Absolute frequency measurement of the molecular iodine hyperfine transitions at 647 nm

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We report absolute frequency measurements of the molecular iodine P(46) 5-4 \(a_{11}\), \(a_{10}\), and \(a_{15}\) hyperfine transitions at 647 nm with a fiber-based frequency comb. The light source is based on a Littrow-type external-cavity diode laser. A frequency stability of \(5 \times 10^{-12}\) at a 200 s integration time when the light source is stabilized to the P(46) 5-4 \(a_{15}\) line. The effect of pressure shift with \(-8.3(7)\) kHz/Pa is discussed. Our determination of the line centers reached a precision of better than 20 kHz. The light source can serve as a reference laser for lithium atom spectroscopy (2\(P \rightarrow 3P\)).

OCIS codes: (300.6320) Spectroscopy, high-resolution; (300.6390) Spectroscopy, molecular; (300.6460) Spectroscopy, saturation; (140.2020) Diode lasers; (140.3425) Laser stabilization; (140.7300) Visible lasers.

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1. INTRODUCTION

Molecular iodine (I\(_2\)) has played a important role in optical frequency standards for many applications. The most striking element of the iodine absorption spectrum is the long series of the \(B \rightarrow X\) system in the range from the green to near-IR and has very strong strength and narrow linewidth in the region close to the dissociation limit [1]. Molecular iodine is commonly used for frequency stabilization of laser. Stabilized laser by sub-Doppler saturation spectroscopy may be called a traditional method in molecular iodine. That good signal-to-noise ratio at the 532 nm of frequency doubled Nd:YAG laser gives very good results [2]. Stabilized laser as reference applies for fundamental metrology [3, 4], atomic or molecular physical [5–10], cavity QED system [11] and optical clocks [12–14].

Iodine absorption lines at 647 nm are very close to doubled wavelength (2\(x=323\) nm) of the 2\(S \rightarrow 3P\) of atomic lithium (Li). Therefore, these iodine lines can be frequency references for Li atom research, e.g., the development of an laser cooling [15, 16] and the measurement of hyperfine intervals [17]. The frequency references at 647 nm using a simple iodine cell are particularly helpful in regards to studying, especially for atomic physics laboratories where no optical frequency combs are available.

In this work, we perform Doppler-free saturation spectroscopy in an iodine vapor cell using modulation transfer spectroscopy. The effect of pressure shift is investigated by changing the cold finger temperature and obtain the absolute transition frequency at zero pressure. The saturated absorption signal is used to lock the laser frequency, and the absolute frequency of the transitions are measured by an optical frequency comb. To our knowledge, there are no precision measurements around this wavelength, and our results provide useful input for the theoretical predictions.

2. EXPERIMENT

The light source is consisted of a Littrow-type external-cavity diode laser (ECDL). We try two different specification laser diodes from Oclaro (model HL6385DG & HL65014DG) in a standard \(\phi=5.6\) mm package and show its the characteristics in Fig. 1 with Littrow configuration. The HL6385DG diode has a free-running wavelength of 642 nm at 25 °C, so we increase its temperature to 40 °C to shift the laser gain profile around 647 nm. However, the HL65014DG diode has a free-running wavelength of 649 nm at room temperature and may be cryogenically cooled to shift gain profile near 647 nm at 18 °C. By grating feedback, the production of high-power single-mode semiconductor laser system operate at 647 nm. As a whole, this diode laser system characteristics are better than HL6385DG diode (e.g. threshold current, gain slope, and power). The laser is assembled in the Littrow configuration in order to establish a frequency selective external cavity. Tuning piezoelectric transducer is achieved the mode-hop free of \(>5\) GHz allowing broad tuning across spectral features of interest for iodine molecular experiment.

The experimental setup is shown in Fig. 2. The laser frequency is stabilized to a Fabry-Pérot cavity to reduce its linewidth by controlling the piezoelectric transducer voltage and driving current of the ECDL. In general we operate that the
The powers of the pump and probe beams are both 15.2 mW. The pressure is related to the cold finger temperature of iodine cell with multilayered glass fibre clothes and a tape heater, and its is maintained at 223 °C. The heating of iodine vapor is necessary in order to access the rovibrational strength of the $B - X$ system originating from high-lying vibrational levels of the ground state.

