

**Theoretical Dynamics and Kinetics of Small Organic
Molecules: Applications and Methods**

by

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Theoretical Dynamics and Kinetics of Small Organic Molecules: Applications and Methods

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Several problems concerning both the dynamics and kinetics of a selection of small organic molecules in different environments are considered. Chapters 2 and 3 concern the photochemistry of the hydrated clusters of the fluoromethanol, $\text{CH}_2(\text{OH})\text{F}$, and methanediol, $\text{CH}_2(\text{OH})_2$, molecules upon vibrational overtone excitation of an OH chromophore within the cluster. Ab initio calculations unambiguously predict a dramatic drop in the barrier height of the reaction $\text{CH}_2\text{OHX}\cdot(\text{H}_2\text{O})_n \rightarrow \text{CH}_2\text{O} + \text{HX}\cdot(\text{H}_2\text{O})_n$ ($\text{X}=\text{F},\text{OH}$). However, analysis of “on-the-fly” trajectory simulations shows a pronounced delayed threshold in the quantum yield for the reaction. This phenomenon originates from a competition between the reaction and the evaporation of water molecules from the cluster, which can quench the possibility of reaction by removing energy from the activated complex. The conclusion of this work is that quantum chemistry calculations at stationary points on the potential energy surface can be insufficient to establish water catalysis in photochemical reactions where the dynamical details are important due to the non-statistical nature of the excitation.

In the second part of this work, an adiabatic semiclassical treatment is proposed for incorporating low frequency torsional motions into molecular state sums. In this treatment, “fast” internal degrees of freedom, often well represented in the harmonic, free, or hindered rotor approximations, can be incorporated quantum mechanically into a local state sum that is a function of the “slow” coordinate. The slow torsional states can then be included using a classical phase space integral over the local state sum. This method is applied to a simple model problem of coupled harmonic oscillators and to the hydrogen peroxide molecule and its isotopomer HOOD. The method is compared to simpler, commonly used state count algorithms.

In the last section, the catalyzed decomposition of methanol on the metal surfaces of Pd(111), Pt(111), and Ni(111) is considered. These reactions are used to construct a microkinetics model

composed of surface symmetry consistent rate coefficients to simulate the relevant surface kinetics. Global sensitivity and stochastic pathway analyses are used to identify reactions to which the model output shows the greatest sensitivity. Due to its modest size, this mechanism is considered as a model problem on which to compare the ability of global sensitivity and stochastic pathway analyses methods to identify and understand competing pathways within a chemical mechanism.

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Chapter 1

Introduction

Advances in computer technology and the development of efficient and accurate *ab initio* quantum chemistry algorithms have greatly expanded the set of chemical systems and phenomena that can be studied on potential energy surfaces calculated from first principles. Traditional theoretical reaction dynamics has largely been concerned with three body reactions [109] of the type $A + B \rightarrow C$ not only because chemical phenomena in such “simple” systems, which nonetheless have a complex and diverse chemistry, lend themselves more to interpretation, but because their low dimensionality makes them less computationally demanding. Most highly accurate potential energy surfaces (PESs), making use of state-of-the-art quantum chemistry calculations, have been constructed for very small molecules composed of only 3 or 4 atoms. The modeling of the dynamics and chemical mechanisms of larger systems necessarily requires some approximation. Statistical theories, such as transition state theory (TST) [200,201] and unimolecular rate theories such as RRKM and phase space theory [118,132], have been highly successful tools when applied in the correct context. Such theories are convenient as they usually only require properties of the reacting species at a few discrete points, or, in more advanced treatments, reduced dimensional cuts [64,230], on the potential energy surface. However, statistical theories rely on the assumption that excitation energy in a molecule is randomly distributed amongst the molecular degrees of freedom and the redistribution of this energy among the degrees of freedom is extremely fast relative to any reactive process. Exceptions to the assumption of facile energy redistribution within a molecule have been noted in many different systems under various conditions, including thermal [19,55,165] and photo-

excited processes [6,171,216]. In such cases, the details of the reaction dynamics become important in making reliable rate and mechanistic predictions. Modeling the full dynamics of molecular systems of moderate size is now possible on ab initio potential energy surfaces using the method of “on-the-fly” dynamics [121,139], which avoids the necessity of fitting a highly accurate PES and integrates the trajectories using potential energy values and derivatives directly obtained from electronic structure methods at each time step. Such methods often rely on more modest applications of electronic structure theory to be computationally practical, and, so, unlike potentials of 3 and 4 atom systems fit to highly accurate electronic structure calculations and empirical data, they tend to be less accurate. Nevertheless, the ability to perform full dimensional dynamics of larger molecules, and even in condensed phase systems [81] and for non-adiabatic dynamics [167], on even semi-quantitative PESs has proven a powerful tool for studying chemical processes of modestly sized chemical systems where non-statistical effects are important.

In this thesis, both statistical and dynamical methods are used to model the chemistry of small organic alcohols and diols in various chemical environments. These small organic molecules can be interesting both due to the abundance of simple organics in many studied chemical systems and as prototype models for understanding the possible chemistry of larger organics. The rest of this section describes the content and motivation of each of the chapters contained in this work.

Chapters 2 and 3 concern the water-mediated elimination reactions of $\text{CH}_2\text{X}(\text{OH}) \rightarrow \text{CH}_2\text{O} + \text{XH}$, $\text{X}=\text{F}$, fluoromethanol, and $\text{X}=\text{OH}$, methanediol. This work was motivated by several problems in the field of atmospheric chemistry. First, it has been found that small water clusters play an important role in atmospheric chemical processes [14,181,205,207,209], also small hydrated complexes are often considered as models for both approximating condensed phase chemistry and bridging the divide between chemistry in the gas phase and corresponding chemistry in the solution phase limit [105,124]. In addition, small water complexes with organic molecules, in particular aldehydes, have been considered as having a potential role in the formation of secondary organic aerosols [2]. Second, atmospheric processes are driven by photochemistry caused by solar radiation [208]. The typically large cross sections of electronic transitions of molecules that fall in the ultraviolet (UV)

region of the electromagnetic spectrum make such electronic photochemistry an important source for generating the reactive radicals that act as reagents in many atmospheric chemical reactions. However, the UV component of solar radiation is lessened in the lower atmosphere by absorption due to O_2 and O_3 at higher altitudes. Moreover, the longer wavelength IR and visible radiation constitutes a far larger component of solar radiation than the higher energy UV. In order to account for an anomalously large production of HO_x radical at dawn and dusk, it has been shown by Donaldson et al. [40] that vibrational overtone excitation of the OH local mode due to absorption in the near infrared and visible region of the solar spectrum is a source of radical production from common atmospheric constituents such as HO_2NO_2 and HNO_3 and for the production of SO_3 from sulfuric acid [41]. Photochemistry resulting from the vibrational overtone excitation of the OH local mode may have an compelling role in reactions in small water clusters.

The ability of water to increase the rate of certain reactions in aqueous solution is well known. Such catalytic behavior has various origins. For example, it has been found by Rideout and Breslow [163] that the Diels-Alder reaction is catalyzed due to hydrophobic effects on the reagent molecules. Also, water solvent can passively catalyze a reaction by stabilizing a transition state or intermediate characterized by a separation of charges [30]. In this thesis, the catalyzing water(s) is considered as an active participant in the reaction mechanism. This active catalysis is common for reactions involving proton or hydrogen atom transfers where water molecules provide an alternative reaction path from the direct hydrogen transfer by contributing to a hydrogen transfer network. The quantum chemistry study of Muguruma and Morokuma [146] showed the ability of just one water molecule to form a hydrogen bonded complex in the conversion of sulfuric acid, H_2SO_4 , to SO_3 and lower the energy barrier to reaction by $\sim 25 \text{ kcal mol}^{-1}$. The water catalysis of this reaction was confirmed experimentally in the gas phase hydrated clusters of H_2SO_4 [86,96,122]. This work, and others [154,215], established that quantum chemistry calculations for the energetics of the equilibrium hydrated cluster geometries and the reaction saddle points are an effective method of identifying water catalysis via barrier lowering. This barrier lowering translates to catalysis under thermal conditions where energy in the reacting complex is Boltzmann distributed. In this

scenario, transition state theory is expected to apply and the effect of barrier lowering reduces the free energy of activation in the TST rate coefficient, $\Delta G^\ddagger$ [201]. However, it is unclear whether the barrier lowering effect alone is sufficient to infer water catalysis in systems excited into non-statistical distributions inconsistent with statistical rate theories. The OH vibrational overtone induced chemistry within water clusters is such an example. Here, the excitation energy is placed in a specific and localized chromophore, and the coupling of this energetically excited bright state to the reaction coordinate and to a competing low barrier evaporation reaction may alter the dynamics from statistical expectations. Chapters 2 and 3 provide analysis of the dynamics of OH overtone initiated reactions in the small hydrated clusters of fluoromethanol and methanediol in order to understand how the presence of catalytic water molecules and their barrier-lowering effect is manifested in the photochemistry.

In Chapter 4, we move away from studying non-statistical dynamics and set out a semi-classical adiabatic method for incorporating “slow” large amplitude degrees of freedom [230] into the molecular state sums that are used to construct statistical based quantities such as partition functions and TST and RRKM rate coefficients. These slow degrees of freedom most often correspond to internal rotations and torsions and are usually treated as completely separable from other internal motions. The most commonly applied methods for incorporating such slow motions into molecular state sums assume they are harmonic or a free rotor and, in more rigorous hindered rotor treatments [?, 45], most famously the Pitzer-Gwinn approximation [76, 155], a more problem-specific classical approximation is used involving a phase space integral along an approximate, or the actual, one dimensional potential energy surface along the torsional coordinate. Such approximations, however, still treat the “slow” and “fast” coordinates as separable. The shape of the molecular potential energy surface along the fast degrees of freedom can change significantly with the variation of the slow degree of freedom. The method we propose treats the “fast”, usually harmonic, degrees of freedom in the state sum using a quantum mechanical sum of states at the each value of the slow coordinate. The slow coordinate is then convolved into the total state sum by a classical phase space integral. Application of the method to a model problem and to various

properties of the H_2O_2 molecule and its HOOD isotopomer, including the RRKM rate coefficient for dissociation into OH radicals, are shown and compared with simpler and more common treatments.

In the last chapter, the metal surface catalyzed decomposition of methanol, CH_3OH , on Pd(111), Pt(111), and Ni(111) is considered. Microkinetics modeling has become an important tool for studying reactive processes in surface science [62,185]. Chemical mechanism optimization strategies utilizing global sensitivity analysis have been developed and applied to simulations in combustion chemistry [37,177]. In this work, microkinetics mechanisms for the dehydrogenation decomposition of methanol on the metal surfaces of Pd(111), Pt(111), and Ni(111) are constructed using density functional theory calculations of Gu and Li [59]. Transition state theory is used to generate surface symmetry consistent rate coefficients for the mechanisms. First and second order global sensitivity analysis is performed on the constructed mechanisms in order to determine the key rate coefficients that have the greatest impact on the simulation results and to study how mechanism structure influences the modeled kinetics. Global sensitivity provides information on how single rate coefficients, and therefore single reactions, influence the observed quantity simulated by the microkinetics model. While such information is quite useful, it is reasonable to expect that entire chemical pathways within the mechanism may also have influence on the simulation result. A pathway study using a stochastic pathway analysis method [229] is given on the small mechanism and the results are contrasted with those of global sensitivity analysis.

A brief presentation of the OH vibrational overtone initiated dynamics of performic acid is given in Appendix A. This system is quite interesting due to its similarity in structure to the hydrogen peroxide molecule, but with an added feature of the hydroxyl group hydrogen bonded to a carbonyl oxygen. The overtone initiated dynamics of the hydrogen peroxide molecule have been well studied experimentally [164] and theoretically [203,216]. However, the H_2O_2 molecule lacks the ability to intramolecularly hydrogen bond, and it has been illustrated that vibrational excitation energy placed in hydrogen bonded OH chromophores tends to dissipate much more quickly than in the absence of hydrogen bonding via IVR and “chattering” mechanisms [189,190]. This system, and the related system of peroxyacetic acid [69], has been studied by Sinha and co-workers [70,174]

by photoacoustic and action spectroscopy. In the work presented here, the overtone initiated dynamics and possible reactions for the O–O dissociation of performic acid are studied using quantum chemistry calculations and “on-the-fly” reaction dynamics studies. Trajectory studies are used to determine the lifetime in the excited OH chromophore. Reactive events observed in the dynamics are discussed and directions for future work are proposed.

Chapter 2

Water Catalysis and Anticatalysis in Photochemical Reactions: Vibrational Overtone Induced Elimination Reaction of Fluoromethanol Hydrated Clusters

The possible catalysis of photochemical reactions by water molecules is considered. Using classical trajectory simulations, where the ab initio potential energy surface is computed “on-the-fly”, we investigate the HF elimination reaction of fluoromethanol in small water clusters. Hydrogen bonding of catalyzing water molecules to the transition state is predicted to lower the energetic barrier of the elimination reaction by over 20 kcal mol⁻¹. However, it is found when excitation energy is deposited in the molecule via a vibrational overtone excitation of an OH chromophore within the hydrogen bonded network of the cluster that the quantum yield of the elimination reaction versus energy shows a pronounced delayed threshold at odds with the catalytic effect. It is concluded that the quantum chemistry calculations of barrier lowering are not sufficient to infer water catalysis in some photochemical reactions, which instead require dynamical modeling.

The contents of this Chapter were published in References [188] and [99] and are presented here with a few modifications.

2.1 Introduction

2.1.1 Vibrational Overtones in Hydrated Clusters

Hydrated clusters, and their photochemistry, have a long been known to play a rich and various role in atmospheric chemistry [1, 20, 36, 80, 94, 96, 108, 172, 205, 207, 209]. Additionally, cluster phase chemistry is an intermediary bridge between the limits of gas phase and solution

phase chemistry, and therefore the study of hydrated clusters is an integral part of understanding the effect of solvation on chemical processes [144,187]. In this chapter and the subsequent chapter, we shall consider the vibrational overtone induced photochemistry of small organic molecules in hydrated clusters on the ground electron potential energy surface. In these studies, the OH stretch vibrational mode is the chromophore carrying the oscillator strength. This chromophore has a relatively large absorption cross section and is well separated due to the high fundamental frequency of OH (although still much smaller than that of an electronic absorption) that decreases by roughly an order of magnitude for each transition to a successively higher overtone state [35]. Indeed, the OH vibrational transition has long been used as a means to study dynamics, mode selective chemistry, and intramolecular vibrational redistribution (IVR) [15, 34, 40, 41, 68, 97, 142, 157, 175, 203, 209], and is a convenient probe into the dynamics of hydrated clusters due not only the OH groups of the clustered water molecules, but also because many solvated organics contain chemically active hydroxyl functional groups. In this chapter, we consider the photochemistry of water catalyzed reactions within small water clusters.

2.1.2 The Catalytic Properties of Water

It is well appreciated that water will catalyze certain neutral chemical reactions so that their rate in solution is substantially higher than in the gas phase. Such enhancements have been observed, either experimentally or in large theoretical simulations, for a variety of reactions including Diels-Alder, dehalogenation, dehydration, and decarboxylation reactions [10, 21, 38, 90, 106, 110, 146, 154, 163, 181, 223]. The origin of the catalytic effect of water often differs between systems. For some reactions, such as the Diels-Alder reaction [163], the catalytic effect of water is due to its ability, as a polar solvent, to force non-polar reactants into close proximity via hydrophobic effects. In others, hydrogen bonding of water to a transition state with a large charge separation can stabilize the reaction system as it passes over the reaction barrier [30], and thus catalyze the reaction without being “directly” involved in the reactive process. In many systems, including those studied in this chapter and the next, water can also have a more interesting and active catalyzing

role. M. Eigen [43], R. P. Bell [5], and others [17] conjectured long ago that water molecules may participate in an essential way in hydrogen atom (or proton) transfer reactions by forming hydrogen bonded complexes at the transition state (TS). In such cases, the water molecule, or molecules, can take a direct part in the reaction mechanism as part of a “water wire” or hydrogen transfer network [129,193], where several hydrogen transfer events occur and provide an alternative, and in the catalytic case lower barrier, reaction pathway. Using finite clusters of reagent and water molecules, quantum chemistry calculations [224] have confirmed that the TS energy for a variety of reactions can be significantly lowered compared to the bare (i. e. non-hydrated) reagent which thus may serve as the basis for the catalytic effect. The calculations of Morokuma and Muguruma [146] demonstrated that the hydrogen bonding of a single water molecule to the reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ lowered the barrier by 25 kcal mol^{-1} through the formation of a very stable six-member ring. This catalytic effect was found to be consistent with the gas phase SO_3 hydration experiments of Molina and co-workers [86,96] and Lovejoy et al. [122]. Tao and co-workers [106] found that further solvation of the SO_3 in larger clusters led to even lower TS barriers which seemed to converge with cluster size which might be regarded as the solution limit. Vohringer-Martinez et al. [215] have seen evidence of water catalysis in the bimolecular reaction $\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO}$ where, again, clustering with a single water molecule was found to significantly lower the barrier to hydrogen abstraction, though this effect has recently been questioned by the theoretical work of Vivier-Bunge et al. [83]. Phillips and co-workers [154] likewise noted that the addition of 1-4 water molecules dramatically lowered the barrier for the dechlorination reaction $\text{CH}_2(\text{OH})\text{Cl} \rightarrow \text{CH}_2\text{O} + \text{HCl}$.

2.1.3 Thermal Versus Photo- Water Catalysis in Hydrated Fluoromethanol Clusters

For thermally activated reactions, a substantial lowering of the TS barrier by hydrogen bonding is expected to accelerate the rate of reaction. Using transition state theory (TST), the rate

coefficient in the presence of water is approximated by,

$$k(T) = \kappa(T) \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{k_B T}} \quad (2.1)$$

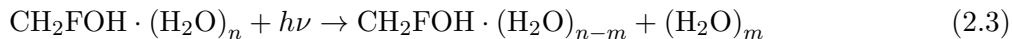
where $\kappa(T)$ is a modest transmission coefficient that takes into account dynamical effects of the solvent [201]. The free energy of activation, $\Delta G^\ddagger$, strongly correlates with the barrier height, ΔE^{TS} , and thus a quantum chemical determination of the barrier energies should provide a reliable gauge of catalytic behavior. However, under more general “non-thermal” conditions, the effect of dynamics may play a role in the reaction and could possibly alter the catalytic behavior. Such general conditions include photochemical processes, such as vibrational overtone excitation, spontaneous internal conversion, or stimulated emission pumping [33, 97]. In any of these excitation processes, the photon energy is deposited “locally” into one or several vibrational modes, and reaction occurs when the energy flows into the reaction coordinate. While the ground state barrier is lowered by hydrogen bonding, the non-equilibrium distribution of the excitation energy creates a possibility that (non-statistical) dynamical effects [121] may play an important role, perhaps even suppressing the catalytic enhancement.

In this chapter, we examine the possibility of water catalysis for photochemical reactions occurring on the ground electronic potential energy surface (PES). As can be deduced from the discussion above, chemical systems exhibiting water catalysis are multifarious and multitudinous, and an exhaustive study of photochemistry of water catalyzed systems is quite impractical. We adopt the viewpoint that the study of the photochemistry of specific and simple example systems exhibiting the water catalytic effect may reveal some of the essential features of the general phenomenon. In this vein, we chose the elimination of HF in fluoromethanol as our prototype system,



While the fluoromethanol molecule is undoubtedly quite unstable, and thus impractical for experimental study, it lends itself to theoretical investigation because of its simplicity. A more experimentally relevant system, methanediol, is treated in Chapter 3. In Equation 2.2, the photon,

represented by $h\nu$, excites the OH stretch local mode chromophore. Since the barrier energy is significantly higher than the hydrogen bonding energy binding a water molecule to the cluster, ΔE^{EVAP} , the elimination reaction must be viewed in competition with the evaporation process,



The reaction in Equation 2.3 represents irreversible energy flow out of the reactive system that can leave the cluster below the barrier thereby deactivating the activated complex and quenching the elimination reaction in Equation 2.2. Since $\Delta E^{\text{TS}} > \Delta E^{\text{EVAP}}$, we expect that if the excitation energy were to randomize quickly within the cluster, then the lower barrier process, in Equation 2.3, would dominate over the reactive process, in Equation 2.2, and the elimination reaction would be effectively suppressed. Thus, the catalyzed reactive process should occur with an appreciable rate only if the dynamics is “direct”, i. e. non-statistical, and occurs on a time scale commensurate with or faster than that of the energy transfer process, $\tau_{\text{ET}} \geq \tau_{\text{RXN}}$. Such time scale restrictions are not expected to apply to thermally induced reactions in solution or cluster phase where evaporation is reversible, and a near-equilibrium distribution of reagent states is maintained. A schematic of the hydrated fluoromethanol cluster system and the relevant photochemistry are shown in Figure 2.1.

Since the photo-activated reagents must lie in a highly non-equilibrium distribution for the chemical reaction to occur at all, we should not necessarily expect statistical-based rate theories, such as RRKM [184], to apply. Thus, we cannot simply rely on the energetics of the TS to determine whether or not the water catalytic effect occurs in a photochemical reaction. Instead we must model the dynamics of the reactive process from reagents to products. The specific objective of the calculations is to obtain the quantum yield for the reaction as a function of excitation energy, $\Phi(E = h\nu)$. For an isolated gas phase molecule, $\text{CH}_2(\text{OH})\text{F}$, $n = 0$ in Equation 2.2, the energy dissipation channel is absent and, in the absence of quantum tunneling, we should observe a threshold,

$$\Phi(E) = \Theta(E - \Delta E^{\text{TS}}(n = 0)) \quad (2.4)$$

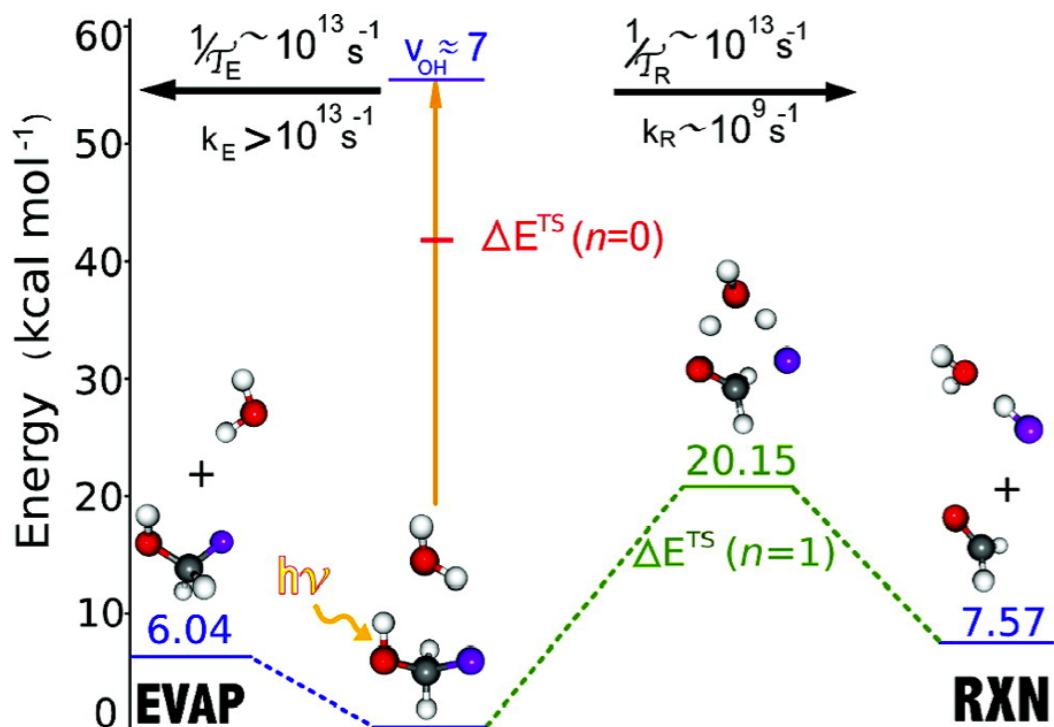


Figure 2.1: This schematic diagram shows the reactive HF elimination and evaporation processes for fluoromethanol monohydrate. The energies shown were calculated at B3LYP/6-31+G(*d,p*) with zero point correction. The transition state energy barriers for the $n = 0$ and 1 clusters are labeled as $\Delta E^{\text{TS}}(n = 0)$ and $\Delta E^{\text{TS}}(n = 1)$, respectively. The τ 's represent timescales observed in the simulated dynamics and the k 's represent statistically expected rate coefficients.

where Θ is the Heaviside step function and $\Delta E^{\text{TS}}(n=0)$ is the “un-catalyzed” reaction barrier in the absence of water. Of course, the time scale for reaction is potentially longer than the typical gas phase collision times in this hypothetical case. For hydrated clusters, with $n \neq 0$, we shall judge the photochemical process to be water catalyzed if we observe the threshold in $\Phi(E)$ to be shifted in energy to a value significantly below $\Delta E^{\text{TS}}(n=0)$. In an ideal catalyzed limit, the threshold might move all the way to the hydrated barrier position. It is also possible to observe anticatalysis, where the threshold for the cluster reaction lies above the TS of the bare, i. e. $n=0$, reaction.

2.1.4 Chapter Outline

The rest of this chapter is organized as follows. In Section 2.2, we describe the quantum chemistry and theoretical methods used construct the simulations of the OH local mode excited states in the fluoromethanol hydrated clusters. In Section 2.3, we discuss the findings from the quantum chemistry calculations and dynamics simulations, including the overall quantum yield for the HF elimination reaction and the time scales deduced from the dynamics. Also in this section, some discussion of the reaction mechanism is given. In Section 2.4, we summarize conclusions of this chapter.

2.2 Methodology

To describe the overtone-induced chemistry of the $\text{CH}_2\text{FOH}\cdot(\text{H}_2\text{O})_n$ clusters, several calculations are required. First, the equilibrium structures for the clusters must be computed using quantum chemistry calculations. Second, the initial excitation of the OH chromophore must be modeled. Third, the dynamics of the activated cluster must be propagated until reaction occurs or until sufficient energy has dissipated from the cluster through evaporation.

2.2.1 Quantum Chemistry Calculations

The equilibrium geometries for the species $\text{CH}_2\text{FOH}\cdot(\text{H}_2\text{O})_n$, for $n = 0, 1, 2$, and 3 are found from a minimum search of the ground PES using the B3LYP/6-31+G(d,p) [4, 26, 49, 65, 71, 107, 136]

method employing the Gaussian03 [50] quantum chemistry package. The relevant saddle points and the associated minimum energy paths (MEPs) for the elimination reaction have also been located to further characterize the system. In previous works on glycolic acid [189] and pyruvic acid [190], it has been established that the level of DFT used here is sufficient to account for spectroscopic line positions and intensities of OH overtones observed in experiment. In order to test the accuracy of the DFT method, we also investigated these structures using higher level theory, i. e. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(*d,p*) [196] using the MOLPRO quantum chemistry package [218].

The B3LYP method employed here has proven to be quite reliable and flexible in a wide variety of problems involving molecular structure and dynamics. However, future work on this or related problems should be aware that much work has been done to develop density functional theory methods specifically hydrogen bonded systems [87]. Indeed, we have test the MPWB1K functional of Zhao and Truhlar [227] and found that the transition state barrier heights and energies are much closer to the CCSD(T) values than B3LYP when using the same basis set. It has also been suggested that the MP2 method gives a more accurate description of the hydrogen bonding interaction, but can strongly dependent upon the choice of basis set, see Appendix A. Also, DFT is much more computationally efficient than MP2 at a given basis set size, particularly in “on-the-fly” dynamics which require many Hessian and/or gradient evaluations.

2.2.2 OH Overtone Trajectory Construction

Since no reasonable analytical potential energy surface is available for use in modeling the full dimensional unimolecular dynamics of the overtone excitation in the fluoromethanol clusters, the classical trajectories comprising the simulation are integrated using ab initio points computed “on-the-fly” at the B3LYP/6-31+G(*d,p*) level of theory. However, in order to model the excitation, it is necessary to construct initial conditions corresponding to the bright state of the OH overtone transition. We adopt the conventional view that the oscillator strength for the transition is carried by the OH stretch local mode. In order to investigate the effects of mode selectivity, we have

modeled the dynamics for two different chromophores. The first is the hydroxyl group in the fluoromethanol molecule that participates in the hydrogen bonded network, which we shall call *a*OH. The second is the terminal water OH group in the hydrogen bonded network that is donating a hydrogen bond to the fluorine of the fluoromethanol, which we shall call the *w*OH chromophore.

In order to determine the overtone excitation energies, we first construct a one dimensional PES computed using B3LYP/6-31+G(*d,p*) by stretching the OH along its bond while keeping all other atoms at their positions in the equilibrium configuration. The one dimensional OH local mode time independent Schrödinger equation, shown in Equation 2.5 below, is then solved,

$$\left(\frac{\hat{p}_{\text{OH}}^2}{2\mu_{\text{OH}}} + \mathcal{V}(\hat{r}_{\text{OH}}) - \mathcal{V}(r_{\text{OH}}^0) \right) \psi_v(r_{\text{OH}}) = \epsilon_v \psi_v(r_{\text{OH}}) \quad v = 0, 1, \dots \quad (2.5)$$

where ϵ_v is the energy eigenstate of the OH local mode, $\mathcal{V}(r_{\text{OH}}) - \mathcal{V}(r_{\text{OH}}^0)$ is the PES relative to the potential energy of the equilibrium OH length, r_{OH}^0 , and μ_{OH} is the reduced mass of the OH diatom moiety. The one dimensional Schrödinger equation is conveniently solved using a grid basis method [191] or discrete variable representation, DVR, [29], where the quantum chemistry calculations for the potential energy can be computed at the DVR grid points. The excitation energy of the v vibrational state of the OH chromophore is then $\epsilon_v - \epsilon_0$.

An ensemble of initial conditions with zero point energy, consistent with the conditions $T = 0$ K and $J = 0$, are generated by taking the equilibrium configuration and performing the fixed normal mode sampling method of Hase et al. [66] as implemented in Gaussian03 [50], where zero point energy is added to all the normal modes in a random phase to each molecule in the ensemble. For each zero point initial condition, a one dimensional OH stretching PES is calculated, slightly different for each initial condition. For each initial condition, the generated OH PES is used to select an OH local mode coordinate and velocity to correspond with the desired excitation energy with a random vibrational phase. If mode coupling effects are significant, a scaling of the velocities of all the atoms [66] in the molecule can be used ensure that all molecules in the ensemble have the same total energy. While there is no unique semiclassical prescription for choosing initial conditions, the present approach does provide a physically reasonable result with no serious anomalies.

2.2.3 Trajectory Propagation and Details

The dynamics of the vibrationally excited cluster is modeled using a classical trajectory simulation. The force field is constructed “on-the-fly” [192, 225] using analytical gradients and Hessians, available for the B3LYP method, and the trajectories were integrated using the Hessian based predictor-corrector method of Schlegel and Hase [139]. The variable time step was selected to maintain energy conservation to five-figure accuracy and was typically between 0.5 and 1.0 fs. Each trajectory was propagated until (1) the distance between the centers of mass of the fluoromethanol and a water molecule becomes greater than $8.5a_0$, (2) the center of mass separation of HF and CH₂O becomes greater than $8.5a_0$, or (3) the time of propagation becomes long and excitation energy dissipates from the OH-chromophore. Some care was taken when classifying non-reactive trajectories that satisfied the stopping criteria to establish non-reactivity. The total propagation time for a trajectory was generally less than 600 fs, with the dynamics of interest occurring mainly within the first 100-150 fs of the trajectory. From previous studies of IVR in polyatomic molecules, we expect that the classical representation of the overtone vibration will be reasonable on short timescales and the quantum effects will contribute significant error if the simulation is extended beyond a “breaktime” [58]. For longer times, the quantum mechanical rate of IVR is typically slower than the classical analog and a quantum mechanical cluster model of the reaction/evaporation competition described here would be an interesting future direction for this work.

For both $n = 1$ and $n = 2$ clusters with an excited *a*OH chromophore, batches of 200 trajectories were run for each overtone excitation simulated. For the $n = 3$ *a*OH chromophore excitations, 100 trajectories were run in each overtone ensemble. For the $n = 1$ and $n = 2$ simulations of the *w*OH chromophore, modest batches of 100 and 75 trajectories, respectively, were run at each excitation energy. The overtone excitation energies and the corresponding vibrational states are shown in Table 2.2.3 for the $n = 1$ and $n = 2$ clusters. Some of the effects of anharmonicity are quite clear upon close observation of Table 2.2.3, particularly for the *a*OH chromophore in the

Table 2.1: The overtone excitation energies, corresponding to the energy of the exciting photon, in kcal mol⁻¹, and the OH local mode vibrational state they correspond to are shown for those overtone states that were simulated in this study.

<i>n</i> = 1 Cluster	
<i>a</i> OH	<i>w</i> OH
43.6 (<i>v</i> = 5)	44.6 (<i>v</i> = 5)
50.5 (<i>v</i> = 6)	53.1 (<i>v</i> = 6)
56.9 (<i>v</i> = 7)	61.4 (<i>v</i> = 7)
67.9 (<i>v</i> = 9)	69.3 (<i>v</i> = 8)
<i>n</i> = 2 Cluster	
35.9 (<i>v</i> = 5)	28.5 (<i>v</i> = 3)
40.9 (<i>v</i> = 6)	37.0 (<i>v</i> = 4)
46.2 (<i>v</i> = 7)	44.8 (<i>v</i> = 5)
51.8 (<i>v</i> = 8)	52.2 (<i>v</i> = 6)

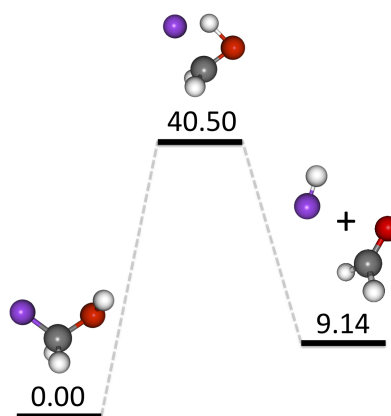


Figure 2.2: The fluoromethanol molecule and stationary points along the minimum energy path of the HF elimination reaction. The energies shown were calculated at B3LYP/6-31+G(*d,p*) and are zero point corrected.

$n = 2$ cluster.

A closely related discussion of trajectory construction and overtone simulation is given in Chapter 3.

2.3 Results & Discussion

2.3.1 Quantum Chemistry and Transition State Barrier Lowering

The energetics of HF elimination reaction for the $n = 0$ bare molecule is shown in Figure 2.2. The transition state for the reaction involves a four-membered, highly strained, hydrogen transfer ring predicted to have a transition state barrier of approximately 40 kcal mol⁻¹. Also apparent from Figure 2.2, the HF elimination reaction is endothermic, a property that carries over to larger clusters. The most stable equilibrium geometries of the $n = 1, 2$, and 3 clusters and their corresponding HF elimination transition states are shown in Figure 2.3. In the $n = 1$ (monohydrate) cluster, two hydrogen bonds to the water molecule yield a six-member ring containing the OH-group, and the F-atom, in the “chair” configuration. Other local minima on the PES were found that correspond to single hydrogen bonded complexes, but these are less stable by at least 3.25 kcal mol⁻¹. When a second water molecule is added to form the $n = 2$ (dihydrate), CH₂FOH·(H₂O)₂, the most stable

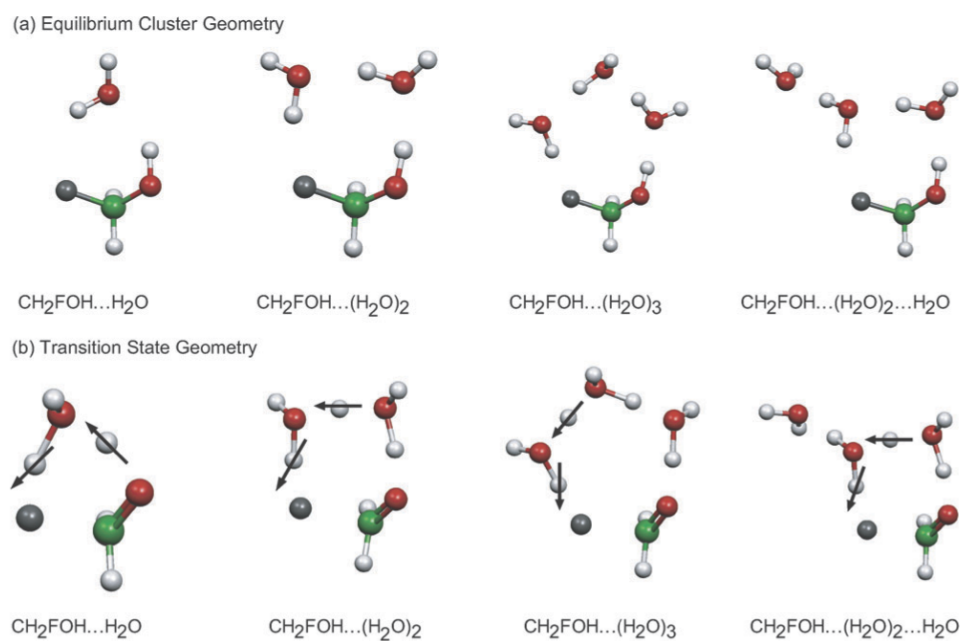


Figure 2.3: Molecular geometries computed for $\text{CH}_2\text{FOH}\cdot(\text{H}_2\text{O})_n$ clusters using B3LYP/6-31+G(*d,p*). In (a), the minimum energy configurations for the clusters with $n = 1, 2$, and 3. In (b), the corresponding HF elimination transition states for each cluster type. The motion corresponding to the minimum energy path is indicated with arrows.

structure is an 8 atom ring where, again, each water molecule participates with two hydrogen bonds in the hydrogen bonded ring network. The next lowest energy cluster conformer for $n = 2$ lies at $3.55 \text{ kcal mol}^{-1}$ above the 8 atom ring configuration. One very important property of the $n = 2$ stable ring cluster is the relatively linear alignment of the αOH chromophore group to its corresponding hydrogen bond acceptor oxygen atom in a water. As we shall see, this structural feature facilitates a more effective hydrogen atom transfer that initiates the overtone induced reaction.

Although we have only carried out a limited analysis of the $n = 3$ (trihydrate) cluster, since its large size requires long computer run times in the trajectory simulations, we have explored the stationary points of its PES. The most stable structure is, similar to the $n = 1$ and $n = 2$ cluster, composed of a hydrogen bonded 10 member ring with each H_2O molecule doubly hydrogen bonded within the ring. Such ring geometries appear to continue as minimum energy conformations as the cluster size grows, at least for small clusters, but these ring geometries become entropically less favored, and we have chosen to investigate the alternative second lowest energy cluster geometry for $n = 3$. This geometry consists of the eight membered hydrogen bond ring, an analog of $n = 2$, while the third water is “excluded” from the hydrogen bond network and accepts a hydrogen bond from a dangling OH of a water molecule within the network. This configuration may be thought of as representing a first approximation to a solvating water that does not directly participate in the reaction.

The transition state saddle point geometries reveal a great deal about the reaction process. The water molecules catalyze the elimination reaction by altering the reaction mechanism via active participation in the hydrogen atom transfer. Indeed, the transition states are characterized by highly concerted multiple hydrogen atom transfers within the hydrogen bond network. These transfers happen in conjunction with the breaking of the C–F bond in fluoromethanol. The saddle point geometries reveal that the transferred hydrogens are all roughly halfway between the donor and acceptor oxygens (and fluorine) as the minimum energy path crosses the reaction barrier and that the heavy atoms in the hydrogen bonded ring are, disregarding the extended C–F bond, closer together than in the equilibrium cluster geometry. The arrows in Figure 2.3(b) denote the largest

amplitude motions tangent to the minimum energy path at the saddle point, which mostly consist of multiple hydrogen transfers. The intrinsic reaction coordinate, calculated for these clusters, reveals that the initial motion along the reaction path is composed of the “shrinking” of the hydrogen bond ring network into a more compact geometry along with the simultaneous extension of the C–F bond. In the vicinity of the saddle point, the motion along the MEP changes to the motion of the light atom hydrogen transfer event. In the monohydrate, the centers of mass of the water and fluoromethanol molecules decrease by approximately 0.5 Å before the concerted hydrogen transfer event. The shrinking of the $n = 2$ backbone also occurs along the MEP, although less prominently than in the monohydrate cluster. The conventional view of light atom transfer reactions [131] is that the motion of the slow “skeletal” coordinates provide the critical configuration required for the rapid H atom transfer, and this study suggests that the dependence of the reaction on the large atom motions is an important feature within these small hydrated clusters.

The B3LYP HF elimination barrier energies and water binding energies are shown in Table 2.3.1 along with reference CCSD(T) calculations. We have chosen in this table to express the water binding energy as the total energy needed to fully move all the individual molecules in the cluster to infinite separation. The one water evaporation energies can also be determined from Table 2.3.1, for instance the B3LYP quantum chemistry predicts the one water evaporation energy for the $n = 2$ cluster is 9.33 kcal mol⁻¹, obtained from subtracting the $n = 3$ full evaporation energy from that of $n = 2$. We note this fact so the reader can see that the property $\Delta E^{\text{TS}} > \Delta E^{\text{EVAP}}$ discussed in Section 2.1 still applies.

The salient feature of Table 2.3.1 is the large and significant drop in the HF elimination barrier energy with the addition of one water molecule. The $n = 0$ transition state barrier height is predicted to be 40.50 kcal mol⁻¹ while the $n = 1$ barrier is only 20.15 kcal mol⁻¹; this is a decrease in the barrier energy by almost 20 kcal mol⁻¹. Such a drop in barrier would be manifested in a TST rate coefficient calculation by an increase in the rate coefficient by many orders of magnitude. Clearly, the hydrated fluoromethanol system is predicted to be water catalyzed by its quantum chemistry. The decrease in the barrier height continues upon the addition of the second water

Table 2.2: Barrier energies and complex binding energies computed using various levels of quantum chemistry are shown. The barrier energy reported is the zero point corrected saddlepoint energy for the process $\text{CH}_2(\text{OH})\text{F}\cdot(\text{H}_2\text{O})_n \rightarrow \text{CH}_2\text{O} + \text{HF}\cdot(\text{H}_2\text{O})_n$. The binding energy is the evaporation energy for $\text{CH}_2(\text{OH})\text{F}\cdot(\text{H}_2\text{O})_n \rightarrow \text{CH}_2\text{O} + n\text{H}_2\text{O}$. The clusters given below correspond to those shown in Figures 2.2 and 2.3.

Method: B3LYP/6-31+G(<i>d,p</i>)		
Molecule	Barrier Height / kcal mol ⁻¹	Total Binding Energy / kcal mol ⁻¹
CH ₂ FOH	40.50 (45.68)	
CH ₂ FOH·(H ₂ O)	20.15 (23.89)	6.04 (8.18)
CH ₂ FOH·(H ₂ O) ₂	15.28 (20.29)	15.37 (20.31)
CH ₂ FOH·(H ₂ O) ₃	16.01 (21.82)	23.55 (30.79)
CH ₂ FOH·(H ₂ O) ₂ (H ₂ O)	14.20 (18.64)	20.14 (27.01)
Method: CCSD(T)/aug-cc-pVDZ //B3LYP/6-31+G(<i>d,p</i>)		
Molecule	Barrier Height/ kcal mol ⁻¹	Total Binding Energy / kcal mol ⁻¹
CH ₂ FOH	42.45 (47.62)	
CH ₂ FOH·(H ₂ O)	24.51 (28.52)	6.35 (8.48)
CH ₂ FOH·(H ₂ O) ₂	21.44 (26.46)	14.49 (19.42)
CH ₂ FOH·(H ₂ O) ₃	23.88 (29.69)	21.33 (28.57)
CH ₂ FOH·(H ₂ O) ₂ (H ₂ O)	19.84 (24.27)	18.64 (25.50)

molecule, where the barrier height is $15.28 \text{ kcal mol}^{-1}$, a decrease of over 25 kcal mol^{-1} from the bare fluoromethanol molecule. The addition of the another water to the ring conformer of the $n = 3$ cluster actually predicts a slight increase in the barrier height. This increase is likely due to the highly stable geometry of the hydrogen atom transfer network at the transition state of the eight membered ring that has an optimally, relative to other cluster geometries, aligned hydrogen transfer $\text{O}_{\text{DONOR}}\text{--H--O}_{\text{ACCEPTOR}}$ configuration with reduced steric strains to facilitate the hydrogen transfer event. Also, it is interesting to note that the excluded water $n = 3$ cluster has a barrier height close to, but slightly lower, than the $n = 2$ cluster, suggesting that the eight membered hydrogen transfer ring may continue to be an important transition state in larger clusters and may even be stabilized by excluded, or hydration shell, water molecules.

