

Sub-Doppler molecular-iodine transitions near the dissociation limit (523–498 nm)

Wang-Yau Cheng,* Lisheng Chen, Tai Hyun Yoon,[†] John L. Hall, and Jun Ye

JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440

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A widely tunable and high-resolution spectrometer based on a frequency-doubled Ti:sapphire laser was used to explore sub-Doppler transitions of iodine molecules in the wavelength range 523–498 nm. The wavelength dependence of the hyperfine transition linewidth of iodine was mapped out in this region, and the narrowest linewidth was ~ 4 kHz near 508 nm. The hyperfine-resolved patterns were found to be largely modified toward the dissociation limit. The observed excellent signal-to-noise ratio should lead to high-quality optical frequency standards that are better than those of the popular 532-nm system. © 2002 Optical Society of America

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Hyperfine-resolved optical transitions in molecular iodine (I_2) often provide stable references for precision spectroscopy.^{1,2} The narrow hyperfine components have also been widely used in laser frequency stabilization, following the lead of an early He-Ne/ $^{127}I_2$ system by intracavity saturated absorption in a red laser at 633 nm.³ Other systems include He-Ne/ $^{127}I_2$ at 640, 612, 576, and 543 nm and Ar/ $^{127}I_2$ at 515 nm as well as the $^{129}I_2$ variants. Most of these systems have wavelengths recommended for realization of the SI Metre.⁴ The I_2 lines near 532 nm are stronger than red transitions, have relatively narrower (200–300-kHz) linewidths, and are readily accessible by frequency-doubled solid-state Nd:YAG lasers.^{5,6} The 532-nm system has proved to be one of the best practical optical frequency standards, with its compact size, reliability, and demonstrated high stability ($< 5 \times 10^{-14}$ at 1 s).⁷ Recent development of wide-bandwidth optical combs shows that such I_2 -based references can be useful not only for precision length metrology but also for generation of high-stability time signals.⁸

To reach higher frequency stability it is useful to explore I_2 transitions at wavelengths below 532 nm, where the natural linewidths may decrease at a faster rate than that for the line strengths. In fact, coincidental overlaps between the I_2 transitions and corresponding Ar⁺-ion laser lines at 515 and 501 nm have already revealed transition linewidths [half-width at half-maximum (HWHM)] as small as 50–100 kHz at these wavelengths.^{9,10} It will be interesting to monitor variations in the transition linewidth when the I_2 molecules approach the dissociation limit. Furthermore, a widely tunable laser system also permits systematic studies of rotation–vibration dynamics and hyperfine interactions near the dissociation limit, providing rich information on molecular dynamics. In this Letter we report a widely tunable yet high-resolution and high-sensitivity I_2 spectrometer based on a frequency-doubled Ti:sapphire laser. We measured the linewidths of the I_2 transitions within the range 523–498 nm; signals were recovered with excellent signal-to-noise ratio (S/N). Our results indicate that I_2 transitions in the

wavelength range 532–501 nm hold great promise for future development of high-quality, portable optical frequency standards, especially in light of the rapid development of all-solid-state Yb:YAG lasers near 1030 nm.¹¹ Further, we show the existence of strong modifications of the hyperfine patterns of I_2 near the dissociation limit.

Figure 1 shows part of the experimental setup that implements precision scan and control of the laser frequency. Our single-mode Ti:sapphire laser is constructed to tune from 1080 to 953 nm and provides ~ 300 mW of useful output power at 1030 nm. A small portion of the fundamental power is used for laser frequency stabilization, based on an evacuated, highly stable optical cavity. An external frequency servo based on an acousto-optic modulator (AOM 1) in combination with a piezo transducer- (PZT-) activated laser cavity mirror is used to stabilize the laser frequency onto the cavity resonance, with an in-loop error signal indicating a relative frequency noise below 0.3 Hz. The operational laser linewidth is limited by the vibration noise and drift associated with the cavity. A heterodyne measurement made between the cavity-stabilized Ti:sapphire laser and a Yb:YAG laser revealed a beat width of 8 kHz rms, probably limited by the free-running linewidth of the Yb:YAG laser. Frequency scanning of the Ti:sapphire

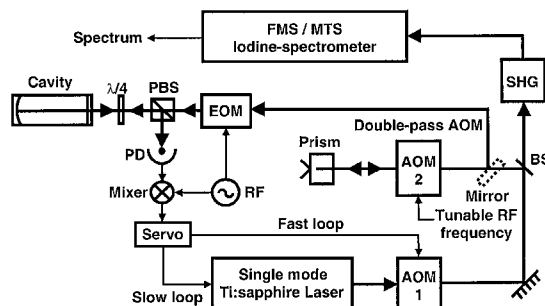


Fig. 1. Part of the experimental setup that controls the laser frequency for the I_2 spectrometer: PD, photodiode; EOM, electro-optic modulator; PBS, polarization beam splitter; $\lambda/4$, quarter-wave plate; BS, beam splitter; other abbreviations defined in the text.

laser is accomplished with a double-passed acousto-optic modulator (AOM 2) that is located at the cavity input. With a fixed cavity length (aside from drift), changing of the drive frequency of AOM 2 will thus tune the stabilized laser frequency, continuously over a 150-MHz range without losing the cavity lock. Because the cavity's free spectral range (mode spacing) is 244 MHz ($<150 \text{ MHz} \times 2$), this AOM-based laser tuning system allows for continuous laser scan over consecutive cavity modes, basically limited only by the single-mode tuning range of the laser itself.