A half-wave plate and a polarization beam splitter (PBS2, see Fig. 2) are used to separate the laser beam into parts. A 5~7 mW portion of this beam is sent to an optical frequency comb with a single-mode fiber. When the laser is locked to the molecular iodine transition, the frequency of the 647 nm laser is measured by optical frequency comb. The frequency comb is based on a mode-locked erbium-doped fiber laser [19, 20] pumped by a diode laser at 980 nm and operated at a repetition rate of approximately 250 MHz. Stabilizing the repetition rate frequency is phase locked to the Cs atomic clock (Hewlett Packard 5071A) by controlling the piezoelectric transducer mounted in cavity. The carrier envelope offset frequency originating from high-lying vibrational levels of the ground state.

A 58 cm long iodine vapor cell with plane windows fused to the cylindrical body at a slightly tilted angle with light path to avoid interference effects is used and the molecular iodine is contained in cold finger. The cold finger temperature is typically set at 20 °C and is allowed to vary from 20 °C to 30 °C in order to study the effect of pressure shift. The stability of the temperature control of the cold finger is better than 10 mK. The iodine vapor pressure is related to the cold finger temperature of iodine cell by [18]

$$\log(P) = -\frac{3512.830}{T} + 2.013 \times \log(T) + 18.37971, \quad (1)$$

where $P$ is the iodine vapor pressure in Pascals and $T$ is the cold finger temperature in Kelvins. The cell body is surrounded with the $B - X$ system originating from high-lying vibrational levels of the ground state.

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A continuous frequency scans across a full spectral range of the hyperfine structure could be realized without mode-hopping in Fig. 3. That is read with frequency counter and recorded number values through program. The accuracy of the fiber comb is achieved by referencing it to the Cs atomic clock. The Cs atomic clock is calibrated with Hydrogen maser by National Time and Frequency Standard Laboratory of Chung Hwa Telecom Co., Ltd. The precision of the fiber comb system has been to $9 \times 10^{-12}/\sqrt{\tau}$ for $\tau$ less than 1000 s (see Fig. 5). Therefore, the fiber comb introduces negligible errors to our measurement. The iodine transition frequency $f_{\text{iodine}}$ can be derived by the relation

$$f_{\text{iodine}} = \frac{f_{\text{pump}} + f_{\text{probe}}}{2} = f_{\text{laser}} + \frac{f_{\text{AOM}}}{2}$$

$$= 2 \cdot f_{\text{comb}} \pm f_{\text{beat}} + \frac{f_{\text{AOM}}}{2}$$

$$= 2(N \cdot f_{\text{rep}} + f_{\text{CEO}}) \pm f_{\text{beat}} + \frac{f_{\text{AOM}}}{2},$$

(2)

where $f_{\text{laser}}$ is the 647 nm laser frequency, $f_{\text{rep}}$ is the repetition rate frequency, $f_{\text{beat}}$ is the carrier envelop offset frequency, $f_{\text{comb}}$ is the beat note frequency between the 647 nm laser and the fiber comb laser, and $f_{\text{AOM}}$ is 40 MHz in our case. Here the mode number $N$ is a large integer to be determined as follows. We first use a wavelength meter to check our laser frequency to be within 200 MHz of the transition as predicted by the IodineSpec program [21] and iodine spectral atlas textbook [22]. We also change the repetition rate and the offset frequency of the comb laser on purpose to further confirm our measurements.

In order to accurately determine the transition frequency at zero pressure, the pressure dependence must be carefully study. We vary the cold finger temperature to change the iodine vapor pressure according to Eq. (1) and wait for minutes to arrive temperature balance. Typical data are shown in Fig. 6. The result shows great linearity at the pressure range between 20 and 65 Pa. A linear fit is employed to extract the slope of the pressure shift.

3. RESULTS AND DISCUSSIONS

The signal-to-noise ratio (SNR) is 200 for $a_{15}$. A time constant of 30 ms and 12 dB/octave slop are used in spectra.