2.3.2 The Delayed Threshold in the Quantum Yield

Suppressed Catalysis & Anticatalysis The main results of this work are displayed in Figure 2.4 summarizing the quantum yield versus excitation energy for the $n = 1$ and $n = 2$ fluoromethanol hydrated clusters. The quantum yield is defined to be,

$$\Phi(E) = \frac{N_{\text{RXN}}(E)}{N_{\text{TOTAL}}(E)} \quad (2.6)$$

where $N_{\text{TOTAL}}(E)$ is the total number of trajectories in the ensemble at excitation energy E and $N_{\text{RXN}}(E)$ is the total number of reactive events observed in the ensemble. A clear and dramatic delayed threshold is apparent in the results where the reaction is not observed until the excitation energy lies far above the hydrated TS energy. Consider first the monohydrate cluster shown with blue symbols (squares for $a\text{OH}$ excitation and circles for $w\text{OH}$ excitation). For both chromophores of the monohydrate, the phenomenological reaction threshold does not occur until the photon energy is above 50 kcal mol^{-1} , which is significantly more than the bare $\text{CH}_2(\text{OH})\text{F}$ transition state at 40 kcal mol^{-1} . The results for the two chromophores are nearly equal near the threshold, but significant mode specificity develops at higher excitations where the $a\text{OH}$ excitation is more effective in promoting the reaction. The dihydrate results are similar to those for the monohydrate

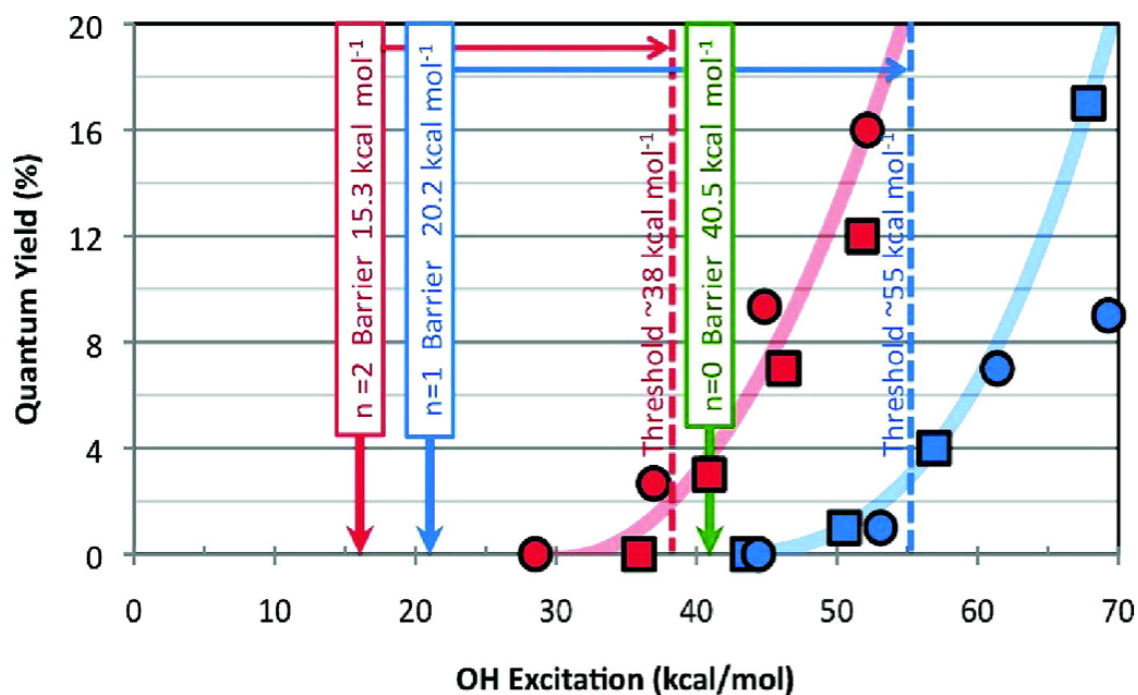


Figure 2.4: The quantum yield, the fraction of reactive trajectories versus photon energy for mono- (blue points) and di- (red points) hydrate clusters obtained from ab initio dynamics simulations with $T = 0$ K and $J = 0$. The circles (squares) represent the alcohol, aOH , (water, wOH , excitation). The curves are drawn to indicate trends and the saddle point and reaction threshold energies are indicated in the plot.

except they are shifted downward, and the mode specificity has mostly disappeared. The threshold for the reaction of the $n = 2$ cluster occurs at roughly 38 kcal mol^{-1} for both chromophores. Thus, the classical threshold is only about 2 kcal mol^{-1} below the bare TS energy. Hence, due to the delayed threshold behavior, we see an anticatalytic effect for the $n = 1$ case and essentially no catalysis for the $n = 2$ case. Naturally, there is an inherent uncertainty in the quantum yield results due to the modest sample sizes of the ab initio trajectories but the existence of a pronounced delayed threshold effect in the elimination reaction is apparent from the results.

Quantum Yield Studies for the $n = 3$ Cluster Trajectories were propagated for the $a\text{OH}$ excitation for both the ring conformation and two possible excluded water conformations of the $n = 3$ clusters at the $v = 8$ OH local mode state, $52.6 \text{ kcal mol}^{-1}$ excitation energy for the ring and 48 and $51.2 \text{ kcal mol}^{-1}$ excitation energies for the excluded water conformers. The quantum yields observed are shown in Figure 2.5. These quantum yields clearly show that the eight membered hydrogen transfer system is very efficient, while the larger $n = 3$ network does not seem to enhance the quantum yield relative to the dihydrate cluster, though it certainly does relative to the monohydrate cluster. Also, the position of the “solvating” excluded water seems to make some difference in the quantum yield. It is possible that the water bound to the water accepting the hydrogen bond of the $a\text{OH}$ chromophore impedes the initial hydrogen transfer.

2.3.3 Analysis of the Dynamics

The rate of energy flow from the excited OH chromophore is a key to understanding the ensuing dynamics, as it determines the time scale during which sufficient energy is maintained in the “relevant” degrees of freedom for the chemical reaction to occur. A measure of the average energy in the OH chromophore over time can be obtained by the ensemble average, at each time, of the quantity,

$$E_{\text{OH}} = \frac{p_{\text{OH}}^2}{2\mu_{\text{OH}}} + \mathcal{V}(r_{\text{OH}}) \quad (2.7)$$

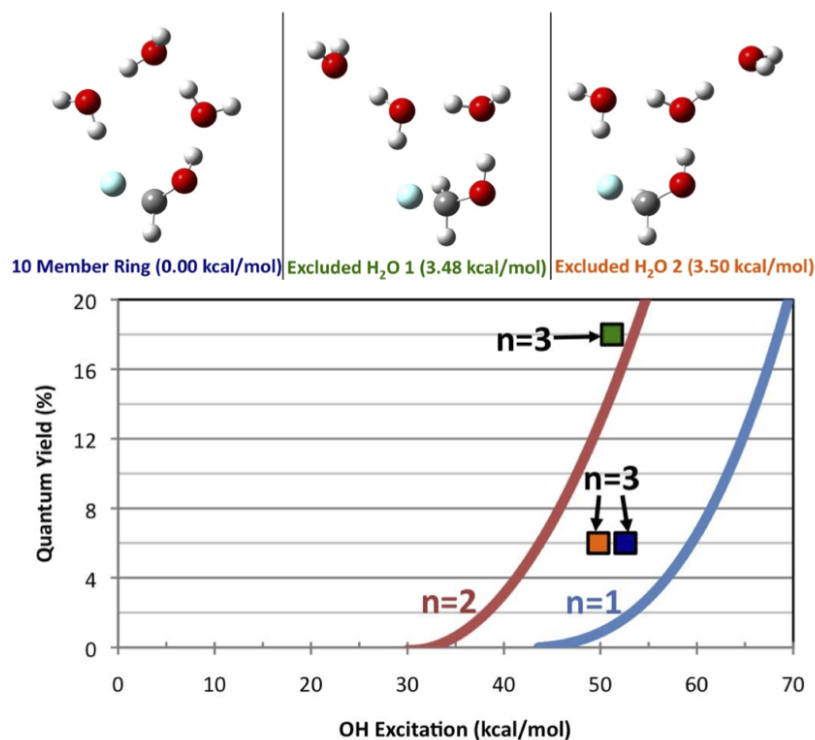


Figure 2.5: The quantum yield, the fraction of reactive trajectories versus photon energy for the $a\text{OH}$ excitation for selected $n = 3$ clusters, the ring (violet), the most stable excluded water cluster (green), and another excluded water conformation (orange). The curves are drawn to indicate trends found in the $n = 1$ and $n = 2$ quantum yields for reference. The structures of the clusters and their relative energies are shown in the top panel for reference.

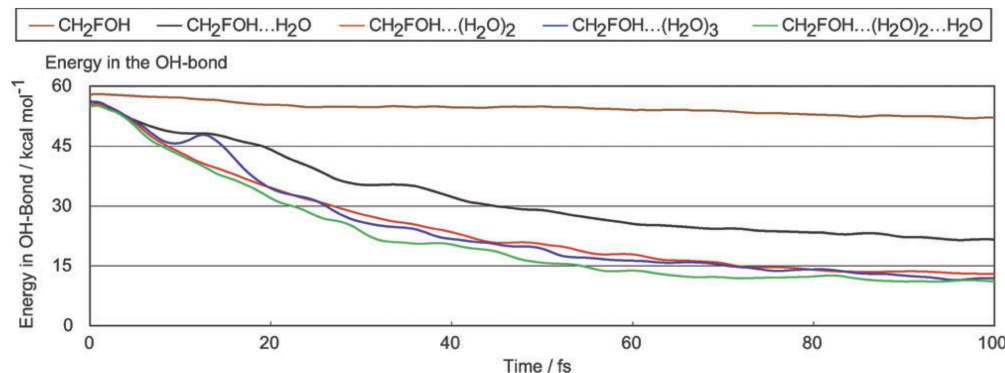


Figure 2.6: The ensemble average of the total energy remaining in the excited *a*OH chromophore versus the time after excitation for different cluster sizes at excitations of 50 kcal mol^{-1} .

where $\mathcal{V}(r_{\text{OH}})$ is the one dimensional local mode potential, we used the potential obtained from the cluster equilibrium geometry. In Figure ??, the average energy in the excited *a*OH chromophore is plotted for an ensemble of trajectories corresponding to the overtone state closest in excitation energy to 50 kcal mol^{-1} for different cluster sizes (for $n = 0$, the excitation is closer to 55 kcal mol^{-1}). The bare, $n = 0$, cluster shows that the excitation energy stays localized in the OH local mode coordinate. Indeed, the excitation energy roughly corresponding $v = 6$ vibrational state remains in the *a*OH chromophore for 400 fs . Energy flow is much more facile in the hydrated clusters, and the energy dissipation occurs within the first 25 to 50 fs after excitation. Consistent with the earlier results of Miyoshi and co-workers [225], the clustering greatly promotes energy transfer from the chromophore. The monohydrate exhibits a somewhat slower rate of energy dissipation than do the larger clusters. This reflects the added anharmonic coupling and higher dimensionality of the larger clusters. The energy relaxation curves for the $n = 2$ and the two $n = 3$ clusters are seen to be essentially equivalent. An inspection of the trajectories reveals that an efficient energy transfer occurs between the OH stretch and the van der Waals (vdW)-stretching modes that lead to water dissipation.

In order to investigate the reaction and evaporation time scales, we construct a diagnostic quantity we refer to as the cumulative event probability that may be applied to either reaction or evaporation. We define a specific “reaction time”, τ_i^{Rxn} , for the i^{th} reactive trajectory. This

reaction time was taken to be the first time where the trajectory satisfied the criteria that all hydrogen transfer events have occurred and the C–F bond distance is greater than or equal to 2.0 Å. If there are N_R reactive trajectories at a certain energy E , then the cumulative event probability for reaction is,

$$S_R(r) = \frac{1}{N_R} \sum_{i=1}^{N_R} \Theta(t - \tau_i^{\text{Rxn}}) \quad (2.8)$$

The cumulative event probability increases monotonically from 0 to 1 and reveals the times at which all, or at least most, of the trajectories react. Likewise, we also define the evaporation time τ_i^{Evap} to be the earliest possible time at which the water molecule can be identified as breaking away from the cluster¹. The cumulative event probability for evaporation is,

$$S_{\text{Evap}}(t) = \frac{1}{N_{\text{Evap}}} \sum_{i=1}^{N_{\text{Evap}}} \Theta(t - \tau_i^{\text{Evap}}) \quad (2.9)$$

The cumulative event probabilities for the $n = 1$ and $n = 2$ clusters are shown in Figure 2.7. The physical origin of the delayed threshold effect is completely understandable in terms of time scales. Because the irreversible water evaporation process is in competition with and quenches the reactive process, photo-excited clusters will tend to evaporate before the dynamics can “find” the low energy TS which requires roughly the statistical lifetime, or at least much stronger coupling of the bright state to the full reaction coordinate. On the short time scale set by the direct evaporation process, the reactive trajectories must cross to products at an unfavorable (higher energy) location of the potential energy surface far from the TS. This stands in contrast to thermally activated reactions where water evaporation is reversible and does not quench the reaction. In that case, the clusters may decay and re-condense many times on the time scale of the reaction. The time scales for the direct reaction and evaporation processes are shown in Figure 2.7. It is clear that the time scale for reaction is quite short, ~ 70 fs, and is not strongly dependent upon the level of excitation. The time scale for evaporation is somewhat longer, ~ 100 -150 fs, and shows little energy

¹ We have adopted a dynamically motivated definition of evaporation time in this study. The evaporation time of a trajectory is defined as follows. An evaporative trajectory is identified using the criterion that the distance, R_{rel} , between the center of mass of the fluoromethanol and any existing water molecule (or dimer) becomes greater than a chosen dissociation length. The evaporation time for that trajectory is defined to occur when the relative velocity v_{rel} achieves its local maximum prior to dissociation.

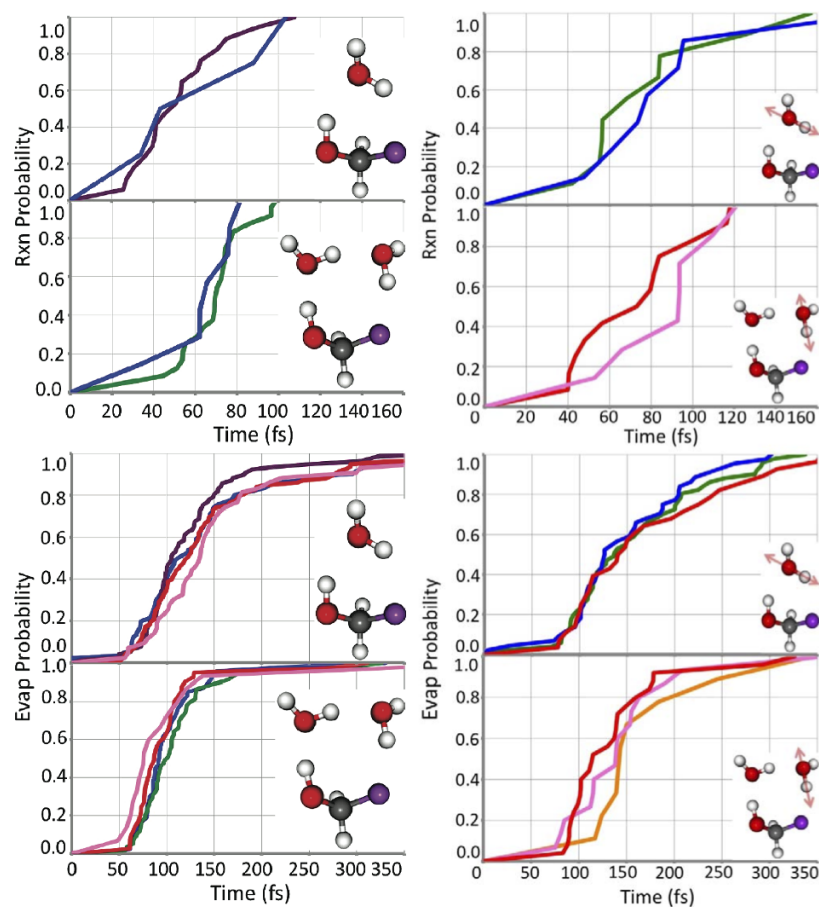


Figure 2.7: The cumulative event probability for the direct reaction (upper panels) and evaporation (lower panels) for the aOH excitation (left) and wOH excitation (right) of both the $n = 1$ and $n = 2$ clusters. Vibrational levels are indicated by color: $v = 4$ (orange), $v = 5$ (pink), $v = 6$ (red), $v = 7$ (blue), $v = 8$ (green), $v = 9$ (violet).

dependence. In the right panels, the event probability curves for the wOH excitation are shown and it is seen that both the direct reaction and evaporation times are somewhat longer for the water excitation case. These longer times indicate a weaker degree of coupling between the wOH local mode to the reaction coordinate which is manifested as the mode specificity seen in the quantum yield of Figure 2.4. The results clearly indicate the presence of a non-statistical direct reaction since the reaction process is effectively over before significant energy randomization takes place. Indeed, if the trajectories did not react quickly, < 200 fs, no reaction was observed in the aOH excited trajectories, although a somewhat longer reaction time scale was observed for the wOH excitations. For comparison, the reaction and evaporation rates were also computed using a crude, harmonic oscillator, microcanonical RRKM theory [53]. As expected, the statistical reaction rates were dramatically lower than the observed dynamical rates with the evaporation rate dominating the reaction. At $\Delta E = 57$ kcal mol $^{-1}$ for $n = 1$, for example, RRKM theory predicts $k_{\text{RXN}} \approx 10^9$ s $^{-1}$ and $k_{\text{Evap}} \geq 10^{13}$.

Since the observed photochemical reaction in the trajectories is clearly non-statistical, it is interesting to contrast the reaction mechanism suggested by the intrinsic reaction path from the potential energy surface to that actually observed in the dynamics. The intrinsic reaction paths emanating from the saddlepoints depicted in Figure 2.8 have been computed for the $n = 1$ and $n = 2$ clusters. Along the reaction path, the two (for $n = 1$) and three (for $n = 2$) hydrogen atoms within the ring are transferred nearly simultaneously. This low energy pathway is a concerted multiple H-atom transfer process. Furthermore, the ring structure at the TS is significantly compressed relative to the equilibrium cluster geometry and the reaction is initiated by the excitation of the low frequency ring breathing mode. A close inspection of the actual trajectories reveals that the true dynamics is quite different. Following the OH excitation, the excited H atom tends to undergo a high frequency chattering motion [176,190] back and forth between the hydrogen bond donor and acceptor oxygen atoms, eventually initiating a sequence of non-concerted hydrogen atom transfers. Furthermore, and just as importantly, the excitation of the low frequency ring mode occurs in the later stages of the reaction process and does not usually collapse, particularly at energies near

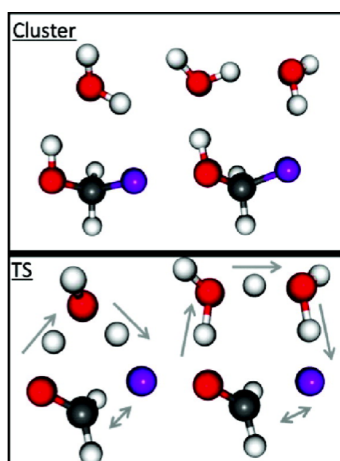


Figure 2.8: The equilibrium and transition state saddle points for the $n = 1$ and $n = 2$ clusters, the same as in Figure 2.3, but with a different perspective and a more detailed description of the reaction coordinates at the saddle points.

the observed reaction threshold, to the small size found at the true saddlepoint of the reaction. Since the dynamical barrier passage problem takes place so far from the low energy TS, it should be expected that a significantly higher minimum level of excitation than ΔE^{TS} is required for reaction.

An example trajectory for the $n = 2$ cluster at selected times is shown in Figure 2.9. The chattering behavior of the H atom is clearly seen during the first 30 fs as the two OH bond lengths rapidly oscillate. The evolution of the slow skeletal coordinates of the ring is found to play a critical role in the reaction. The water-to-water and CH₂FOH-to-water O–O distances are seen to slowly decrease from the cluster values near 2.8 Å to about 2.4 Å at 60 fs. The size of the hydrogen bond ring network does shrink to a geometry closer to that of the saddlepoint; however, by the time the full compression occurs, the hydrogen atom transfers are well underway. This is much different than the distinct initial slow atom motions followed by the H atom transfers predicted by the MEP. The network compression is also systematic in all the trajectories and does not represent random energy flow into the van der Waals bonds.

Some attempt was made to try and isolate a possible H₃O⁺ intermediate to the elimination reaction in this, and the methanediol system of Chapter 3, but, at least in the small cluster sizes considered here, such an intermediate was not found as a stable minimum on the potential energy surface. However, some explanation of the *a*OH excitation dynamics may be understood in terms of charge separations occurring throughout the reaction process. As the C–F bond length slowly increases from 1.4 Å to near 2 Å, an analysis of the Mulliken charges indicates that the F atom acquires a significant negative charge during this phase of the trajectory. Thus, due to the stability of the F[−] anion, the C–F bond greatly weakens and, therefore, lengthens. After several exchanges, the initially excited H atom becomes “permanently” transferred to the water molecule. At this time, the secondary water-to-water H atom transfer process commences. This process may also be accompanied by a chattering H atom exchange, although often only a single step is observed. During this stage of the reaction, a charge separation is apparent between the fluoro-methoxy anion moiety and the protonated water molecule. The final phase of the reactive trajectory involves the hydrogen transfer to the F atom to yield the HF product. Based on the charge assignments, this

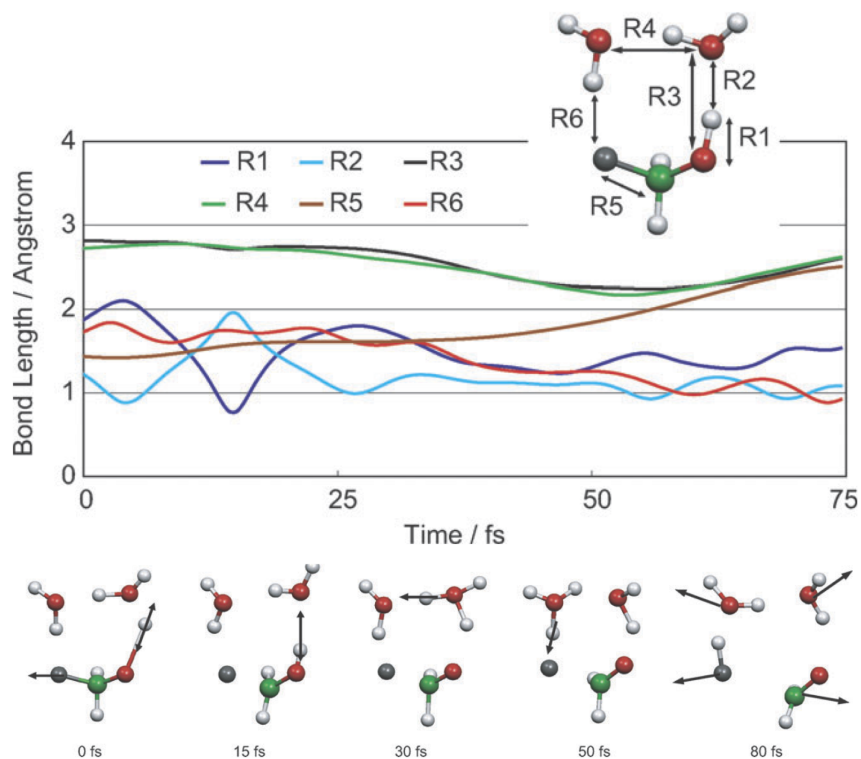


Figure 2.9: An example trajectory at excitation energy $51.8 \text{ kcal mol}^{-1}$ for the αOH chromophore of the $n = 2$ cluster. In the upper panel, several atomic distances are shown over the course of the trajectory. In the lower panel, snapshots of the fluoromethanol molecule at different times are shown.

last step of the reaction has a character similar to a H^+ and F^- ionic recombination. Hence, the last step tends to be quite rapid and direct. Similar dynamics were seen in the $w\text{OH}$ excitation, where significant negative charge buildup on the fluorine was necessary prior to the hydrogen atom transfer event.

2.4 Conclusion

Several conclusions can be drawn from this work. First and foremost, a quantum chemistry prediction of a TS barrier lowering through hydrogen bonding can be insufficient to establish the existence of water catalysis for some photochemical reactions. The competition occurring from the bright state between the reaction and evaporation coordinates must often be modeled dynamically because of the irreversible and non-equilibrium character of the photochemical process. Second, it is apparent from Figure 2.4 that there is a strong effect on the quantum yield $\Phi(E)$ and other dynamical quantities due to the clustering water molecules. Indeed, the difference in the threshold energy for $n = 1$ and $n = 2$ is about 13 kcal mol^{-1} which is even larger than between $\Delta E^{\text{TS}}(n = 2)$ and $\Delta E^{\text{TS}}(n = 1)$. The presence of one or multiple water molecules in the cluster greatly modifies the HF elimination reaction mechanism observed from the isolated molecule. While the presence of the water molecules dramatically lowers the TS saddlepoint barriers, it also provides a low barrier competing evaporation pathway. The elimination pathway is insignificant to the evaporation process if the energy in the molecule is completely randomized, and the large values of the quantum yield, despite the delayed threshold of their onset, indicate that the OH overtone induced elimination reaction is direct rather than statistical.

It would be interesting to model the dynamics in larger clusters to address the issue of whether water catalysis may occur in the solution phase limit $n \rightarrow \infty$. Of course, for a very large cluster, the notion of evaporation is fully replaced by intermolecular energy transfer [44]. We note that the pronounced shift in the observed threshold position with cluster size opens the possibility of photochemical size selectivity in atmospheric processes where the distributions of cluster sizes are known to occur. Finally, while the limitations of the present methods that employed classical

mechanics and DFT will likely result in some quantitative error, we believe the generic delayed threshold behavior observed here will exist, or be a contributing component in the dynamics, in more realistic simulations.

Chapter 3

Will Water Act as a Photocatalyst for Cluster Phase Chemical Reactions? Vibrational Overtone-induced Dehydration Reaction of Methanediol

The possibility of water catalysis in the vibrational overtone-induced dehydration reaction of methanediol is investigated using ab initio dynamical simulations of small methanediol-water clusters. Quantum chemistry calculations employing clusters with one or two water molecules reveal that the barrier to dehydration is lowered by over 20 kcal mol⁻¹ because of hydrogen-bonding at the transition state. Nevertheless, the simulations of the reaction dynamics following OH-stretch excitation show little catalytic effect of water and, in some cases, even show an anticatalytic effect. The quantum yield for the dehydration reaction exhibits a delayed threshold effect where reaction is not observed until the photon energy is far above the barrier energy. Unlike thermally induced reactions, it is argued that competition between reaction and the irreversible dissipation of photon energy may be expected to raise the dynamical threshold for the reaction above the transition state energy. It is concluded that quantum chemistry calculations showing barrier lowering are not sufficient to infer water catalysis in photochemical reactions, which instead require dynamical modeling.

This contents of this Chapter is published in Ref. [100] and is presented here with few modifications.

3.1 Introduction

3.1.1 An Overview of Water Catalysis

Water-mediated chemistry is of central importance to the understanding of chemical, biological, and atmospheric processes that occur in nature. Of interest here is the role of water as a catalyst for non-ionic chemical reactions. It is well known that many such chemical reactions occur at much faster rates in an aqueous environment than in gas phase or in non-polar solvents [10, 16, 163]. The catalytic effect of water may result from one of several mechanisms that include various hydrophobic effects or transition state (TS) stabilization through hydrogen bonding. In the latter scenario, the reaction sometimes proceeds through multiple H-atom transfer processes via a “water wire.” Interestingly, the catalytic properties of water are not restricted to the condensed phase. It has been shown that small gas phase clusters of reagent molecules with water can similarly exhibit catalysis. Molecular clusters have been used to investigate the transition between reactions in gas phase and in solvent environments since they allow a high level of control over the reaction [51, 117, 148, 161, 221]. Such hydrated cluster environments may play a key role in interpreting chemical reactions that occur in the atmosphere where these species exist [1, 63, 94, 108, 150, 172, 181, 205–207, 209, 214, 215]. As a practical matter, theoretical simulations of the reaction dynamics can be greatly simplified in a cluster environment compared to solution since only a few water molecules need to be represented. While the detailed connection between cluster phase and solution phase chemistry has been the subject of great interest, it is not clear when a cluster is sufficiently large to model the solution. In this study, we shall consider catalysis in small water clusters as a problem in its own right rather than as a model for chemistry in aqueous solution.

Theoretical treatments of reactions catalyzed by a barrier lowering mechanism have been presented for a variety of reactions occurring in small water clusters. Following the seminal work of Fukui and co-workers [224], it was realized that the methods of quantum chemistry could be used to find the catalyzed TS barriers defined relative to the most stable van der Waals configuration of the water cluster. A well-known early example was the $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ reaction. Motivated

by experimental observation [86, 96], Morokuma and Muruguma [146] showed that the addition of just one water molecule lowered the transition state barrier by over 25 kcal mol⁻¹ via the formation of a six-membered ring in which the reaction proceeds through a double H-atom transfer [143, 206]. Extending this work to larger water clusters, Tao and co-workers [106] found even lower TS barriers and mechanisms that involved multiple H-atom transfers. An interesting example is the TS stabilization for the $\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$ [215]. Phillips et al. [154] have studied the dechlorination reaction $\text{CH}_2\text{Cl}(\text{OH}) \rightarrow \text{H}_2\text{CO} + \text{HCl}$ and again noted a strong catalytic effect of water in cluster of size $n = 1, 2, \dots$ and 3. Brudnik et al. [11] likewise noted barrier lowering for dehalogenation reactions of trichloro-, trifluoro-, and tribromomethanol. In previous works, we have demonstrated substantial lowering of the TS barrier by water complexation for the reaction $\text{CH}_2\text{FOH} \rightarrow \text{CH}_2\text{O} + \text{HF}$ reaction, described in detail in Chapter 2, for clusters containing up to three water molecules [99, 188]. Numerous other theoretical studies can also be cited that demonstrate the power of quantum chemistry methods to reveal TS barrier lowering for reactions in water clusters [8, 38, 82, 84, 90, 120, 182, 231].

3.1.2 Water Molecules as Catalysts in Photochemistry

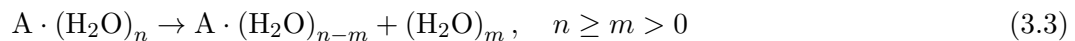
Our primary objective is to elucidate the role of water molecules as possible catalysts for photochemical reactions. The intellectual centerpiece of our work is the essential difference between photo-induced and thermally induced chemical reactions. We shall focus on chemical reactions in that occur on the ground electronic state potential energy surface, which could be photo-initiated by vibrational overtone excitation, rapid internal conversion, or stimulated emission pumping. Overtone excitation, in particular, has been used successfully to observe the competition between reaction and energy flow. The excitation process is simple and the excited system evolves on the better characterized ground state potential energy surface [15, 34, 41, 61, 117]. We further specialize to cases where clustering with a few water molecules leads to a significant lowering of the transition state barrier relative to reagents. For thermally induced reactions, we expect that such “barrier lowering” should strongly signal catalytic behavior. Indeed, it is reasonable to

believe that a conventional transition state theory (TST) viewpoint would be valid since, under thermal conditions, a near equilibrium distribution of reagent clusters is maintained. Hence, the free energy of activation, $\Delta G^\ddagger$, should track downward with the barrier upon complexation and the rate coefficient (that multiplies the cluster concentration in the rate law) should grow according to the standard expression [201],

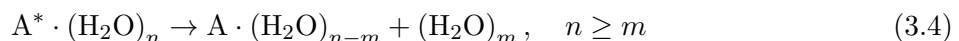
$$k(T) = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{k_B T}} \quad (3.1)$$

In Equation 3.1, we ignore complexities such as quantum tunneling and “dynamical solvent” effects due to clustering.

In the previous chapter, we have argued that the distinction between thermal and photochemical reactions should be analyzed in terms of the competition between processes of reaction and cluster evaporation. If we consider a generic unimolecular chemical reaction of the form $A \rightarrow$, then we have two cluster phase processes,



For neutral reactions, we presume that the barrier for the reactive process, Equation 3.2, is significantly higher than that of the evaporative process, Equation 3.3. Indeed, for the case of fluoromethanol, which we have considered previously [99, 188], the catalyzed reaction barriers are on the order of 20 kcal mol⁻¹ while the evaporative energy per water is on the order of 5 kcal mol⁻¹. For thermal processes, the rate of evaporation is thus much higher than that of the reaction. Nevertheless, the existence of a rapid evaporative channel, Equation 3.3, does not fundamentally alter the validity of the TS rate expression, given by Equation 3.1, which is to be applied to the cluster concentration. The equilibrium distribution of reagent complexes, $A \cdots (H_2O)_n$ is maintained since the clusters may evaporate and reform many times on the time scale of the chemical reaction. In other words, the evaporative process in Equation 3.3 is reversible under thermal conditions. For photochemical reactions, $A + h\nu \rightarrow A^* \rightarrow B$, the situation is different. The evaporative process,



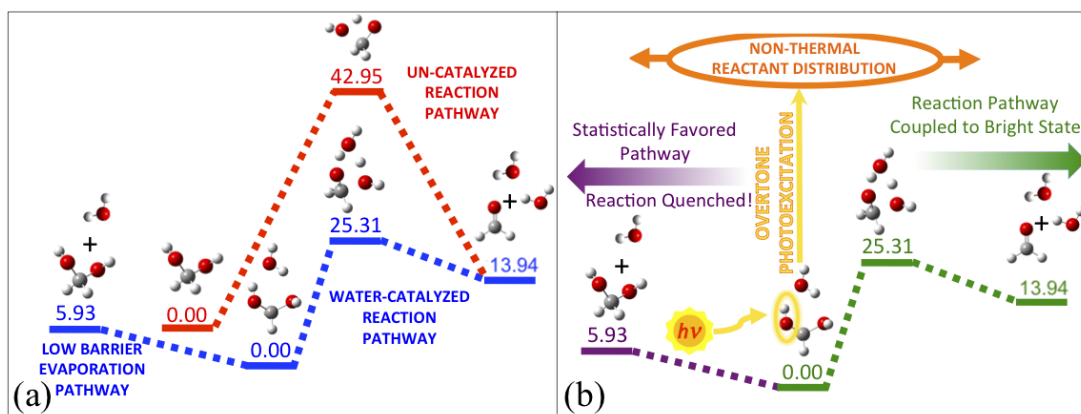


Figure 3.1: In (a), a schematic of how complexation of one water molecule lowers the barrier to dehydration of methanediol by almost 18 kcal mol⁻¹. In (b), the competing processes of reaction and evaporation. In a photo-excitation, e. g. an overtone OH-vibration, the cluster is excited into a non-thermal distribution where thermal predictions may no longer hold. The zero point corrected energies shown are in kcal mol⁻¹ and are calculated from B3LYP/6-31+G(*d,p*), see Table 3.2.

is now irreversible. That is, the photon energy cannot be “redeposited” into the cluster when the cluster is reformed through collision, $A^* \cdot (H_2O)_{n-1} + H_2O \rightarrow A \cdot (H_2O)_n$. Thus, the evaporation can quench the reaction by dissipating the photon energy and it is therefore necessary to construct a model in which both processes Equations 3.2 and 3.3 act in competition. Because of the low barrier to evaporation, the evaporation typically occurs on a sub-picosecond time scale. Since such times are generally too short to allow energy randomization within the molecular clusters, statistical theories such as TST or Rice-Ramsperger-Kassel-Marcus (RRKM) theory are unreliable and the rates must be obtained through dynamical simulation.

3.1.3 The Water Catalyzed Dehydration of Methanediol

In this work, we consider the possibility of water catalysis for the vibrational overtone-induced dehydration reaction of methanediol (also known as methylene glycol),



It is well known that in aqueous solution, formaldehyde (CH_2O) rapidly hydrates to form methanediol, $\text{CH}_2(\text{OH})_2$, by the reverse of Equation 3.5,



It is observed that the molecule is mostly in methanediol form in solution phase while it is dominantly in formaldehyde form in the gas phase [134, 147, 222]. This makes a study of the reaction in small water clusters particularly interesting as a transition regime. The solution phase rate coefficients for the hydration and dehydration reactions have been extracted from conventional kinetic measurements [219, 220]. In dilute solution at ambient temperatures $T = 300$ K, the rate coefficient, k_d , for the reaction in Equation 3.5 was observed to be about $9.7 \times 10^{-3} \text{ s}^{-1}$, while the activation energy for the reaction in Equation 3.6 was found to be $13.3 \text{ kcal mol}^{-1}$. The rate coefficient was fitted to the form,

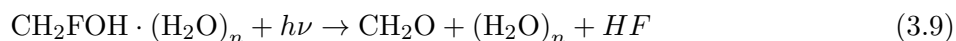
$$k_d = (4.96 \times 10^7 \text{ s}^{-1}) e^{-\frac{6705}{T(\text{K})}} \quad (3.7)$$

The pseudo-first order rate coefficient for the hydration reaction in Equation 3.6 in dilute solution was,

$$k_h = (2.04 \times 10^5 \text{ s}^{-1}) e^{-\frac{2936}{T(\text{K})}} \quad (3.8)$$

The activation energy for the reaction in Equation 3.5 is $5.83 \text{ kcal mol}^{-1}$, while the overall enthalpy of hydration under these conditions was $-7.50 \text{ kcal mol}^{-1}$. The gas phase thermochemistry of the reaction in Equation 3.5 was determined theoretically by Goddard and co-workers [84]. The methanediol is energetically favored at 298.15 K with $\Delta H = 9.8 \text{ kcal mol}^{-1}$ for reaction 3.5, but formaldehyde is thermodynamically favored with $\Delta G = -1.1 \text{ kcal mol}^{-1}$. Interestingly, the zero point corrected barrier to dehydration is found to be $44.3 \text{ kcal mol}^{-1}$, a number vastly higher than the activation energy measured in solution phase. In light of these results, the case for water catalysis of the dehydration reaction of methanediol in solution phase is strong.

The present work on methanediol is closely related to our previous study of the overtone-induced defluorination reaction of fluoromethanol-water clusters [99, 188],



In that work it was found that, despite significant lowering of the TS barrier by water complexation, the photochemical reaction was not appreciably water catalyzed. Dynamical simulations of the photo-reaction dynamics indicated that the quantum yield for reaction was zero until the photon energy had actually exceeded the uncatalyzed barrier energy for $\text{CH}_2\text{FOH} \rightarrow \text{CH}_2\text{O} + \text{HF}$. This delayed threshold effect was understood in terms of a competition between the reactive process and the energy dissipation process of water evaporation. The present study illustrates the generality of those earlier results. Furthermore, the methanediol system is more amenable to experimental study and is also of practical importance since $\text{CH}_2\text{O}/\text{CH}_2(\text{OH})_2$ is an important atmospheric species.

3.1.4 Chapter Overview

The remainder of this report is organized as follows. In Section 3.2, we review the theoretical methods used in this study. Since the approach used here is quite similar to that employed by us previously [99, 188], the discussion is brief. In Section 3.3, we present the main result obtained, namely, the observation of a pronounced delayed threshold effect in the quantum yield for the reaction in the methanediol-water clusters. It is argued that this delayed threshold largely suppresses the catalytic activity of water. In Section 3.4, the dynamics of the photo-excited clusters is discussed in detail. A relatively simple picture is advanced to rationalize the existence of the delayed threshold. Finally, in Section 3.5, we summarize our conclusions.

3.2 Quantum Chemistry Methodology: Reactive Dynamics Simulations in Hydrated Clusters

The dehydration reaction of methanediol-water clusters is studied using ab initio dynamics simulations. Our specific objective in these computations is to extract the quantum yield for overtone-induced reaction as a function of the photon energy. The theoretical methodology we used in this study is essentially the same as those employed in our previous study of overtone-induced reactions for fluoromethanol-water clusters [99, 188]. Here, we shall only briefly review the computational strategy and refer the interested reader to a more detailed discussion presented in

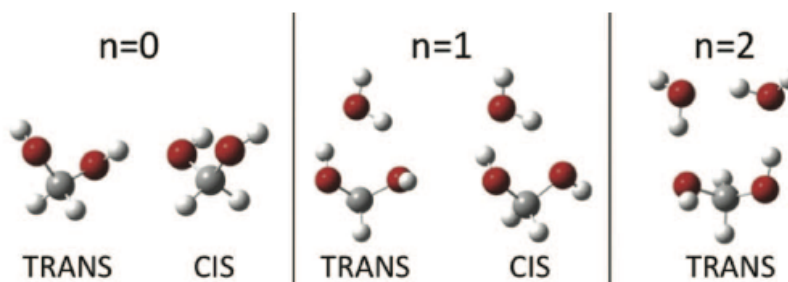


Figure 3.2: Equilibrium geometries of methanediol and its first two hydrated clusters calculated using B3LYP/6-31+G(*d,p*). The tran- and cis- conformers differ by the relative orientation of the OH-groups. Only the the eight-membered ring conformer is presented for the $n = 2$ cluster. Another conformer was found for the bare molecule using B3LYP/6-31+G(*d,p*), but was not found using the higher level quantum chemistry and is not included in our discussion.

Chapter 2.

The initial configuration of the reagent species is assumed to be the most stable van der Waals structure of the methanediol hydrated complexes $\text{CH}_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_n$ for $n = 0, 1$, and 2. The equilibrium structures were optimized using B3LYP/6-31+G(*d,p*) [4, 26, 49, 65, 71, 107, 136] using the Gaussian03 package [50]. This level of quantum chemistry is consistent with that used for the dynamical simulations. To judge the accuracy of the calculations, and for certain comparisons to experiment, higher level computations were also carried out. Using the Molpro quantum chemistry package [218], coupled-cluster energies were computed at MP2 geometries employing the CCSD(T)/aug-cc-pVTZ//MP2/6-311++G(3*df*,2*pd*) method [196]. For both the bare methanediol molecule and the monohydrate complex ($n=1$), two low-lying equilibrium structures were located. As shown in Figure 3.2, the structures differ in the orientation of the two OH-groups of the diol. When the two OH-groups of the diol point parallel to each other, we have the cis-conformer, while if the OH-groups point in opposite directions we have the trans-conformer. The zero point corrected energies of these structures differ by just under 3 kcal mol⁻¹ for both $n = 0$ and $n = 1$ with the trans-conformer being the more stable (see Table 3.2). Thus, we expect the trans conformer to dominate the equilibrium distribution at room temperature and it will be used to define the initial conditions of the simulations. For $n = 2$, the cis-conformer was not found for the eight-membered

Table 3.1: Calculated energetics of hydrated methanediol cluster ($n = 0, 1, 2, 3$) decomposition reactions and hydrated formaldehyde water binding, in kcal mol⁻¹, with zero point energy corrections at B3LYP/6-31+G(*d,p*) (CCSD(T)/aug-cc-pVTZ//MP2/6-311+G(3*df*,2*pd*)). Basis set superposition error corrected values [9] of evaporation energy are shown in ‘[]’. See text for more details.

H ₂ C(OH) ₂ cluster (n)	TS barrier	Endothermicity	1 st Evaporation	H ₂ O-binding per H ₂ O
0 trans	42.95 (44.62)	8.01 (8.08)		
0 cis	40.15 (42.29)	4.95 (5.75)		
1 trans	25.31 (29.56)	13.94 (14.36)	5.93 (6.28)	5.93 (6.28) [5.17]
1 cis	22.56 (27.14)	10.96 (11.47)	5.75 (5.72)	5.75 (5.72) [4.90]
2 trans	20.41	23.75	9.80	7.87
3 ring	20.62	31.95	8.21	7.98
H ₂ CO cluster (n)			1 st Evaporation	H ₂ O-binding per H ₂ O
1			3.15 (3.60)	3.15 (3.60) [2.80]
2			6.94 (6.36)	5.04 (4.98)
3 ring			7.87	5.98
4 ring			6.34	6.07

ring and does not exist as a stationary point at this level of theory. The $n = 1$ and the $n = 2$ clusters form puckered, hydrogen-bonded six- and eight-membered-ring structures, respectively, that incorporate one OH-group from each water molecule. As seen in Figure 3.2, only one of the diol OH-groups is included as part of the hydrogen-bonded ring while the other OH-group is oriented away from the ring. We note that in the dynamical simulations it is the diol OH-group lying within the ring that will receive the photon energy. There are also other higher energy conformers that do not form eight-member rings that exist for $n = 2$. These conformers form the six-membered ring structure, similar to $n = 1$, but with another water molecule excluded outside the ring system and hydrogen bonded to one of the ring’s “dangling” OH groups. We do not include them in our study, as we expect the $n = 1$ cluster to be somewhat representative of them (their TS energies for dehydration are similar to the $n = 1$ cluster) since they share similar ring conformations. The water evaporation energies were computed from the energy differences of the ground vibrational states,

$$\Delta E_{\text{EVAP}}(n) = E_0 [\text{H}_2\text{O} + \text{CH}_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_{n-1}] - E_0 [\text{CH}_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_n] \quad (3.10)$$

The second water molecule in the $n = 2$ eight-membered ring conformation is seen to be bound much more strongly than the first. The energetics of the most stable, ring, conformation for the $n = 3$ is also included. It is seen that the third water molecule is bound less strongly than the second, and the binding energy per water molecule remains approximately constant between adding the second and third water. This trend continues with more water molecule additions and indicates the eight-membered hydrogen bond ring in this system is a particularly stable conformation. Basis set superposition error (BSSE) is present in the calculations [211] and BSSE corrected [9] binding energies at the B3LYP/6-31+G(d,p) level are shown for reference. The BSSE correction, however, is both computationally time consuming and ambiguous to incorporate into the “on-the-fly” dynamics calculations, and since most of the dynamics occur in the cluster rather than the dissociated product, we do not treat it beyond brief mention. That BSSE generally over stabilizes the water binding and evaporation energies is evident from Table 3.2. The most stable conformations of the hydrated

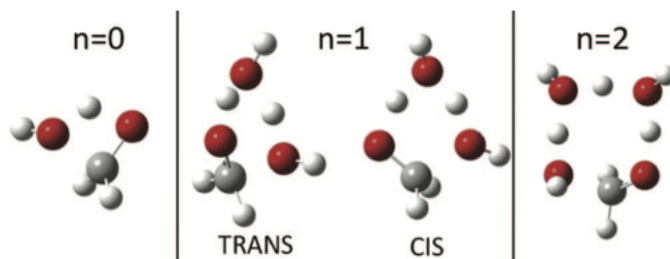


Figure 3.3: Transition state geometries for methanediol dehydration for $n = 0, 1$ and 2 obtained using B3LYP/6-31+G(d,p). The trans- and cis-conformations observed in the equilibrium clusters carry over to the TS for $n = 1$. All transferred hydrogen atoms lie roughly halfway between the donor and acceptor oxygen atoms at the saddle point.

clusters of the formaldehyde products are also given in Table 3.2 for comparison. The formaldehyde clusters have lower water binding energies than the corresponding methanediol clusters, though the $n = 3$, which is the product of the reaction of the eight-membered $n = 2$ methanediol cluster, has a relatively high first evaporation energy. A comparison of the B3LYP energies to the more accurate CCSD(T) results, shown in parentheses in Table 3.2 suggest that the B3LYP results are expected to have errors on the order of several kcal mol⁻¹. This level of accuracy is consistent with our previous studies of intramolecularly hydrogen-bonded systems such as glycolic acid [67], glyoxylic acid [156, 189], and fluoromethanol [99, 188]. In Table 3.2, the endothermicity is defined to be the zero point corrected energy between dissociated formaldehyde and water molecules and the stable methanediol cluster reactant. Water binding energies in the $n = 1$ clusters are defined to be relative to the bare methanediol conformations they are connected to by a minimum energy path (MEP) along the evaporation channel.