For second-harmonic generation, a KNbO_3 crystal ($3 \text{ mm} \times 5 \text{ mm} \times 3 \text{ mm}$; b cut) is placed inside a buildup cavity as the crystal temperature is varied from 172 to 71 °C to achieve noncritical phase matching at wavelengths that range from 523 to 498 nm. The cavity-output second-harmonic generation power is 82 mW, with a 235-mW mode-matched fundamental power just in front of the doubling cavity. The I_2 spectrometer is similar to that described in Ref. 7 but has the added flexibility of using either frequency-modulation spectroscopy (FMS) or modulation-transfer spectroscopy (MTS) for appropriate recovery of a saturated-absorption signal. The high-purity I_2 cell was prepared by the Bureau International des Poids et Mesures and is 8 cm long, with a Brewster window at each ends. The I_2 pressure is controlled by the temperature stabilization of the cell's cold finger.

Figure 2 shows some typical modulation-transfer spectra of I_2 transitions from 523 to 500 nm. These spectra were obtained with a vapor pressure of 4.12 Pa. The I_2 transitions are identified by the CNRS I_2 spectral atlas.¹² However, spectra obtained below 500.53 nm are out of the range of the I_2 atlas. Our I_2 spectrometer is found to have a constant noise floor throughout the wavelength range of interest. Strong transitions (with strengths comparable to that of 532-nm lines) are relatively common in the range from 530 to 510 nm, as shown in Fig. 2. Near the dissociation limit (499.5 nm),¹³ the line strengths and associated S/Ns decrease substantially.

With such a widely tunable spectrometer, a large range of rovibrational quantum numbers can be addressed, permitting a detailed parametric study of transition strengths, hyperfine interactions, and collision physics. For example, Fig. 2(a) shows that the spectrum of $P(54)38-0$ at 522.474 nm (even rotational quantum number) follows the usual 15-line hyperfine pattern (1-4-4-1-4-1), whereas the spectrum of $P(61)43-0$ at 516.505 nm (odd rotational number) shown in Fig. 2(b) displays the typical 21 hyperfine components (3-4-4-3-4-3). However, as the transition wavelength approaches the predissociation region, for example, line $P(61)53-0$ at 507.949 nm [Fig. 2(c)], the hyperfine splitting pattern starts to change. When the wavelength approaches the dissociation limit, as at 500.506 nm, the 15-line pattern is completely modified [Fig. 2(d)]. Similar observations are made for other lines near 500 nm. Clearly the hyperfine interactions are dramatically influenced by the dissociation effect. Systematic frequency measurement for the corresponding hyperfine constants in this wavelength region is under way in our lab.

The search for the best candidate for an I_2 -based optical frequency reference requires systematic studies of the linewidth and strength of many transitions in this wavelength region. To obtain the zero-power, zero-pressure linewidth of a particular line we typically vary the I_2 cell's pressure from 0.4 to 4 Pa. At each pressure we measure the light-power dependence of the linewidth and determine its zero-power value. We fit the linewidth versus pressure to find the zero-pressure linewidth. Near each wavelength we usually measure and compare a few lines that either have different rovibrational quantum numbers in the excited state or are different hyperfine components within the same transition. Figure 3(a) shows a few pressure-fitted curves. We notice that, even at nearly the same wavelength, natural linewidths of transitions with vastly different rotational quantum numbers can differ by as much as 40 kHz and exhibit quite different collision broadening coefficients. Figure 3(b) displays a number of measured zero-pressure linewidths. For comparison, the 543-nm (Ref. 14) and 532-nm data points are also included. The dashed line (37-kHz) in Fig. 3(b) represents the remediable technical limit to the measured linewidth, including contributions from wave-front curvature and transit time ($\sim 24 \text{ kHz}$), laser linewidth (in the green, $\sim 8 \text{ kHz}$), recoil ($\sim 5 \text{ kHz}$). The natural linewidth can be estimated from deconvolution of the measured Voigt profile. The narrowest natural linewidth that we have found so far is $\sim 43 \text{ kHz}$ HWHM for $R(20)50-0:b5$ at 508.077 nm.