![Fig. 4. Modulation transfer signals of the P(46) 5-4 transition. The signal-to-noise ratio (SNR) is 200 for $a_{15}$. A time constant of 30 ms and 12 dB/octave slop are used in spectra.](image)

![Fig. 5. (solid circle): Allan deviation $\sigma_\tau(\tau)$ is calculated from measuring beat frequency datas between the laser and frequency comb. The stability of the stabilized laser reaches a level of $5 \times 10^{-12}$ at a 200 s integration time. (open circle): Allan deviation of the Cs atomic clock [23]. (red line): $\sigma_\tau(\tau) = 9 \times 10^{-12}/\sqrt{\tau}$.](image)

![Fig. 6. Pressure shift of the $a_{15}$ transition frequency. The negative slope of 8.3(7) kHz/Pa shows that the interaction due to collision is attractive. Each data point is obtained by a constant fit of 5 measurements.](image)
At our level of precision, we do not observe differences in the slopes among the three components we measure. Therefore, we combine all the results and obtain a coefficient of pressure shift as -8.3±0.7 kHz/Pa. We then use this coefficient to correct all the measured results to obtain the zero-pressure values.

Figure 7 shows the results 10 sessions of each for the three components obtained over several days. Each data point consists of 2000 measurements with cold finger of 20 °C. During the 10 session points, We repeated the process of locking and unlocking laser. The servo electronic offset, for example, a dc voltage offset between the baseline of the spectrum and the lock point, was adjusted servo parameter to <0.5 mV with average time to avoid the offset in the laser frequency. An estimate of the frequency stability (Δf) can be obtained by dividing the linewidth by the signal-to-noise ratio (SNR), leading to Δf ≈ 23 kHz. The sources of measurement uncertainties are summarized in Table 1.

Table 1. Sources of Uncertainties (kHz)

| Source          | Correction | Error |
|-----------------|------------|-------|
| Pressure shift  | 224        | 19    |
| Statistical stability $a_1$: | —          | 6     |
| $a_{10}$:       | —          | 7     |
| $a_{15}$:       | —          | 6     |

Table 2. Results of the Transition Frequency and Hyperfine Splittings and Comparison to the Calculated Values (kHz)

| $a$     | Measured $a$ | Calculated | Measured - Calculated |
|---------|--------------|------------|-----------------------|
| $a_1$   | 463 556 678 565(19) | 463 556 679 461 | -896 |
| $a_{10}$ | 463 557 264 549(20) | 463 557 265 431 | -882 |
| $a_{15}$ | 463 557 558 050(19) | 463 557 558 984 | -934 |
| $a_{15} - a_{10}$ | 293 501(27) | 293 553 | -52 |
| $a_{10} - a_1$   | 585 984(27)  | 585 970 | 14 |

$^a$ The uncertainty is the combined error of the value in Fig. 7 and the uncertainties listed in Table 1.

4. CONCLUSION

In summary, we have measured the absolute transition frequency of the P(46) 5-4 $a_1$, $a_{10}$, and $a_{15}$ hyperfine transitions at 647 nm by modulation transfer saturation spectroscopy with the aid of an optical frequency comb. The results (see Table 2) are in marginal agreement with the prediction of IodineSpec5, in which the expected uncertainty (2σ) in this wavelength is quoted to be ±3 MHz [21]. The effect of pressure shift is important at our level of precision, and our measurement yields a linear dependence with a slope of -8.3(7) kHz/Pa. Our precision measurements at 647 nm will help to reduce the uncertainties of the iodine atlas. In addition, our laser system can serve as a reference for $2S \rightarrow 3P$ of the lithium atomic spectroscopy.

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REFERENCES

1. W.-Y. Cheng, L. Chen, T. H. Yoon, J. L. Hall, and J. Ye, “Sub-doppler molecular-iodine transitions near the dissociation limit (523–498 nm),” Opt. Lett. 27, 571–573 (2002).
2. H.-M. Fang, S. Wang, and J.-T. Shy, “Pressure and power broadening of the $a_{10}$ component of R(56) 32-0 transition of molecular iodine at 532 nm,” Opt. Commun. 257, 76–83 (2006).
3. Y.-C. Huang, H.-C. Chen, S.-E. Chen, J.-T. Shy, and L.-B. Wang, “Precise frequency measurements of iodine hyperfine transitions at 671 nm,” Appl. Opt. 52, 1448–1452 (2013).
4. Y.-C. Hsiao, C.-Y. Kao, H.-C. Chen, S.-E. Chen, J.-L. Peng, and L.-B. Wang, “Absolute frequency measurement of the molecular iodine hyperfine transitions at 548 nm,” J. Opt. Soc. Am. B 30, 328–332 (2013).