For the purpose of comparing dynamical simulation to statistical theory, we have also located and characterized the transition state structures. For the $n = 1$ species, a cis- and trans-conformation of the TS were found; for $n = 0$ and $n = 2$, only the trans-conformation was found. As shown in Figure 3.3, these structures are analogous to the equilibrium cluster structures shown in Figure 3.2. The water complexation introduces a strong barrier lowering of the TS. The TS energies shown in Table 3.2 reveal that complexation with two water molecules already leads to a

lowering of the barrier by over 22 kcal mol⁻¹. An interesting consequence of the eight-member ring stability for the $n = 2$ cluster is seen in the energetics, where the transition state of the $n = 2$ ring is lower than both that of the $n = 1$ and the $n = 3$ ring conformers. Apparently, the eight-membered ring provides a much more optimal configuration for the hydrogen transfer event transition state crossing. In the $n = 2$ cluster, the angles formed by all the O_{DONOR}-H_{TRANSFER}-O_{ACCEPTOR} are much closer to 180° than in the other hydrated clusters. This can be seen in the TS geometries in Figure 3.3.

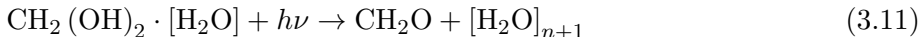
It is important to point out that the quantum chemistry calculations of the TS clearly indicate that the mechanism of the catalyzed reaction is strongly “concerted” for both $n = 1$ and $n = 2$. That is, at the barrier configuration, all the exchanged hydrogen atoms move simultaneously and synchronously from the donor to the acceptor oxygen.

The ab initio “on-the-fly” trajectory simulations were carried out using ensembles of 100-200 statistically selected initial conditions at each photon energy studied. Zero point energy was placed into the vibrational normal modes with random phases using fixed normal mode sampling to create an ensemble of initial conditions. The initial (pre-excitation) cluster thus corresponds to $T = 0$ K and $J = 0$ [123]. For most of the calculations, the chromophore for overtone excitation was taken to be the OH-stretching local mode of the “donor” OH-group of methanediol, see Figure 3.1, that lies within the hydrogen bonded ring. We shall refer to this mode as *a*OH. For the $n = 1$ case, we also investigated a different chromophore, specifically the water OH stretching mode within the ring, hereafter denoted as *w*OH. We adopt the conventional view that the oscillator strength for the transition is carried by the OH-local mode, so the overtone excitation energies (i. e. the photon energies) are taken to be the eigenstates on the one dimensional potential curve obtained from the stretching the OH chromophore along its local mode coordinate with the remaining coordinates frozen at the equilibrium cluster geometry values. For the OH overtone levels, the appropriate quantized photon energy was deposited into the classical local mode coordinate of each initial condition with a random phase. The trajectories within each excitation energy ensemble were constructed to have the same energy so that comparison to statistical theories was sensical [188].

While there is no unique semiclassical prescription for choosing initial conditions in this problem, the present approach does provide a physically reasonable result with no serious anomalies. We note that it is also possible to employ other sampling schemes for the initial conditions, such as the Wigner distribution, although we have not used these methods here [186]. A comparison of the results using a different sampling method may be interesting, but since we are exciting the OH chromophore to a relatively high overtone state, with a likely more classical phase space distribution than the lower vibrational states, we have taken the classical sampling to be adequate.

The trajectories were integrated using the variable step-size Hessian based predictor-corrector method of Miller et al. [139]. The potential energy surface and forces are computed “on-the-fly” using ab initio calculations from Gaussian03 at the B3LYP/6-31+G(*d,p*) level. The trajectories were integrated with a step size in the range of 0.5 to 1 fs and the total propagation time was generally less than 600 fs¹. From previous studies of IVR in polyatomic molecules, we expect that the classical representation of the vibrational dynamics will be reasonable on short timescales and the quantum effects will only prove crucial if the simulation is extended beyond a “breaktime” [58]. For longer times, the quantum mechanical rate of IVR is typically slower than the classical analog. However, in the present problem, the excitation energy is well above the barrier height and reaction dynamics of interest occurs quickly (usually on the order of 100 fs), so it seems likely that the classical model will be reasonable.

The quantum yield for the dehydration reaction,



is defined as the fraction of reactive trajectories within each ensemble. The reactivity of each trajectory is determined by a distance criterion applied to all the transferred hydrogen atoms and the breaking of the C–O bond length. While reactive trajectories usually produced free (unclustered) CH₂O molecules, occasionally reactions did yield a product CH₂O in a cluster with one water molecule. In general, a great deal of the reaction energy was transferred to formaldehyde transla-

¹ Subsets of trajectories, particularly near the reaction threshold were propagated much longer, usually between 1 to 1.5 ps to study trajectories classified as “non-reactive” for reactivity. No reactive events were observed.

tion in the product. In all cases, the final excitation energy of the product cluster was lower than the barrier and back reaction to form methanediol was ignored. The propagation for non-reactive trajectories was halted when the cluster evaporated or at long times when the initial excitation energy was randomized within the cluster. A conservative definition of evaporation was used in this study, defined in terms of water-methanediol center of mass distance and escape velocity [188], and identifying a specific time for an evaporation event was sometimes quite ambiguous, particularly at lower excitation energies. However, extended trajectory propagation times confirmed that all events classified as evaporations were certainly evaporations, and those that were not generally reached the unambiguous evaporation criteria at longer time scales.

3.3 The Observation of a Delayed Threshold Effect in the Quantum Yield

3.3.1 The Delayed Threshold and Anticatalysis

The main numerical result of this work is presented in Figure ?? . The observed quantum yield for the methanediol dehydration reaction, $\Phi(E)$, is shown as a function of the photon energy $E = h\nu$. The square symbols represent the quantum yield for excitation of the *a*OH-chromophore at the photon energies corresponding to the $\text{OH}(\nu' \leftarrow 0)$ overtone transitions with $\nu' = 4 - 8$. The results for the dihydrate cluster ($n = 2$) are shown with red, while those for the monohydrate cluster ($n = 1$) are shown in blue. The blue circles depict the quantum yield for the *w*OH chromophore for the $n = 1$ cluster. For reference, we indicate in the figure the energies of the TS for $n = 0, 1$, and 2. The most salient feature apparent in this plot is the occurrence of a clear delayed threshold; for clarity, the thresholds are depicted with dashed red and blue lines. The onset of reaction for both $n = 1$ and $n = 2$ clusters occurs well above the corresponding transition state barrier. The delayed threshold is most pronounced for the monohydrate that occurs at approximately 50 kcal mol⁻¹ excitation energy, almost 25 kcal mol⁻¹ above the calculated $n = 1$ transition state barrier. In fact, the dynamical threshold lies about 7 kcal mol⁻¹ above the transition state barrier of the bare ($n = 0$) methanediol implying that clustering with water is actually “anticatalytic” in this

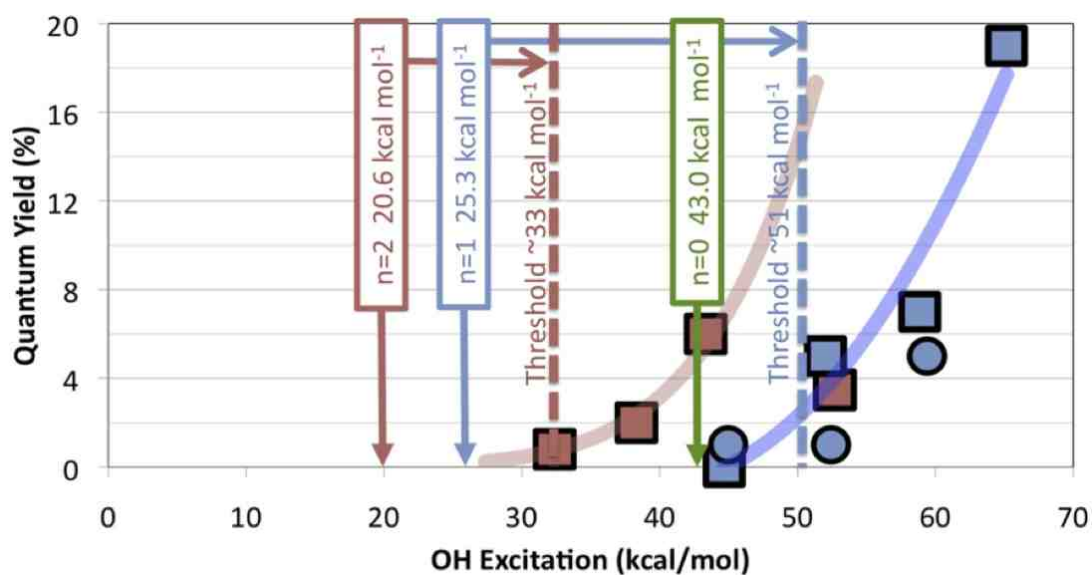


Figure 3.4: The observed dehydration quantum yield, the fraction of reactive trajectories, versus the photon energy for the $n = 1$ (blue) and $n = 2$ (red) clusters obtained from ab initio simulations with $T = 0$ K and $J = 0$. The squares represent excitation of the diol chromophore, aOH , while the circles represent excitation of the water chromophore, wOH . The solid curves are drawn to emphasize the location of the dynamical thresholds.

case. The delayed threshold effect is less dramatic, but still present, in the $n = 2$ cluster. The threshold for the $n = 2$ reaction lies at approximately 33 kcal mol^{-1} above the predicted transition state barrier, and 10 kcal mol^{-1} below the $n = 0$ barrier. Therefore, while the addition of the second water molecule is not anticatalytic, it does suppress the catalytic effect of the water from what is expected from the barrier-lowering.

3.3.2 Effects of Mode Specificity

It is also interesting to compare the results obtained for the two chromophores for the $n = 1$ species. While the position of the dynamical threshold is roughly comparable, we note a significant difference in the quantum yield for the two cases. Apparently, the *a*OH excitation leads to significantly more reaction than does the *w*OH excitation at comparable energy. There are obviously other OH-groups within the water cluster than are also capable of overtone excitation and so the present results indicate that there is likely to be significant mode specificity. Of particular interest, due to the suggested concerted nature of the hydrogen transfers along the reaction path, are possible excitations of combinations of the OH stretches with the hydrogen bonded network. Indeed, two batches of 50 trajectories were propagated for 250 fs for the $n = 2$ case with energies of $33.4 \text{ kcal mol}^{-1}$ and $53.5 \text{ kcal mol}^{-1}$ placed in a normal mode corresponding to the concerted stretches of all three OH groups in the hydrogen bonded network. While it is intuitive that such a bright state should enhance the reaction probability, the observed quantum yields for the 33.4 and $53.5 \text{ kcal mol}^{-1}$ excitations, 2% and 16%, respectively, do not contradict the threshold behavior observed in Figure 3.4. At the low excitation energy of 33 kcal mol^{-1} , little or no mode specificity can be seen in the quantum yield. At the higher energy of 53 kcal mol^{-1} , the concerted excitation results in a much higher quantum yield than the local mode excitation. The local mode excitation experiences an anomalous drop in quantum yield at this particular energy and whether this trend continues at higher energy or the quantum yield rebounds to follow the earlier progression was not explored. However, enhancement of the reaction near the threshold resulting from distributing the excitation energy among the OH groups within the hydrogen bond network seems, if perceptible,

non-dramatic.

3.3.3 Comparisons of Dynamical Results to Statistical Expectations

It is useful to contrast the present dynamical results with our naïve expectations about how the reaction should proceed based on statistical theory. In the absence of the evaporative channel, Equation 3.3, or collision with a buffer gas, the energized n -hydrate cluster should react with unit probability when the photon energy excites the molecule above the TS barrier, $E^{\text{TS}}(n)$. Thus, if the initial cluster is at $T = 0$ K, the classical quantum yield should be a step function, $\Phi(E = h\nu) = \Theta(E - E^{\text{TS}}(n))$. When the cluster can dissipate the excitation energy by collision or evaporation, then the time scale of the reaction must be taken into account. Consider low pressures where collisions can be neglected, but evaporation and reaction are competitive unimolecular processes². If the photon energy rapidly randomizes in the complex, then the quantum yield can be written in terms of RRKM microcanonical rate coefficients for reaction and evaporation,

$$\Phi_{\text{RRKM}}(E) = \frac{k_{\text{rxn}}(E)}{k_{\text{rxn}}(E) + k_{\text{evap}}(E)} \quad (3.12)$$

where the photon energy, E , is added to the zero point energy of the complex. Since the barrier to evaporation is low compared to the TS barrier, the evaporation rate dominates and $\Phi_{\text{RRKM}}(E)$ is expected to be very small. In Figure 3.5, we show the RRKM results computed for the $n = 1$ cluster. The calculations were carried out by computing the RRKM rate coefficients in the harmonic oscillator rigid rotor approximation, see Chapter 4, assuming $J = 0$ and using the Beyer-Swinehart state counting method [7] to compute the necessary sums and densities of states. The evaporation RRKM rate constant was somewhat more difficult to calculate, as no saddle point geometry was found for the process. Instead, the degree of freedom corresponding to the translation between the water and methanediol molecules was taken as a reaction coordinate, and the rate coefficient was calculated as a function of this coordinate as well as the energy. The evaporation rate constant used was the minimum as a function of the relative translation between the two dissociating molecules.

² These “low” pressures may actually be quite substantial since we require only that the collision frequency be lower than the unimolecular reaction rate.

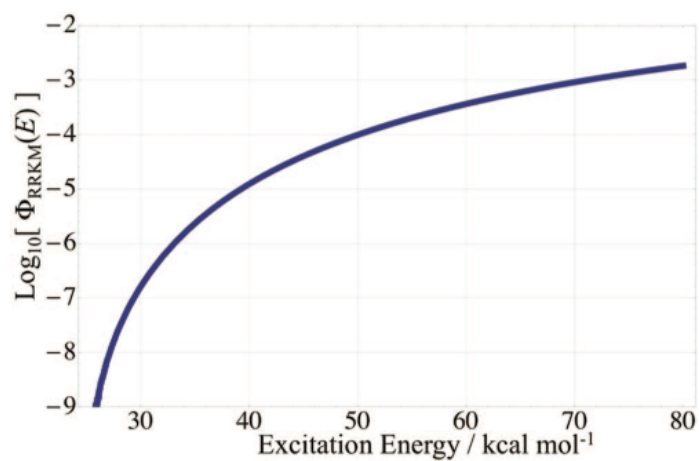


Figure 3.5: The quantum yield for the reaction of the $n = 1$ cluster, $\text{CH}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, computed using RRKM. The excitation energy equals the photon energy for the $T = 0$ K cluster. The result is independent of chromophore for this statistical treatment. At 5 kcal mol⁻¹ above the catalyzed barrier of 25.3 kcal mol⁻¹, the quantum yield is seen to be about 10^{-7} .

For the excitation energies we have simulated, the statistical prediction for the quantum yield is seen to be orders of magnitude smaller than that observed in the dynamical calculations.

The disagreement between the statistical predictions and the dynamical simulations clearly indicate a direct character in the reaction dynamics. In Section 3.4, we discuss the mechanistic details of the direct reaction process.

3.4 Discussion of the Reaction Mechanism

3.4.1 Reaction Probabilities and Time Scales

To understand the origin of the delayed threshold effect and the concomitant suppression of water catalysis, we have analyzed the behavior of the ab initio trajectories that were generated in the simulations. In a general mechanistic sense, the trajectory dynamics were straightforward. Consistent with the TS geometries shown in Figure 3.3, the dehydration reaction always proceeded via a multiple hydrogen atom transfer process with the hydrogen bonded ring, i. e. the “water wire”. For $n = 1$, this involves two hydrogen atom transfers while for $n = 2$ there were three hydrogen atom transfer steps. For reactive trajectories, the ring structure remained intact until all the hydrogen atom transfer steps were complete. On the other hand, evaporative trajectories were heralded by the rupturing of hydrogen bonds within the ring before the reaction is complete, although the excited hydrogen atom may “chatter” back and forth between donor and acceptor oxygen atoms following excitation. The detailed features of the reactive motion, and of the energy flow within the activated cluster, are found to be rather complicated and require a more in-depth discussion.

To establish the times scales for the direct reactive and evaporative events, we have constructed a diagnostic quantity we refer to as the cumulative event probability that may be applied to either reaction or to evaporation. We define a unique “reaction time”, τ_i^R for the i^{th} reactive trajectory as the earliest time at which the distance criteria for the reaction are satisfied, that is all the hydrogen atoms are transferred and the C–O bond length is sufficiently large. If there are

N_R reactive trajectories at a certain energy E , then the cumulative event probability for reaction is,

$$S_R(t) = \frac{1}{N_R} \sum_{i=1}^{N_R} \Theta(t - \tau_i^R) \quad (3.13)$$

As a function of time, t , $S_R(t)$, goes monotonically from 0 to 1 and reveals the times at which most of the trajectories react. Likewise, if we define an evaporation time τ_i^{Evap} to be the earliest time for which a water molecule has broken from the cluster with sufficient velocity to escape, we may define the cumulative event probability for evaporation as,

$$S_{\text{Evap}}(t) = \frac{1}{N_{\text{Evap}}} \sum_{i=1}^{N_{\text{Evap}}} \Theta(t - \tau_i^{\text{Evap}}) \quad (3.14)$$

In Figure 3.6, we show the cumulative event probabilities for reaction (left panels) and evaporation (right panels) for $n = 1$ and $n = 2$ clusters excited through the αOH chromophore, the dotted line in the first panel shows one of the $w\text{OH}$ excitations for reference. The line coloring indicates the level of excitation energy. The mean reaction time is 50 ± 15 fs for both $n = 1$ and $n = 2$. The reaction is essentially complete by $t = 100$ fs with the exception of a single “unusual” trajectory for the $v = 6$ ensemble of the $n = 2$ cluster.

The observed evaporation process occurs on a somewhat slower time scale than does the reaction. The $n = 1$ ensembles have a mean evaporation time of about 100 fs. Furthermore, the evaporation events for $n = 1$ are seen to be remarkably insensitive to the level of excitation. The mean evaporation times for the $n = 2$ ensembles are longer and the ensembles are more distinct from one another. However, we believe that some of the difference between the $n = 1$ and $n = 2$ cumulative evaporation probability comes from technical difficulties from precisely defining the evaporation time for the $n = 2$ clusters. The insensitivity of the results to excitation energy shown in Figure 3.6, is completely consistent with a direct reaction mechanism. Indeed, the time scale for the reaction is far too short to permit energy randomization within the complex. The RRKM rate for $n = 1$ is over 10^4 times slower than the dynamical rate at 40 kcal mol⁻¹. Some quantitative appreciation for the rate of intramolecular energy relaxation (IVR) is provided by the numerical results shown in Figure 3.7. The the classical energy of the excited OH stretch local

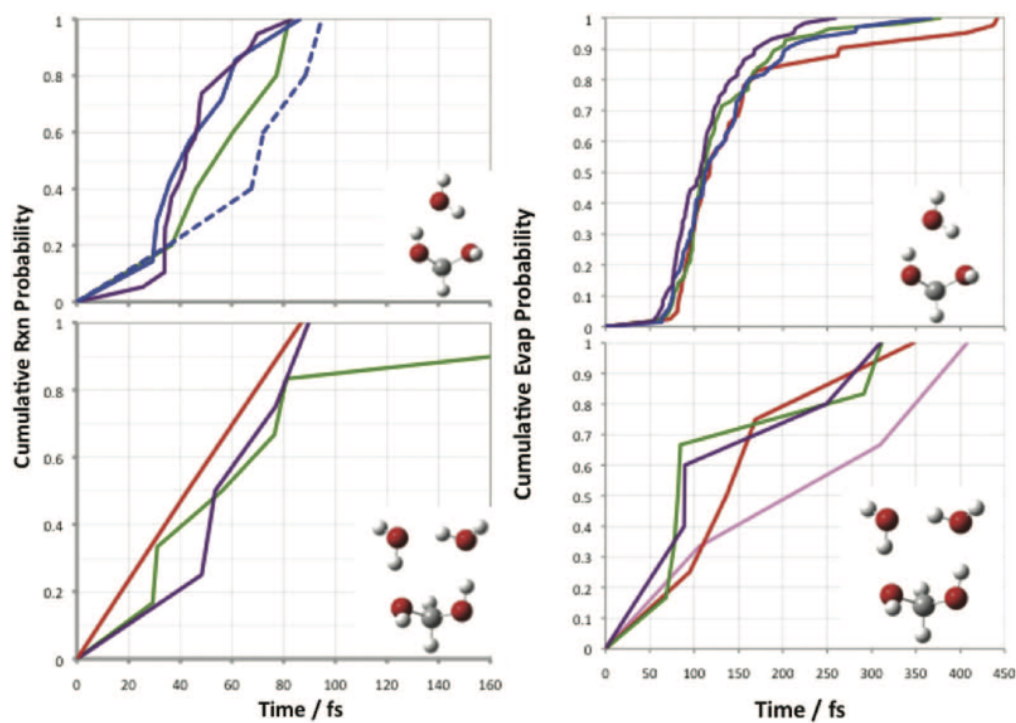


Figure 3.6: Cumulative reaction and evaporation probability functions for the reaction (left panels) and evaporative (right panels) trajectories for $n = 1$ (upper panels) and $n = 2$ clusters (lower panels). The excited vibrational states are labeled by $v = 4$ (pink), $v = 5$ (red), $v = 6$ (green), $v = 7$ (blue), and $v = 8$ (violet).

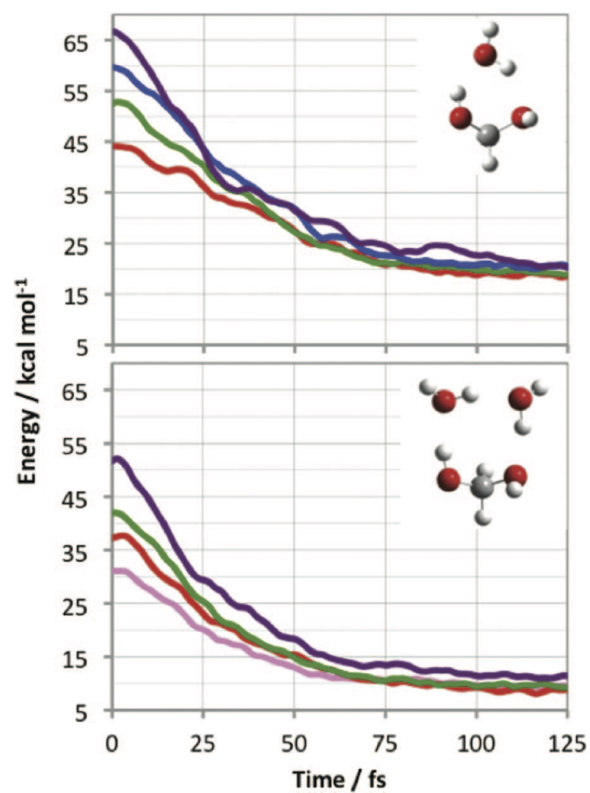


Figure 3.7: The average excitation energy above the zero point energy for the $a\text{OH}$ excitation of the $n = 1$ and $n = 2$ clusters. The results are the average of the classical local mode energies of the OH stretch over all non-reactive trajectories in the ensemble. The vibrational states are labeled by $v = 4$ (pink), $v = 5$ (red), $v = 6$ (green), $v = 7$ (blue), and $v = 8$ (violet).

mode is plotted versus time after excitation. The mean OH energy decays monotonically at a rate that is not strongly dependent on the initial excitation. It is seen that the $1/e$ excitation lifetime is roughly the same as the mean time of reaction, roughly 50 fs.

The origin of the delayed threshold effect of the quantum yield can be understood conceptually in terms of the time scales. Because the irreversible water evaporation process is in competition with the reactive process, photo-excited clusters will tend to evaporate and quench the reaction before for the dynamics can “find” the low energy regions of the transition state surface. Indeed, the mean time to encounter the TS is the statistical lifetime of $\sim 10^{-10}$ s which is far greater than the observed reaction time, $\sim 10^{-13}$ s. On the short time scale set by evaporation, the reactive trajectories must cross to products at an unfavorable (higher energy) location of the potential energy surface that is distant from the saddle point. This stands in contrast to thermally activated reactions where water evaporation is reversible and does not quench the reaction. In that case, the clusters may decay and re-condense many times on the time scale of the reaction. The cluster evaporation/condensation is modeled in thermal environments by the steady state cluster concentration and not by the activation energy. To understand how the reaction mechanism differs from the low energy pathway passing through the TS, we must examine the atomic motions that occur during the reaction.

3.4.2 Dynamical Pathway Versus Minimum Energy Pathway

We first consider how the reaction is predicted to occur if it follows the minimum energy path (MEP). The minimum energy path is characterized by two somewhat distinct steps as it approaches and crosses the transition state. In the first, the donor and acceptor oxygen atoms in the hydrogen bonded network move closer together, that is, the six ($n = 1$) or eight ($n = 2$) membered rings that characterize the clusters compress. Concurrently, the bond between the carbon and the terminal oxygen bond in the hydrogen bond network begins to lengthen. Once the hydrogen bond ring has contracted and the C–O bond has lengthened, the system then proceeds and crosses to the transition state at the barrier by the simultaneous and concerted transfer of two, for $n = 1$, or three, for $n = 2$, hydrogen atoms between donor and acceptor oxygen atoms in the hydrogen bonded network. Thus,

the early phase of the minimum energy path is dominated by the low frequency modes of the heavy backbone atoms of the cluster, and it is not until the path is in proximity to the saddle point that the multiple hydrogen atom transfer occurs.

In contrast, the excited OH bright state created in the trajectory ensembles places the initial excitation energy into a single OH bond, a mode that has some character of the hydrogen transfer mode needed for reaction, but leaves the slow atom motions with only zero point energy. A hydrogen transfer with the heavy atoms fixed in their reactant configuration requires more than 75 kcal mol^{-1} of energy in the $n = 1$ cluster and more than 65 kcal mol^{-1} in the $n = 2$ cluster. This is clearly far greater than both the transition state barrier energy and the observed threshold energy. Therefore, some coupling of the OH local mode must occur with the large atom motions for reaction to occur.

The compression of the hydrogen bonded network ring is not only a harbinger to reaction in the dynamics, but an excitation of the van der Waals mode between the methanediol and the water molecule that can lead to evaporation. Therefore, the OH stretch-ring compression coupling results in excitation both along the reaction and evaporation coordinates. Although the coupling to the van der Waals was usually insufficient in the trajectories to cause a complete and simultaneous collapse of the donor-acceptor oxygen distances in the hydrogen bonded network to their transition state values prior to hydrogen transfer events, it was sufficient to effectively lower the energy enough to make the transfer possible. The collapse, however, occurs at the expense of exciting the evaporation mode. Indeed, if the hydrogen transfer does not occur during the short time the oxygen distances can lower the transfer energy, the van der Waals mode will reach its inner turning point, reverse, and the water will be evaporated eliminating the catalytic effect and removing excitation energy from the complex. Figure ?? shows the average separation of the water and methanediol centers of mass averaged at each time over the ensemble for each excitation energy of the $n = 1$ $a\text{OH}$ excitation. Regardless of the excitation energy, the ring compression begins after about 20 fs, roughly the time of two OH vibrations. The compression achieves a minimum at approximately 40 fs and the water is on its well way along the evaporation coordinate by 60 fs. The minimum distance achieved by the ring compression depends strongly on the excitation energy. At high OH excitation energy,

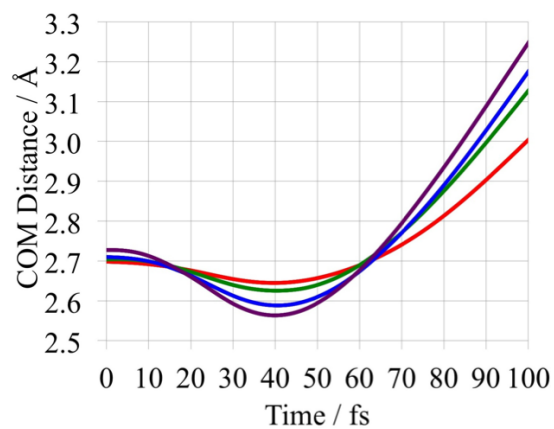


Figure 3.8: The distance between the water and methanediol centers of mass in $a\text{OH}$ excitation of the $n = 1$ cluster averaged at each time over the ensemble of unreactive trajectories at each excitation energy. The vibrational states are labeled by $v = 4$ (pink), $v = 5$ (red), $v = 6$ (green), $v = 7$ (blue), and $v = 8$ (violet).

chattering of the excited hydrogen atom between the donor and acceptor oxygen atoms becomes more feasible and more frequent, facilitating greater energy transfer to the van der Waals mode. All reactions at low OH excitation energy and almost all reactions at high OH excitation energies were preceded or accompanied by pronounced donor/acceptor distance shrinking and the reaction times, see Figure 3.6, are commensurate with the time window of the collapse of the van der Waals motion. While the dynamics the $n = 2$ cluster ring compression coordinate are more complex than that for the $n = 1$ cluster, they exhibit analogous behavior.

The compression of the hydrogen bonded network ring is the most obvious large atom motion associated with the reaction, but not the only important one. The bond between the carbon and the terminal oxygen in the hydrogen bonded network lengthens by approximately 0.3 Å along the MEP between the equilibrium geometry and the TS. In the trajectories, the steady and uninterrupted lengthening of the C–O bond was the most reliable indicator that the reaction was complete. The chattering of hydrogens in the transfer network was effectively terminated as the CO bond completely broke. In addition, a large amount of the excitation energy of the reaction was generally released into the relative translation between the formaldehyde product and the water molecules. In the reactive trajectories, the CO bond dissociation, once initiated, occurred very quickly, on the same timescale as a hydrogen transfer, and prior to or simultaneously with the final hydrogen transfer. This is very different from the MEP where the CO bond lengthening occurred prior to the hydrogen atom transfer.

As we have mentioned above, the initial excitation lies in the high frequency OH chromophore, and the dynamics often exhibits rapid hydrogen atom chattering between donor and acceptor oxygens. While energy does flow into the low frequency “ring compression” and CO stretch coordinates (R_{comp}, R_{CO}), where R_{comp} is taken to be the center of mass distance between the methanediol and water molecules, on the 50 to 100 fs time scale, energy transfer is inefficient due to the frequency mismatch between the excited OH and large atom motions. Therefore, low frequencies modes do not reach their TS configurations. An ensemble of reactive trajectories for $h\nu = 59 \text{ kcal mol}^{-1}$ and $n = 1$ are plotted in the (R_{comp}, R_{CO}) coordinates in Figure 3.9. The orbits do not achieve suffi-

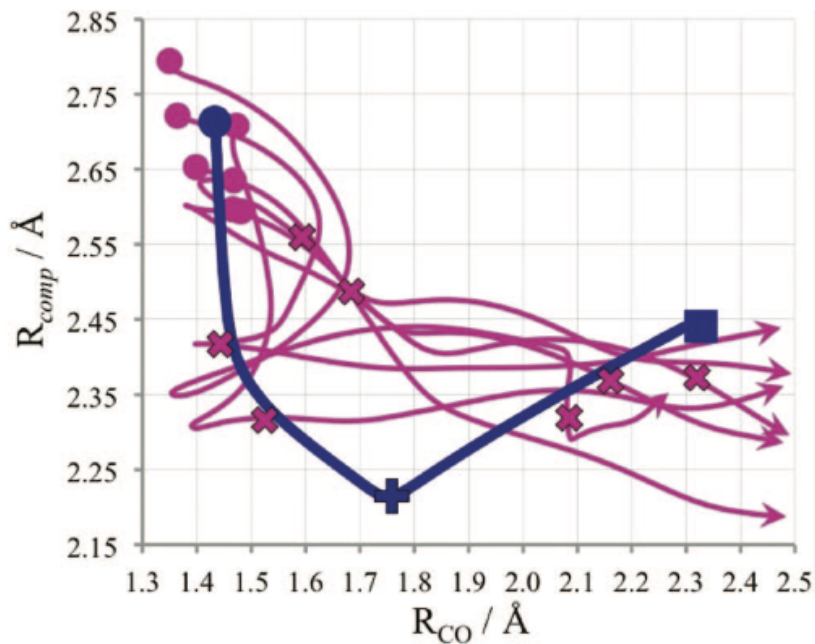


Figure 3.9: Several reactive trajectories for the $v = 7$ excitation of the $a\text{OH}$ chromophore, 59 kcal mol^{-1} , of the $n = 1$ methanediol cluster are plotted in the coordinates $(R_{\text{comp}}, R_{\text{CO}})$, where R_{comp} is taken to be the center of mass distance between the methanediol and water molecules. The position of the final hydrogen atom exchange is marked with an 'x'. The initial condition for each trajectory is marked with a 'o'. For reference, we show the MEP with a thick blue line. The saddle point is marked with a '+'. The equilibrium geometry of the product $n = 2$ cluster of formaldehyde is marked with a '□'.

cient compression to cross from reagents to products near the saddle point. Instead, instantaneous crossing of the transition state hypersurface occurs at larger values of R_{comp} , indicated by $\times$ on each trajectory, at which the potential energy is much higher. The deviation of the trajectory dynamics from the MEP is also apparent in the motion of the hydrogen atoms. While the MEP near the saddle point shows all active hydrogen atoms exchange synchronously from donor to acceptor, the true dynamics reveals that the hydrogen atom transfer steps appear to occur sequentially. In Figure 3.10, we show a representation of the hydrogen atom transfer process for four randomly chosen reactive trajectories for $n = 2$ and $v = 5 - 8$. The status of the three hydrogen atoms in the transfer network versus time is as follows: each hydrogen atom is assigned ‘0’ if it resides on the donor oxygen atom and ‘1’ if it resides on the acceptor oxygen atom so that the exchange process is clearly visible. The red curve denotes the status of the initially excited α OH hydrogen atom. It is seen that this hydrogen atom is exchanged several times before the reaction is completed. To a lesser degree, the other hydrogen atoms also chatter after an induction time. While the hydrogen atom transfer processes are not totally uncorrelated, we can see from Figure 3.10 that the transfers are clearly not simultaneous.

3.5 Conclusion

We have investigated the overtone-induced dehydration reaction of methanediol-water clusters. Our primary objective was to ascertain whether a catalytic effect due to hydrogen bonding with water would be observed in this photochemical reaction. Quantum chemistry calculations unambiguously established a dramatic lowering of the TS barrier by one or two water molecules clustered to the methanediol species. Furthermore, previous experiments of the reaction in solution phase [219, 220] yielded an activation energy that was clearly consistent with the catalyzed barrier and inconsistent with the gas phase uncatalyzed barrier. Thus, it appeared very likely that the thermally activated dehydration reaction was indeed water catalyzed.

From our earlier work on the fluoromethanol system [99, 188], we concluded that the mere observation of barrier lowering by water complexation was insufficient ground to establish water

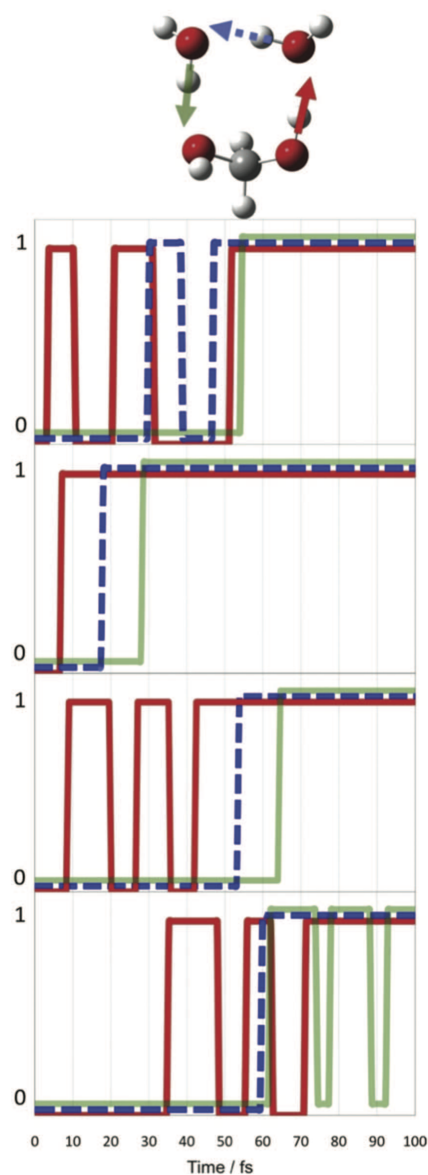


Figure 3.10: The position of the three exchanged hydrogen atoms versus time for four reactive trajectories of the $n = 2$ cluster at various excitations. The trajectory is assigned the value 0 if it instantaneously lies closer to the donor oxygen atom, while it is assigned 1 if it lies closer to the acceptor oxygen atom. The red line corresponds to the *a*OH atom that is initially excited, the blue dashed line is the middle hydrogen atom, and the green line is the terminal hydrogen atom.

catalysis in photochemical reactions. Instead, full dynamical simulation was required to establish catalysis. Following this principle, we simulated the reaction dynamics of the methanediol-water complexes using an ab initio trajectory method. A strong delayed threshold effect was observed in the quantum yield for the dehydration reaction of methanediol. Since the quantum yield was zero until the photon energy exceeded the bare transition state energy, $E^{\text{TS}}(n=0)$, the catalytic effect of water was negated for the $n=1$ cluster. We termed this behavior “anticatalytic” since the reaction actually had a higher threshold energy than in the absence of water. A delayed threshold was also obtained for $n=2$, although some reaction does occur at energies slightly lower than $E^{\text{TS}}(n=0)$. Our conclusion is that water will do little to promote, and may even suppress overtone-induced reaction.

The analysis of the delayed threshold effect in the photochemical reaction of the methanediol-water clusters suggests that the reactive process must be viewed in competition with that of water evaporation. Since evaporation “cools” the photo-excited cluster in an irreversible way, the evaporation and reaction should be viewed as exclusive processes. Since water evaporation occurs with a much lower barrier than does reaction, evaporation would totally dominate if the reaction occurred in a statistical (slow) manner over the course of nanoseconds. Thus reaction, if it is to occur at all, must happen rapidly by a non-statistical direct mechanism. Inspection of the ab initio trajectories does, in fact, reveal a direct mechanism in which the hydrogen atoms within a hydrogen bonded ring are exchanged in a sequential reaction mechanism within the first 100 fs following excitation. The observed mechanism is quite distinct from the computed reaction path that corresponds to a concerted reaction process where the H-atoms in the water wire are simultaneously transferred. The dynamical excitation of the low-frequency ring modes of the cluster is insufficient to achieve the compressed configuration of the low energy saddle point and but still excites the van der Waals motion directly connected to the evaporation channel.

Chapter 4

Adiabatic Treatment of Torsional Anharmonicity and Mode Coupling in Molecular State Sums, Partition Functions, and Statistical Rate Coefficients: Application to Hydrogen Peroxide

A semiclassical method is proposed for accurately incorporating torsional degrees of freedom into molecular state sums and partition functions in a computationally economic way. This method applies an adiabatic separation of the “slow” torsional mode from the other “fast” internal degrees of freedom. The state sum is carried out quantum mechanically over the fast vibrations and the molecular rotations as a local function of the slow torsion coordinate. The torsional states are then included as a classical phase space integral over the local state sum with a zero point energy correction. The method is formulated for both bound and reactive systems. This method was applied to two test cases: (a) a simple coupled-harmonic oscillators model problem and (b) the H_2O_2 molecule, its isotopomer DOOH , and with the explicit calculation of the unimolecular rate coefficient for the dissociation reaction. The results are compared with those obtained from the usual separable treatments, including the harmonic oscillator-rigid rotor (HO-RR) and Pitzer-Gwinn separable hinder rotor methods. The coupled oscillator model shows the tendency of the HO-RR model to significantly miscount states at high energy. It is generally observed that the separable models tend to underestimate the state count of the H_2O_2 molecule at lower energies relative to the more rigorous semiclassical method. The RRKM rate constants predicted for the O-O bond breaking of H_2O_2 are higher for the semiclassical model than those of the separable models. These differences highlight the necessity of accounting for the coupling between torsional motion

and other degrees of freedom in any sophisticated model and we recommend the semiclassical adiabatic torsion method in future applications.

4.1 Introduction

The computation of internal state densities and partition functions for polyatomic molecules is an essential task in the theoretical treatment of molecular gases. A first principles approach to the statistical thermodynamics of polyatomic gases requires the computation of the internal molecular energy levels based on an ab initio quantum chemical (QM) determination of portions of the potential energy surface [212]. Likewise, statistical theories of chemical reactions, such as Rice-Ramsberger-Kassel-Marcus (RRKM) theory or transition state theory (TST) permits the computation of reaction rate coefficients without the need for dynamical modeling provided that partition functions for the activated complex and the reagent molecules can be accurately obtained. The traditional approach to the calculation of molecular partition functions makes use of a separable normal mode approximation for molecular vibrations and a rigid rotor treatment of molecular rotations obtained from single point QM determination of energies, structures and frequencies. This simple approach is often found to be adequate for many practical purposes, even though significant numerical errors may be incurred. With the advent of powerful computers, it has become possible to compute QM energies for hundreds or thousands of molecular geometries of reasonably large molecules. In principle, this makes possible the computation of partition functions that go beyond the harmonic oscillator-rigid rotor (HO-RR) approximation. Despite these advances, it is still not possible to obtain an accurate ro-vibrational eigenvalue spectrum for most polyatomic molecules. It is, however, of great importance to develop methods that at least partly incorporate the effects of anharmonicity, mode coupling, and non-rigidity into first principles computations of statistical quantities.

A particularly challenging problem in the statistical thermodynamics of gases involves the treatment of torsional motions such as internal rotations [119]. These torsional motions are often of low frequency and high amplitude and are poorly described by a normal mode description at

most elevated temperatures. Furthermore, it is quite common for multiple minima to occur along the torsion coordinate. When the barrier to torsional isomerization is not too high, the influence of these conformers must be fully included. For chemical reactions, this may lead to multiple non-equivalent transition states that contribute in toto to the overall rate. In general, the frequencies of the remaining vibrational modes will be functions of the torsional coordinate, and hence the conformation isomer, as will be the rotational constants. The anharmonic coupling to the torsional motion is often found to lead to much larger breakdowns of the HO-RR model than coupling between other higher frequency normal modes.

There have been numerous attempts to treat torsional motion in molecular statistical mechanics, and we do not attempt to review this vast literature here. We do note, however, the ground breaking early work of Pitzer and Gwinn [155] who proposed a separable hindered rotor model. This approach, and closely related variations, is still widely used today as the most common method to go beyond the HO-RR model [45, 153]. We also point out that several nonseparable methods have recently been developed that appear to be promising [128, 162, 173, 213, 217, 228].

Our approach to the treatment of torsional anharmonicity makes use of the vibrationally adiabatic approximation. We originally introduced this analysis in our previous treatment of the $\text{HO}_2 + \text{HO}_2$ reaction where torsional motion played a key role [230]. The adiabatic approximation is a common scheme to treat mode coupling for systems that exhibit a separation of time scales [89, 201]. Since torsional motion is typically a very low frequency molecular vibration, the adiabatic approximation appears well suited to this problem. Hence we take the torsional coordinate, τ , as “slow” while the remaining normal modes are “fast”. We adopt the most basic version of the adiabatic approximation in which nonadiabatic couplings between the vibrational modes and to the rotation are ignored. For problems that exhibit chemical reaction, we include a second slow coordinate, the reaction coordinate s . We need to make no additional assumptions about the relative timescales of τ and s . For reactive problems, we note that the conventional saddle point, $\vec{X}_0$, associated with the transition state is replaced by a ridge line, $\vec{X}_0(\tau)$. The ridgeline passes through the conventional saddlepoint as well as any other conformers of the transition state. The

reactive flux is computed through a generalized dividing surface that coincides with $\vec{X}_0(\tau)$. In this scheme, the reactive flux occurring at all values of the torsional angle is included in an even-handed way. The molecular rotational partition functions are likewise parameterized by the torsional coordinate in addition to the reaction coordinate. When necessary, the effects of quantum tunneling can be included in terms of tunneling through a series of barriers computed for frozen values of the torsional angle.

While it is generally straightforward to construct the adiabatic Hamiltonian for a bound or reactive problem, the full computation of the coupled partition function can be problematic. For each set of quantum numbers describing excitations of the fast vibrational modes, a distinct vibrationally adiabatic potential curve is generated for the torsion. In principle, this may require the solution of thousands or even millions of one-dimensional Schrödinger equations to obtain the required level positions. To circumvent this computational bottleneck, we introduce a semiclassical method where the torsion is treated classically by phase space integration while the remaining fast modes are modeled as fully quantum mechanical. We shall demonstrate that this approach generally yields excellent results.

In this work we shall investigate the influence of the torsional motion on the statistical description of the hydrogen peroxide molecule. Hydrogen peroxide provides a good system for study since it is the simplest molecule to exhibit torsion, and has been thoroughly studied in all its isotopic variants [98]. Furthermore, a high quality potential energy surface (PES) is available due to Kuhn et al. [104]. The equilibrium geometry of the H_2O_2 molecule is nonplanar, which leads to a double barrier potential energy profile along the dihedral angle. The higher barrier to internal rotation, in the cis configuration, is approximately $7.6 \text{ kcal mol}^{-1}$. The O–O bond can rupture at excitation energy of $48.4 \text{ kcal mol}^{-1}$ and higher. In addition to numerous theoretical treatments of H_2O_2 [28, 52, 60, 199, 203], including the recent six-dimensional wavepacket treatment of the reaction dynamics [216], there have been experimental studies carried out for this system which provide useful data for comparison [15, 18, 33, 47, 93, 103, 125–127, 164, 197].

In Section 4.2, the formal theory of the adiabatic approach to the computation of thermody-

namics functions with emphasis on the high amplitude torsional motion is presented. For simplicity, only cases with a single torsional degree of freedom are addressed. An algorithm is presented for the computation of rotational-vibrational state sums with the torsional motion adiabatically coupled to the remaining rotational-vibrational degrees of freedom. The calculations are made feasible with the introduction of a semiclassical technique for the torsional state sum that obviates the need for repeated diagonalization of the vibrationally adiabatic Hamiltonian. The methodology required for reactive problems is introduced in Section 4.3. In this case, the density of states is now written as an explicit function of two slow coordinates, the torsion and the reaction coordinates. A technique to include quantum tunneling through the reactive ridge is discussed. In Section 4.4, the numerical results for the hydrogen peroxide molecule are presented. It is found that that molecular partition functions and thermodynamic functions are modified by factors on the order of 10% when the torsional coupling is included. The RRKM reaction rate coefficient is modified by a similar amount. Section 4.5 summarizes several conclusions of this work.

4.2 Adiabatic theory of molecular state density for nonseparable large amplitude motion: Bound Motion

The basic approach adopted in the adiabatic method is quite simple and the formalism is briefly presented for bound molecules in this section and then, in Section 4.3, for reactive systems. Further details may be found in a proceeding work [230].