From Fig. 3 we can observe a clear trend of linewidth narrowing with decreasing transition wavelength. However, this tendency is complicated by variations in linewidths among various rotational or hyperfine components when the transitions approach the predissociation region. The initial linewidth narrowing at shorter wavelength may indicate among other interesting effects that the Frank-Condon factor in the transition probability is reduced when the excited state reaches a higher vibration level. As the excited state approaches the dissociation threshold,

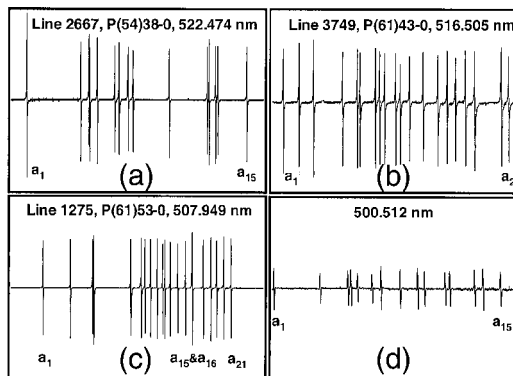


Fig. 2. Typical spectra of molecular I_2 hyperfine transitions from 523 nm to 500 nm. (a), (b), (c) MTS, 273-kHz modulation frequency; (d) FMS, 6-MHz modulation frequency. The quoted¹² line strengths are (a) 80, (b) 79, (c) 55. The time constant is 5 ms for (a)–(c) and 100 ms for (d). Length of I_2 cell, 8 cm; vapor pressure, 4.12 Pa.

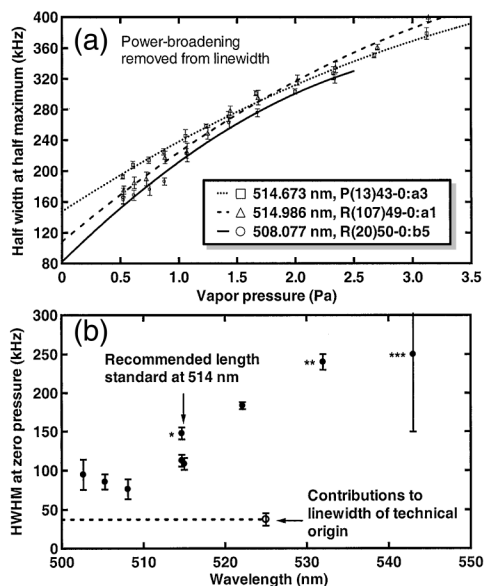


Fig. 3. (a) Three typical curves of zero-power transition linewidth (HWHM) versus pressure. (b) Wavelength dependency of linewidth: *, wavelength standard $P(13)43-0, a3$ at 514.673 nm^4 ; **, measured by Nd:YAG laser; ***, measured by He-Ne laser.¹⁴

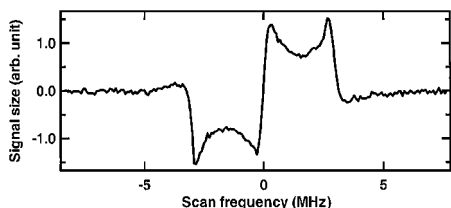


Fig. 4. Typical FMS S/N of a hyperfine transition of $R(86)57-0$ at 508.060 nm . Laser frequency stabilization with this discrimination slope will lead to a projected (in)stability of 1.6×10^{-13} at 1 s, or 1×10^{-14} at 1 s for a 120-cm-long I_2 cell.

the limit on lifetime imposed by predissociation will need to be taken into consideration.¹⁵

To stabilize the frequency of the Ti:sapphire laser we simply feed back the molecular resonance information to the drive frequency of AOM2, which basically suppresses the drift and low-frequency noise from the prestabilization cavity. Currently we use a femtosecond-laser-based wide-bandwidth optical comb to check system performance, which we expect to surpass that of the Nd:YAG/ I_2 system. A preliminary estimate of the system performance at 508 nm can be made based on the S/N of the discrimination curve shown in Fig. 4. The transition is one of the hyperfine components of $R(86)57-0$ at 508.060 nm , and the signal is recovered with FM spectroscopy with a modulation frequency of 6 MHz and a 1-ms time constant. The cold finger temperature of the I_2 cell is -15°C , which corresponds to 0.79-Pa vapor pressure. The projected frequency noise of a laser locked to this error signal is 3 kHz, corresponding to a fractional noise of 5×10^{-12} at 1 ms or 1.6×10^{-13} at 1 s. The best (in)stability reported in an I_2 -stabilized laser system is $<5 \times 10^{-14}$ at 1 s

with a 120-cm long I_2 cell, also at -15°C .⁷ Therefore the performance of the new system, if it is scaled to the same I_2 cell length, would have an (in)stability of 1×10^{-14} at 1 s. Placing the I_2 cell inside a multipass cavity will further improve system performance.

I_2 transitions in the important wavelength region of 523–498 nm yield a number of highly promising candidates for future optical frequency standards. Using a wide-bandwidth precision optical frequency comb, we are measuring the absolute frequencies and the associated systematic shifts of these new reference lines. We intend to perform detailed studies of molecular dynamics including hyperfine interactions in the region of predissociation as well as to check systematically the formula for the predicted hyperfine-induced predissociation broadening.¹⁵ Portable systems based on Yb:YAG laser are under investigation.

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*Present address, Department of Physics, National Dong Hwa University, Taiwan, China.

†Present address, Korea Research Institute of Standards and Science, Daejeon, Korea.

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