5. I. Fan, C.-Y. Chang, L.-B. Wang, S. L. Cornish, J.-T. Shy, and Y.-W. Liu, “Refined determination of the muonium-deuterium 1S-2S isotope shift through improved frequency calibration of iodine lines,” Phys. Rev. A 89, 032513 (2014).

6. Y.-C. Huang, W.-J. Luo, Y.-T. Kuo, and L.-B. Wang, “Precision measurement of hyperfine intervals in the D_1 lines of atomic ^7Li,” J. Phys. B: At., Mol. Opt. Phys. 46, 075004 (2013).

7. C.-C. Liao, Y.-H. Lien, K.-Y. Wu, Y.-R. Lin, and J.-T. Shy, “Widely tunable difference frequency generation source for high-precision mid-infrared spectroscopy,” Opt. Express 21, 9238–9246 (2013).

8. P.-L. Luo, J.-L. Peng, J.-T. Shy, and L.-B. Wang, “Precision frequency metrology of helium ^2S_0→^2P_1 transition,” Phys. Rev. Lett. 111, 013002 (2013).

9. P.-L. Luo, Y.-C. Guan, J.-L. Peng, J.-T. Shy, and L.-B. Wang, “Measurement of the ^2P_1→^3D_2 transition frequency in ^4He,” Phys. Rev. A 88, 054501 (2013).

10. P.-L. Luo, J. Hu, Y. Feng, L.-B. Wang, and J.-T. Shy, “Doppler-free intermodulated fluorescence spectroscopy of ^4He ^2P_3/2→^3D_2 transitions at 588 nm with a 1-W compact laser system,” Appl. Phys. B 120, 279–284 (2015).

11. A. J. Daley, “Quantum computing and quantum simulation with group-ii atoms,” Quantum Inf. Proc. 10, 865–894 (2011).

12. A. Dareau, M. Scholl, Q. Beauvill, D. Dörrig, J. Beugnon, and F. Gerbier, “Doppler spectroscopy of an ytterbium bose-einstein condensate on the clock transition,” Phys. Rev. A 91, 023626 (2015).

13. T. Kobayashi, D. Akamatsu, K. Hosaka, H. Inaba, S. Okubo, T. Tanabe, M. Yasuda, A. Onae, and F.-L. Hong, “Absolute frequency measurements and hyperfine structures of the molecular iodine transitions at 578 nm,” J. Opt. Soc. Am. B 33, 725–734 (2016).

14. A. J. Daley, “Quantum computing and quantum simulation with group-ii atoms,” Quantum Inf. Proc. 10, 865–894 (2011).

15. J.-L. Peng, H. Ahn, R.-H. Shu, H.-C. Chui, and J. Nicholson, “Highly stable, frequency-controlled mode-locked erbium fiber laser comb,” Appl. Phys. B 86, 49–53 (2007).

16. H. Inaba, Y. Daimon, F.-L. Hong, A. Onae, K. Minoshima, T. R. Schibli, H. Matsumoto, M. Hirano, T. Okuno, M. Onishi, and M. Nakazawa, “Long-term measurement of optical frequencies using a simple, robust and low-noise fiber based frequency comb,” Opt. Express 14, 5223–5231 (2006).

21. We have used IodineSpec version 5 to simulate these transitions. For the actual status of the program, contact knoeckel@iqo.unihannover.de.

22. H. Katô, M. Baba, S. Kasahara, K. Ishikawa, M. Misono, Y. Kimura, J. O’Reilly, H. Kawan, T. Shimamoto, T. Shinano, C. Fujiwara, M. Ikeuchi, N. Fujita, M. H. Kabir, M. Ushino, R. Takahashi, and Y. Matsunobu, Doppler-Free High Resolution Spectral Atlas of Iodine Molecule 15000 to 19000 cm-1. (Japan Society for the Promotion of Science, 2000).

23. The Cs atomic clock is calibrated with Hydrogen maser by National Time and Frequency Standard Laboratory of Chunghwa Telecom Co., Ltd.