For a bound nonlinear polyatomic molecule consisting of n -atoms, we imagine that a well-defined large amplitude coordinate, such as torsion, can be defined based on physical considerations. For a typical internal rotation, this coordinate might be selected to be a dihedral angle. In other applications we might pick the large amplitude coordinate to follow a numerically determined path of steepest descent from a saddlepoint of the barrier to internal rotation. This coordinate is denoted as τ and there is no strict mathematical requirement that this coordinate is periodic. For simplicity, in this presentation, the curvilinear torsional coordinate is assumed to coincide with a normal mode vibration near the minimum of the potential well although it is not strictly necessary.

The $3n$ -dimensional quantum Hamiltonian is decomposed into three terms,

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{trans}} + \hat{H}_{\text{rot}}(\tau) + \hat{H}_{\text{vib}}(\hat{p}_\tau, \tau, \hat{\mathbf{p}}, \hat{\mathbf{q}}) \quad (4.1)$$

where the vectors $\mathbf{p}$ and $\mathbf{q}$ describe the $3n - 7$ small amplitude vibrations. The coupling between rotation and vibration is neglected except for the (possibly large) dependence of the rotation constants on τ . Focusing on the vibrational dynamics, the adiabatic approximation is invoked by assuming that each vibrational eigenstate takes the product form $\psi(\tau) \times \phi(\mathbf{q}; \tau)$ (for brevity, the “vib” subscript is left out). The constituent wavefunctions satisfy

$$\hat{H}(\hat{p}_\tau = 0, \tau, \hat{\mathbf{p}}, \hat{\mathbf{q}}) \phi_n(\mathbf{q}; \tau) = \epsilon_n(\tau) \phi_n(\mathbf{q}; \tau) \quad (4.2)$$

$$\left(\hat{T}_\tau + \epsilon_n(\tau) \right) \psi_{\mathbf{n}, n_\tau}(\tau) = E(n_\tau, \mathbf{n}) \psi_{\mathbf{n}, n_\tau}(\tau) \quad (4.3)$$

where $\hat{T}_\tau$ is the kinetic energy operator for τ and $\mathbf{n} = (n_1, n_2, \dots, n_{3n-7})$ are the quantum numbers for the “fast” vibrational degrees of freedom.

A primary quantity of interest in this work is the cumulative sum of states $N(E)$ and the density of states $\rho(E)$ formally defined by the exact expressions,

$$N(E) = \sum_i \Theta(E - E_i) = \text{Tr} \left(\Theta(E - \hat{H}) \right) \quad (4.4)$$

$$\rho(E) = \sum_i \delta(E - E_i) = \text{Tr} \left(\delta(E - \hat{H}) \right) \quad (4.5)$$

where E_i are the exact eigenvalues, Θ is the Heaviside step function, and δ is the Dirac delta function. The usual canonical partition function is the Laplace transform of $\rho(E)$. The vibrationally adiabatic potential functions $\epsilon_{\mathbf{n}}(\tau)$ may be approximated by a separable model for the $3n - 7$ fast vibrational modes, invoked at each τ , or through a low order perturbation treatment. Unfortunately, the low frequency mode τ is a high amplitude degree of freedom, such as a torsion, that is not expected to be separable at all. To find the density of vibrational states within the vibrationally adiabatic approximation, it is necessary to solve the one dimensional Schrödinger equation 4.3 for each set of quantum numbers $\mathbf{n}$ up to a sufficiently high level of excitation. While this is not overly burdensome for triatomic molecules, for larger polyatomics the number of required Schrödinger

equations can become astronomical. Hence, we propose a method to obtain the state counts which is more computationally feasible while not resorting to unrealistic separable approximations.

The classical approximation to the cumulative distribution of vibrational states can be written as,

$$N_{\text{classical}}(E) = \frac{1}{h^{3n-6}} \int \int \cdots \int \Theta(E - H) \prod_{i=1}^{3n-6} dp_i dq_i \quad (4.6)$$

where H is the classical Hamiltonian. This classical approximation, while often useful, is known to exhibit serious errors, especially associated with the significant zero point energy of high frequency modes. This chapter adopts a mixed semiclassical representation in which the high frequency modes are represented quantally while the low frequency τ -mode is treated classically. Hence, the zero point errors incurred should be quite modest since the zero point is included for the high frequency, fast, degrees of freedom using exact quantum mechanics. The semiclassical expression for the cumulative state sum is,

$$N_{\text{mixed}}(E) = \frac{1}{h} \int \int Tr'[\Theta(E - H_{\text{mixed}})] dp_\tau d\tau \quad (4.7)$$

with,

$$H_{\text{mixed}} = T_\tau + H(p_\tau = 0, \tau, \mathbf{p}, \mathbf{q}) \quad (4.8)$$

where T_τ is the classical kinetic energy of the τ -mode. Consistent with the adiabatic approximation, we assume in this treatment any $\mathbf{q}$ -dependence of the T_τ is either absent or can be averaged out. The partial trace Tr' is taken over all the $3n - 7$ high frequency quantum mechanical vibrational modes. Thus, we can abbreviate Equation 4.7 in terms of the τ -dependent cumulative sum of states $\tilde{N}(E, \tau)$ of the high frequency modes, which is a purely quantum state sum for the non-torsional degrees of freedom,

$$N_{\text{mixed}}(E) = \frac{1}{h} \int \int \tilde{N}(E - T_\tau, \tau) dp_\tau d\tau. \quad (4.9)$$

As a practical note, the energy argument in $\tilde{N}$ from Equation 4.9, $E - T_\tau$, is the energy available to the high frequency modes when the torsional degree of freedom is in the classical state (p_τ, τ) . The actual value of the energy argument depends on how the energy scale is referenced and we shall make no assumptions on the referencing.

In the simplest case, we can use a harmonic approximation and normal mode analysis for the energy levels of the fast $\mathbf{q}$ -vibrations. Since the τ -mode is potentially a high amplitude degree of freedom, we should employ instantaneous normal modes. In this treatment, the frequencies and normal mode coordinates are obtained by diagonalizing the projected force constant matrix,

$$\mathbf{F}_{\text{proj}} = \mathbb{P}\mathbf{F}\mathbb{P}^{-1}. \quad (4.10)$$

Here, $\mathbf{F}$ is the conventional Hessian matrix in mass-weighted Cartesian coordinates of the full configuration space and $\mathbb{P}$ is a projection operator. The projector $\mathbb{P}$ can be constructed as a product of one-dimensional projectors that locally eliminate the subspaces for translation, overall rotation, and the torsion. The projector matrix, $\mathbb{P}$, can also be constructed similar to the prescription set out in the classic paper by Miller et al. [141]. In that paper, the authors showed how make a projector for the elimination of the translations, overall rotations, and the gradient. In our prescription, we project out the torsion, which can be easily incorporated into the projector construction of Miller et al. by including the tangent vector to the torsion [42] in mass-weighted coordinates rather than the gradient.

Thus, we can obtain the frequencies of the high frequency modes $\omega_i^2(\tau)$ as functions of the slow torsional coordinate. The Hamiltonian operator of the adiabatically separated high frequency modes, in mass-weighted coordinates $\mathbf{q}$ is,

$$\hat{H}_{\text{mixed}} = \frac{p_\tau^2}{2I_\tau} + V(\tau) + \sum_{i=1}^{3n-7} \left(\frac{\hat{p}_i^2}{2} + \frac{1}{2}\omega_i^2(\tau)\hat{q}_i^2 \right) \quad (4.11)$$

where $V(\tau) = V(\tau, \mathbf{q} = \mathbf{0})$. The quantity $\tilde{N}(E, \tau)$ can be very efficiently computed using the Beyer-Swinehart algorithm as a function of the two arguments [7, 183].

A dominant source of error in Equation 4.9 is the treatment of the zero point energy for the classical coordinate τ . This zero point energy can be approximated, as conveniently expressed by Truhlar et al. [45] as,

$$\epsilon_0^\tau = \frac{1}{2}\hbar\omega_\tau \quad (4.12)$$

where,

$$\omega_\tau = \sqrt{\left(\frac{1}{I_\tau(\tau)} \frac{d^2 V(\tau)}{d\tau^2} \right) \Big|_{\tau=\tau_{eq}}} \quad (4.13)$$

where τ_{eq} is the global minimum equilibrium dihedral angle of the potential $V(\tau)$ defined above. Following the traditional approach of Marcus and Rice [132] we add the zero point energy of the separable torsional mode to the argument of the Heaviside function to obtain the final result,

$$N_{\text{mixed}}(E) = \frac{1}{h} \int \int \tilde{N}(E + \epsilon_0^\tau - T_\tau, \tau) dp_\tau d\tau. \quad (4.14)$$

The addition of the torsion zero point energy to $\tilde{N}$ may seem counterintuitive at a glance, but the addition of ϵ_0^τ is included to approximately account for the undercounting of states in the classical picture. The corresponding density of states, $\rho_{\text{mixed}}(E)$ can be obtained by differentiating $N_{\text{mixed}}(E)$.

The inclusion of overall molecular rotation into the state sums may be carried out using either classical or quantum mechanics. A quite common and convenient approximation that we shall use in this work involves the symmetric top approximation in which two of the moments of inertia, those closest in magnitude, are set equal to their geometric average. We present here the explicit formulae of the quantum mechanical approach in the symmetric top approximation, and extensions to symmetric top and, when absolutely necessary, asymmetric top systems can be made by appropriately modifying the rotational terms and sums in the expressions that follow. The key assumption necessary for this treatment is that the rotational constants are instantaneous functions of the large amplitude coordinate, τ , but that the rotation is otherwise separable from the vibration. The symmetric top moments of inertia $I_d(\tau)$, the degenerate moment, and $I_u(\tau)$, the unique moment, are obtained from a principal axis analysis at the geometry $(\tau, \mathbf{q} = \mathbf{0})$ which is presumed to be at the minimum of the potential well $V(\tau, \mathbf{q} = \mathbf{0})$ holding τ fixed. The rotational energy levels are given by,

$$E_{jk} = \frac{\hbar^2}{2I_d(\tau)} + \hbar^2 k^2 \left(\frac{1}{2I_u(\tau)} - \frac{1}{2I_d(\tau)} \right) \quad J = 0, 1, 2, \dots \quad k = -J, -J+1, \dots, J \quad (4.15)$$

and each energy level above has a degeneracy of $2J+1$ due to the M_J quantum number of the

symmetric top. The total internal cumulative state sum is,

$$N_{\text{mixed}}(E, J) = \frac{1}{h} \int \int \tilde{N} \left(E + \epsilon_0^\tau - T_\tau - \frac{p_\tau^2}{2I_\tau(\tau)} - \frac{\hbar^2}{2I_d(\tau)} J(J+1), \tau \right) dp_\tau d\tau + 2 \sum_{k=1}^J \frac{1}{h} \int \int \tilde{N} \left(E + \epsilon_0^\tau - T_\tau - \frac{\hbar^2}{2I_d(\tau)} J(J+1) - \hbar^2 k^2 \left(\frac{1}{2I_u(\tau)} - \frac{1}{2I_d(\tau)} \right), \tau \right) dp_\tau d\tau \quad (4.16)$$

where the $2J+1$ degeneracy factors of the rotational levels are not included in the expression above and can be included in the usual way,

$$N_{\text{mixed}}(E) = \sum_{j=0}^J (2J+1) N_{\text{mixed}}(E, J). \quad (4.17)$$

When required, Equation 4.16 should be divided by a symmetry factor to account for the interchange of identical nuclei in symmetric molecules [137]. While Equation 4.16 may at first sight seem difficult to evaluate, it can actually be computed quite efficiently. The quantity $\tilde{N}(E, \tau)$ can be precalculated on a large grid of (E, τ) values and the numerical integrations can then be carried out rapidly using numerical quadrature.

As a simple preliminary test of the semiclassical adiabatic state counting algorithm, consider the generalized anharmonically-coupled harmonic system,

$$H = \frac{p_\tau^2}{2} + \frac{1}{2} \omega_\tau^2 \tau^2 + \sum_{i=1}^{N-1} \left(\frac{p_i^2}{2} + \frac{1}{2} \omega_i^2(\tau) q_i^2 \right) \quad (4.18)$$

where the coupling factor is,

$$\omega_i^2(\tau) = \omega_i^0 + \frac{1}{2} \delta_i \tau^2 \quad (4.19)$$

with ω_τ and ω_i^0 being constants of the model. Here, τ will be the example “slow” coordinate, expressed as mass-weighted in Equation 4.18, but is not connected to a torsional rotation but rather, for simplicity, to coupled harmonic degree of freedom in this example. Clearly, the potential is a 6th order polynomial and the exact eigenvalues are not analytically known. On the other hand, the levels in the vibrationally adiabatic approximation can be computed exactly. In the limit where the frequency ω_τ is low compared to the remaining $N-1$ frequencies, the adiabatic potential for

the τ degree of freedom is,

$$\begin{aligned} V_{\text{ad}} &= \frac{1}{2}\omega_{\tau}^2\tau^2 + \sum_{i=1}^{N-1} \hbar\omega_i(\tau) \\ &= \frac{1}{2}\left(\omega_{\tau}^2 + \sum_{i=1}^{N-1} \hbar\delta_i\left(n_i + \frac{1}{2}\right)\right)\tau^2 + E_0(n_1, n_2, \dots) \end{aligned} \quad (4.20)$$

where,

$$E_0(n_1, n_2, \dots) = \sum_{i=1}^{N-1} \hbar\omega_i^0\left(n_i + \frac{1}{2}\right). \quad (4.21)$$

Hence, the adiabatic levels are given by,

$$E_{\text{ad}}(n_{\tau}, n_1, n_2, \dots) = \hbar\omega_{\text{eff}}\left(n_{\tau} + \frac{1}{2}\right) + E_0(n_1, n_2, \dots) \quad (4.22)$$

with,

$$\omega_{\text{eff}} = \sqrt{\omega_{\tau}^2 + \sum_{i=1}^{N-1} \hbar\delta_i\left(n_i + \frac{1}{2}\right)}. \quad (4.23)$$

Provided that ω_{eff} doesn't become too large, the adiabatic approximation is expected to be accurate.

To assess the performance of the semiclassical method, we have evaluated the cumulative state sums for the anharmonically-coupled harmonic model described above $N = 3$, $\omega_{\tau} = 1$, $\omega_1 = 4$, $\omega_2 = 5$, $\delta_1 = 0.1$, and $\delta_2 = 0.11$. In Figure 4.1 we show the “exact” adiabatic cumulative state sum using Equation 4.22 with the red line. The semiclassical result obtained using Equation 4.14 is given by the green line and is seen to be virtually indistinguishable from the exact adiabatic result. For reference, we have also plotted the traditional separable (quantum) harmonic approximation in Figure 4.1 which clearly shows serious error. From this result and other similar tests, it seems that the semiclassical model is capable of accurately reproducing the adiabatic state counting without the need to explicitly evaluate the energy levels for the myriad of adiabatic potential curves $V(n_1, n_2, \dots, ; \tau)$.

4.3 Adiabatic Theory for Reactive Systems

The adiabatic model for reactive problems is formulated in a manner similar to that outlined above for bound polyatomic molecules. The basic distinction is that the reactive problem requires

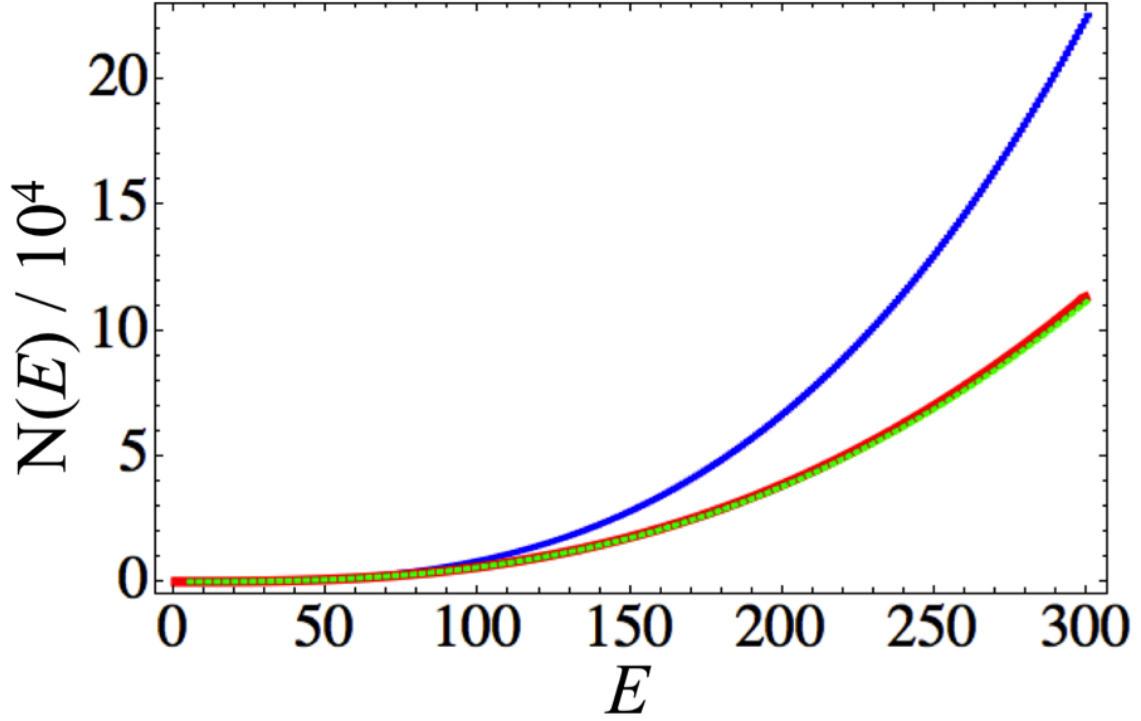


Figure 4.1: The cumulative sum of states for a system of three coupled oscillators. The Hamiltonian is given by Equation 4.18 with $\omega_\tau = 1$, $\omega_1 = 4$, $\omega_2 = 5$, $\delta_1 = 0.1$, and $\delta_2 = 0.11$. The red line is the “exact” adiabatic state count using the levels given by Equation 4.22. The dotted green line is a result of the semiclassical adiabatic method, Equation 4.14. The blue line is the traditional uncoupled harmonic description based on harmonic frequencies computed at the potential minimum.

the use of two slow large amplitude degrees freedom, the torsion, τ , and the reaction coordinate, s . The reaction coordinate may be described as the path of steepest descent from the saddlepoint, or through some other convenient method. Both of degrees of freedom (τ, s) are treated adiabatically and thus are assumed to be slow compared to the $\mathbf{q}$ -vibrations, although no particular time scale separation is presumed to exist between τ and s themselves. To obtain the rate coefficient, the cumulative sum of states must be computed as a function of s , i. e. $N(E, J; s)$. In particular for a unimolecular reaction such as $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$, if the transition state (TS) bottleneck occurs at $s = s_0$, so that $N^\ddagger(E, J) = N(E, J; s_0)$, the (E, J) dependent rate coefficient is [78],

$$k(E, J) = \frac{1}{h} \frac{N^\ddagger(E, J)}{\rho(E, J)} \quad (4.24)$$

where $\rho(E, J)$ is the reagent density of states.

The key construction for the reactive problem is the reaction path as a function of the torsional coordinate τ , i. e. $\mathbf{X}(s, \tau)$. Here, $\mathbf{X}$ is a $3n$ -dimensional vector and $\mathbf{X}(s, \tau)$ is assumed to be a smooth surface. Hence, in place of the usual saddle point $\mathbf{X}_0$, one has a ridge line of saddle points, $\mathbf{X}_0(\tau)$, defined through $\nabla V = 0$ when τ is held fixed. The reaction surface can be viewed as composed of individual paths of steepest descent, at fixed τ , that issue from the reduced saddle points along the ridgeline. Along each path of fixed τ , we carry out an instantaneous normal mode analysis by projecting out both the torsion and the reaction coordinate motions from the Hessian matrix, i. e. $\mathbf{F}_{\text{proj}} = \mathbb{P}\mathbf{F}\mathbb{P}^{-1}$. Assuming the torsion and the reaction coordinate are treated classically while the remaining $3n - 8$ vibrations are treated quantum mechanically, we have the semiclassical vibrational Hamiltonian,

$$H_{\text{mixed}} = \frac{1}{2} \frac{p_\tau^2}{I_\tau} + \frac{1}{2} \frac{p_s^2}{\mu_s} + V(\tau, s) + \sum_{i=1}^{3n-8} \left(\frac{1}{2} p_i^2 + \frac{1}{2} \omega_i^2(\tau, s) q_i^2 \right). \quad (4.25)$$

Assuming the TS is associated with the ridgeline at $s = s_0$, the semiclassical method gives the vibrational cumulative sum of states as,

$$N_{\text{mixed}}^\ddagger(E) = \frac{1}{h} \int \int \tilde{N}^\ddagger(E + \epsilon_0^\tau - T_\tau, \tau) dp_\tau d\tau \quad (4.26)$$

where $\tilde{N}^\ddagger(E, \tau)$ is evaluated by carrying out the trace for the $3n - 8$ high frequency vibrational degrees of freedom orthogonal to s and τ using the TS ridgeline frequencies $\omega_i(\tau, s_0)$ for $i = 1, 2, \dots, 3n - 8$. The zero point energies, including that of the τ -mode, ϵ_0^τ , are computed for the potential $V(\tau, s_0)$.

The inclusion of overall rotation into the reactive problem proceeds analogously to the formalism introduced for the bound problem. A principal axis analysis of the complex with fixed values of (τ, s) produces rotational constants that explicitly depend upon τ and s , $I_i(\tau, s)$ where $i = 1, 2, 3$. Under the symmetric top assumption for the rotational energy levels, we get the ro-vibrational cumulative sum of states at the TS as,

$$\begin{aligned} N_{\text{mixed}}^\ddagger(E, J) = & \frac{1}{h} \int \int \tilde{N}^\ddagger \left(E + \epsilon_0^\tau - T_\tau - \frac{p_\tau^2}{2I_\tau(\tau, s_0)} - \frac{\hbar^2}{2I_d(\tau, s_0)} J(J+1), \tau \right) dp_\tau d\tau \\ & + 2 \sum_{k=1}^J \frac{1}{h} \int \int \tilde{N}^\ddagger \left(E + \epsilon_0^\tau - T_\tau - \frac{\hbar^2}{2I_d(\tau, s_0)} J(J+1) \right. \\ & \left. - \hbar^2 k^2 \left(\frac{1}{2I_u(\tau, s_0)} - \frac{1}{2I_d(\tau, s_0)} \right), \tau \right) dp_\tau d\tau \end{aligned} \quad (4.27)$$

where, the rotational degeneracy factor of $2J + 1$ is not been included.

Although quantum tunneling is not important for the H_2O_2 system, for completeness, we note the methodology for incorporating tunneling into the adiabatic model. Including quantum tunneling into the RRKM determination of the rate is typically accomplished by replacing the classical cumulative sum of states $N^\ddagger$, that, by definition, does not include tunneling, with [78],

$$N_Q^\ddagger = \int_{E_{TS}}^{\infty} \rho^\ddagger(\epsilon) P(E - \epsilon) d\epsilon \quad (4.28)$$

where the state density is $\rho^\ddagger(\epsilon) = \frac{dN^\ddagger(\epsilon)}{d\epsilon}$ and $P(E - \epsilon)$ is the quantum transmission probability at the energy of the translation along the reaction coordinate $E - \epsilon$. We define the energy ϵ as the total excitation energy of the $3n - 8$ vibrational modes. Tunneling occurs through the ridge surface in the adiabatic approximation. For simplicity, we assume that the tunneling dynamics occurs at fixed τ , or, in other words, that the torsion is dynamically frozen. Thus, a tunneling probability at each τ -value, $P(E - \epsilon, \tau)$ may be determined by applying the tunneling method to

the torsionally constrained Hamiltonian, $H|_{\tau=\text{constant}}$. We can calculate the quantum transmission probability at fixed τ by simply applying Equation 4.28 separately to each value of τ . Thus, in place of the classical $\tilde{N}^\dagger(E, \tau)$ we have the quantum expression,

$$\tilde{N}_Q^\dagger = \int_{E_{TS}}^{\infty} \tilde{\rho}^\dagger(\epsilon, \tau) P(E - \epsilon, \tau) d\epsilon \quad (4.29)$$

where $\tilde{\rho}^\dagger(\epsilon, \tau) = \frac{d\tilde{N}^\dagger(E, \tau)}{dE}$. The choice of tunneling method, such as the small curvature method [178], should be adapted to the problem at hand.

4.4 Results for H₂O₂ and HOOD

The H₂O₂ molecule provides a thoroughly studied and well understood problem that possesses a nonseparable torsional coordinate which we shall use to test our method. While the nonseparable torsional coupling in this system is modest, the deviation from separable behavior is clear and, potentially, observable. Furthermore, this system is efficient for study since an accurate global potential energy surface (PES) has been constructed by Kuhn et al. [104] using spectroscopic observation and ab initio calculations.

Based on this PES, the frequencies of the H₂O₂ normal modes are 3777.4, 3761.9, 1453.4, 1297.2, 888.5, and 392.1 cm⁻¹ corresponding to the two OH-stretches, the two OOH angle bends, the O–O stretch, and the torsional mode, respectively. As shown in Figure 4.2, the equilibrium geometry is nonplanar. Thus, there are two barriers to internal rotation of 361 cm⁻¹ (trans) and 2645 cm⁻¹ (cis). The dihedral angle τ is found to closely correspond to the lowest frequency normal mode at the equilibrium geometry. Indeed, the frequency of small amplitude motion along the dihedral angle is 397 cm⁻¹, within about 1% of the value of the torsional normal mode. For heuristic purposes, we have constructed a simple separable model of the torsion that is described by the one dimensional Schrödinger equation in the dihedral angle τ ,

$$\left(-\frac{\hbar^2}{2I_\tau} \frac{d^2}{d\tau^2} + V(\tau) \right) \phi_k(\tau) = \epsilon_k \phi_k(\tau) \quad (4.30)$$

where,

$$I_\tau = \frac{\iota_1 \iota_2}{\iota_1 + \iota_2} \quad (4.31)$$

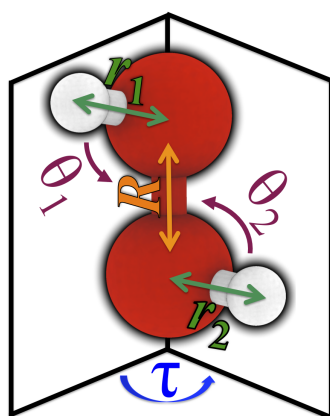


Figure 4.2: The internal degrees of freedom of the H_2O_2 molecule are shown. The r 's are the OH stretches, the θ 's the OOH bends, R is the O-O stretch coordinate, and τ is the torsion.

with,

$$\iota_1 = m_{\text{H}} (r_1 \sin \theta_1)^2 \quad (4.32)$$

$$\iota_2 = m_{\text{H}} (r_2 \sin \theta_2)^2 \quad (4.33)$$

where we have made use of notation consistent with that shown in Figure 4.2. The potential $V(\tau)$ is defined as the relaxed potential optimized at each fixed value of τ and no zero point correction from the other modes is included. The torsional levels from Equation 4.30 are shown in Figure 4.3. Including states of both even and odd symmetry, there are 2 states below the lower barrier and 13 states below the higher barrier.

We first focus on properties of the bound molecule and consider the effects of nonseparability on the molecular partition function and density of states. The potential nonseparability is reflected by the variation of the normal mode frequencies as a function of τ . Projecting out the torsional motion from the Hessian matrix, we obtain the quadratic form for the potential in terms of the instantaneous normal mode coordinates, q_i for $i = 1, 2, \dots, 5$,

$$\mathcal{V}(q_1, q_2, \dots, q_5, \tau) = V(\tau) + \frac{1}{2} \sum_{i=1}^5 \omega_i^2(\tau) q_i^2. \quad (4.34)$$

The potential $V(\tau)$ is shown in Figure 4.3 while the normal mode frequencies versus τ are presented in Figure 4.4. The bending frequencies in particular are seen to have a strong dependence on the torsional angle, up to 20%. Another source of coupling that can be included in our formalism is the torsional dependence of the rotation constants. The rotational constants are computed from the principal moments of inertia by,

$$B_i(I_i) = \frac{\hbar^2}{2I_i}. \quad (4.35)$$

In Figure 4.5 we show the B -constants versus τ computed from the relaxed geometries at fixed τ . The variation of the rotational constants with τ is seen to be about 10%. The torsional moment of inertia, I_τ , also depends on the dihedral angle. Although this coordinate dependent mass can lead to a factor ordering ambiguity in a fully quantum treatment of torsion, it is easily incorporated into the semiclassical integration in Equation 4.16 [179].

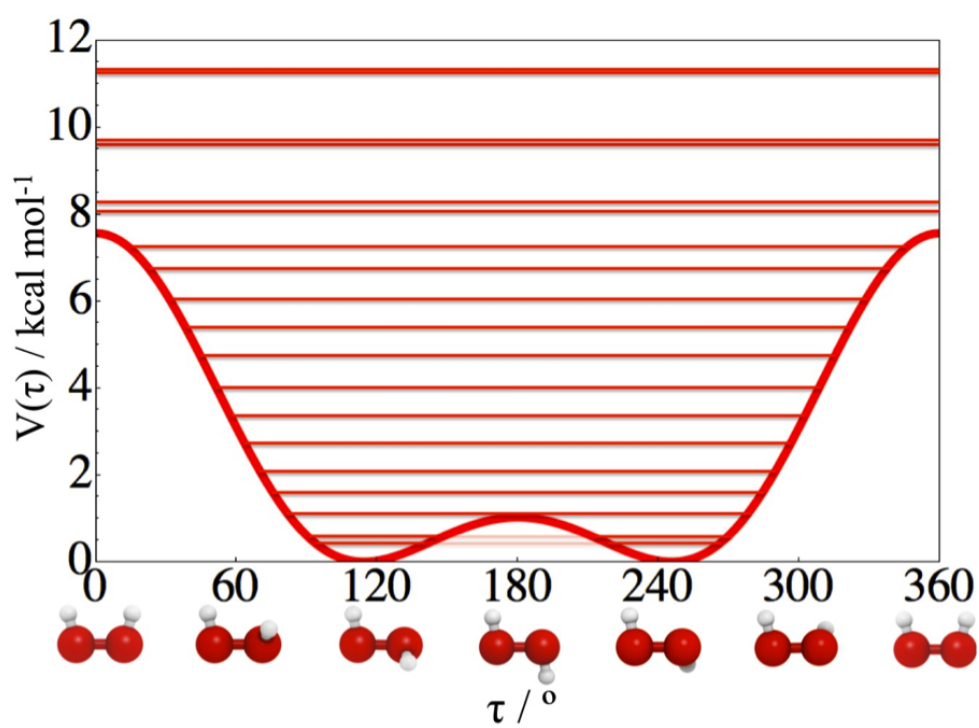


Figure 4.3: The energy levels for the separable torsional motion in H_2O_2 along with the potential versus dihedral angle. No zero point energy is included from the high frequency vibrations.

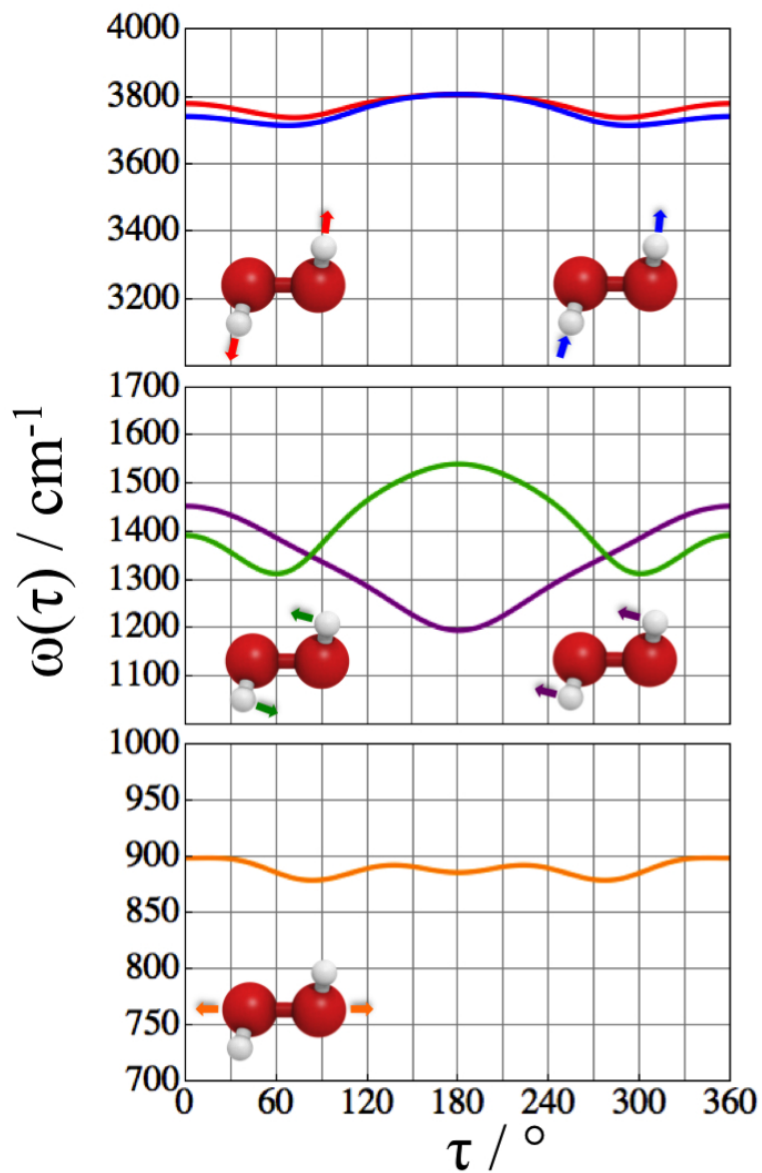


Figure 4.4: The normal mode frequencies of H_2O_2 versus the torsional angle τ computed from diagonalizing the projected force constant matrix of Equation 4.10. The OH-stretch frequencies are shown in the upper panel, the OOH-bending frequencies in the middle panel, and the O–O stretch frequency is given in the lower panel.

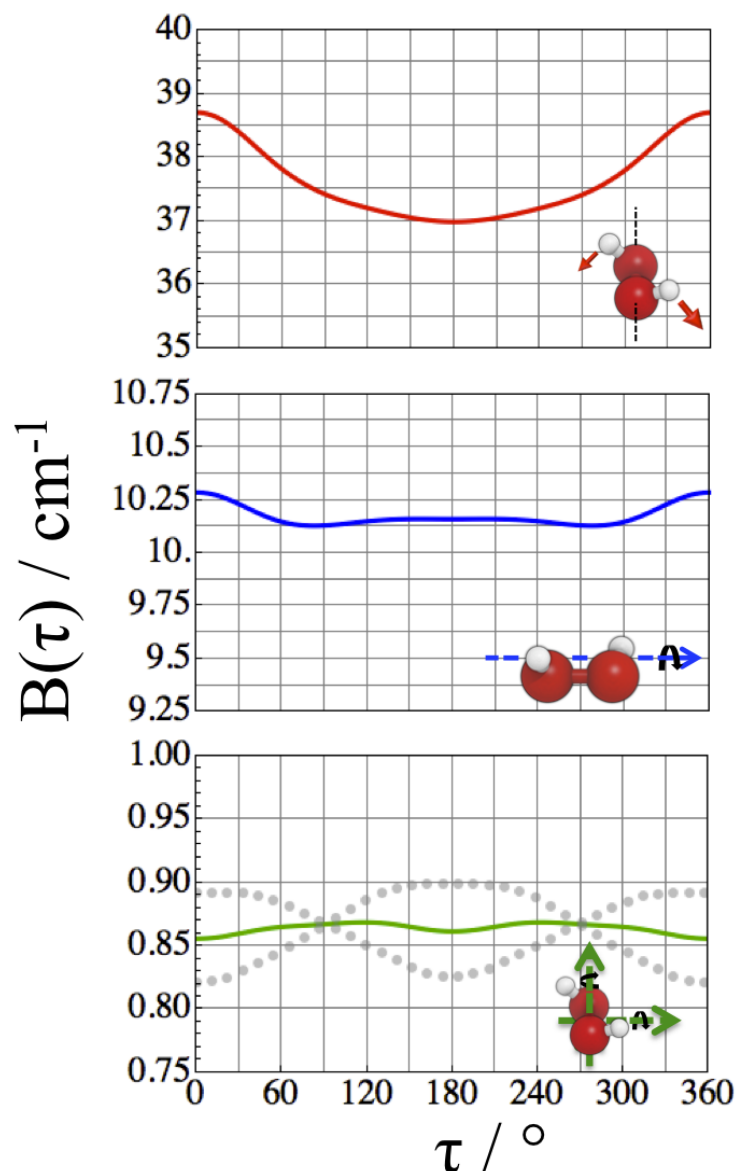


Figure 4.5: The top panel shows the internal torsional rotational constant computed using the internal moment of inertia from Equation 4.31. The middle panel gives the rotational constant calculated using the smallest, and unique in the symmetric top approximation, principal moment of inertia from the principal axis, I_u . The lowest panel shows the rotational constants calculated using the two largest principle moments of inertia, shown as grey dots. The green line in the lowest panel is the rotational constant calculated using a geometric average of the two largest principle moments of inertia, I_d , used in the prolate symmetric top treatment of the H_2O_2 molecule. All constants were computed for the relaxed H_2O_2 for fixed τ .

In Figure 4.6, we show the cumulative density of ro-vibrational states for H_2O_2 as a function of the excitation energy above the zero point energy.

In Figure 4.7, the density of the ro-vibrational states for H_2O_2 , $\rho(E)$, is shown as a function of the excitation energy above the zero point. We computed $\rho(E)$ by a high order polynomial fit of the finite difference computed derivative of the cumulative sum of states. We also show the results obtained using the separable harmonic oscillator-rigid rotor (HO-RR) method, where the quantum rotational levels and the assumed harmonic normal mode vibrational levels are computed under the separable approximation using the Beyer-Swinehart state count algorithm, and the separable τ -hindered rotor approximation. Both the HO-RR method and the τ -hindered rotor method are separable models unlike the adiabatic semiclassical method of Equation 4.16. It is seen that the conventional HO-RR approximation is in error by roughly 10% at high energy. Although HO-RR apparently undercounts the state density at low energy, it overcounts the state density at high E since it omits the torsional anharmonicity. We have also constructed the separable τ -hindered rotor representation of the state density. This method treats all vibrational modes as harmonic oscillators with frequencies set to those as the equilibrium geometry except for the torsion; the torsional energy eigenvalues of the one dimensional torsional Schrödinger equation shown in Equation 4.30 are explicitly included in the state count. The rotational constants are set to their values at the equilibrium geometry. It is seen that at low energies the hindered rotor model gives results similar to the HO-RR method, but the two methods begin to clearly deviate from each other at energies above the barrier to internal rotation of $7.6 \text{ kcal mol}^{-1}$. The hindered rotor model undercounts the state density at high E by 10% due to its neglect of mode coupling. While the difference from the adiabatic model and the conventional treatments is fairly modest, it is still potentially observable. For example, the “microcanonical entropy”, $k_B \ln[\rho(E)]$ shown in Figure 4.9 indicates that deviations from the separable models are apparent. The influence of torsional nonseparability is found to be equally important for canonical ensembles. The canonical partition function $Q(T)$ is obtained from the Laplace transform of $\rho(E)$. Its behavior versus temperature is shown in Figure 4.10. The nonseparable effects are again seen to be on the quite significant over the full temperature

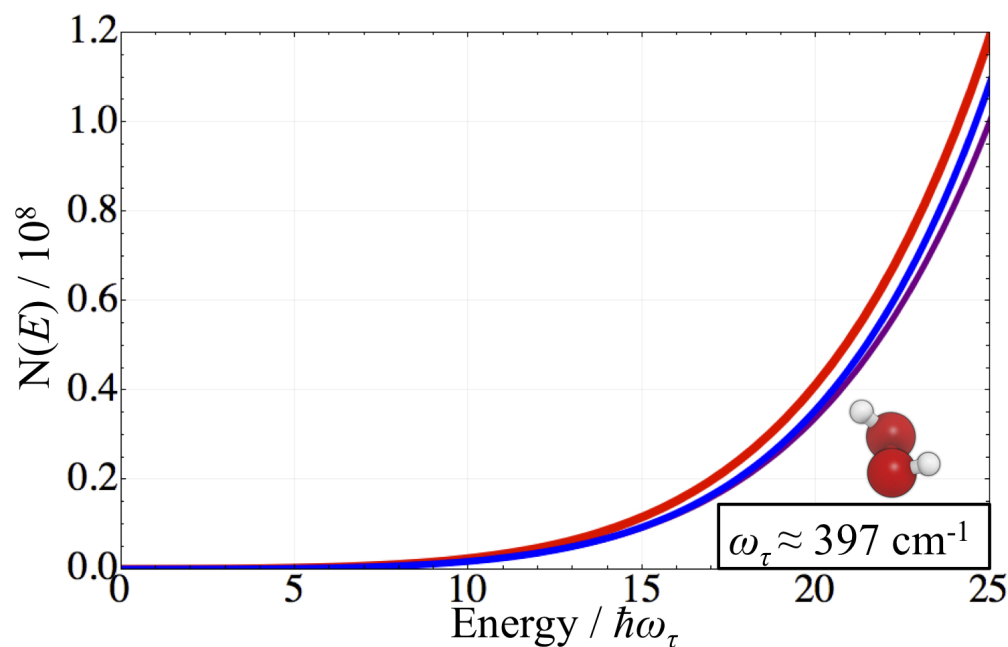


Figure 4.6: The cumulative sum of states versus excitation energy above the zero point for H_2O_2 computed using three different methods. The red curve is the semiclassical adiabatic method, the blue curve is the HO-RR method, and the purple curve is the separable hindered rotor approximation for torsion using the relaxed PES.

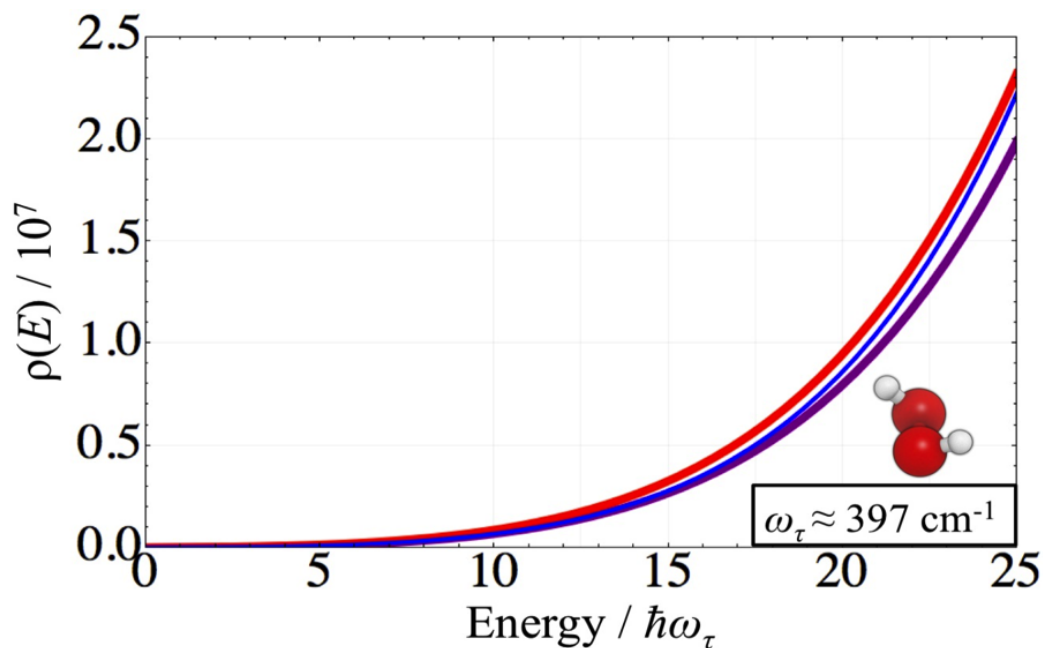


Figure 4.7: The density of states for H_2O_2 versus excitation energy (in units of torsional quanta) computed using three methods. The semiclassical adiabatic method, from Equation 4.16 is shown with the red curve, the convention HO-RR method is shown with blue, while the separable τ -hindered rotor torsional model is shown with purple.

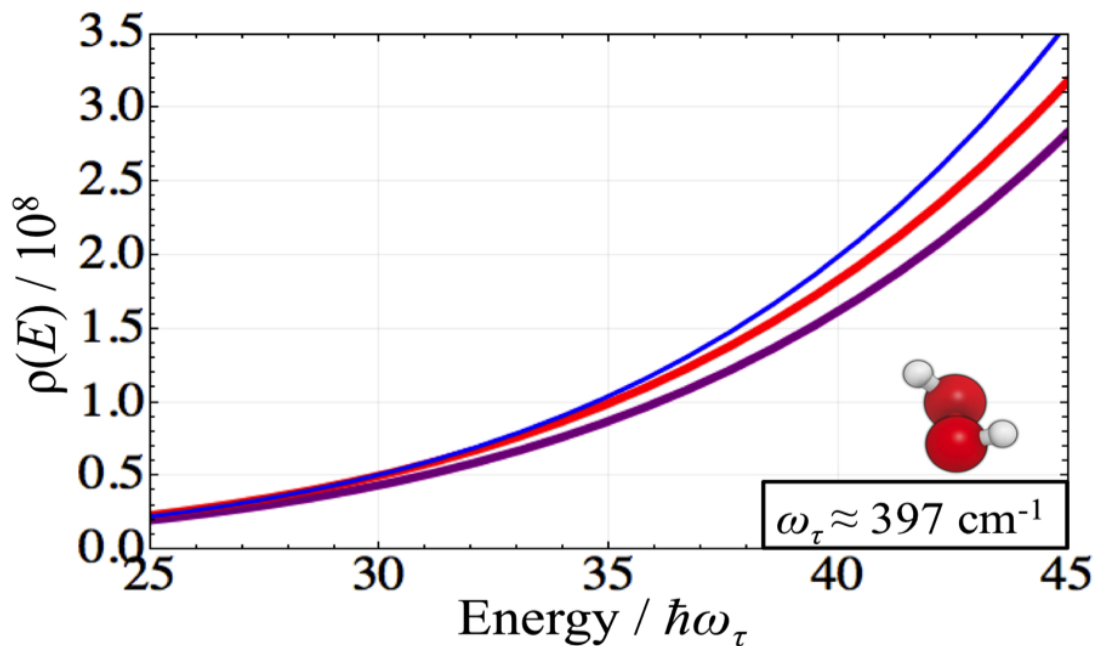


Figure 4.8: The same as Figure 4.7 except for a higher excitation energy range.

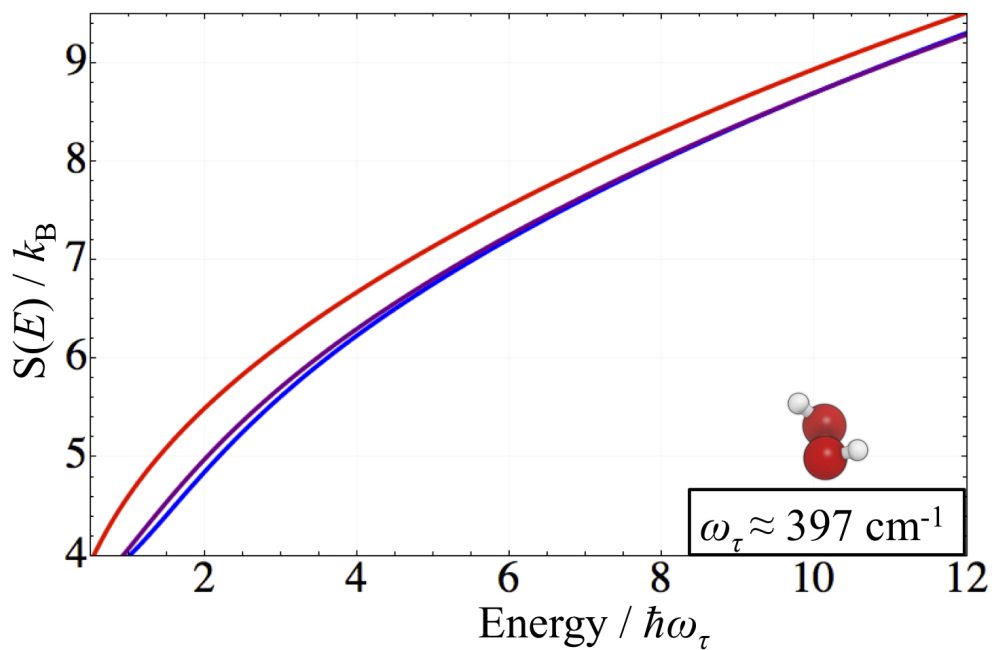


Figure 4.9: The microcanonical entropy, $k_B \ln [\rho(E)]$, of H_2O_2 computed versus excitation energy above the zero point. The red curve is the semiclassical adiabatic method, the blue curve is the HO-RR method, and the purple curve is the separable hindered rotor model.

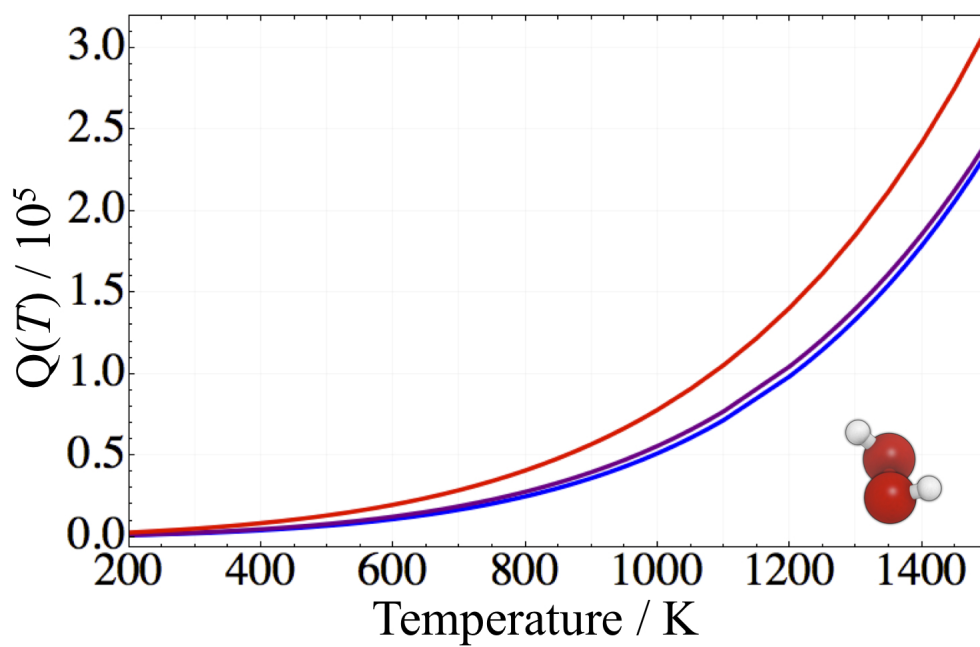


Figure 4.10: The canonical partition function versus temperature for H_2O_2 computed by three methods. The red curve is the semiclassical adiabatic method, the blue curve is the HO-RR method, and the purple curve is the HO-RR model but with the Pitzer-Gwinn approximation for the torsion [155].

range, particularly at high temperatures where the separable models severely underestimate the partition function.

Using the same methodology, it is a straightforward exercise to compute the state density for the isotopomer HOOD. In addition to the frequency shifts and changes in rotational constants due to the mass substitution $m_{\text{H}} \rightarrow m_{\text{D}}$, there is also a modification due to a loss of symmetry, so that the symmetry number changes from $\sigma = 1$ to $\sigma = 2$. In Figures 4.11 and 4.12, we show the state density versus the excitation energy above the zero point energy. It is seen that the separable HO-RR and hindered rotor approximation show a somewhat higher level of error than was seen for the H_2O_2 species.

The Kuhn et al. [104] predicts a HO–OH dissociation energy of $D_0 = 48.4 \text{ kcal mol}^{-1}$ for the $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$ reaction. The reaction coordinate consists primarily of the O–O bond stretching coordinate. In Figure 4.13, the potential energy profile along the reaction coordinate is depicted. It was noted by Kuhn et al. that a cusp in the PES as a function of the reaction coordinate is observed at large R distances, using the notation shown in Figure 4.2. We therefore adopt and approximate transition state which is shifted inward to $R = 5.2a_0$, slightly before the cusp located at $5.36a_0$, where a_0 is the Bohr radius. To compensate for this modification, those states with energy less than the dissociation energy are explicitly excluded from the state sums. This technical difficulty is not essential in the present work, which aims to test the adiabatic method, since the HO-RR and hindered rotor models use the identically modified TS. In Figure 4.14, we show the potential energy along the TS ridgeline. The barrier to internal rotation is seen to have fallen to from $7.6 \text{ kcal mol}^{-1}$ to about 2 kcal mol^{-1} on the relaxed reactant τ PES.

The RRKM rate coefficients were computed using Equation 4.24 for the reaction $\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$. The cumulative state sum at the TS, $N^\ddagger(E, J)$ in the semiclassical adiabatic approximation is given by Equation 4.27. The molecular density of states, $\rho(E, J)$ is obtained by the derivative of Equation 4.16. The rotational degeneracy factor of $2J + 1$, not included in these formulae, thus cancels in the final expression. The result for $J = 0$ versus excitation energy above the dissociation limit, $48.4 \text{ kcal mol}^{-1}$, is shown in Figure 4.15. For comparison, the HO-RR and hindered rotor

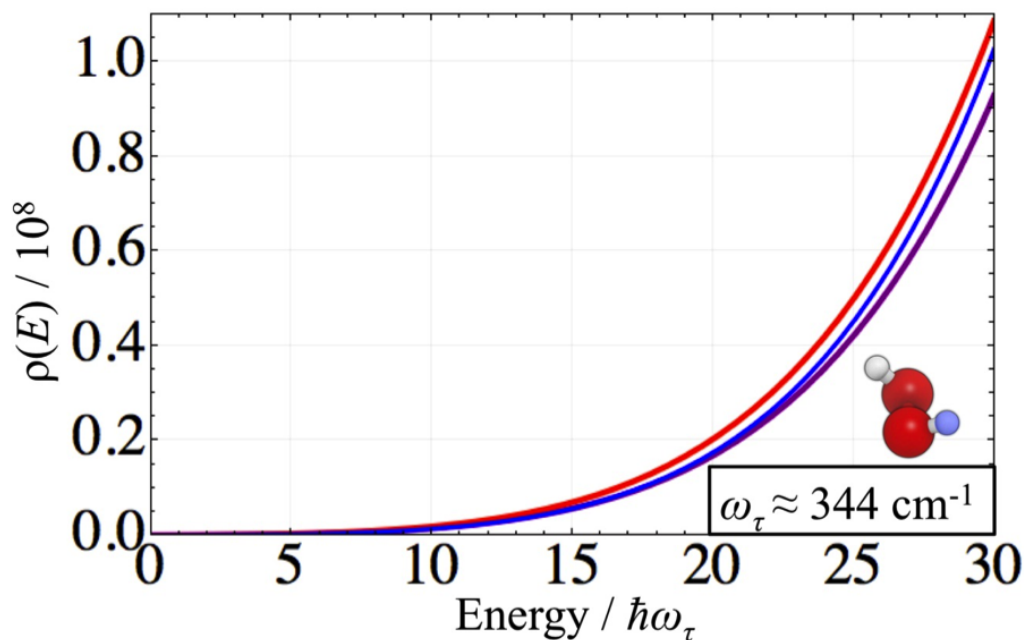


Figure 4.11: The density of states for HOOD as a function of energy above zero point. The red curve is the semiclassical adiabatic model, the blue is HO-RR method, and the purple curve is the separable hindered rotor model.

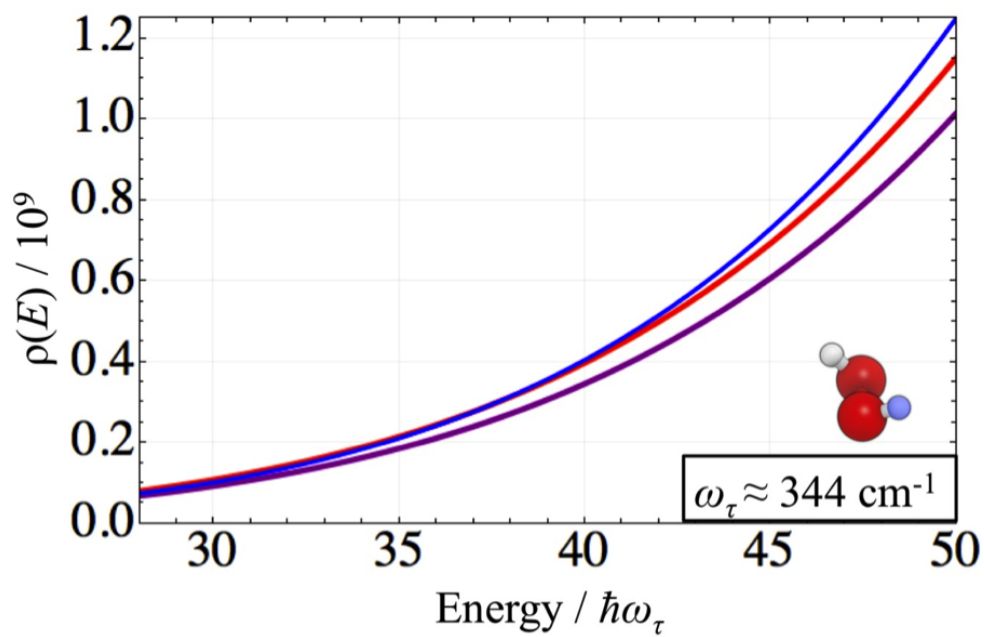


Figure 4.12: Same as Figure 4.11, except at higher energy.

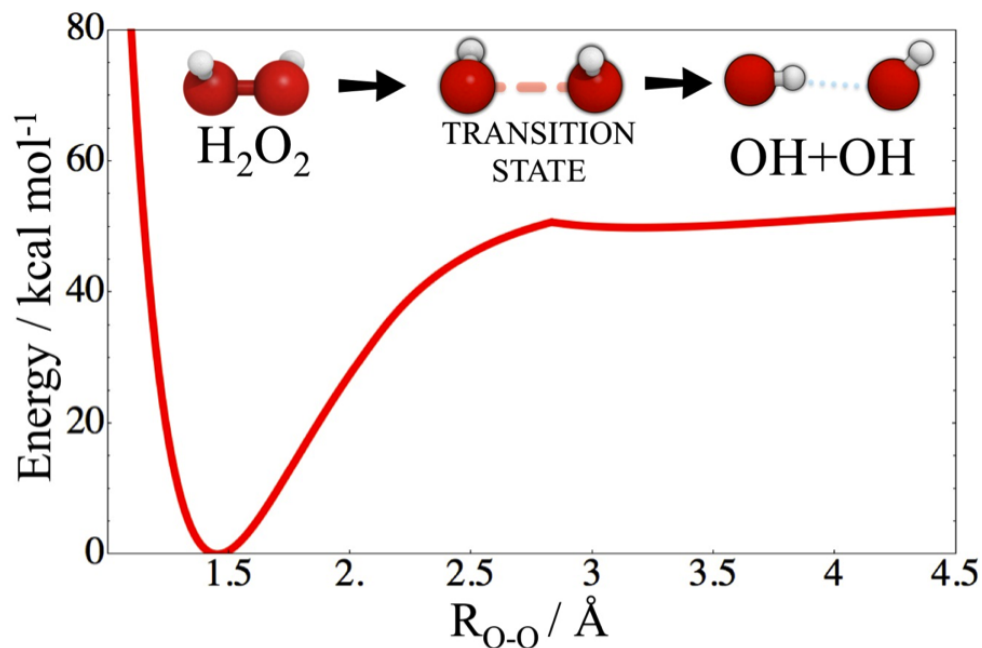


Figure 4.13: The potential energy from the PES of Kuhn et al. [104] computed along the coordinate versus the R bond length. The transition state is taken to be situated slightly before the potential kink.

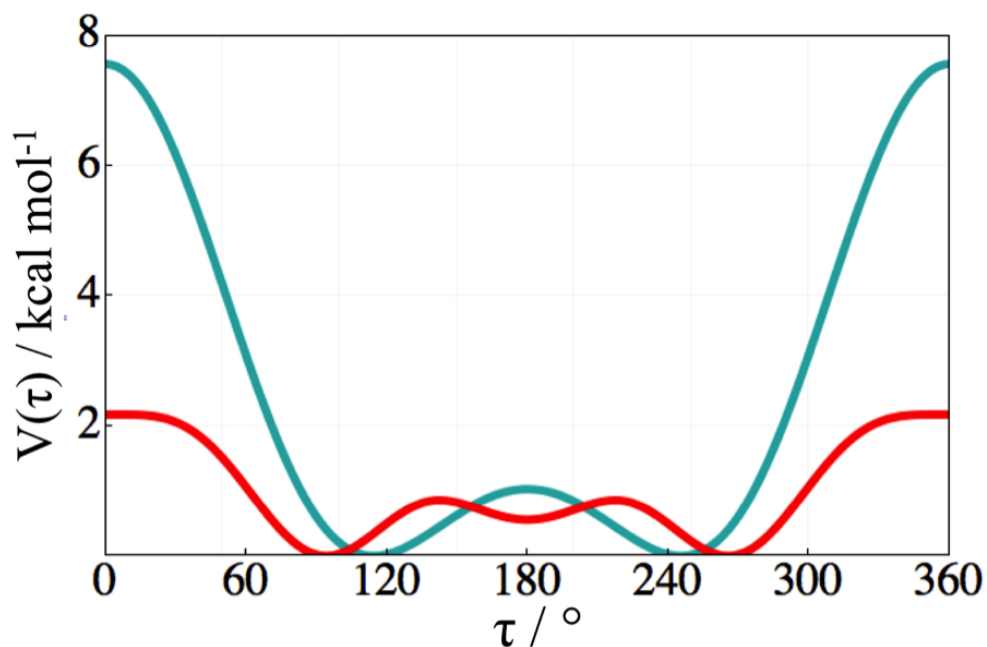


Figure 4.14: The torsional potential for H_2O_2 computed at relaxed geometries given in kcal mol^{-1} . The potential along the ridgeline is shown with the red curve while the potential at the equilibrium geometry is shown with the green curve.

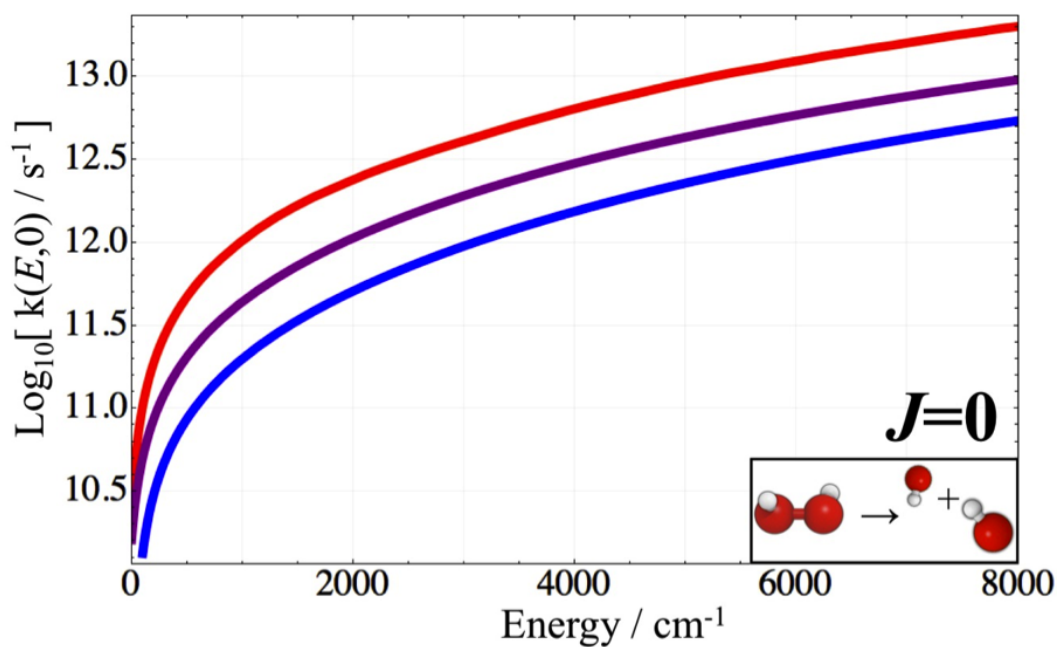


Figure 4.15: The microcanonical rate coefficient versus energy above dissociation for the reaction $\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$ with $J = 0$ computed using three methods. The red curve is the semiclassical adiabatic model, the blue curve is the HO-RR method, and the purple curve shows the result of the separable τ -hindered rotor approximation.

approximations are also presented. It is seen that the HO-RR method gives results that are about a factor 2 to 3 times too low at most energies. Clearly, the harmonic approximation is inappropriate for the transition state. The separable hindered rotor approximation gives an improvement over the HO-RR method. It corrects about half of that error, but still yields results that are about a factor of 1.5 too small. The coupling induced by the torsional dependence of the vibrational frequencies and rotational constants is seen to have a clear and potentially observable effect upon the rate coefficient.

Finally, the influence of overall rotation can be easily determined by constructing the rate coefficients using the state sums and densities obtained from Equations 4.27 and 4.16 for higher values of angular momentum quantum number J . In these calculations, we do not include the shift of location of the transition state with J since this would create difficulty with the potential cusp. The results obtained using the semiclassical adiabatic model are shown in Figure 4.16.

4.5 Conclusions

This work proposes a new method for the inclusion of coupling between a torsional mode and other degrees of freedom in a valid statistical model of a molecule. While totally separable approximations, like the HO-RR method, are quite often useful, they should be used cautiously in quantitative work. The semiclassical adiabatic method developed here accounts for torsional coupling while circumventing the necessity for repeated quantum determinations of torsional eigenenergies at all levels in internal excitation of the molecule. Since the torsional motion is typically of low frequency, this semiclassical approximation is generally good.

Application of the semiclassical adiabatic method to a model system of coupled harmonic oscillators showed that the usual separable model severely overestimates the number of states at higher energy, while the semiclassical method is indistinguishable from the exact state count. The method was successfully tested for many choices of system parameters indicating that the state counting algorithm was reliable.

The density of states for H_2O_2 , and its isotopomer HOOD, were calculated using the semi-

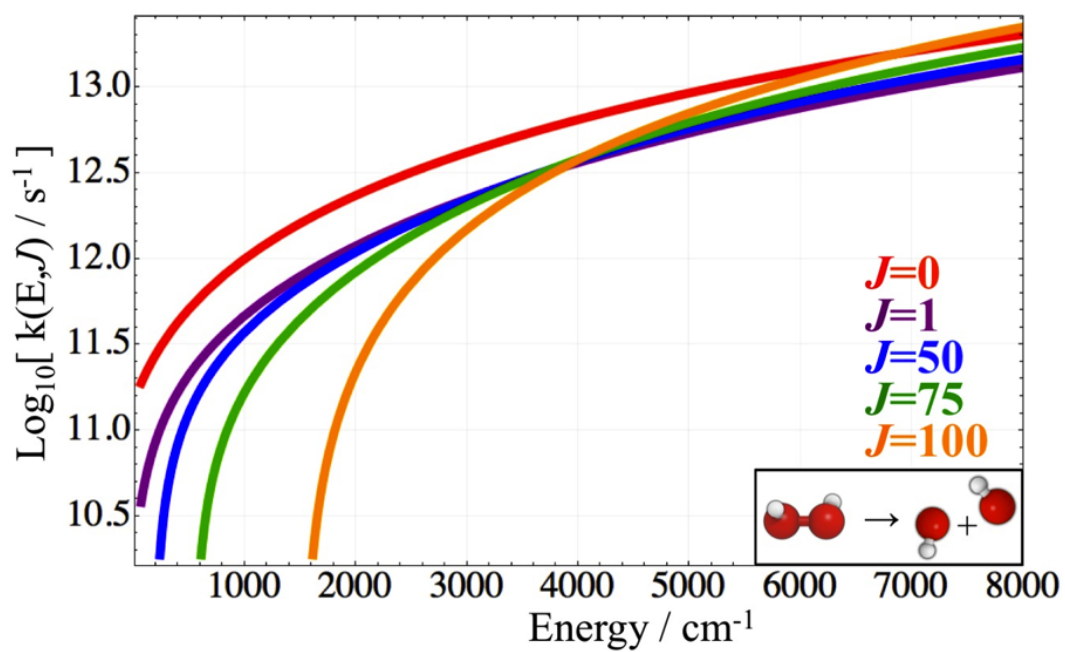


Figure 4.16: The microcanonical rate coefficient versus energy above dissociation calculated using the semiclassical adiabatic model evaluated at five values of the overall angular momentum.

classical adiabatic method and the separable HO-RR and hindered rotor models. Both separable models showed a discrepancy from the semiclassical adiabatic model that included the torsional coupling. At low energies, the HO-RR model underestimated the state density due to the omission of mode coupling while at high energies it over counted the state density due to its omission of torsional anharmonicity. The hindered rotor approximation predicted a state density that was too low due to the neglect of mode coupling. It is clear that while the differences between the adiabatic model and the separable models are on the order of 10%, these differences do appear in observable quantities amenable to experimental verification.

The RRKM rate coefficients for the dissociation of hydrogen peroxide into OH radicals were calculated using the semiclassical adiabatic, τ -hindered rotor, and HO-RR models. The rate coefficients predicted by the methods were significantly different. The HO-RR underestimates the rate by a factor of 2 or 3. The harmonic treatment of torsion at the TS is clearly a poor approximation. The τ -hindered rotor approximation reduces the error to about a factor of 1.5. These deviations between the separable models and the semiclassical adiabatic model are much greater for the rate coefficient than for the thermodynamics of the bound molecule. This is due to both the higher level of torsion coupling at high energies in the reactant and to the importance of torsional coupling at the transition state.

While the adiabatic model has been shown to work well for the case of one slow torsional mode, it is an open question how it will perform for systems with additional torsional modes. Since multiple torsional coordinates exist commonly for many polyatomic systems this is an important avenue for future work.

Chapter 5

Mechanism Construction and Global Sensitivity and Pathway Analyses: Application to a Model of Surface-Catalyzed Decomposition of Methanol on Pd(111), Pt(111), and Ni(111)

The decomposition of methanol on metal surfaces is an important catalytic process in many fuel cell systems. In this work, we construct a microkinetics model of the surface kinetics of the decomposition of methanol on the Pd(111), Pt(111), and Ni(111) metal surfaces using density functional theory calculations performed by Gu and Li [59]. The model is constructed by calculating surface symmetry consistent rate coefficients using conventional transition state theory. We perform first and second order global sensitivity analysis in order to identify the key reactions of the mechanisms and to understand the dependence of the model upon the rate coefficient parameters. In Pd(111) and Ni(111), the reaction $\text{COH} \rightarrow \text{CO} + \text{H}$ is found to be rate limiting and the mechanisms are highly dependent upon the decomposition time of the COH intermediate. Reactions at branches in the reaction network are also particularly important in the modeled kinetics. A stochastic atom-following trajectory based pathway analysis is used to elucidate both the pathway probabilities in the modeled kinetics and the dependence of the pathways on the values of the key rate coefficients of the mechanisms. On Pd(111) and Ni(111) there exists significant competition between the pathway containing the slow step and faster pathways that bypass the slow step. A small discussion is given on the dependence of the model target's probability density function on the chemical pathways.

5.1 Introduction

5.1.1 Complex Chemical Kinetics Models

Complex chemical systems occur in processes where excessive energy or alternative low energy barrier reaction pathways diversify the chemistry available to the involved reactants [166]. Such complex systems are ubiquitous in all areas of chemistry, including combustion [95, 140], heterogeneous catalysis [185], atmospheric chemistry [23, 32], and biological systems [24]. The chemistry of even relatively small molecules in combustion or catalytic environments can be quite varied. For example, the decomposition of methanol on the metal surfaces studied in this paper is composed of 10 possible surface reactions [59] and their corresponding reverse reactions. In the combustion mechanism of methanol, a current mechanism lists 93 reactions and their reverse reactions [116]. Experimental study of complex chemical systems is an interesting but daunting task as often, in addition to the large number of possible chemical reactions, such complex chemistry occurs in environments where experimental observation is difficult or infeasible. Theoretical modeling and kinetics simulations have proved to be invaluable tools for studies involving complex systems, and indeed have become part of the standard tool set employed by practicing researchers for complementing experimental efforts and elucidating interesting chemistry.

Modeling chemical kinetics requires a parameterized chemical mechanism. A model chemical mechanism is composed of a set of elementary chemical reaction steps and their forward and reverse rate coefficient parameters, denoted as k . Depending on the modeled system, thermodynamic and chemical transport properties may also need to be included [177]. The elementary steps and rate coefficients define the system of differential equations that determine the time evolution of the reacting chemical species as the reaction proceeds. In other words, a model is composed of a set of

reacting species $\{A_1, A_2, \dots, A_N\}$ and the set of differential equations,

$$\begin{aligned}\frac{d[A_1]}{dt} &= \sum_j k_j f_{j1}(\{A_1, A_2, \dots, A_N\}) \\ \frac{d[A_2]}{dt} &= \sum_j k_j f_{j2}(\{A_1, A_2, \dots, A_N\}) \\ &\vdots \\ \frac{d[A_N]}{dt} &= \sum_j k_j f_{jN}(\{A_1, A_2, \dots, A_N\})\end{aligned}\tag{5.1}$$

parameterized by the rate coefficients¹. Depending on the process modeled, the number of rate coefficient parameters, k_j , may be quite large. There are many ways to choose such parameters. For instance, rate coefficients can be set to experimentally derived values or can be chosen so that the entire simulation reproduces some empirical quantity of interest. On the other hand, rate coefficients can be calculated from first principles using the results of quantum chemistry calculations [149, 230] and theories such as unimolecular rate theory [130] and transition state theory [201]. While experimentally determined rate coefficients are desirable, they are difficult to determine under some possible reaction conditions, for example, in high pressure environments found in internal combustion engines or in surface catalysis where the changes in surface coverage can have profound effects on reaction rate [57, 73]. Parameters chosen so the model can reproduce an observable measurement can be useful for reproducing chemistry under similar conditions of the benchmark property, but there is no guarantee that such parameters or models are representative of the underlying chemistry. The reliability of such parameters in applications where conditions are different from the conditions under which the parameters were constructed is dubious at best. An ideal model is representative of the underlying chemistry of the system and is grounded on the physical and chemical properties of the reacting species. It is, therefore, desirable to determine the rate coefficients from first principles when accurate calculations are possible.

In most freshman chemistry courses, reaction mechanisms are presented in the context of often containing a “slow”, or “rate-limiting”, elementary step. The same concept is often true in

¹ Other differential equations for properties like temperature and pressure may appear in Equation 5.1 depending on the modeled system.

more complex reaction systems, where a subset of elementary steps may prove to be a bottleneck in the reaction kinetics, or, in a more general sense, may strongly influence the simulated results. Very simply put, some elementary steps are often much more important than others. We shall call such important elementary steps “key” reactions in this work. It is important to note that the set of key reactions can change with the reaction conditions and may be different for different observables being modeled- we will call a modeled observable a “target” and denote it as τ . The accuracy of the model rate coefficients corresponding to the key reactions is, therefore, more critical to the quality of the model than the accuracy of the other parameters. This is actually quite fortuitous, as a high accuracy determination, even from first principles calculations, of all the rate coefficients in a mechanism is extraordinarily time consuming for most modestly sized chemical mechanisms, and, currently, impossible for large and complex mechanisms. Efficient parameterization of a kinetics model should, therefore, be preceded by identification of the key reaction parameters for the target observable. The rate coefficients of the identified key reactions can then be determined to higher precision, while more crude estimates can be used for the other parameters. Skodje et al. [37,177] have proposed a such a scheme by making use of a randomly sampled high dimensional model representation (RS-HDMR) representation [112] of the target τ of the simulation and using global sensitivity analysis [113] to identify the key reactions in the chemical mechanism. They applied their systematic mechanism improvement scheme to several problems in combustion chemistry [37,177,229].

While individual key chemical reactions are often quite important to the simulated chemistry of the model, it is possible that effects originating from interplay between entire chemical pathways, sets of reactions in the reaction network connected by shared reacting chemical species, can also contribute to the quality of the chemical mechanism. Indeed, it is expected that the topology of the reaction network will have an effect on the described chemistry and will have a fundamental connection to why certain reactions are identified as key in global sensitivity analysis. Zhou and Skodje [229] have developed a method to analyze the importance of pathways in a chemical mechanism. In their method, an ensemble of stochastic kinetics trajectories [54,210] are performed

following a single discrete atom, common within the trajectory ensemble, as it proceeds through the chemical mechanism. Pathway probabilities can then be determined by averaging the frequency of an observed pathway in the atom-following ensemble of trajectories. This method goes beyond the traditional kinetics pathway methods involving flux analysis, which are limited since they still rely on calculating flux through individual reactions rather than treating reaction pathways holistically.

5.1.2 Methanol Decomposition on Pd(111), Ni(111), and Pt(111)

The metal surface catalyzed decomposition of methanol is of great interest in fuel cell research [79] due to methanol's high hydrogen to carbon ratio, its availability, and its ability to be transported in liquid form. It is an important process in both direct methanol fuel cells (DMFCs) [13] and in the chemistry of methanol steam reforming (MSR) to hydrogen gas, $\text{H}_3\text{COH} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$. Both DMFC and MSR that have been studied as a fuel source for low emissions vehicles [59, 198]. The decomposition of methanol is also interesting because it shares many chemical characteristics with more complex carbohydrates used in fuel cell research [31, 56] and its surface decomposition mechanism may include many of the same elementary reactions as surface catalyzed mechanisms involving more complicated molecules. Therefore, surface reactions of methanol are of practical interest and of interest as a prototype system for larger fuel cell components.

There have been many studies, both experimental and theoretical, of the surface catalyzed decomposition of methanol on various metal surfaces, particularly Pt, Pd, and Cu, [56, 77, 92] and even on Pd nanocrystals [226]. The mechanism of the decomposition reaction of methanol on Pd(111), Pt(111), and Ni(111) has been characterized using density functional theory in several studies [39, 56, 59, 88]. Indeed, Greeley and Mavrikakis [56] have noted that there is a competition between the reaction pathways in methanol decomposition, which we shall further explore in this study. As we shall similarly observe later in this chapter, they noted that the pathway initialized by the extraction of the methyl hydrogen from methanol dominates over pathways that begin with hydrogen extraction from the hydroxyl hydrogen.

Quantum chemistry calculations of surface catalyzed reactions, primarily plane wave periodic

DFT calculations, have not yet achieved the level of chemical accuracy that can be provided for small gas phase molecules using multireference methods. However, since DFT has become the most commonly applied electronic structure method in both chemistry and material science, DFT is an active area of research and new functionals and implementations, along with maturing computer technology, suggest a promising future for electronic structure calculations of surface catalyzed reactions [12]. In this work, rate coefficients for methanol decomposition on metal surfaces are calculated from ab initio data, but the precision of these coefficients is likely to be relatively low. Even if key reactions are identified, the use of ab initio calculations to achieve highly accurate rate coefficients is unlikely unless the DFT of surface reactions progresses closer to the level of chemical accuracy. This study, however, still recommends the Skodje and Davis' implementation of global sensitivity analysis [177] for improving and optimizing microkinetics simulations of surface catalysis systems. The identification of key reactions alone gives insight into a chemical model and which components of the chemical mechanism are important. Furthermore, both global sensitivity analysis and pathway analysis provide model information and provide a connection between the model results and the reaction network topology. Lastly, if electronic structure theory reaches chemical accuracy in surface science systems, this work suggests a framework for using the results of state-of-the-art ab initio calculations to improve the routine practice of microkinetic simulation. Our purpose here is to present global sensitivity and pathway analyses in the context of a small model surface science problem, and to discuss the implications and connections between the two types of analyses on a non-trivial, but still manageably small, reaction network. Our emphasis will be on the system as a motivating and physically relevant model rather than a highly accurate representation the physical process.

5.1.3 Overview of Methanol Decomposition Mechanism and Analyses

In Section 5.2, we will construct dehydrogenation decomposition of methanol mechanisms on the Pd(111), Pt(111), and Ni(111) metal surfaces using the DFT calculations of Gu and Li [59]. In Section 5.3, we review the global sensitivity analysis implementation and then apply the global

sensitivity analysis methods outlined by Skodje et al. [177] to the decomposition of methanol on the metal surfaces in order to identify the key reactions in the decomposition process. The methanol decomposition mechanism constructed in this work has a relatively simple topology, and is, therefore, a useful trial system for applying the pathway analysis method of Zhou and Skodje. In Section 5.4, we use the atom following trajectory method of Zhou and Skodje to explore the pathway dependence of the methanol decomposition reaction on the chemical mechanism parameters. Also in this section, we will compare the pathway analysis to the first and second order global sensitivity analyses and give a heuristic discussion on how reaction topology and pathway importance influence the identity of key reactions. Manifestations of pathway switching in the target probability density function are also discussed. In Section 5.5, we summarize the conclusions of this work.

5.2 Construction of the Model Methanol Decomposition Mechanism

5.2.1 Density Functional Calculations & Energetics

The DFT calculations for the reaction energetics of the mechanism were all performed by, and generously provided by, Xiang-Kui Gu and Wei-Xue Li. We describe their calculations here as necessary to understand the context of this work, and I take responsibility for any mistakes made describing them below.

Periodic plane wave DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) [101,102]. The exchange-correlation energy was calculated within the generalized gradient approximation (GGA) [151] using the Perdew-Wang 1991 functional (PW91) [152]. A plane-wave basis set with a kinetic energy cutoff of 400 eV was used. A periodic 3×3 unit cell with nine atoms in each layer, corresponding to an adsorbate surface coverage of $\frac{1}{9}$ of a monolayer, was chosen to represent the system. The surface Brillouin zone was sampled with a $5 \times 5 \times 1$ Monkhorst-Pack k -point grid [145]. Four layer slabs were used to model the surface with a 12 Å vacuum separating slabs. The top two layers of the surface and the adsorbate atoms were allowed to relax in optimization calculations, while the bottom two slabs were held in their bulk configuration.

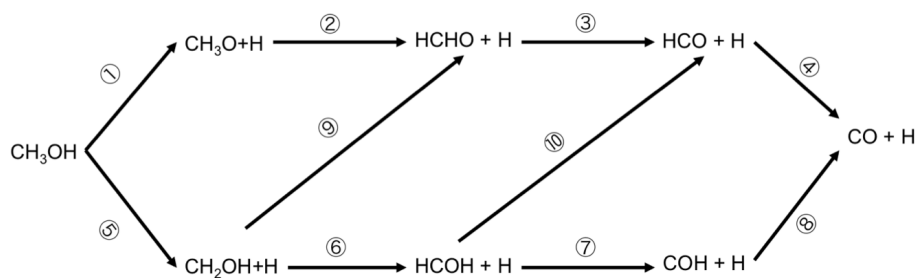


Figure 5.1: The reaction network of the decomposition of methanol via dehydrogenation determined by Gu and Li. Each reaction is referred to by a number and each step results in the loss of a hydrogen from the carbohydrate adsorbate.

Transition states were calculated using the climbing image nudged elastic band method (CI-NEB) [74, 75] with 8 images separating the initial and final states. The transition state was taken as the highest image along the minimum energy path defined by the NEB calculation. Vibrational frequencies were calculated for the equilibrium and transition state structures by diagonalizing the force constant matrix, including only the adsorbate degrees of freedom, obtained from finite differences of the potential performed by VASP. For further details, we refer the reader to the paper by Gu and Li [59] in the bibliography.

In Figure 5.1, the reaction network of the decomposition of methanol via dehydrogenation determined by Gu and Li is shown. A number is assigned to each reaction in Figure 5.1, and we will refer to the reactions by their number throughout the rest of this chapter. Each reaction results in a loss of a hydrogen atom from the carbohydrate adsorbate. In Figure 5.2, the optimized structures of the reactant adsorbates calculated by Li and Gu are shown. In the notation used, notice that HCHO and HCOH are different adsorbates, the first being formaldehyde and the later being an adsorbate with one hydrogen on the carbon and the other on the oxygen. Likewise, H₃CO and H₂COH, and HCO and COH, are all different adsorbates. The first column of structures are those found on Pd(111) and Ni(111), and the second column shows those adsorbates on Pt(111) that had markedly different stable binding configurations than those found on Pd(111) and Ni(111). Only the most stable adsorbates are shown, though some of the adsorbates, particularly H, are known to have other stable binding sites of comparable energy. Only the most stable adsorbates are included

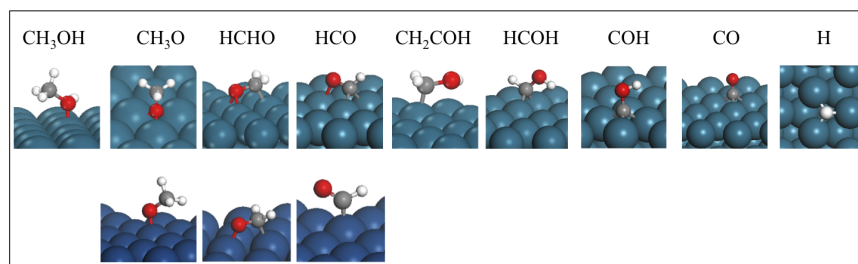


Figure 5.2: The reactant adsorbates in the most stable adsorption sites on Pd(111) and Ni(111) are shown on the first row. Some of the equilibrium structures of Pt(111) were visibly different from those on Pd(111) and Ni(111), and these structures are shown in the second row. Calculations were done by Gu and Li.

in the model, but those included are connected to the transition states found using CI-NEB. The transition state geometries for each reaction in the mechanism are shown in Figure 5.3, and the reaction barrier heights and reverse barrier heights are shown in Figure 5.4. The reverse reaction barrier heights shown in Figure 5.4 are generally very high compared to those of the corresponding forward reactions. The high reverse energetic barriers mean that the reverse reactions will be mostly insignificant at temperatures of practical interest and the forward reactions will be dominant, as will be seen later. Also, each hydrogen extraction is highly exothermic, as the loss of a hydrogen usually results in either an increase in the number of adsorption bonds to the surface or at least the development of a more stable adsorption bond. There are several other common trends for the mechanism on the three metals. First, the initial hydrogen extraction from the methyl group has a lower energy barrier, particularly on Pd and Pt, than the initial extraction from the hydroxyl group. The last hydrogen extraction in reaction 8 has a relatively high barrier and is very exothermic in all three reactions. The two branching reactions 6 and 9 have comparable energetic barriers on all three metals. The vibrational frequencies for each equilibrium adsorbate and transition state are given in Table 5.2.1. The lowest frequencies in Tables 5.2.1 and 5.2.1 roughly correspond to the translation of the adsorbates along the surface and, usually, the rotation of the adsorbate about its adsorption bond. The lowest frequencies of the saddle point geometries are, in general, higher than the lowest frequencies of the equilibrium energy geometries since the mechanism of surface

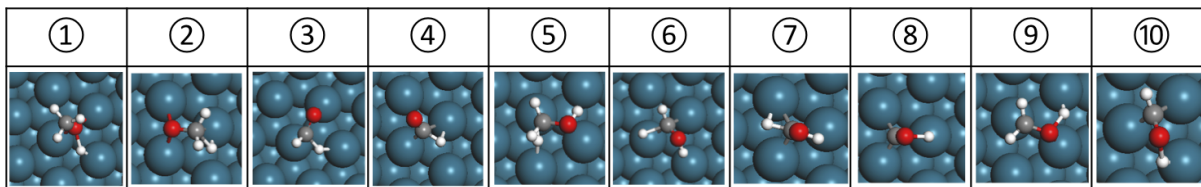


Figure 5.3: The transition states for each reaction on Pd(111) in Figure 5.1. Calculations were done by Gu and Li.

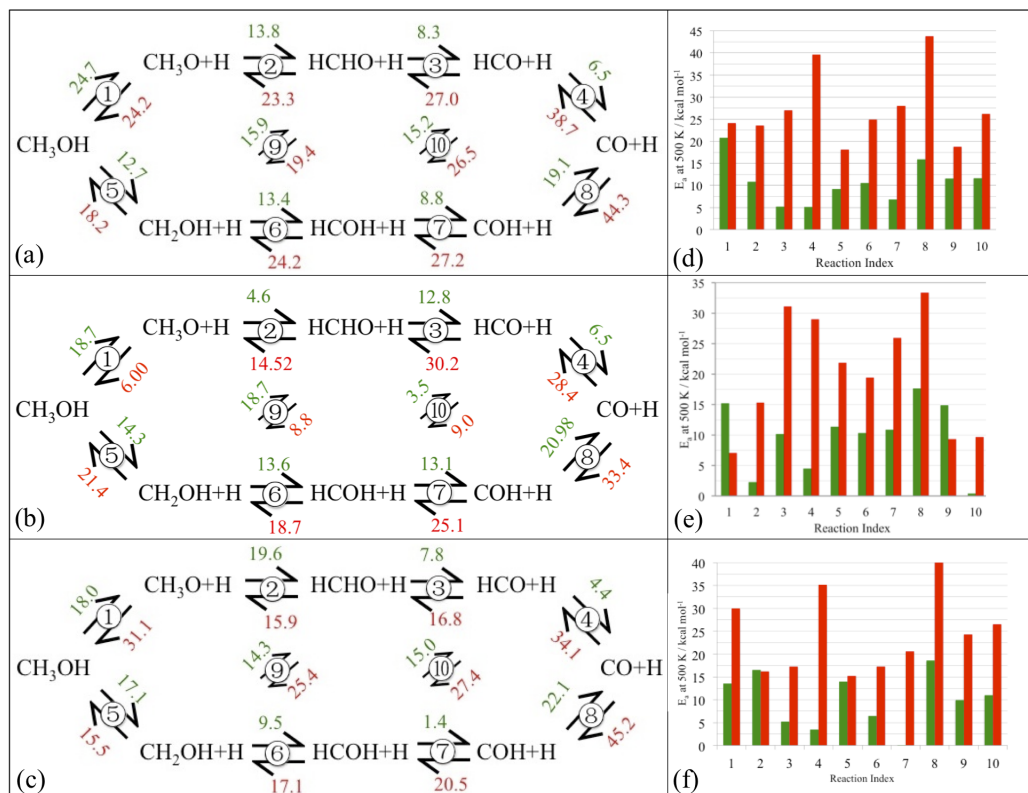


Figure 5.4: In (a), (b), and (c) the forward and reverse reaction barrier energies are shown on the reaction network on Pd(111), Pt(111), and Ni(111), respectively. The zero point energy is not included. In (d), (e), and (f) the forward (green) and reverse (red) activation energies calculated at a temperature of 500 K are shown for Pd(111), Pt(111), and Ni(111), respectively. All energies shown are in kcal mol⁻¹.

Table 5.1: Vibrational frequencies, in cm^{-1} of each equilibrium adsorbate in the reaction mechanism calculated using DFT by Gu and Li. Very small imaginary frequencies have been left out and are treated as free rotations in subsequent calculations.

Adsorbate	Pd(111)	Pt(111)	Ni(111)
CH ₃ OH	3676, 3078, 3038, 2964, 1450 1442, 1417, 1298, 1131, 1038, 973, 405, 197, 128, 112, 56, 46	3651, 3081, 3055, 2975, 1447, 1440, 1414, 1291, 1129, 1037, 972, 472, 220, 145, 133, 70, 57	3598, 3088, 3054, 3040, 1455, 1446, 1414, 1293, 1135, 1045, 971, 425, 219, 143, 118, 63, 49
CH ₃ O	3046, 3045, 2959, 1432, 1431, 1405, 1107, 1106, 962, 292, 291, 245, 100, 90	2975, 2930, 2872, 1419, 1391, 1380, 1094, 1090, 1004, 460, 245, 187, 92, 80, 40	3065, 3062, 3040, 1445, 1442, 1412, 1134, 1132, 977, 305, 292, 286, 107, 96
CH ₂ OH	3502, 3082, 2981, 1408, 1316, 1115, 1062, 945, 686, 481, 440, 220 118, 73, 57	3571, 3090, 2983, 1423, 1334, 1165, 1089, 1011, 752, 504, 432, 229, 105, 62, 51	3520, 3078, 3008, 1395, 1284, 1112, 1051, 835, 598, 542, 469, 250, 116, 84, 69
HCHO	3023, 2927, 1421, 1160, 1139, 919, 569, 440, 281, 215, 170, 121	2983, 2902, 1421, 1171, 1134, 959, 622, 505, 359, 180, 121, 37	3041, 2966, 1423, 1138, 1110, 902, 596, 442, 331, 235, 123, 113
HCOH	3252, 2955, 1335, 1151, 1124, 850, 485, 462, 354, 259, 138, 92	3185, 3011, 1349, 1170, 1147, 893, 538, 530, 351, 304, 167, 125	3319, 2940, 1361, 1156, 1103, 811, 462, 417, 297, 253, 83, 51
HCO	2887, 1370, 1120, 666, 473, 311, 295, 187, 176	2862, 1726, 1159, 806, 553, 291, 124, 44, 40	2902, 1282, 1173, 631, 477, 313, 233, 152, 67
COH	3577, 1235, 1070, 499, 484, 355, 166, 165, 101	3596, 1256, 1100, 512, 466, 386, 210, 180, 155	3586, 1258, 1088, 451, 412, 390, 237, 136, 99
CO	1771, 347, 346, 317, 157, 155	1747, 338, 314, 313, 170, 162	1765, 347, 282, 270, 133, 95
H	920, 879, 867	1028, 652, 650	1130, 906, 894

Table 5.2: Vibrational frequencies, in cm^{-1} of each transition state in the reaction mechanism calculated using DFT by Gu and Li. The imaginary frequencies are included.

TS	Pd(111)	Pt(111)	Ni(111)
1	3019, 3011, 2936, 1431, 1427, 1399, 1203, 1108, 1099, 970, 532, 242, 235, 126, 93, 86, 57, 699 <i>i</i>	3006, 2988, 2917, 1550, 1431, 1407, 1389, 1110, 1108, 985, 565, 432, 279, 214, 183, 116, 64, 281 <i>i</i>	2998, 2962, 2889, 1426, 1423, 1397, 1112, 1106, 985, 838, 644, 364, 199, 189, 126, 94, 61, 847 <i>i</i>
2	2997, 2930, 1609, 1417, 1169, 1140, 1043, 772, 542, 340, 243, 222, 161, 111, 948 <i>i</i>	3009, 2912, 1681, 1454, 1309, 1165, 1028, 755, 517, 355, 280, 201, 145, 92, 600 <i>i</i>	3040, 2967, 1775, 1421, 1192, 1144, 1009, 791, 461, 336, 302, 251, 157, 134, 946 <i>i</i>
3	2937, 1467, 1210, 994, 917, 819, 467, 291, 233, 156, 110, 688 <i>i</i>	2986, 1577, 1414, 1223, 917, 736, 529, 296, 154, 142, 47, 832 <i>i</i>	2935, 1845, 1237, 1208, 862, 592, 474, 350, 208, 188, 121, 810 <i>i</i>
4	2063, 1653, 919, 402, 344, 258, 122, 50, 323 <i>i</i>	1837, 1304, 942, 694, 334, 255, 211, 52, 265 <i>i</i>	2395, 1400, 1059, 528, 325, 276, 174, 138, 270 <i>i</i>
5	3372, 3092, 2970, 1456, 1389, 1323, 1151, 1103, 1039, 708, 582, 493, 324, 182, 158, 71, 65, 750 <i>i</i>	3404, 3090, 3016, 1751, 1423, 1340, 1172, 1112, 1053, 739, 611, 510, 342, 184, 108, 76, 62, 902 <i>i</i>	3362, 3084, 2957, 1599, 1407, 1407, 1320, 1148, 1106, 1021, 667, 551, 475, 329, 191, 145, 65, 61, 855 <i>i</i>
6	3304, 2997, 1875, 1340, 1159, 1102, 971, 547, 536, 433, 256, 238, 112, 93, 794 <i>i</i>	3285, 3046, 1624, 1343, 1210, 1144, 958, 681, 606, 551, 287, 222, 96, 90, 801 <i>i</i>	3479, 2819, 1823, 1362, 1168, 1056, 966, 553, 475, 410, 227, 219, 111, 47, 846 <i>i</i>
7	3586, 1592, 1224, 1152, 3554, 1948, 1198, 1084, 3610, 1826, 1217, 1121,	1083, 573, 452, 358, 693, 562, 391, 374, 564, 476, 369, 320	260, 231, 136, 173 <i>i</i> 271, 256, 149, 412 <i>i</i> 203, 170, 31, 588 <i>i</i>
8	1495, 1347, 565, 411, 403, 375, 229, 157, 1428 <i>i</i>	1513, 1366, 630, 427, 411, 382, 239, 189, 1530 <i>i</i>	1474, 1273, 502, 427, 345, 324, 189, 121, 1541 <i>i</i>
9	2996, 2900, 1425, 1205, 1145, 1045, 886, 570, 548, 423, 312, 230, 113, 105, 709 <i>i</i>	3023, 2936, 1548, 1413, 1146, 1140, 948, 741, 670, 500, 327, 273, 174, 168, 513 <i>i</i>	3010, 2929, 1398, 1138, 1099, 963, 919, 715, 526, 427, 323, 188, 137, 93, 1245 <i>i</i>
10	2844, 1480, 1269, 1104, 687, 585, 418, 296, 225, 142, 44, 959 <i>i</i>	2958, 1568, 1255, 1115, 857, 733, 630, 478, 198, 197, 86, 772 <i>i</i>	2885, 1278, 1185, 1015, 705, 575, 442, 291, 232, 165, 59, 1295 <i>i</i>

catalyzed reactions usually involves the transition state forming multiple bonds with the surface. The multiple surface bonds restrict diffusional and in-site rotational motions. This is also observed for the equilibrium adsorbate frequencies with multiple or strong surface-adsorbate bonds. While each of the adsorbates and saddle points should have $3N$ frequencies, where N is the number of atoms, fewer frequencies are listed for some of the adsorbates in Table 5.2.1. These frequencies were very small and were reported as imaginary in the final converged calculation, although the imaginary values are likely due to small errors rather than significant instability. The normal modes corresponding to these “zero” frequencies were associated with in-site rotations of the adsorbates about their adsorbate bonds. The in-site rotations with this property were treated as free rotors in the subsequent analysis.

5.2.2 Transition State Theory Rate Constant Calculation

Rate coefficients for the kinetics mechanism in Figure 5.1 were calculated with conventional transition state theory (TST),

$$k_{\text{TST}} = \left(\frac{k_B T}{h} \right) \frac{Q_{\text{TS}}^\ddagger}{Q_{\text{R}}} e^{-\frac{E^\ddagger}{k_B T}} \quad (5.2)$$

where Q ’s are the canonical molecular partition functions per volume, or on a surface per surface area, and $E^\ddagger$ is the reaction barrier energy. The imaginary degree of freedom corresponding to the reaction coordinate in $Q_{\text{TS}}^\ddagger$. The molecular partition functions are constructed, according to the usual practice [184], as a product of all the partition functions of individual degrees of freedom within the molecule. In contrast to gas phase systems, the translational and rotational degrees of freedom of surface adsorbates are, in general, restricted by the surface bonds. In the simplest approximation, all degrees of freedom can be treated either as harmonic oscillators or free rotors, which we adopt here. This is an excellent place to start the global sensitivity analysis improvement scheme, since the identification of the key reactions in the microkinetics model can proceed by updating only the key rate coefficients with a more rigorous TST treatment. Free rotors are used to approximate in-site adsorbate rotational degrees of freedom about the adsorption bond for the methanol and methoxy adsorbates, which were found to have rotational temperatures of 1.85 K

and 7.53 K (2.12 K on Pt), respectively. The vibrational partition function used for a mode of frequency ω is,

$$q_{\text{vib}} = \frac{e^{-\frac{\hbar\omega}{2k_B T}}}{1 - e^{-\frac{\hbar\omega}{k_B T}}} \quad (5.3)$$

and the classical free rotor partition function used is,

$$q_{\text{FR}} = \frac{1}{\sigma} \left(\frac{T}{\Theta_R} \right)^{\frac{1}{2}} \quad (5.4)$$

where Θ_R is the rotational temperature and σ is the symmetry number of the rotation, 1 for the methanol rotation and the methoxy rotation in Pt, and 3 for the methoxy rotation in Pd and Ni.

Symmetry is another consideration when constructing transition state theory rate coefficients for surface reactions, and symmetry considerations can, and perhaps sometimes should, be extended beyond the traditional symmetry number corrections due to degrees of freedom that exchange identical nuclei [138]. Achiral molecules can become chiral adsorbates when bound to the surface, and the high degree of symmetry on the surface provides reaction path degeneracies for each of the rate coefficients depending on how the molecular degrees of freedom are treated in the partition functions. This symmetry effect is given in the limit of very low coverage as,

$$k_{\text{uni}}(T) = \left(\frac{k_B T}{h} \right) \left(\frac{N_{TS}}{N_R} \right) \left(\frac{n_{TS}}{n_R} \right) \left(\frac{\sigma_R}{\sigma_{TS}} \right) \frac{Q_{\text{TS}}^{0\dagger}}{Q_R^0} e^{-\frac{E^\ddagger}{k_B T}} \quad (5.5)$$

and for a bimolecular reaction, when reactant adsorbate concentrations are expressed per unit area,

$$k_{\text{uni}}(T) = \alpha_u \left(\frac{k_B T}{h} \right) \left(\frac{N_{TS}}{N_{R_1} \times N_{R_2}} \right) \left(\frac{n_{TS}}{n_{R_1} \times n_{R_2}} \right) \left(\frac{\sigma_{R_1 R_2}}{\sigma_{TS}} \right) \frac{Q_{\text{TS}}^{0\dagger}}{Q_{R_1}^0 \times Q_{R_2}^0} e^{-\frac{E^\ddagger}{k_B T}} \quad (5.6)$$

where the Q^0 are molecular partition functions that contain no symmetry whatsoever. The symmetry number σ accounts for the exclusion of certain states in the molecular state sum over degrees of freedom that exchange indistinguishable nuclei. The chiral number n_i is the number of chiral conformations of species i . Both the symmetry number and chiral number effects are well described in the literature [46, 158]. A description of the factor N_i is more difficult to find in the literature and is most commonly referred to in reference to surface diffusion [76, 202]. The factor N_i counts all possible adsorption sites and orientations of adsorbate i within the context of how the degrees of

Table 5.3: Symmetry prefactors to the transition state theory rate constants shown in Equations 5.5 and 5.6. Parenthesis are put in when Pt(111) factors differ from Pd(111) and Ni(111). The ‘*’ indicates a free rotor partition function is used for in-site rotation of one of the reactants.

Rxn	Forward Rxn	Reverse Rxn
1 ^{*(*)}	3	2
2 ^{*(*)}	6	2/3 (1/3)
3	2 (1)	2/3 (2)
4 ^(*)	2 (6)	2
5 ^{*(*)}	3	1/3
6	1	2/3
7	1	1/3
8	1	1
9	1	2/3 (1/3)
10	2	2/3

freedom are incorporated into Q_i^0 , e.g. whether the adsorbate is allowed to rotate in its adsorption site, in a surface unit cell of area α_u . The area α_u is large enough so that it contains all the surface symmetry elements and all possible adsorbate orientations for all the included adsorption sites, and is usually intuitive for a given problem. The cell can be chosen to be arbitrarily large, but usually the simplest cell that contains all the orientations and connecting reaction paths to the species is usually the most convenient. The same surface cell of area α_u must be used for both the transition state and the reactant adsorbates to calculate N_{TS} and N_R .

We give the values of the symmetry factors, including N , n , and σ terms, used in each rate coefficient calculation in Table 5.2.1. The bimolecular symmetry factors must be multiplied by the area of the site on which they were determined. A hexagonal site of the (111) surface was used, composed of 7 surface atoms. The areas of these sites are given in Table 5.2.2. In Figures 5.5(a), (b), and (c), the calculated forward TST rate constants are shown on Pd(111), Pt(111), and Ni(111), respectively. It is readily apparent that the model chemical mechanism of the reaction is very different for different metals, although the reaction network topology is the same for each. However, on the Pd and Pt metals, we clearly see that reaction 1 has a very small forward rate constant relative to reaction 5. This is consistent with the kinetics findings of

Table 5.4: The areas, in units of $\text{\AA}^2$, of the hexagonal unit (111) surface sites used to calculate the bimolecular symmetry factors given in Table 5.2.2.

Pd(111)	Pt(111)	Ni(111)
21.1	20.7	16.4

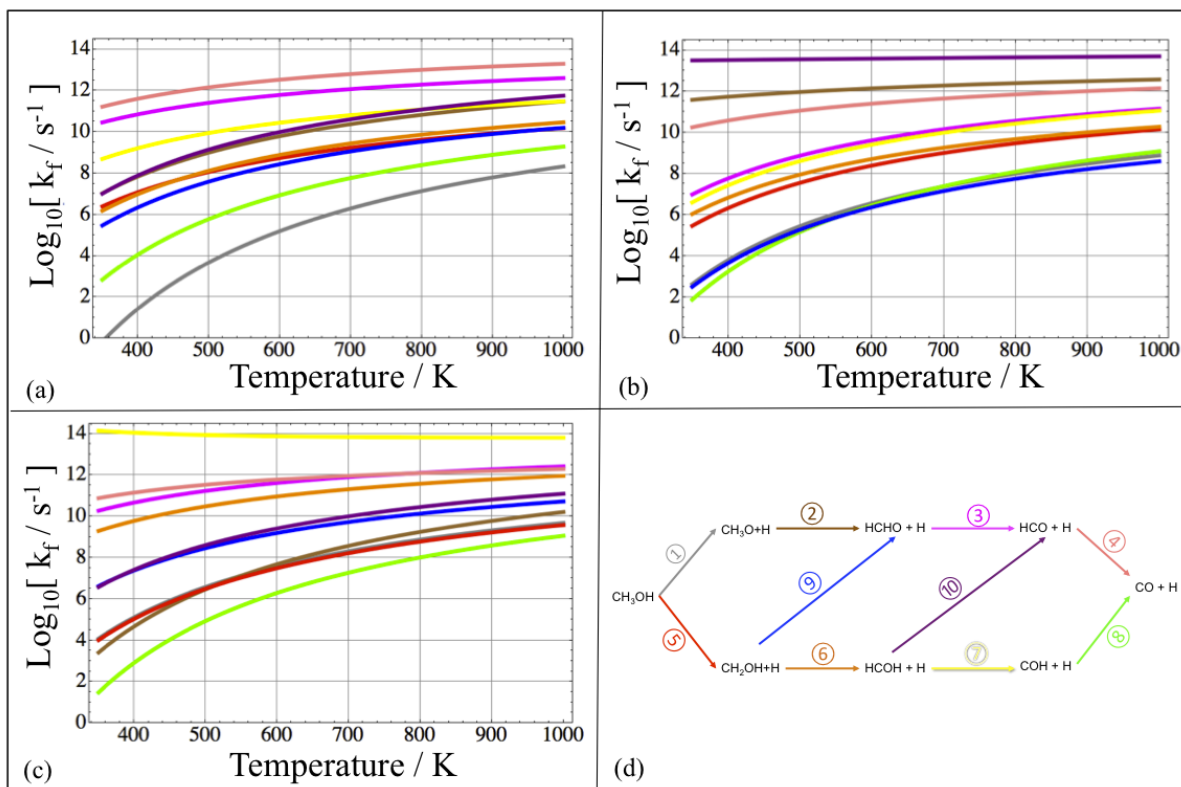


Figure 5.5: In (a), the orders of magnitude for the forward rate constants in the reaction mechanism on Pd(111) as a function of temperature. In (b), same as (a) but on Pt(111). In (c), same as (a) but on Ni(111). In (d), a color coded reaction network that is a legend for (a), (b), and (c).

Greeley and Mavrikakis [56] on Pt. Both Pt(111) and Ni(111) have a large rate coefficient, for step 10 on Pt and step 7 on Ni, that result from very small reaction barriers, see Figure 5.4. For step 7 on Ni, the barrier is low enough that the zero point corrected barrier height is actually negative, suggesting that the HCOH adsorbate is unstable on Ni(111). We include reaction 7 in the Ni mechanism with its calculated TST rate coefficient within our global sensitivity and pathway analyses without modification. Although the negative activation energy is likely incorrect, since the order of magnitude of this rate coefficient for step 7 on Ni is so much greater than all the other reactions, even within our rate coefficient sample space, it can approximately be thought of as happening “instantly”. This is roughly consistent with the HCOH being unstable. Lastly, it is important to compare the rate coefficients for reactions at branches in the reaction mechanism. Reactions 1 and 5 have very similar rate coefficients on Ni and some competition is expected at this junction. Similarly, reactions 6 and 9 on Pd are quite close together. As temperature increases, all of the rate coefficients become closer in value, and we expect pathway competition to increase as the temperature increases.

5.2.3 Model Limitations

While only dehydrogenation and the corresponding reverse reactions are included in the model mechanism, these are not the only possible surface reactions. Reactions between carbohydrate intermediates are not considered, and Mavrikakis et al. [92] found that while some of these reactions have a relatively low barrier on Pt, their inclusion in a microkinetics model did not cause significant changes to their modeled result. Since Greeley and Mavrikakis’s [56] model well represented experimental data, this suggests that the inclusion of these non-dehydrogenation reactions are not critical to the model on Pt(111). We do not include these reactions in any of our mechanisms in the absence of evidence that they play a key role in the kinetics.

On a last note, we have not included adsorption and desorption within our model. We acknowledge that this is physically unrealistic; however, our primary purpose in this work is to compare the results of global sensitivity and pathway analyses methods on a simple test reaction

network. Our model test problem is based on the decomposition of methanol and we expect that many of the main conclusions of our model can be extrapolated, or are at least relevant to, a more complete mechanism. In particular, the key surface reactions can be identified within the framework of the surface model presented here, as the reaction network is simple and feedback loops in the kinetics are insignificant, at least within the model, as the back reactions have large barriers. Future work should include incorporation of the adsorption and desorption into the model mechanism and simulation of a more relevant physical result, such as H_2 turnover frequency [92].

5.3 Global Sensitivity of Analysis of Methanol Decomposition

5.3.1 Global Sensitivity Methodology

This section gives an overview of the global sensitivity analysis method, based on the work by Sobol [180] and the HDMR method of Rabitz [159], given by Skodje et al. [177]. In this method, each rate coefficient parameter has an associated uncertainty, Δk_i , originating from experimental or theoretical error bars. The purpose of global sensitivity analysis is to determine how the uncertainty in all the model parameters translates to the uncertainty in the model result. Therefore, random sets of model parameters are sampled [180], rate coefficients $\{k_1^i, k_2^i, \dots\}$, where i stands for the i^{th} sample, from the full parameter uncertainty space and the model is run for each sampled set. This generates a set of values of the target that define a probability distribution of the target variable. From this probability distribution, a variance of the target can be found and decomposed into contributions from the uncertainty of individual parameters. Figure 5.6 shows a schematic of the global sensitivity analysis process.

Skodje et al. [177] describe the advantages of global sensitivity analysis over the much more commonly applied local sensitivity analysis. Specifically, global sensitivity analysis samples all of the parameter uncertainty space of the model, in other words all uncertainty space of the rate coefficients, simultaneously. Local sensitivity analysis, the derivative of the target model result with respect to one or multiple parameters, measures variation only about the set of nominal values of

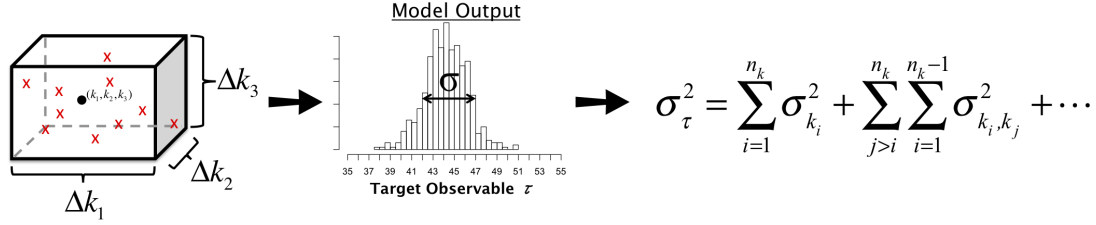


Figure 5.6: Schematic of the global sensitivity analysis process. The parameter sample space is randomly sampled. A probability density function is defined, and therefore a variance. The variance is then decomposed into contributions from each parameter and set of parameters.

the rate coefficients. If the true, that is most physically relevant, model parameter set lies far from the nominal values of the rate coefficients, then local sensitivity may not accurately describe the true variation of the model with respect to the rate coefficients [168]. Because of the simultaneous sampling over all uncertainty space, the covariation of the model result with respect to two or more of the model parameters can also be more clearly resolved using the global method. Dependence on the model result due to one or several rate coefficient parameters can also be judged based on the probability density function (PDF) of the target result as sampled over the rate coefficient uncertainty space [37].

The initial conditions of our microkinetics model were taken to be an initial methanol coverage on the surface of θ_{MeOH}^0 , and all other species at zero coverage, at a constant temperature, T . The chosen target for the model is the time it takes to convert 80% of the initial methanol concentration to CO, and which we shall call $\tau_{80\%}$. We denote this target variable as τ , and note that it can be represented as a function of the parameter space,

$$\tau = \tau(k_1, k_2, \dots, k_N, T, \theta_{\text{MeOH}}^0) \quad (5.7)$$

where θ_{MeOH}^0 is the initial methanol coverage on the surface. We shall leave out the T and θ_{MeOH}^0 hereafter for simplicity. According to the HDMR representation of Rabitz [113–115, 159, 232], we can expand the target function as a function of each of its parameters,

$$\tau(k_1, k_2, \dots, k_{n_k}) = \tau_0 + \sum_{i=1}^{n_k} A_i(k_i) + \sum_{i>j} \sum_{j=1}^{n_k} B_{ij}(k_i, k_j) \quad (5.8)$$

where $A_i(k_i)$ are functions that represent the dependence of the target on a single rate coefficient, and $B_{ij}(k_i, k_j)$ are functions that represent dependence with respect to the coupling of two rate coefficients. Higher order terms can be used, but it has been observed that many physical systems can accurately be represented by the truncation of Equation 5.8 at the second order term [159]. We shall not consider orders beyond the 2nd. The term τ_0 is a constant. The A and B functions are conveniently expressed in terms of an orthogonal polynomial basis, so that they satisfy the relations,

$$\begin{aligned}\langle A_i \rangle &= 0, & \langle A_i A_j \rangle &= \delta_{ij} \\ \langle B_{n,m} \rangle &= \langle A_i B_{n,m} \rangle = 0 \\ \langle B_{n,m} B_{j,k} \rangle &= \delta_{nj} \delta_{mk} \\ &\vdots\end{aligned}\tag{5.9}$$

where $\langle \dots \rangle$ denotes an average over all rate coefficient uncertainty space. In this study, orthonormal Legendre polynomials were used,

$$\begin{aligned}L_0(x) &= 1 \\ L_1(x) &= \sqrt{3}(2x - 1) \\ L_2(x) &= \sqrt{5}(6x^2 - 6x + 1) \\ &\vdots\end{aligned}\tag{5.10}$$

The first and second order terms in Equation 5.8 are expressed as,

$$A_i(k_i) = \sum_{\ell=1}^{\eta_i} \alpha_{\ell}^i L_{\ell}(\kappa_i)\tag{5.11}$$

$$B_{ij}(k_i, k_j) = \sum_{\ell=1}^{\eta_i} \sum_{\delta=1}^{\eta_j} \beta_{\ell\delta}^{ij} L_{\ell}(\kappa_i) L_{\delta}(\kappa_j)\tag{5.12}$$

where κ_i represents a scaled variable needed since the Legendre polynomials in Equation 5.10 are defined in the space $x \in [0, 1]$. The κ_i factor is defined as,

$$\kappa_i = \frac{k_i - k_i^{\text{MIN}}}{k_i^{\text{MAX}} - k_i^{\text{MIN}}}\tag{5.13}$$

The terms k_i^{MIN} and k_i^{MAX} are the minimum and maximum values considered in the uncertainty sample space of rate coefficient k_i .²

The sampling space of the rate coefficients is defined by a probability distribution function $P_{\mathbf{k}}(\mathbf{k})$, where $\mathbf{k}$ stands for the set of the rate coefficients in the mechanism. In the orthogonal polynomial representation, the functions in Equation 5.8 can be determined knowing $P_{\mathbf{k}}(\mathbf{k})$, by,

$$\tau_0 = \oint_{\Omega_{\text{FULL}}} P_{\mathbf{k}}(\mathbf{k}) \tau(\mathbf{k}) dk_1 dk_2 \cdots dk_N \quad (5.14)$$

$$A_i(k_i) = \oint_{\Omega_{-i}} P_{\mathbf{k}}(\mathbf{k}) \tau(\mathbf{k}) dk_1 dk_2 \cdots dk_{i-1} dk_{i+1} \cdots dk_N - \tau_0 \quad (5.15)$$

$$\begin{aligned} B_{ij}(k_i, k_j) = & \oint_{\Omega_{-i-j}} P_{\mathbf{k}}(\mathbf{k}) \tau(\mathbf{k}) dk_1 dk_2 \cdots dk_{j-1} dk_{j+1} \cdots dk_{i-1} dk_{i+1} \cdots dk_N \\ & - A_i(k_i) - A_j(k_j) - \tau_0 \end{aligned} \quad (5.16)$$

where Ω is the full rate coefficient uncertainty space, and Ω_{-i} signifies the reduced rate constant uncertainty space for at a specific set value of k_i . It follows that the partial variances can be defined by the low dimensional integrals,

$$\sigma_i^2 = \int_{\text{All } k_i \text{ Space}} P_i(k_i) A_i^2(k_i) dk_i = \sum_{\ell=1}^{\eta_i} \alpha_{\ell}^i{}^2 \quad (5.17)$$

$$\sigma_{ij}^2 = \int_{\text{All } k_j} \int_{\text{All } k_i \text{ Space}} P_i(k_i) P_j(k_j) B_{i,j}^2(k_i, k_j) dk_i dk_j = \sum_{\ell}^{\eta_i} \sum_{\delta}^{\eta_j} \beta_{\ell\delta}^{ij}{}^2 \quad (5.18)$$

where the second terms follow from the properties of the orthonormal Legendre polynomial representations of Equation 5.9, and α and β coefficients are defined in Equations 5.11 and 5.12.

While it is possible to obtain the expressions for the polynomial expansion of the target using Equations 5.14, 5.15, and 5.16, even for mechanisms of moderate size, the multidimensional integrations can become computationally expensive or prohibitive. An alternate scheme can be used to obtain the coefficients α and β in Equations 5.11 and 5.12. The uncertainty space of $\mathbf{k}$ is randomly sampled according to its probability distribution $P_{\mathbf{k}}(\mathbf{k})$ a number N times. This can be done using Monte Carlo sampling [177] and the random sampling HDMR (RS-HDMR) technique

² Of course Equations 5.13, 5.11, and 5.12 assume that the parameter space is bounded, and is most convenient if $P_{\mathbf{k}}(\mathbf{k})$ is uniform, but a different orthogonal basis can be used if it is not. In a chemical mechanism, there are certainly limits on the magnitude of k_i .

of Rabitz et al. [112,113]. The model is run for each of the N set of samples of $\mathbf{k}$, N target values are generated, and the total variance is determined according to,

$$\sigma_{\text{TOT}}^2 = \langle \tau^2 \rangle - \langle \tau \rangle^2. \quad (5.19)$$

Since there are now N samples of the target over the $\mathbf{k}$ sample space, the computation of the means in Equation 5.19 is straightforward as a sum over a discrete set of data. The coefficients can be approximately determined using least squares linear regression [177]. In this work, the coefficients α for each first order function of the form given in 5.11 for each k_j were fit to the residuals of the sampled target values, τ_i from the mean,

$$R_i^1 = \tau_i - \tau_0 \quad (5.20)$$

individually. The second order coefficients, β , to fit the second order functions in Equation 5.12 were determined by linear regression of the residuals [113] of the sampled target values from the mean and the first order fits³,

$$R_i^2 = \tau_i - \tau_0 - \sum_{i=1}^{n_k} A_i(k_i) \quad (5.21)$$

The first and second order sensitivities can then be determined from,

$$S_i = \frac{\sigma_i^2}{\sigma_{\text{TOT}}^2} \quad (5.22)$$

$$S_{ij} = \frac{\sigma_{ij}^2}{\sigma_{\text{TOT}}^2} \quad (5.23)$$

using Equations 5.17 and 5.18.

The probability distribution function for each of the 10 forward rate coefficients was assumed to be uniform,

$$p_{k_i}(k_i) = \frac{1}{k_i^{\text{MAX}} - k_i^{\text{MIN}}} \quad (5.24)$$

Similarly to Skodje et al. [177], we adopt a definition of the maximum and minimum values of k_i

³ Equations 5.11 and 5.12 can also be fit simultaneously; however, the scheme above was of sufficient accuracy to provide reasonable values of sensitivity and is not expected to show significant error for the modest sized reaction mechanism used.

according to,

$$k_i^{\text{MAX}} = k_i^{\text{TST}} (|\Delta \log k_i|) \quad (5.25)$$

$$k_i^{\text{MIN}} = k_i^{\text{TST}} (|\Delta \log k_i|)^{-1} \quad (5.26)$$

and the values of $|\Delta \log k_i|$ were capped at 5. Although the true uncertainty may be larger, this value was deemed sufficient as a preliminary test of the global sensitivity of the given mechanism. The full PDF, $P_{\mathbf{k}}(\mathbf{k})$, is a product of all the individual PDFs in Equation 5.24. The reverse reactions are related to the forward rate coefficients through the equilibrium constant,

$$k_i^b = \frac{k_i^f}{K_{\text{eq}}} \quad (5.27)$$

and throughout the sensitivity analysis process, the nominal values of the equilibrium constant are held constant. Thus, the 10 forward rate coefficients are sampled while the reverse rate constants are calculated using Equation 5.27. Usually the thermochemistry of a reaction can be calculated or measured much more accurately than rate coefficients, so the constraint in Equation 5.27 is especially valid if the thermochemistry is well defined. We maintain the constraint in this work, as the model is relatively insensitive to the backward reactions due to their high reaction barriers, and preliminary tests of their explicit inclusion in the sensitivity analysis suggested they make little difference in results within the chosen uncertainty space.

5.3.2 Simulation and Fitting Details

In this study, the kinetics simulation was run at several initial concentrations of methanol, between 0.0001 ML and 1.0 ML, and at several temperatures, between 350 K and 1000 K, in order to determine the key reactions under various reaction conditions on each metal. The temperature range was chosen so that both the regimes of low and high temperature kinetics were represented.

For each calculation at a chosen θ_{MeOH}^0 and T , the nominal TST forward and reverse rate coefficients were calculated. The uncertainty space of the forward rate coefficients was sampled

according to the uniform PDFs of Equation 5.24 using a random number generator. The total number of samples in every case was $N = 50000$, and for each set $\mathbf{k}$ of rate coefficients in the sample the kinetics simulation was integrated using the LSODE [160] integrator to find $\tau_{80\%}$. The RS-HDMR representation of $\tau_{80\%}$ was fit to the 50000 Monte Carlo sampled $\tau_{80\%}$ data points and the first and second order sensitivities were computed.

Several applications of RS-HDMR have noted that the order of the Legendre polynomial fitting functions can be a source of error [23,37]. If the maximum order of the Legendre polynomials used to fit Equations 5.11 and 5.12 is too low, the HDMR of the target will be of poor quality. If the maximum allowed order of the polynomials is too high, over fitting can result. In order to determine if over or under fitting present in our HDMR of $\tau_{80\%}$, we have performed the sensitivity calculation using several different maximum polynomial orders. The results on Pd(111) at various temperatures and an initial methanol coverage of 0.01 ML are shown in Figure 5.7. Davis et al. [37] have noted in their study of the H_2/O_2 combustion mechanism, with 25 elementary reactions, that sensitivities were well converged at a maximum polynomial order of 4 and significant over fitting effects were not observed until a maximum polynomial order of 15. The results in Figure 5.7 reveal similar behavior, where the first order sensitivities seem to stabilize by a maximum polynomial order of 6. Significant shifts in the sensitivities of the key rate coefficients, see Figures 5.7(b) and (c), are not observed, even at very high values of the maximum polynomial order. Only in the relatively unimportant rate coefficients, see Figure 5.7(d), with sensitivities that have a error bar on the order of their value, are sudden significant shifts in sensitivity seen for maximum orders greater than 15. Similar tests for over fitting were done on different metals and at different θ_{MeOH}^0 with similar results. Therefore, a maximum order of 12 was used for the polynomial fitting functions for the first order fits and a maximum order of 10 was used for the polynomial functions in the second order fits.

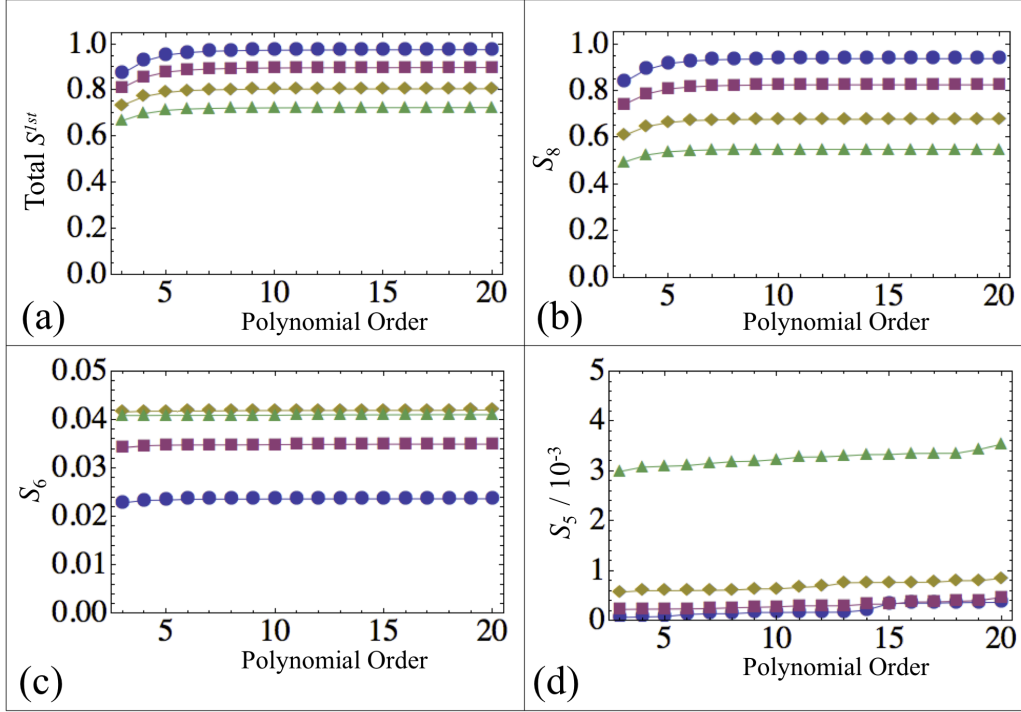


Figure 5.7: In (a), the total of the first order sensitivities as a function of the maximum polynomial function used to fit the first order functions in the expansion of $\tau_{80\%}$ for the Pd(111) mechanism at an initial methanol coverage of 0.01 ML. In (b), the first order sensitivity for reaction 8 in the Pd(111) mechanism as a function of the maximum polynomial used to fit $A_8(k_8^f)$. In (c), similar to (b), but for reaction 6 instead of 8. In (d), similar to (b), but for reaction 5 instead of 8. The blue, red, yellow, and green curves represent the sensitivities computed at $T = 400$ K, 500 K, 600 K, and 700 K, respectively.

5.3.3 First Order Global Sensitivity Results

In order to determine whether the sensitivity was dependent upon the initial methanol coverage, the first order sensitivity for each rate coefficient was determined as a function of the initial methanol surface concentration. The results are summarized in Figure 5.8. The salient feature in all the plots in Figure 5.8 is that the sensitivity is independent of the starting methanol coverage. Indeed, the target, $\tau_{80\%}$, is approximately independent of the initial surface methanol concentration as well, since the first order forward reactions dominate the mechanism⁴. The independence of $\tau_{80\%}$ from the initial methanol coverage, while convenient in the context of this model problem, is likely unphysical over some range of initial methanol coverage conditions as reaction dependence of surface catalyzed processes on surface coverage is well documented in the literature [57, 194, 195]. Such effects are likely most prominent under high coverage conditions where the low number of available adsorption sites for the reacting species will have definite consequences on the reaction rates. However, in their microkinetics study of methanol decomposition on Pt(111), Mavrikakis et al. [92], have successfully reproduced experimental H_2 turnover frequencies with limited assumptions of coverage dependence. We shall present the rest of the results assuming a relatively low initial methanol coverage of 0.01 ML, both since our results are independent of the starting concentration and since we expect our model, constructed from DFT calculations assuming relatively low coverage, to be most valid under low coverage conditions.

The global sensitivity analysis was performed at many different temperatures between 350 K and 1000 K. Temperature dependence of the model is readily apparent from Figure 5.8, and the

⁴ The reaction mechanism, within the rate coefficient uncertainty space, is essentially a directed circuit of first order reactions beginning at the methanol adsorbate and terminating at the carbon monoxide. In the approximation the back reactions are completely ignored, the chemical rate equations are a straightforward system of first order differential equations with an analytical solution for the time evolution for the species. The rate equations and their analytical solution in the no reverse reaction approximation can be expressed as,

$$\frac{d\vec{\theta}_t}{dt} = \underline{\underline{\mathbf{J}}}\vec{\theta}_t \quad (5.28)$$

$$\vec{\theta}_t = e^{\underline{\underline{\mathbf{J}}}t}\vec{\theta}_{t=0} \quad (5.29)$$

respectively, where $\vec{\theta}_t$ is a vector containing the concentrations of all the surface species at time t . The time independent matrix $\underline{\underline{\mathbf{J}}}$ is simply the Jacobian matrix of the system of rate equations. However, in this simpler approximation, there is not a general analytical solution for $\tau_{80\%}$.

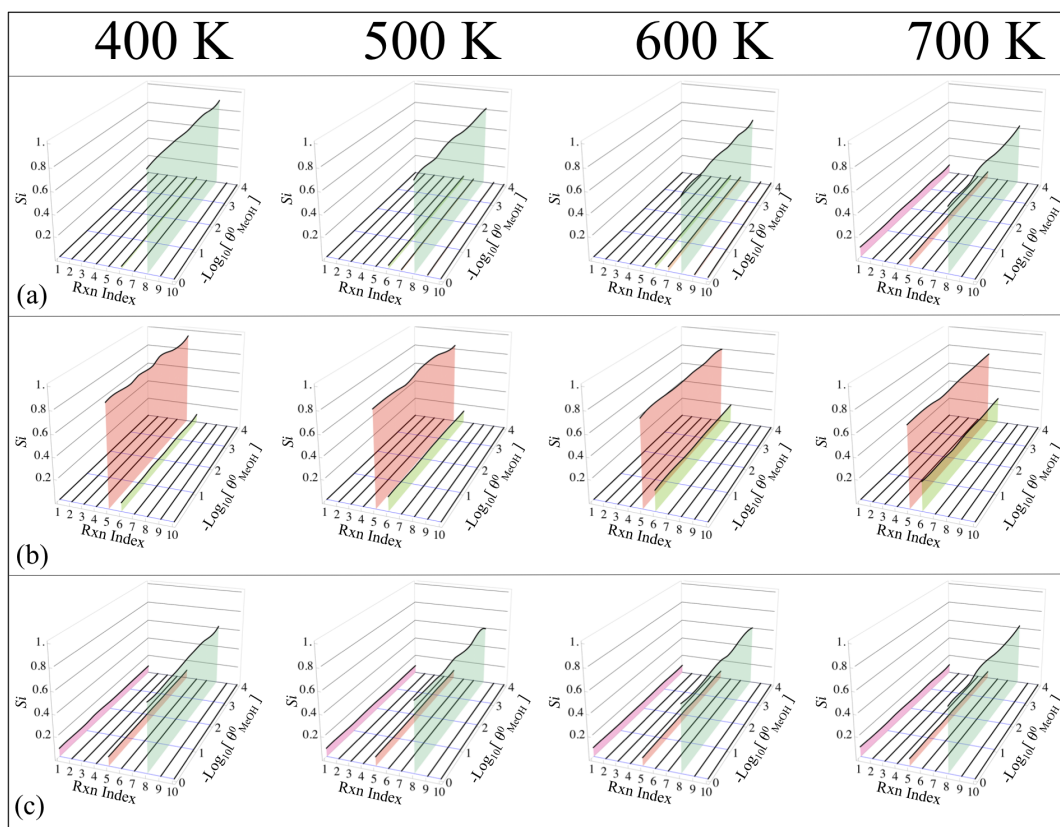


Figure 5.8: In (a), the first order sensitivity for each of the rate coefficients of the elementary steps listed in Figure 5.1 on Pd(111) at various temperature as a function of the starting methanol surface coverage, θ_{MeOH}^0 . In (b), the same as (a) except on Pt(111). In (c), the same as (a) except on Ni(111).

identity of the metal catalyst has a definite influence on the chemical mechanism since the identities of the key reactions vary between the metals. The temperature dependence of the sensitivities of the mechanisms are shown in Figure 5.9. The first order sensitivity is greatest for reaction 8, $\text{COH} \rightarrow \text{CO} + \text{H}$, in Pd(111), particularly at low temperature. This can be rationalized by looking at the barriers in Figure 5.4 and the nominal values of the rate coefficients in Figure 5.5. Reactions 8 and 1 are the “slow” steps of the mechanism on Pd(111), as they have the smallest rate coefficients and highest barriers. However, Reaction 1, extraction of the hydrogen from the hydroxyl group on the methanol, competes with the reaction 5 in the mechanism, extraction of a hydrogen from the methyl group of methanol, which is a faster step over the entire rate coefficient uncertainty space being sampled. Most of the reacted methanol will, therefore, pass through reaction 5. Reaction 8 is in competition with no other forward reactions, and is the slow step along its pathway. Therefore, the significant amount of reaction flux that reaches the COH intermediate must then proceed through the slow step, which has a considerable effect on $\tau_{80\%}$. Other reactions with significant sensitivity mainly corresponded to those at reaction junctures, reactions 6 and 9 and reactions 7 and 10. These reactions have rate coefficients with magnitudes that are similar, or at least not completely disparate within, the sampled uncertainty space and influence the pathway of the chemical kinetics. Sensitivity with respect to the competing reactions rises with temperature as the rate coefficients become closer in value and the junction reactions become more competitive.

It is convenient for the further discussion to have labels for the pathways through the mechanism. Figure 5.10 shows four pathways through the mechanism along with a moniker by which we will refer to them. The “low road” path corresponds to the extraction of hydrogens from the carbon until the last step, reaction 8. The “high road” path corresponds to the initial extraction of the hydrogen from the hydroxyl group and then from the methyl group. The two “shortcut” paths involve extractions of the hydrogen from the hydroxyl after a methyl hydrogen has already been extracted. In the Pd(111) mechanism, the “low” pathway is dominant, and reaction 8 is the slow step along this path. Therefore, it has the highest sensitivity.

In the Pt(111) mechanism, the highest first order sensitivity is for the initial methyl hydrogen

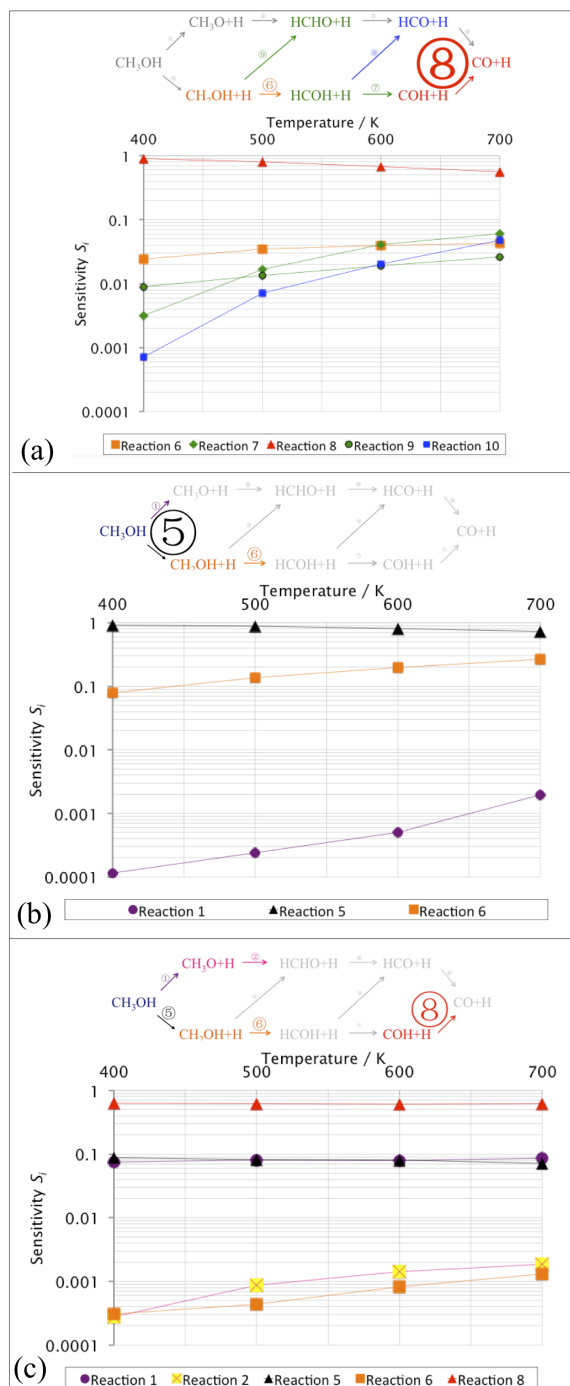


Figure 5.9: The first order sensitivities in the mechanism as functions of temperature. Only reactions to which the mechanism had significant sensitivity are included. The panels (a), (b), and (c) correspond to the mechanism on Pd(111), Pt(111), and Ni(111). All calculations were performed with an $\theta_{\text{MeOH}}^0=0.01$ ML. Above each plot, a labeled reaction scheme is shown with the size of the reaction label roughly corresponding to the magnitude of the first order sensitivity for the reaction in the mechanism.

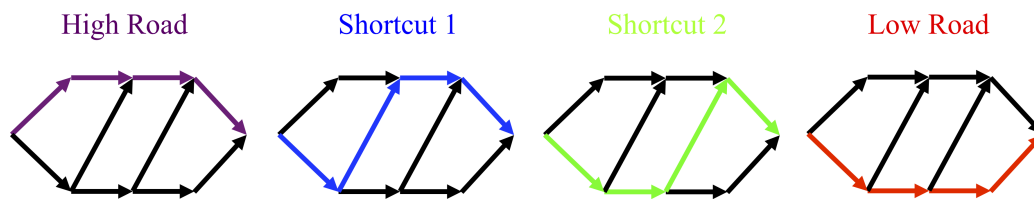


Figure 5.10: Four pathways through the methanol decomposition mechanism corresponding that shown in Figure 5.1. Above the pathway schemes are the labels for each individual pathway used in the text.

extraction. This reaction is in competition with reaction 1, to which the model seems only slightly sensitive. Reaction 1 in the Pt(111) mechanism is one of the few instances where the back reaction may be dominant over the forward reaction, particularly as the reaction proceeds and the surface concentration of hydrogen adsorbates increases. The dominant pathway in this mechanism is the shortcut 2 path, since the shortcut 2 bridge, reaction 10, happens essentially instantly and reaction 9 is a slow step of the mechanism. A small sensitivity to reaction 6 is also present since its rate coefficient is of similar value to reaction 5.

In the Ni(111) mechanism, reaction 8, the $\text{COH} \rightarrow \text{CO} + \text{H}$ slow step, dominates the first order sensitivity and is the slow step of the low pathway. Significant sensitivity to the competing reactions 1 and 5, the initial extractions of the hydrogens from the hydroxyl and methyl respectively, is also present. While the largest sensitivities seem approximately constant with temperature, a very small sensitivity to reactions 2 and 6 along the high and low pathways grows with temperature.

A more concrete picture of the sensitivity of the mechanisms to particular rate coefficient parameters can be obtained from looking at the first order RS-HDMR fitting functions, $A_i(k_i)$ from Equation 5.15. In Figure 5.11, the first order fits are shown of $\tau_{80\%}$ on Pd(111) as functions of κ_1 and κ_8 , corresponding to reactions 1 and 8, respectively, where the quantity κ_i is proportional to the rate coefficient k_i^f and is defined in Equation 5.13. Reaction 1 was chosen for Figure 5.11 to illustrate the fact that the target value shows very little change with the variation of rate coefficients with low sensitivities. The target values are very strongly correlated with the value of reaction 8, the key reaction in the Pd(111) mechanism. Indeed, the value of the rate coefficient for reaction 8

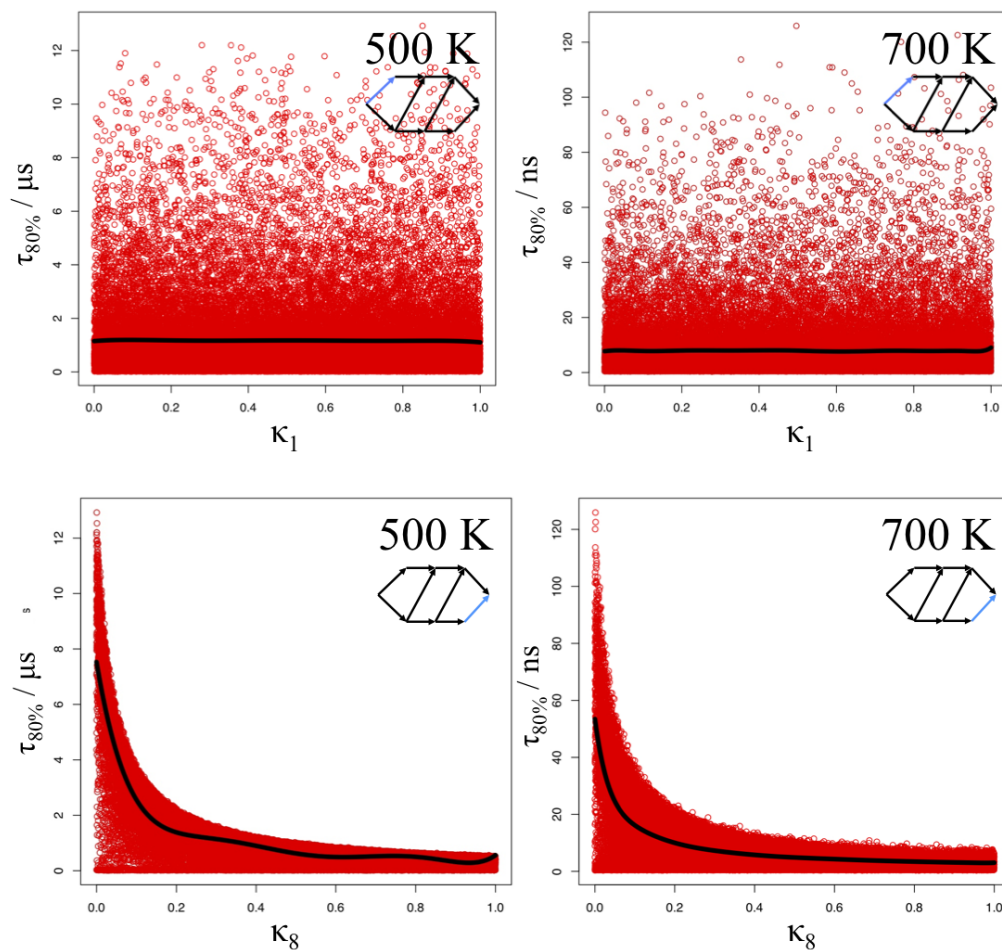


Figure 5.11: The RS-HDMR first order fits, $A_1(k_1^f) + \tau_0$ and $A_8(k_8^f) + \tau_0$, of $\tau_{80\%}$ on Pd(111). The fits are shown as values of the scaled κ variables rather than the actual rate coefficients. The plots are shown for analyses performed at two different temperatures, 500 K and 700 K. The initial methanol coverage was 0.01 ML.

seems to dictate the upper bound, but interestingly not the lower bound, of $\tau_{80\%}$, and a decrease in the target time strongly resembles the decaying exponential dependence that is expected of a first order forward passage through reaction 8 if it is the slow step of the mechanism. In the discussion below, only the first order fit plots, that is those similar to Figure 5.11, that correspond to key reactions are shown, as the plots corresponding to reactions with low sensitivity indices are similar to the upper panel of Figure 5.11.

In Figure 5.12, the first order fits for reactions 6 and 9 and reactions 7 and 10 on Pd(111) are shown. Though the dependence of the target on these reactions is less noticeable, a small increase of $\tau_{80\%}$ is observed as the rate of reactions 6 and 7 are increased, and a small decrease of $\tau_{80\%}$ is observed for increasing the rate of reactions 9 and 10. Recall that these sets of reactions correspond to junctions in the mechanism where changes in reaction pathway can occur.

The scatter plots of the key reactions for the Pt(111) and Ni(111) mechanisms are shown in Figure 5.13. For Pt(111), reactions 5 and 6 are the rate limiting step along the dominant low pathway. For Ni(111), the scatter plots reveal kinetics analogous to the Pd(111) mechanism, with reaction 8 as the key reaction, and small but noticeable trending with the pathway juncture reactions 1 and 5.

5.3.4 Second Order Global Sensitivity Results

Second order sensitivity analysis was also performed on all three metals. All of the variance of $\tau_{80\%}$ was attributed to first order effects in the Pt(111) mechanism. On Pd(111), the second order sensitivity was significant and grew with increasing temperature. On Ni(111), the second order effect was both significant and constant over the temperature range. Figure 5.14 summarizes the distribution of the sensitivities between first and second orders for each metal at several different values of temperature. A small error in the total sensitivity for the Pt(111) can be seen at 500 K on this plot. This effect is likely due to small fitting errors and was deemed insignificant.

Interestingly, the second order sensitivity effects in $\tau_{80\%}$ on Pd(111) and Ni(111) are between the key reaction 8, the “slow” step along the dominant pathway in both mechanisms, and the

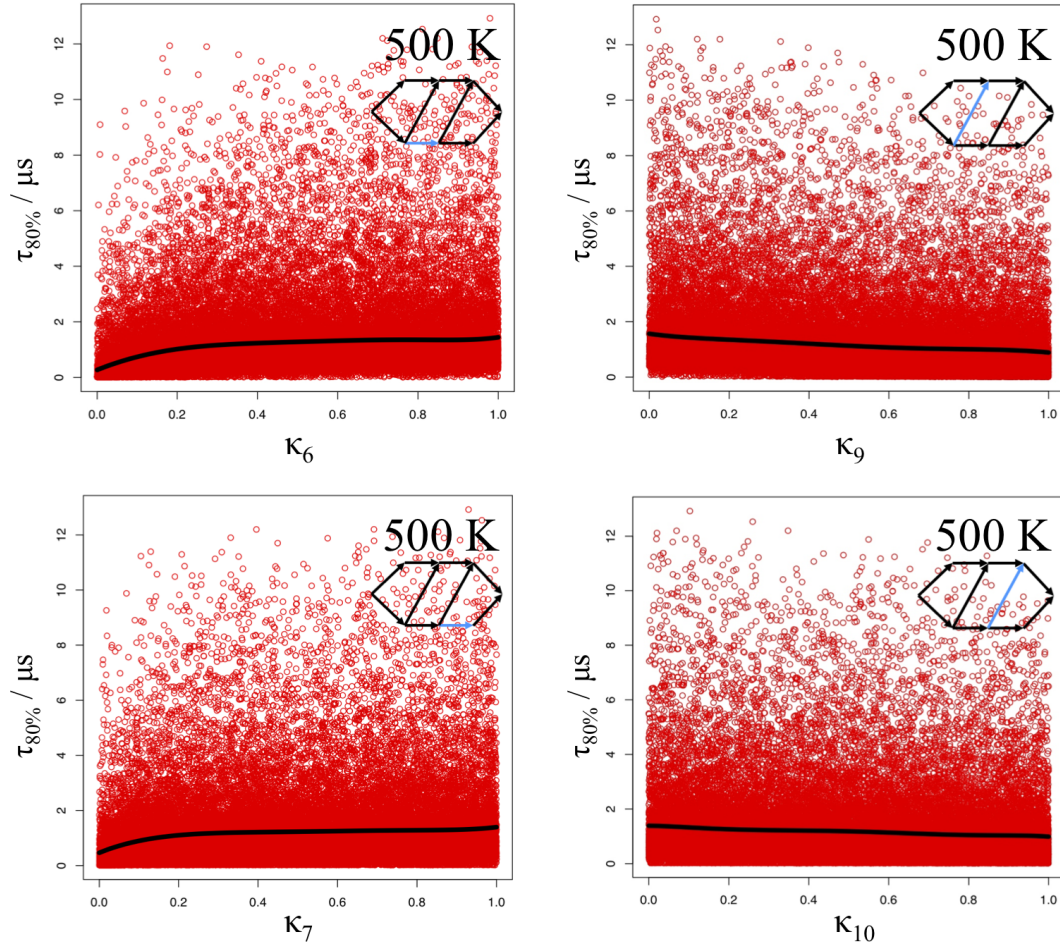


Figure 5.12: The RS-HDMR first order fits, $A_6 + \tau_0$ and $A_9 + \tau_0$ (top panels), and $A_7 + \tau_0$ and $A_{10} + \tau_0$ (bottom panels), of $\tau_{80\%}$ on Pd(111). The fits are shown as values of the scaled κ variables rather than the actual rate coefficients. The plots are shown for $T = 500$ K and $\theta_{\text{MeOH}}^0 = 0.01$ ML.

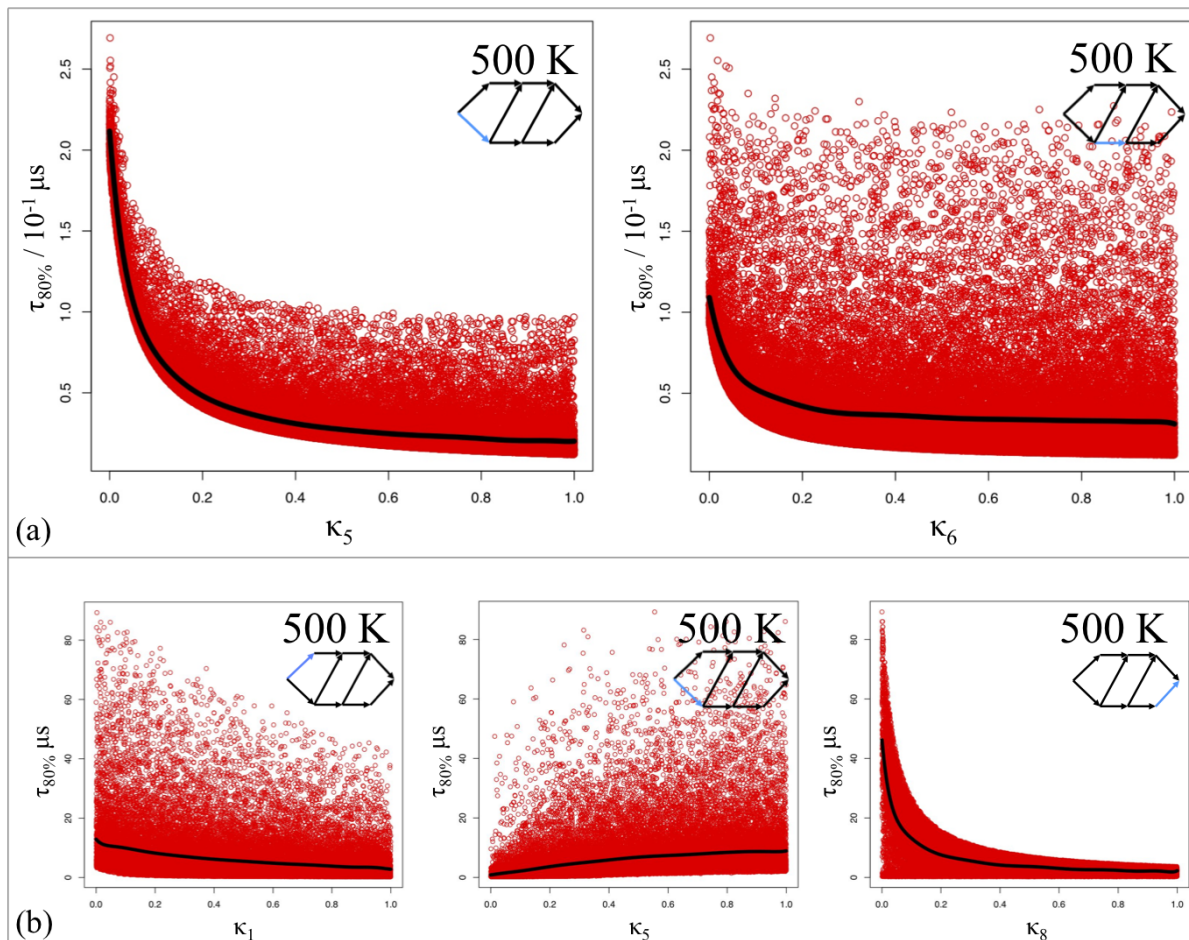


Figure 5.13: Similar to Figures 5.11 and 5.12, the first order fits, $A_i + \tau_0$, of the target, $\tau_{80\%}$, to the key reaction rate constants on Pt(111) and Ni(111) in panels (a) and (b), respectively. The plots are shown for $T = 500 \text{ K}$ and $\theta_{\text{MeOH}}^0 = 0.01 \text{ ML}$.

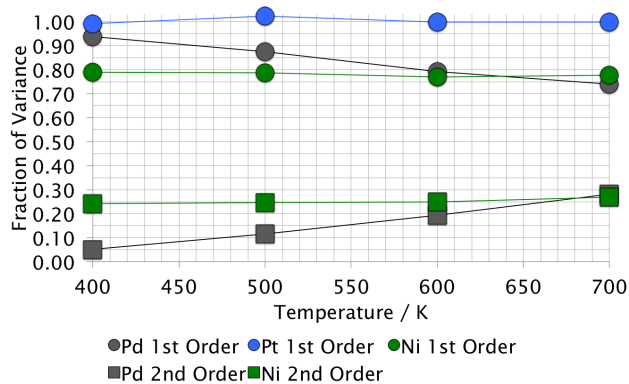


Figure 5.14: The totals of the first and second order sensitivities for the mechanism on the three metals. The plots are shown for $\theta_{\text{MeOH}}^0 = 0.01 \text{ ML}$.

important pathway junction reactions, rather than between the junction reactions themselves. On Pd(111), the largest second order effect is between reactions 8 and 6 at lower temperatures, but effects between reactions 8 and the junction reactions 7 and 10 become dominant as the temperature is raised. The results of the second order sensitivity analysis on Pd(111) are summarized in Figure 5.15. The second order effects of Ni(111) are independent of temperature and are primarily due to the reaction pair 8 and 1 and the reaction pair 8 and 5. The Ni(111) second order analysis is summarized in Figure 5.16. In terms of pathway information, the second order sensitivity analysis does not follow the naïve expectation that the coupling should be between reactions at pathway junctures. It is necessary to remember that the second order sensitivity depends on a fit to the target $\tau_{80\%}$, and therefore, those reactions that most strongly influence the value of the target along a pathway will be those most influential to the second order sensitivity. If significant reactive flux is directed along different chemical pathways, the reactions along each given pathway that have the greatest influence on the target variable will be those in competition and will contribute to both the first and second order sensitivity.

5.4 Reaction Pathways of Methanol Decomposition

5.4.1 Pathway Analysis Methodology

Stochastic chemical kinetics simulations were made popular by Gillespie [54] as a way to account for the importance of the discrete nature of the reacting molecules, and therefore random fluctuations, within a chemical system. One advantage of stochastic kinetics is that chemical events are considered in a discretized manner rather than affecting the reactant population as part of a collective of all possible reactions, as is done in the integration of the differential equations of the reaction rate equations, e.g. as in Equation 5.1. Therefore, individual reaction events can be specifically recorded throughout the kinetics process. Zhou and Skodje [229] have harnessed this property of stochastic kinetics to compute kinetic pathway probabilities. Their method employs using an ensemble of stochastic chemical trajectories. They chose a particular atom to follow,

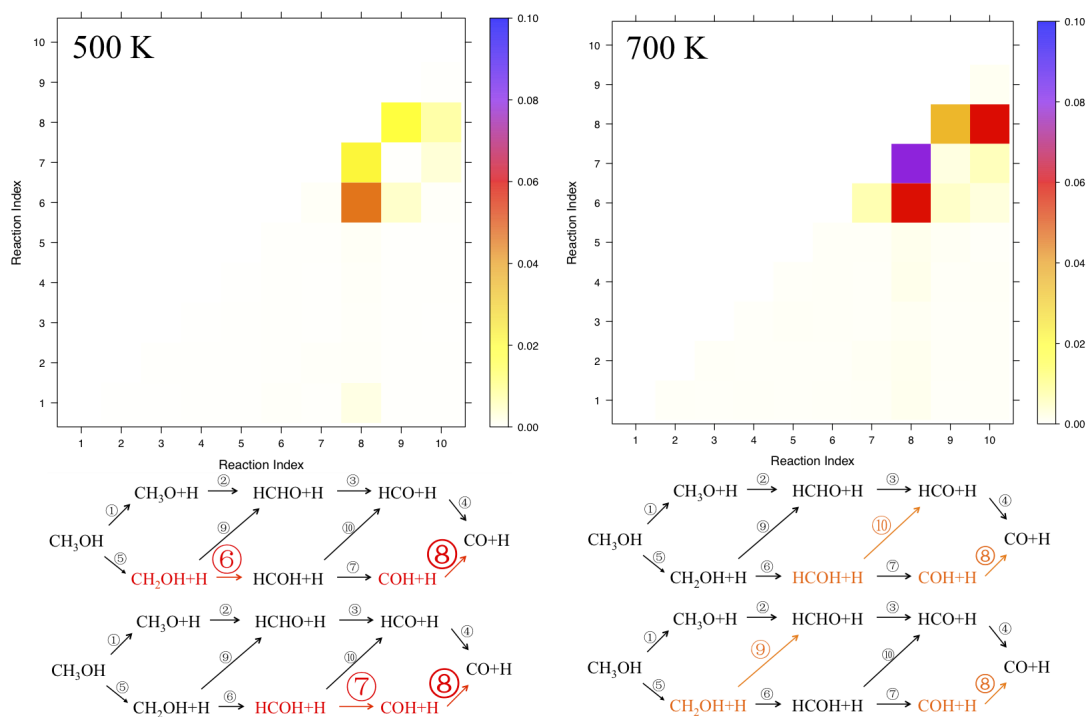


Figure 5.15: The second order sensitivities on Pd(111) at temperatures 500 K and 700 K are shown in the color coded matrix plot, where the axes are the reaction indices. The lower panels show reaction schemes with reaction pairs with significant second order effects having large indices. The plots are shown for $\theta_{\text{MeOH}}^0 = 0.01$ ML.

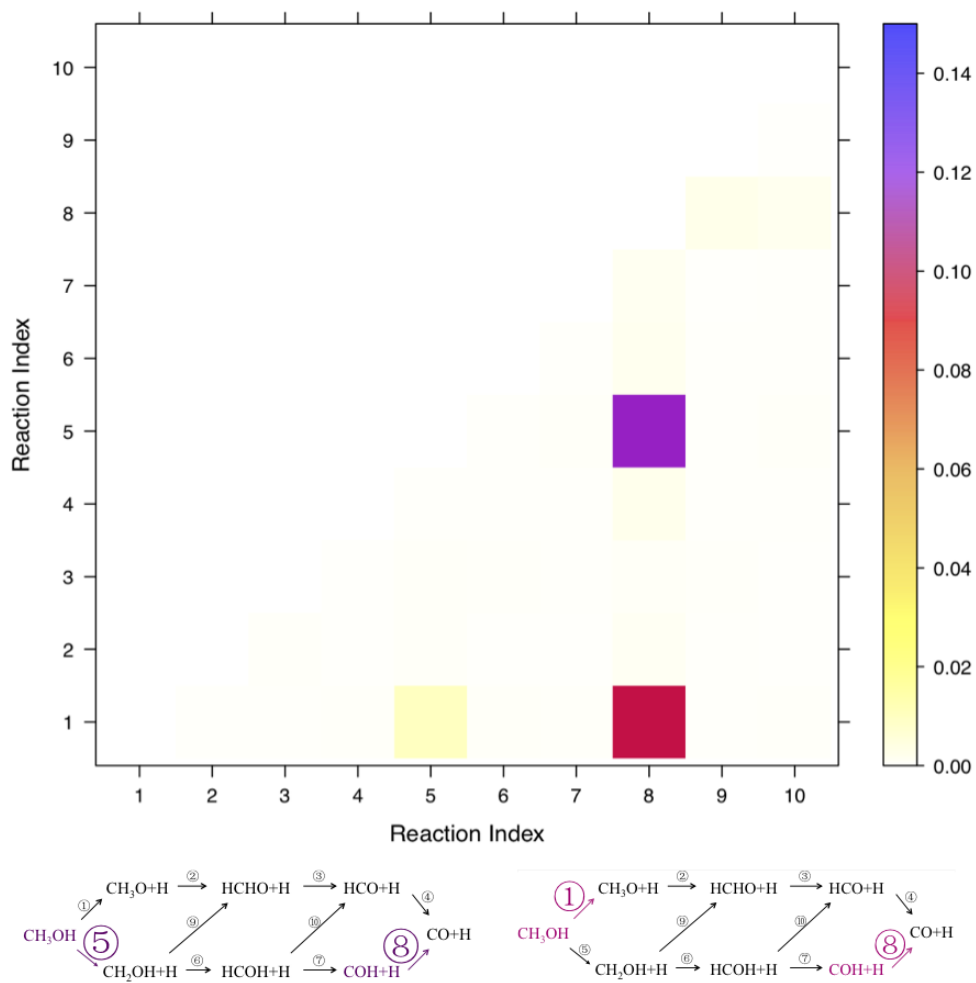


Figure 5.16: The second order sensitivities on Ni(111) at a temperature of 500 K are shown in the color coded matrix plot, where the axes are the reaction indices. The lower panels show reaction schemes with reaction pairs with significant second order effects having large indices. The plots are shown for $\theta_{\text{MeOH}}^0 = 0.01$ ML.

which we shall call the “followed-atom”, throughout the kinetics problem. The followed-atom is then labelled and followed in each trajectory in the ensemble of stochastic simulations, each a sample representation of the same kinetics process. At each reaction event in a trajectory, the followed-atom has a probability of “hopping” from the reactant to the product species. A reaction event is determined by Monte Carlo sampling according to the reaction probabilities. Rather than using the Gillespie stochastic simulation algorithm [54], Zhou and Skodje computed the reaction probabilities using a reference reaction rate kinetics simulation⁵ (integration of the continuous system defined in Equations 5.1) common throughout the ensemble, and constructing the specific reaction probabilities from the ratio of the amount of reactant species that react through a specific reaction, R_i within a small time interval between t and $t + \Delta t$ to the total amount of reactant species at t ,

$$P(t, \Delta t, R_i, S \rightarrow S') = \frac{\int_t^{t+\Delta t} \frac{d[S]_t}{dt} |_{R_i} dt}{[S]_t} \mu(r_i, S, S', A) \quad (5.30)$$

where $\frac{d[S]_t}{dt} |_{R_i}$ is the portion of the reaction rate of species S through reaction R_i , which maps the reactant S to the product S' . The factor μ is a stoichiometric factor which accounts for the number of chemically equivalent atoms in the reactant S to the number of chemically equivalent atoms in the product S' to which the followed-atom “hops”. Each hop is recorded throughout the simulations, and the cumulative list of hops that occurred in the simulation defines the chemical pathway taken by the atom. The total number of times a pathway is observed in the ensemble of stochastic trajectories divided by the total number of trajectories defines the pathway probability,

$$P(p_i) = \frac{n_{p_i}}{N_{tot}} \quad (5.31)$$

where n_{p_i} is the number of trajectories in the ensemble where path p_i was observed and N_{tot} is the total number of trajectories in the ensemble. The pathway probability distribution depends on the atom chosen as the followed-atom. However, in the methanol decomposition mechanism, the most interesting choice for following the conversion of methanol to CO is either the carbon or oxygen

⁵ The use of the reference reaction rate kinetics simulation to compute the reaction probabilities results in a much more computationally efficient method at the expense of losing some of the stochastic character of the fully stochastic simulation.

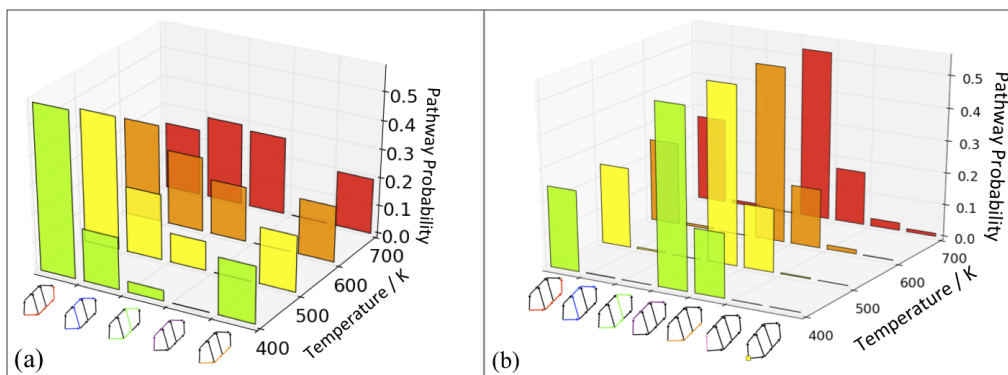


Figure 5.17: The pathway probability distribution function over a range of temperatures for the decomposition of methanol on Pd(111), (a), and on Ni(111), (b), for the nominal (TST) values of the rate coefficients of the mechanism. The results correspond to $\theta_{\text{MeOH}}^0 = 0.01$ ML. The paths are given on the axis in bright colored arrows in the mechanism (closed reactions are in black). In (b), the last pathway on the axis is the “no net reaction” pathway.

atom. In this study, the carbon in methanol was chosen as the followed-atom. The chosen size of a trajectory ensemble for each pathway analysis was 50000 stochastic trajectories. Numerical tests for the convergence of the pathway probabilities with respect to the size of the trajectory ensemble indicated well converged distributions. Though some reverse reaction events were observed on all metals, they were usually rare and only relative forward motion of the reaction along the mechanism was treated as a pathway (reverse reaction and any circular reaction paths were included in the probability analysis only in terms of their relative forward motion from methanol to CO).

5.4.2 Pathway Analysis of Methanol Decomposition on Pd(111) and Ni(111)

The pathway analysis was applied to the methanol decomposition mechanism on both Pd(111) and Ni(111) due to the interesting results of the global sensitivity analyses. The most commonly observed pathways were those shown in Figure 5.10. Although pathways that included reverse reaction were included allowed in the analysis, they were very rarely observed. The pathway probability distribution function (pPDF) as a function of temperature on both Pd(111) and Ni(111), using the nominal, TST computed, rate coefficients, is shown in Figure 5.17. The temperature effects on the Pd(111) pathway probability show that at the lower temperature of 400 K, the low

road pathway, on which reaction 8 is the rate limiting step, is dominant. However, as the temperature is raised, the two shortcut pathways become more accessible since the shortcut reactions, 9 and 10, at junctions along the low road pathway with reactions 6 and 7, respectively, become more competitive. The pathway probability for the high road pathway is never significant, since the reaction energy barrier for the initial hydrogen extraction from the hydroxyl is prohibitively high. The last pathway shown on the axis in 5.17(a) is the incomplete pathway on the low road ending at the COH intermediate. Clearly, at all temperatures, the stable COH intermediate, the reactant in reaction 8, is the most abundant non-product species at the time $\tau_{80\%}$. The pathway probability on the Ni(111) mechanism as a function of temperature shows the same approximate independence of the temperature that was observed in the global sensitivity analysis. The shortcut pathways are relatively unimportant on Ni, and the truncated pathway leading to the COH intermediate reveals that COH is the most abundant carbohydrate on the surface at the $\tau_{80\%}$ target time. The high and low road pathways are in competition on Ni, and the ratio of their probabilities, appropriately summing in the incomplete pathways that overlap with them, is approximately equal to the ratio of the first order rate coefficients $\frac{k_1^f}{k_5^f}$ expected if the reaction process depended only upon the competing first order forward reactions 1 and 5 at the initial mechanism junction. The pathway analysis for Ni(111) is therefore expected, with the only interesting features being which incomplete pathways have been taken prior to $\tau_{80\%}$.

In order to complement the results of the global sensitivity analysis, we computed the pPDFs for Pd(111) and Ni(111) as functions of the key reactions found for both mechanisms. The pPDF with the variation of the key rate coefficients and at several different temperatures is shown in Figure 5.18 for the Pd(111) mechanism. Clearly, the reactions at the branching points of the chemical mechanism have a strong influence on the pPDF, and this influence increases as the temperature is raised. Specifically, the competing reactions 6, Figure 5.18(a), and 9, Figure 5.18(c) have opposite effects. If the forward rate coefficient of reaction 6 is small, then the “shortcut 1” pathway (pathway 2 in Figure 5.18) is highly favored. If the rate through reaction 6 is increased, the low road and “short cut 2” (pathway 3 in Figure 5.18) pathways dominate. If the forward rate

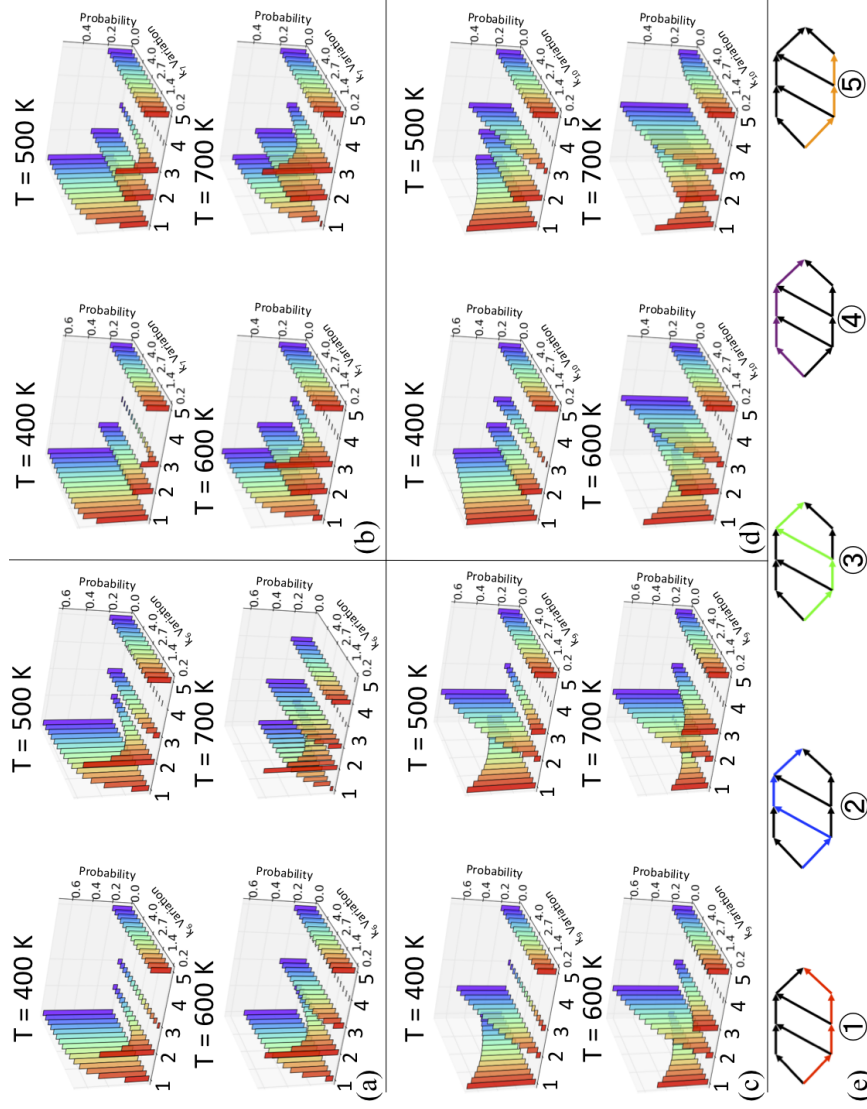


Figure 5.18: The pathway probability distribution functions (pPDFs) on Pd(111) as functions of the rate coefficients. In (a), k_6 is varied. In (b), k_7 is allowed to varied. In (c), k_9 is varied. In (d), k_{10} is varied. In (e), a legend is given labeling each pathway with a number for reference in the plots above. The rate coefficients are expressed in terms of their values as ratios to their corresponding TST nominal values. The results correspond to $\theta_{\text{MeOH}}^0 = 0.01$ ML, and each panel shows the results at $T = 400$ K, 500 K, 600 K, and 700 K.

coefficient of reaction 9 is small, then the low road path and shortcut 2 are the dominant pathways, as the reaction flux through reaction 9 is effectively turned off. A similar correlation in the pPDFs exist between reactions 7 and 10, which are competing pathways. These two reactions occur at a branching point later in the mechanism, and this results in the constant probability of the shortcut 1 pathway in Figures 5.18(b) and (d). The sensitivity of the pPDFs to reactions 7 and 10 is much more prominent at higher temperatures. Intuitively, a higher rate coefficient for reaction 7 favors the low road pathway, and the higher rate coefficient for reaction 10 favors the shortcut 2 pathway. The pathway probabilities also reveal that 20% of the methanol that has not been converted to CO at $\tau_{80\%}$ is mainly COH that has be stalled before passing through the rate limiting step, reaction 8, along the low road pathway.

The main key reaction in the Pd(111) mechanism was reaction 8. However, the pPDF was unaffected by the variation of rate coefficient of reaction 8, and the pPDF dependence on k_8 is not shown as a figure. Since reaction 8 occurs farther down the mechanism than any possible branching point, and since there is no significant backward reaction within the sampling space of the rate coefficients on the Pd mechanism, there is no possibility of feedback from COH reactant buildup. Therefore, although reaction 8 is the main key reaction in the global sensitivity analyses, being an important reaction according to both the first and second order sensitivities, it has no influence on the reaction pathway probabilities.

On Ni(111), the results of the variation of the rate coefficients are shown in Figure 5.19. Again, the two key reactions at the branching points are those that influence the pathway probability. The shortcut pathways have very small probabilities, since the rate coefficients 9 and 10 are too small within the rate coefficient sampling space to be competitive. The pPDFs have the expected inverse response to the variation of the rate coefficients of reactions 1 and 5, just as it did for the competing reactions in the Pd(111) mechanism. One interesting feature of the pathway probabilities, particularly present when reaction 1 is larger than reaction 5 and at higher temperatures, is that the unreacted product at $\tau_{80\%}$ is not all a result of the incomplete low road pathway (pathway 5 in Figure 5.19) terminating at COH. Rather, if the reaction flux along the lower path

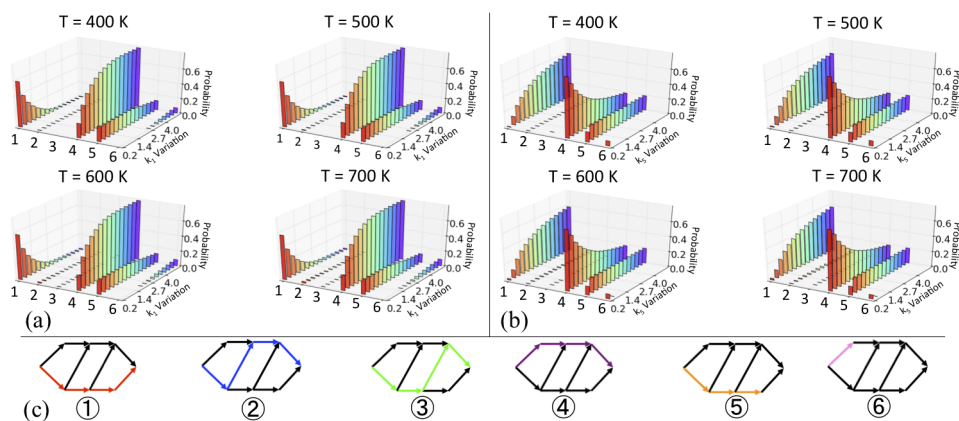


Figure 5.19: The pathway probability distribution functions (pPDFs) on Ni(111) as functions of the forward rate coefficient of reactions 1, (a) and 5, (b). The rate coefficients are expressed in terms of their values as ratios to their corresponding TST nominal values. The results correspond to $\theta_{\text{MeOH}}^0 = 0.01$ ML, and results are given at temperatures $T = 400$ K, 500 K, 600 K, and 700 K. In (c), the legend for the plots labeling each pathway with a number is given.

is reduced, the conversion of methanol to CO along the high road path occurs so quickly that a significant concentration of the methoxy remains unreacted.

The main key reaction of the Ni(111) mechanism was reaction 8, and analogous to the Pd(111) mechanism, the pPDF does not vary much with reaction 8 in the given rate coefficient variation space. However, when the forward rate coefficient of reaction 8 is very large so that the kinetics is very fast, the unreacted reactant at the target time $\tau_{80\%}$ is divided between the stable COH intermediate and methoxy. Therefore, the target time under these conditions has some dependence on reaction 1, beyond the simple competition between reaction 1 and reaction 5. The pPDF as a function of the rate coefficient of reaction 8 is shown in Figure 5.20.

5.4.3 The Target Probability Density Function and Pathway on Pd(111)

Davis et al. [37] have suggested that the probability density function of the target (tPDF) is useful for understanding the dependence of the target upon the individual reactions. The tPDF also presumably depends upon the available pathways in the reaction network, and some elements of the individual pathways in the mechanism may manifest in the tPDF.

In order to obtain a preliminary understanding of signatures of pathway dependence in the tPDF, we have run the Monte Carlo sampling of the target function $\tau_{80\%}$ over the rate coefficient sampling space, but with only certain pathways through the mechanism allowed to be active⁶. The results for Pd(111) at 600 K are shown in Figure 5.21. The tPDF shown is slightly bimodal, with a broader portion at longer times and a small peak at very small times. When the tPDF for the low road pathway is over-layed on that of the full simulation, it can be seen that it shares similar shape and position with the broad peak of the tPDF of the full simulation. However, the tPDF of the low road pathway is shifted toward longer times, even relative to the higher peak of the full simulation tPDF. The shortcut pathways' tPDFs are very sharply peaked, almost on top of the smaller peak of the full simulation tPDF. This suggests that the two features of the tPDF of the full simulation can be understood qualitatively in terms of the effects of the slow low road pathway

⁶ The rate coefficients off the sampled pathway were set to zero.

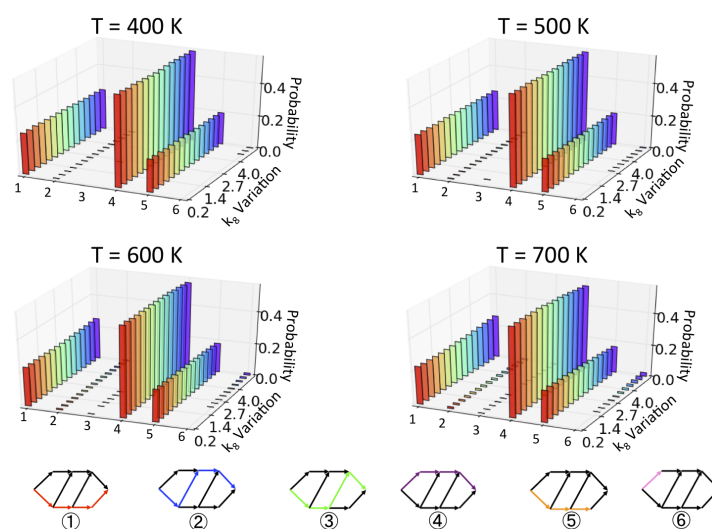


Figure 5.20: The pathway probability distribution functions (pPDFs) as a function of the forward rate coefficient of reaction 8 on Ni(111). The rate coefficient is expressed in terms of its value as a ratio to its corresponding TST nominal value. The results correspond to $\theta_{\text{MeOH}}^0 = 0.01\text{ ML}$, and results are given at temperatures $T = 400\text{ K}$, 500 K , 600 K , and 700 K . A legend for the plots labeling each pathway with a number is shown below the plots.

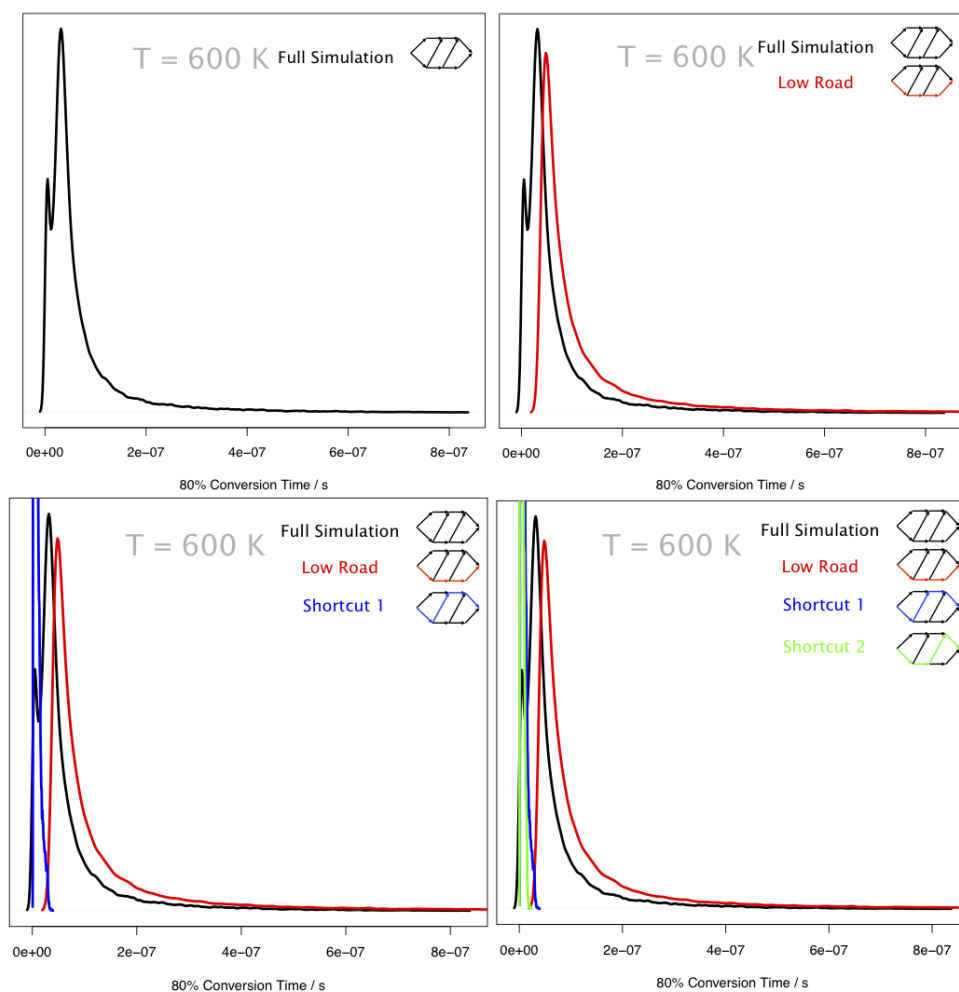


Figure 5.21: The probability density function of the target $\tau_{80\%}$ for the full simulation on Pd(111) (black), and only along certain pathways in the mechanism (red, blue, and green).

and the fast shortcut pathways, where the broad peak at long times represents the $\tau_{80\%}$ samples generated when the low road pathway was dominant, and the small peak at fast times corresponds to the dominant shortcut pathways. Although the shapes of the pathway specific tPDFs do give a picture of the kinetics within the tPDF, and give insight into the origins of its structure, it is not true that the tPDF of the full simulation can be represented completely in terms of the individual pathway contributions. Even in this very simple mechanism, pathway “interference” effects are substantial, particularly within regions of the rate coefficient uncertainty space where pathway probabilities between the fast and slow paths are similar. In this case, the reaction flux along one path is greatly influenced by the amount of reaction flux along the other paths. The results for the Ni(111) tPDF analysis are not shown, since they are analogous to that of Pd(111). A possible decomposition of the structure of the tPDF into pathway contributions would be an interesting future direction for this work.

5.5 Conclusion

In this chapter, we have considered the decomposition of methanol on three metal surfaces, Pd(111), Pt(111), and Ni(111). The density functional theory calculations of Gu and Li [59] and conventional transition state theory were used to construct symmetry consistent rate coefficients and a microkinetics model of the surface catalyzed process. This model was then analyzed by means of global sensitivity and pathway analyses in order to explore the dependence of the mechanism upon the rate coefficient parameters.

First order global sensitivity analysis revealed that, within the sampled uncertainty space of the rate coefficients, the model was insensitive to changes in the initial methanol surface coverage. This implies that the decomposition of methanol proceeds as a sequence of dehydrogenation steps to the CO product with little significant reverse reaction. On Pd(111) and Ni(111), first order sensitivity analysis showed that the 80% CO conversion target time was very sensitive to the reaction step $\text{COH} \rightarrow \text{CO} + \text{H}$, since this step is the rate limiting step within the mechanism. Significant first order sensitivity is also observed for the reactions at branching points in the mechanism,

particularly at higher temperatures. The importance of these reactions are thought to originate from their ability to redirect reaction flux along different pathways within the mechanism. For Pt(111), it was seen that the conversion of methanol to CH_2OH is the clear limiting step along the pathway within the rate constant uncertainty space used.

Second order global sensitivity was performed on Pd(111) and Ni(111). In both mechanisms, the main second order effects were between the $\text{COH} \rightarrow \text{CO}$ slow step and the reactions at pathway junctions. In Pd(111), the results of the sensitivity analysis were sensitive to the temperature, however, the Ni(111) sensitivities were approximately independent of temperature. This independence was the result of very disparate values of rate coefficients at junctions, except at the initial step where the two reactions for the decomposition had approximately equal rate coefficient values.

In order to understand the influence of pathways on the mechanism and the target observable, the 80% CO conversion time, an atom-following stochastic pathway analysis was performed on Pd(111) and Ni(111) and the pathway probability density functions were determined. These pPDFs revealed that dominant pathways in the mechanism were highly dependent functions of the values of the rate coefficients at the junctions, but were independent of the rate coefficient of the $\text{COH} \rightarrow \text{CO}$ slow step. The independence of the pPDFs from the slow step is a result of the topology of the mechanism, since the slow step lies at the terminal end of its pathway, and since backward reactions were insignificant in this highly exothermic process. Indeed, while the results of the pathway analysis are somewhat intuitive, the pPDFs do give a concise representation of the reaction flow observed within the mechanism and the response of this flow to the variation of the rate coefficient parameters.

The manifestation of pathways in the target probability density function (tPDF) were also observed. The bimodal shape of the tPDF was attributed to the dominance of different chemical pathways within different regions of the rate coefficient uncertainty space. The first peak at fast reaction times in the tPDF resulted when the dominant pathways avoided the $\text{COH} \rightarrow \text{CO}$ slow step. The second peak resulted when the dominant pathway did pass through the slow step.

The results suggest that the COH intermediate is quite stable and much of the reactive flux

is restricted at this step in the kinetics. Furthermore, we have illustrated that pathway analysis gives useful insight into a microkinetics model of a surface catalyzed process and drawn comparisons between the pathway analysis and first and second order global sensitivity methods. The stochastic atom-following trajectory pathway analysis and the global sensitivity analysis are useful tools not only for determining the validity of a chemical mechanism, but also are proposed as particularly useful, and relatively easy-to-implement, tools for optimizing such models.

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Appendix A

Overtone Induced Dynamics of Performic Acid: Semiclassical Study of Reaction and Lifetime

A.1 Introduction: Mode Specific Chemistry and Intramolecular Hydrogen Bonds

The study of unimolecular reaction dynamics has been of fundamental importance to our understanding of how intramolecular structure and interactions influence molecular chemistry [48,184]. While studies of thermally excited molecules have certainly provided insights and have motivated the development of many of the, now routinely applied, theories of unimolecular kinetics [118,132], the renaissance in the field began with the ability to selectively deposit an excitation energy, with a relatively low uncertainty value, into specific localized chromophores of a molecule [35]. This mode specific chemistry provides researchers with a way to study energy flow within activated molecules and to determine how the method of excitation influences ensuing chemistry.

Certainly, one of the most studied systems in mode selective chemistry is the decomposition of H_2O_2 into hydroxy radicals upon vibrational overtone excitation of the OH bond. The OH overtone excitation is a convenient chromophore, since it has a relatively significant and distinct absorption cross section for a vibrational transition, that decreases by about an order of magnitude for each subsequent overtone transition [35]. The most notable experimental work on the overtone chemistry of H_2O_2 was done by Crim, Rizzo, and co-workers [15,33,103,164,197], and numerous theoretical studies exist, of which we cite only a selection, on the subject [15,27,91,104,199,204]. The hydrogen peroxide system provided benchmark studies of the role of intramolecular vibrational

redistribution (IVR) in unimolecular reactions [58]. The IVR in this system was predicted to be relatively slow at energies of 50-55 kcal mol⁻¹ ($\nu_{\text{OH}} = 6$), ~ 6 ps in classical simulations [204] and quantum simulations predicted both that the lifetime was ~ 8.4 ps [216] but that even on a time scale of 30 fs IVR was not complete.

More efficient energy flow from a vibrationally excited OH chromophore can be achieved when the OH group participates in a hydrogen bond. Overtone excitation studies of hydrogen bonded hydroxyl groups have been performed for many different systems [22, 25, 69, 111, 133, 170, 175, 190]. This appendix focuses upon the OH overtone excitation of the peroxyformic, or performic, acid molecule, HCO(OOH), and is inspired by experimental and theoretical work done by Sinha et al. [70]. The performic acid molecule is interesting for several reasons. First, it is quite similar in structure and, perhaps photochemically, to the well-studied hydrogen peroxide molecule. Indeed, Sinha and co-workers have studied the O–O bond dissociation upon the overtone excitation of the OH in performic acid using action spectroscopy [174] and have observed OH radical product upon the excitation. This system is of particular interest due to its similar structure to hydrogen peroxide, but with the added feature of a hydrogen bonded OH chromophore to increase the rate of IVR. Second, as mentioned in Chapter 2 and the references cited there, the photochemistry of clusters held together by hydrogen bonding have vital implications in atmospheric chemistry. However, the photochemistry of such clusters is somewhat difficult to study experimentally due to the large number and highly variable environment of the OH chromophores, which is manifested in a greatly broadened lineshape of the OH absorption [209]. Small intramolecularly hydrogen bonded systems such as performic acid are therefore useful as model systems to understand the dynamics of the OH bond in hydrogen bonded environments.

The purpose of this appendix is to report some of my initial findings of the performic acid dynamics upon the overtone excitation of its hydroxyl group and to suggest further directions in which to extend the study. The rest of this appendix is divided as follows. In the first section, we discuss some of the methodology used to study the system along with results of quantum chemistry calculations performed for this system. In the second section, we present the results of statistical

and dynamics calculations for the lifetimes of the excitations. In the third section, we suggest future directions for work on this system.

A.2 Methodology and Quantum Chemistry of Performic Acid

The MP2/6-31+G(d,p) method has been used to determine the equilibrium and saddlepoint geometries on the performic acid potential energy surface (PES). The results are summarized in Figure A.1. The energetics shown were calculated using the Gaussian03 quantum chemistry package [50]. The overtone excitation energies were calculated according to the methodology described in Chapter 2, except using the MP2/6-31+G(d,p) level of theory rather than at the B3LYP/6-31+G(d,p) level. The two most stable conformers of performic acid found are shown in Figure A.1. The first, using similar notation to McCoy and co-workers in their work on HOONO [111], is the cis-cis, or *cc*, conformer that contains the intramolecular hydrogen bond. This conformer was found to be the most stable at all levels of quantum chemistry. The second, just to the right of the *cc* conformed in Figure A.1, is the trans-perp, or *tp*, conformer. Other stable minima on the performic acid PES were also found and are pictured in Figure A.2, which we denote as cis-perp, or *cp*, and cis-trans, or *ct* structures. The stability of these latter two structures was found to be basis set dependent and we do not refer to them as “conformers” for reasons elaborated below. The structure on the left in Figure A.2 was not found as a stable point on the MP2/6-31+G(d,p) PES and the structure on the right was not found as a stable point at other levels of theory tested, namely MP2/aug-cc-pVTZ and MP2/aug-cc-pVDZ. It is also seen that the CCSD(T) calculations suggest a much higher barrier to the OH torsion, with the peroxy group fixed in the cis position with respect to the carbonyl group, than does the smaller MP2/6-31+G(d,p) calculation. Indeed, MP2/6-31+G(d,p) underestimates the barrier to OH torsional rotation by more than 1.5 kcal mol⁻¹ relative to the larger methods used. The energy difference between the *cc* conformer and the *tp* conformer, where the peroxy group has been rotated about 180° relative to the *cp* structure on the right of Figure A.2, is also underestimated. The larger basis set calculations predict the *cp* conformer is less stable than the *cc* by 3.29 kcal mol⁻¹, while the MP2/6-31+G(d,p) method predicts only

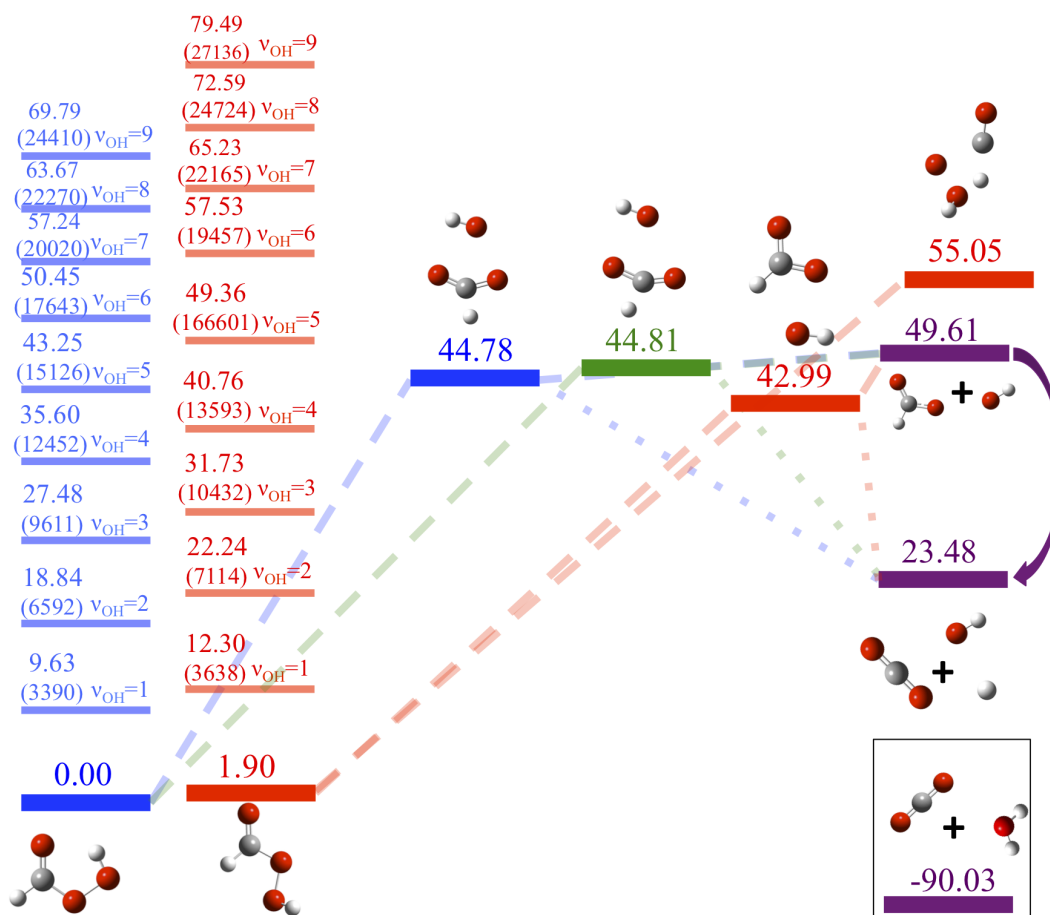


Figure A.1: Zero point corrected energies of the equilibrium and relevant saddlepoints of the performic acid O-O dissociation reaction. Energetics are relative to the zero point of the minimum energy conformer. Also included are the overtone excitation levels for two of the stable performic acid conformers, denoted *cis-cis* (*cc*) and *trans-perp* (*tp*), the energies are reported relative to the most stable conformer, *cc*, and those in parentheses are the excitation energies from the given conformers in cm⁻¹. All energies, outside of parentheses are in kcal mol⁻¹ and are calculated using the MP2/6-31+G(*d,p*) method.

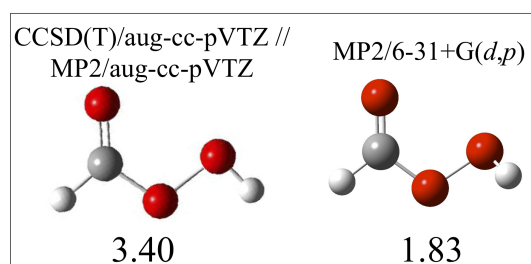


Figure A.2: Two stable structures of performic acid found at two different levels of quantum chemistry. The left shows a structure optimized at MP2/aug-cc-pVTZ [196] with absolute energies calculated at CCSD(T)/aug-cc-pVTZ and the right shows the other structure optimized at the MP2/6-31+G(*d,p*) level of theory that was used in the trajectories. The energies are the zero point corrected and relative to the most stable *cc* conformer shown in Figure A.1. The two structures are referred to as *ct* and *cp*, respectively, in the text.

1.90 kcal mol⁻¹. Therefore, the MP2/6-31+G(*d,p*) method underestimates the stability of the hydrogen bond under the torsion by approximately 1.6 kcal mol⁻¹ relative to the more rigorous quantum chemistry treatments. Increasing the basis set size from 6-31+G(*d,p*) to aug-cc-pVDZ shows a drastic improvement in accuracy relative to the values calculated by CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ. However, such an increase in size of the basis set is quite costly if used in “on-the-fly” trajectories. The B3LYP/6-31+G(*d,p*) method seems to out perform the MP2/6-31+G(*d,p*) in its ability to predict conformer structure (the structure on the right of Figure A.2 is not a stable minimum using B3LYP/6-31+G(*d,p*), but the structure on the left is), but relative conformer energies were still found to be ~ 1 kcal mol⁻¹ lower than those predicted by the more rigorous quantum chemistry methods tested.

Sinha and co-workers [70] provide a relaxed one-dimensional torsional potential energy surface along both the COOH dihedral angle and the O=COO dihedral angle, updated versions from those reported by Bach et al. [3], at the MP2/aug-cc-pVDZ level of theory. The barrier to the rotation from the *cc* conformer to the *tp* conformer is predicted to be around 15 kcal mol⁻¹ (no zero point correction which is likely to reduce the barrier by about 1 kcal mol⁻¹). The salient feature on COOH dihedral PES is the “shelf” feature in the vicinity where the *cp* and *ct* conformers in Figure A.2 are predicted to lie. For illustration, we show the relaxed one dimensional torsion about O–O bond, similar to Sinha and coworkers, shown in black in Figure A.3 calculated at the MP2/aug-cc-pVDZ level of theory and optimized at each value of the HCOO–OH dihedral angle about the O–O bond, denoted τ_{COOH} held constant during the optimization. The minimum corresponding to the *ct* conformer predicted by the quantum chemistry optimization should appear at $\tau_{\text{COOH}} = 180^\circ$. The stabilization here is very small (with a barrier to rotation ≤ 0.1 kcal mol⁻¹). We also diagonalized the one dimensional OH stretch Hamiltonian at each point on the τ_{COOH} PES, to obtain the OH local mode energy eigenvalues as a function of τ_{COOH} . We used these quantities to define adiabatic potential energy surfaces for each OH stretch vibrational state, the first six of which appear in Figure A.3. It is quite apparent that the *ct* and *cp* conformers are not stabilized more on the adiabatic potential energy surfaces than on the absolute surface. The *cc* conformer, however, is

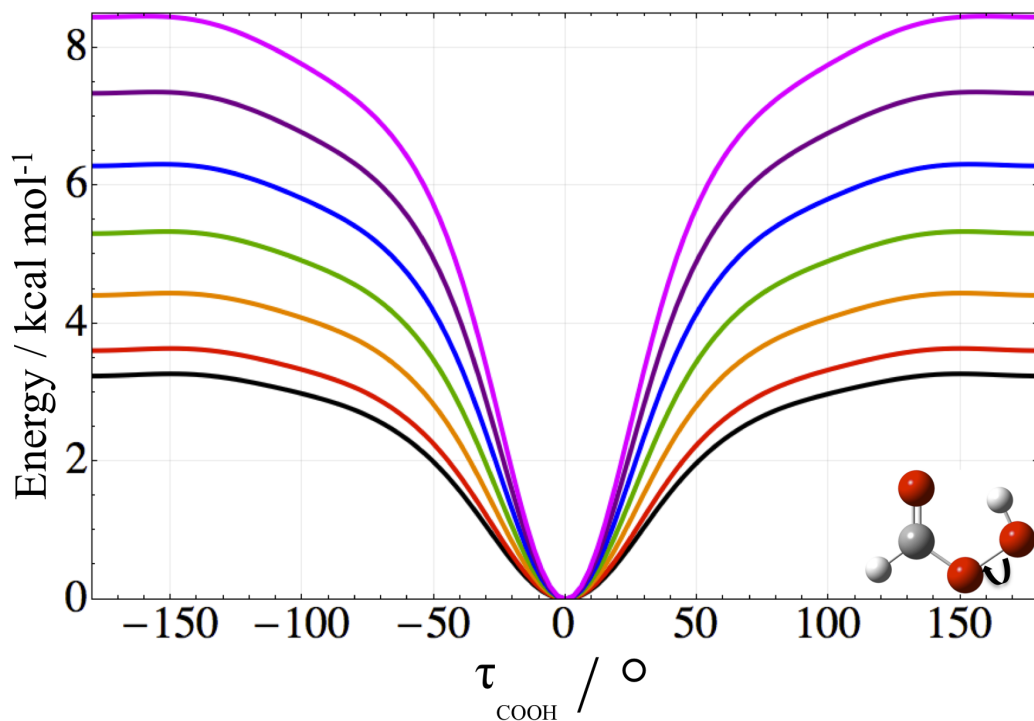


Figure A.3: The one dimensional adiabatic potential energy surfaces as τ_{COOH} is varied, all other degrees of freedom are optimized at each τ_{COOH} . The OH stretch degree of freedom, r_{OH} , is treated as the “fast” degree of freedom and the torsion PESs are calculated for each r_{OH} energy level. Each PES is expressed with relative to its minimum value rather to an absolute reference. All calculations were done at the MP2/aug-cc-pVDZ level. The absolute potential (black), $v_{\text{OH}} = 0$ (red), $v_{\text{OH}} = 1$ (orange), $v_{\text{OH}} = 2$ (green), $v_{\text{OH}} = 3$ (blue), $v_{\text{OH}} = 4$ (purple), $v_{\text{OH}} = 5$ (magenta).

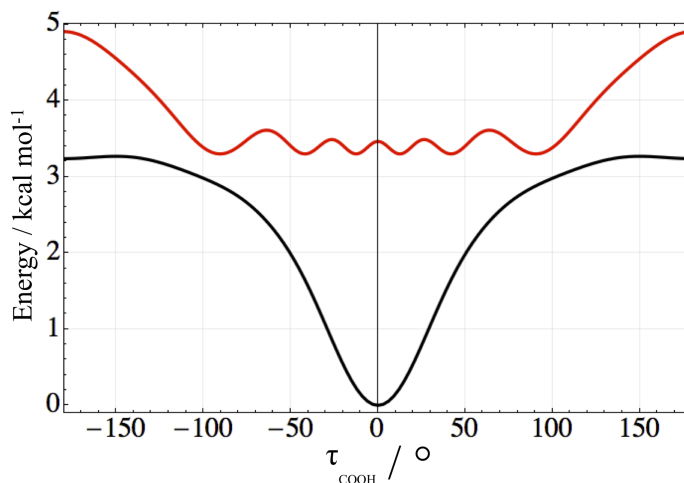


Figure A.4: The probability density of the lowest energy one dimensional τ_{COOH} energy eigenstate (red) found that had significant amplitude in the *ct* region of the torsion PES (black) is shown.

more stabilized at higher OH stretch excitations. To determine if the small well at $\tau_{\text{COOH}} = 180^\circ$ can support a bound state, we solved a one dimensional torsional Schrödinger equation, see Chapter 4 for a similar procedure, using the relaxed τ_{COOH} PES to obtain the torsion energy eigenstates. The first torsion energy eigenstate with significant amplitude in the *ct/cp* region of the torsion PES is shown in Figure A.4, along with the absolute τ_{COOH} PES for reference, and is clearly not a bound state. Rather, this “shelf” state is simply the result of the torsion “slowing” down as it passes over shelf, causing resonance in the shelf region. A bound state was not observed that had significant amplitude in the $\tau_{\text{COOH}} = 180^\circ$ *ct* conformer region. Since the *cp* and *ct* conformers do not seem to correspond to a bound state, they are not included in Figure A.1. However, they may have interesting implications in the photodynamics of the molecule [111,135].

The transition state energies of the first two O–O dissociation transition states shown in Figure A.1 were also calculated at the higher level of quantum chemistry. For the transition states, both the structures and the barrier energies of the MP2/6-31+G(*d,p*) method compared quite well with MP2/aug-cc-pVXZ, X=D and T, with barrier energies that underestimated those of the larger basis set methods by approximately 1 kcal mol^{−1}. Using CCSD(T)/aug-cc-pVTZ//MP2/auc-cc-pVTZ, the barrier energy for transition state along the blue reaction path in Figure A.1 was higher

than the MP2/6-31+G(*d,p*) barrier by 1.6 kcal mol⁻¹. The second barrier energy, for the saddle point along the red reaction path, had a significantly lower energy for the CCSD(T) quantum chemistry, 41.57 kcal mol⁻¹, which is a decrease by 3.2 kcal mol⁻¹ from the modest MP2/6-31+G(*d,p*) method. We also note here, for the benefit of future studies, that the *T1* diagnostic [85] found when performing the coupled cluster theory on the reactants and on transition states shown in Figure A.1 was greater than the 0.02 cutoff signaling multiconfigurational effects for the performic acid system may be significant. Future work on this problem should include multireference quantum chemistry methods, such as complete active space self consistent field (CASSCF), or other methods to characterize the potential energy surface and stationary points. “On-the-fly” dynamics using CASSCF methods are feasible for a molecule of size of performic acid with a modest basis and access to computational resources, and determination of the effects of multiconfigurational character of the molecule on the overtone dynamics may be both interesting and useful for understanding such issues in analogous problems.

Overtone vibrational transitions are forbidden in the harmonic picture, and thus overtone absorptions are attributable to the anharmonic character of the PES. To generate the OH local mode overtone excitation levels shown in Figure A.1, a one dimensional OH local mode PES was computed and is shown in Figure A.5(a) for both the *cc* and *tp* conformer. A clear anharmonic broadening of the hydrogen bonded *cc* OH local mode PES (in blue) relative to the free OH local mode in the *tp* (green) conformer. The anharmonic character of the *cc* conformer OH is even more evident on a relaxed r_{OH} PES shown in Figure A.5(b). In this figure, the full anharmonic character of the OH local mode is evident. The broad shelf in the relaxed PES results from the stabilizing effect of the hydrogen bond accepting carbonyl oxygen on the displaced hydrogen atom. It is interesting to note that the transfer of the hydrogen between the donor and acceptor oxygen atoms in the intramolecular hydrogen bond does not support a stable intermediate when the hydrogen is within a bond length of the carbonyl oxygen, but rather is manifested as a very broad shelf that essentially serves to slow the hydrogen motion in this region. Of course, this is not to say that hydrogen transfer events are not observed in the dynamics, where, particularly at higher

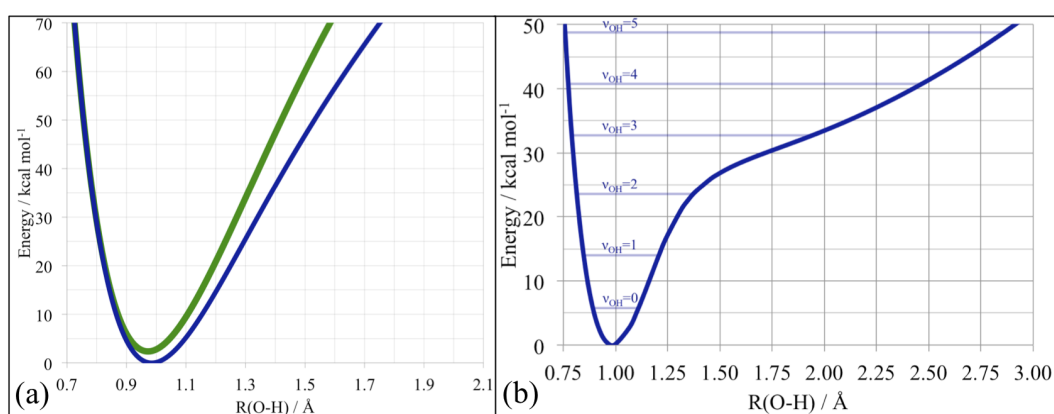


Figure A.5: In (a), the one dimensional OH local mode potential energy surface calculated for both the *cc* (blue) and *tp* (green) conformers of performic acid. These PESs were calculated on the PES holding all other atoms but the OH moiety fixed. In (b), the one dimensional OH local mode PES of the *cc* conformer where at each point on the PES, the OH local mode coordinate r_{OH} was fixed and the rest of the molecule was optimized. The *cc* r_{OH} energy eigenvalues calculated on the rigid PES are shown to emphasize the anharmonic nature of the the higher vibrational states. Energy calculations were performed at MP2/6-31+G(*d,p*).

excitation energies, the hydrogen can transfer to the carbonyl oxygen and vibrate there for one or several vibrational periods. But this occurs when the large atoms are not at their equilibrium configuration, and so a stable transferred hydrogen atom on the carbonyl is not an intermediate given by a minimum on the PES, but rather a transient dynamical intermediate.

The broad OH shelf does indicate the onset of hydrogen “chattering” [99,188,190], where the hydrogen does undergo multiple exchange events between the donor and acceptor oxygens in the hydrogen bond, where the hydrogen at least slows down or spends an amount of time in closer proximity to the acceptor atom as is consistent with the shelf of Figure A.5(b). Takahashi et al. [190] found that OH chattering greatly facilitated energy transfer in pyruvic acid from the bright state OH to the rest of the molecule and broadened the overtone absorption lineshapes of a hydrogen bonded conformer of the pyruvic acid molecule. From the relaxed potential energy surface, we expect hydrogen chattering onset at the $v_{\text{OH}} = 3$ vibrational state of performic acid. We shall see later how this result is manifested in the dynamics.

A.3 Dynamics Initiated by OH Overtone Excitation in Performic Acid

Trajectories of vibrationally excited performic acid were constructed according to the prescription discussed in Chapter 2 with some modifications in the quantum chemistry. We discuss the method briefly again here. For this system, we chose to use the MP2/6-31+G(d,p) method and basis for the “on-the-fly” dynamics. The OH local mode vibrational levels were determined by diagonalizing a one dimensional Schrödinger equation for the mode,

$$\left(\frac{\hat{p}_{\text{OH}}^2}{2\mu_{\text{OH}}} + \mathcal{V}_{\text{OH}}(\hat{r}_{\text{OH}}) - \mathcal{V}_{\text{OH}}(r_{\text{OH}}^{\text{eq}}) \right) \psi_v(r_{\text{OH}}) = \epsilon_v \psi_v(r_{\text{OH}}) \quad (\text{A.1})$$

where $\mathcal{V}_{\text{OH}}(\hat{r}_{\text{OH}}) - \mathcal{V}_{\text{OH}}(r_{\text{OH}}^{\text{eq}})$ is the potential energy obtained by stretching the OH local mode coordinate while keeping the rest of the atoms at their conformer equilibrium value and all energies are measured relative to the equilibrium conformer energy, given by the term $\mathcal{V}_{\text{OH}}(r_{\text{OH}}^{\text{eq}})$ in Equation A.2. This author preferred the use of the Colbert and Miller DVR basis [29] to represent the Hamiltonian matrix in Equation A.2 as the potential energy matrix is diagonal in this representation

and equal to the value of the potential energy at the DVR grid points. Hence, quantum chemistry calculations for the potential need only be calculated at the DVR points.

Sets of initial conditions were constructed at $T = 0$ K and $J = 0$ using the fixed normal mode sampling of Hase et al. [66] as implemented in the Gaussian 03 quantum chemistry package [50]. In each trajectory in an ensemble of initial conditions, zero point energy was placed in each normal mode with a random vibrational phase. Then an OH local mode PES was generated for each initial condition, similar to that described above, but still slightly different for each initial condition. These initial condition PESs were used to construct an OH local mode orbit with energies corresponding to the overtone energies, where the appropriate energy was placed in the OH bond with random phase for each trajectory. Velocity scaling [66] was used to account for mode coupling, which was minimal in this system, and to scale all the molecules to the same energy so comparison to statistical theories was sensible.

Trajectory calculations are presented for various OH vibrational levels for both the *cc* and *tp* conformers of performic acid. Each ensemble of trajectories for each conformer at each excitation energy contained between 50 and 125 trajectories (the *tp* conformer ensembles contained ~ 50 -75 trajectories and the *cc* conformer ensembles contained ~ 100 -150 trajectories). These trajectories were propagated, in general, until a reactive event was observed or the propagation time is in excess of 1 ps but less than 1.5 ps. For the *cc* conformer, trajectories were propagated using the method of Schlegel et al. [139] as implemented in the Gaussian03 quantum chemistry package [50]. The *tp* trajectories were propagated according to the dynamical reaction coordinate implementation in the GAMESS quantum chemistry package [169] with a time step usually around 0.05 fs, although larger time steps were used for lower excitations.

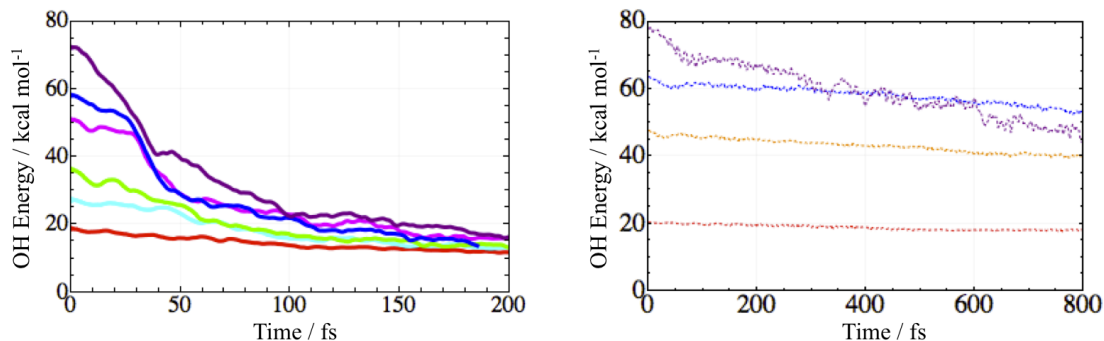


Figure A.6: On the left, the average OH energy for the *cc* conformer over time. On the right, the average OH energy for the *tp* conformer over time. The OH vibrational levels are specified by color: $v = 2$ (red), $v = 3$ (cyan), $v = 4$ (green), $v = 5$ (orange), $v = 6$ (magenta), $v = 7$ (blue), $v = 9$ (violet).

A.4 Dynamics Results

In order to determine the rate of IVR, the energy in the OH local mode was computed as an average over each trajectory ensemble,

$$E_{\text{AVG}} = \left\langle \frac{p_{\text{OH}}^2}{2\mu_{\text{OH}}} + \mathcal{V}_{\text{OH}}(r_{\text{OH}}) - \mathcal{V}_{\text{OH}}(r_{\text{OH}}^{\text{eq}}) \right\rangle \quad (\text{A.2})$$

The result is shown in Figure A.6. The difference in energy between the two conformers is quite clear. In the hydrogen bonded conformer, the energy in the OH chromophore for highly excited vibrational states has substantially dissipated by 100 fs. It is interesting to note some structure in E_{AVG} in the region between 0 and 75 fs, where the average energy decay is much slower. The origin of this region was not explored, but is likely due either to trajectories where energy initially flows to the OH torsion and the OH keeps its energy as the OH bond rotates about the torsion angle until reaching the region of the hydrogen bond again, or to OH “chattering” where the OH bond remains extended for a substantial amount of time. The average OH energy for the *tp* conformer is shown on the right. The energy decay is far slower in this conformer since it contains no hydrogen bond. Indeed, only at the very high vibrational levels is there significant energy dissipation on the observed time scale.

In order to determine the lifetime of the initial OH excited state, we performed a procedure

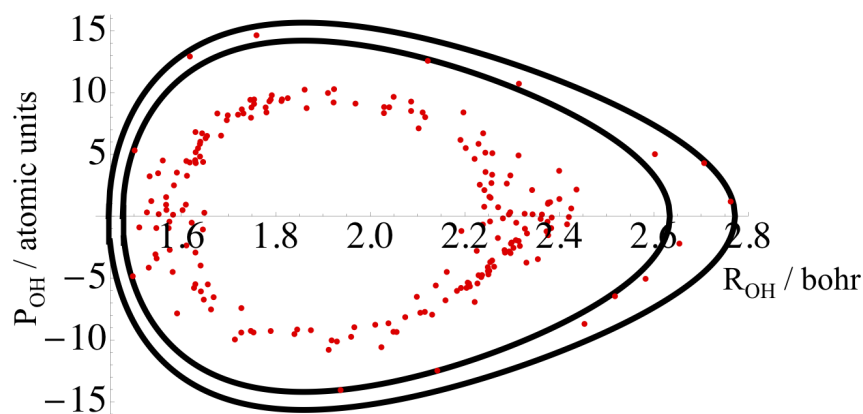


Figure A.7: The $v_{\text{OH}} = 4$ phase space orbit boundaries, in black, and time points for an example trajectory of the *cc* conformer used in computing a classical autocorrelation function for the state is shown.

similar to that of Takahashi et al. [190], and which we describe again here. A representation of the autocorrelation function of the OH local mode bright state, $\langle \phi(0) | \phi(t) \rangle$, where $|\phi(0)\rangle$ represents the bright state, is constructed using a classical analog [72] using a phase space definition of the bright state. Two phase space orbits, with energies halfway between the overtone vibrational state of interest and the energies of the states above and below, respectively, were constructed from an OH stretch PES calculated from the given geometry of the molecule at the beginning of the trajectory. This was done for every trajectory. As each trajectory proceeded in time, the fraction of trajectories that had OH local mode momentum and coordinate values that lay between the two test phase space curves is equated to the autocorrelation function¹. An example trajectory in the OH local mode phase space, along with the higher and lower bounds for the overtone state orbit, is shown in Figure A.7. The probability curves were fit to decaying exponentials in order to obtain the lifetimes. The obtained lifetimes are summarized in Figure A.8. The difference in the lifetimes between the two conformers is striking. The hydrogen bonded *cc* conformer has an excitation lifetime that is an order of magnitude lower than the *tp* conformer at the lowest energy considered, $v = 2$ ($\sim 20 \text{ kcal mol}^{-1}$). The *cc* conformer drops dramatically between the $v = 2$ and $v = 6$ vibrational states by 2.5 orders of magnitude. A substantial part of this decrease in lifetime

¹ Another classical approximation of the autocorrelation function, using the OH energy rather than phase space orbits in the bright state definition, was also tested and the results changed very little between the two approximations.

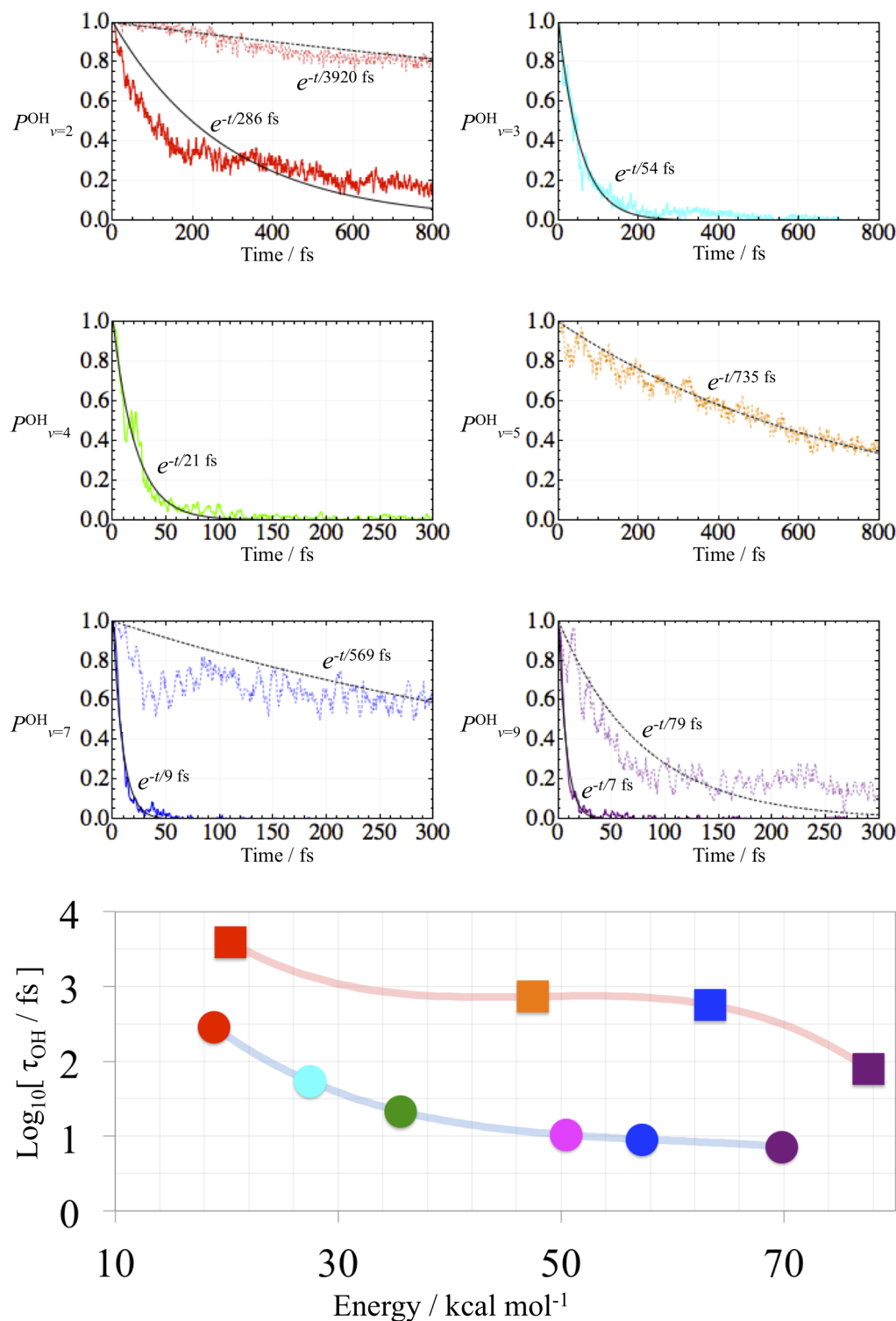


Figure A.8: The probability curves, the approximations to the OH overtone autocorrelation functions, are shown along with their fits to decaying exponentials. The *cc* conformer results are solid colored lines and the *tp* results are dashed colored lines. The OH vibrational levels are specified by color: $v = 2$ (red), $v = 3$ (cyan), $v = 4$ (green), $v = 5$ (orange), $v = 6$ (magenta), $v = 7$ (blue), $v = 9$ (violet). The bottom figure summarizes the lifetime data, where the circles are for the *cc* conformer and the squares are for the *tp* conformer. Energies for the overtone states can be found in Figure A.1.

occurs between $v = 2$ and $v = 3$ and between $v = 3$ and $v = 4$. At $v = 3$, chattering events begin to occur and energy transfer from the excited chromophore becomes markedly more pronounced. This chattering threshold at $v = 3$ was predicted in the relaxed OH PES shown in Figure A.5. At $v = 4$, the lifetime has decreased to the time scale of approximately two OH vibrational periods. The phase space model of the autocorrelation function predicts sub-OH vibrational period lifetimes² that suggest the localization OH excitation energy in the chromophore is quite transient. The short lifetimes of the OH local mode suggest that excitation of this mode to high vibrational states will manifest in an absorption spectra as a very broad feature. Indeed, the homogenous broadening we compute for the $v = 2$ excitation and, in particular, the $v = 3$ excitation is approximately consistent with the observed peak widths observed by Sinha et al. [70]. The experimental spectra peak widths are wider than those expected for the *tp* conformer from the trajectories. The lifetime plots for this conformer reveal that the excited state is relatively long lived, on the order of 0.5 to 1 ps for excitations between $v = 2$ and $v = 7$. Not until $v = 9$, at extremely high energies, is a significant decrease in the lifetime seen.

The overtone spectra of Sinha et al. [70, 174] also show an interesting feature in the OH absorption peaks, which usually consist of two peaks separated by 342 cm^{-1} . In peroxyntrous acid, which is somewhat similar in structure to performic acid, McCoy and co-workers showed the importance of including the OH torsional mode in calculating the OH overtone spectrum [111, 135]. It is reasonable that the performic acid system, particularly with its low barrier to OH torsion, see Figure A.5, also requires consideration of this torsion. Excitation to a OH stretch-torsion combination state may prolong the lifetime of the excitation if there is significant amplitude of the bright state in the shelf region of the torsion potential.

² This may be a somewhat unphysical result due to limitations of our classical treatment of the overtone excited state generated on an unrelaxed potential energy surface and also may be due to other limitations of our phase space autocorrelation function approximation. Nevertheless, the results are indicative of a very short lifetime of the excitation.

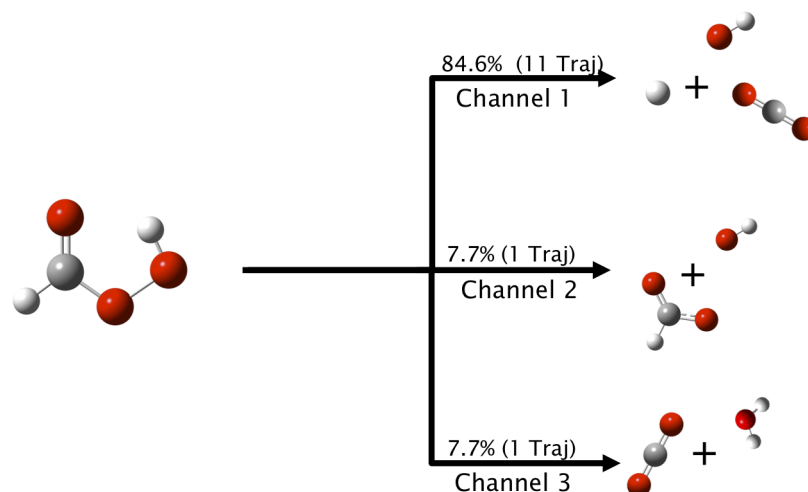


Figure A.9: The results of the trajectory simulations of the OH overtone induced chemical reaction for $v = 9$ excitation observed on the simulation time scale. All the $v = 7$ trajectories reacted through the first channel shown but are not counted in the shown percentages.

A.5 The O–O Dissociation Reaction of Performic Acid

The O–O dissociation reaction of performic acid was also studied using classical trajectory simulations similar to those described in Chapters 2 and 3. Reactions were observed in the trajectories only for the highest energy excitations considered for the *cc* conformer, $v = 7$ and $v = 9$. No reaction was observed on the time scale of the trajectories for the *tp* conformer. The favored reactive channel was the production of HCO_2 , where the H is attached to the C, and an OH radical. In most cases, HCO_2 was unstable with the CO_2 bending motion and the radical decayed to H and CO_2 . Other reactive channels were observed, and the most interesting was the production of CO_2 and H_2O . An summary of the observed reactive channels is given in Figure A.9. Some of these reactions occurred at very long simulation times beyond the time scale where the classical dynamics coincide with the quantum evolution of the bright state [58], ≥ 1 ps, and elementary product analysis suggests that issues with zero point energy leakage are possible. Also, for trajectories that reached one of the diradical reactive channels, obtaining converged quantum chemistry calculations became difficult, and it is probable that multiconfigurational effects of the electronic wavefunction may be important as the reaction passes through the transition state dividing surface.

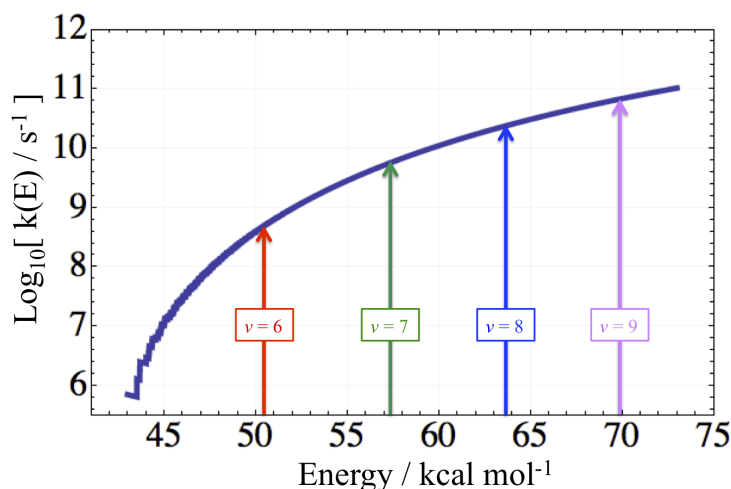


Figure A.10: The RRKM rate coefficient for the dissociation of the O–O bond in the unimolecular decomposition of performic acid.

Nevertheless, reactive events were observed in these high energy excitations and may be indicative of an accelerated reaction rate upon OH overtone absorption. We have computed a crude RRKM rate constant, where OH torsion modes are treated as a hindered rotors along relaxed torsional PESs, similar to the separable rotor approximation described in Chapter 4, in both the reactant density of states and the transition state sum of states, as a function of excitation energy, shown in Figure A.10. All other degrees of freedom are assumed to be harmonic with frequency values equal to that found in a normal mode analysis of the lowest energy structure. As seen in Figure A.10, the RRKM calculation predicts reactive lifetimes at the $v = 7$ and $v = 9$ OH overtone states of about 150-200 ps and 15-20 ps, respectively. While these lifetime estimates are slightly longer than the reaction lifetimes implied by the dynamics of the trajectory studies, they are not suggestively inconsistent with the observed dynamics from the trajectories within the uncertainty of both the crude RRKM model and the simulations. Indeed, the trajectories indicate that IVR occurs on a relatively short time scale relative to reaction which is consistent with the statistical model and a salient non-statistical reactive process is not evident in the results presented in this appendix. The IVR process is expected to dominate the linewidth of the frequency domain spectrum for the hydrogen bonded conformer.

A.6 Future Work

Several major steps should be accomplished in elucidating the OH overtone initiated dynamics of performic acid. First, the role of the torsional coordinates about the O–O and C–O bond should be understood in terms of the experimental spectra of Sinha et al. [70], in particular the splitting of the OH overtone absorption into two peaks separated by 342 cm^{-1} and the effect on the homogeneous broadening due to torsional “shelf” states. The role of the two possible torsional coordinates in the performic acid spectra should be further explored along with other low frequency large atom coordinates that participate in the initial IVR of the excitation energy in the OH bright state. Second, the possible multiconfigurational effects of the performic reactants and transition states should be computed. This system is small enough that relatively high level ab initio calculations may be performed to characterize important features of the potential energy. With accurate quantum chemistry data, a more rigorous RRKM calculation should be performed, particularly one utilizing the methods outlined in Chapter 4 of this thesis, in order to provide a better estimate of the statistical lifetime of the performic acid molecule upon excitation.