

Spectroscopy of doubly resonant third-harmonic generation in I_2

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A technique of third-harmonic generation based on simultaneous resonances in one- and two-quantum transitions was applied to find a level of symmetry $^1O_g^+$ of molecular iodine. The energy of this level is given, in cm^{-1} , by $E_T(n, J) = (35972.4 \pm 0.5) + (132.9 \pm 0.2)(n + 1/2) - (0.34 \pm 0.02)(n + 1/2)^2 + [(0.02857 \pm 0.00015) - (0.00015 \pm 0.00002)n](J(J+1))$, where n is an integer differing from the vibrational quantum number v by an undetermined integer and J is the angular momentum. This technique has relatively high efficiency in third-harmonic generation and may provide a basis for a new Doppler-free spectroscopy.

I. INTRODUCTION

Third-harmonic generation (THG) in metal vapors and inert gases has received attention as a means of extending the range of coherent radiation sources beyond the absorption limit of nonlinear crystal frequency converters.¹⁻²⁰ Although an energy conversion ratio of over 10% has been reported,¹² very high power of the primary laser beam ($\sim 10^{10} \text{ W/cm}^2$) was required. Approaches based on the resonant enhancement of the two-quantum state reported for cesium,^{9,15} thallium,¹⁶ strontium,¹¹ and argon,¹⁸ as well as the enhanced resonance in the three-quantum state in mercury²¹ all have low conversion efficiency ($\sim 10^{-10}$ at laser power $\sim 10^7 \text{ W/cm}^2$). A limitation on the conversion efficiency for the two-quantum resonant THG in the phase-matched alkali-metal vapors is due to the loss of atoms and the break of the phase-matching condition through multiphoton ionization.^{7,12,19}

Here we describe the THG in I_2 by the method of simultaneous resonances in one- and two-quantum transitions. This method is not as seriously limited by the photoionization process as the single resonant method. It also has a high third-harmonic conversion efficiency, even with a primary laser of moderate power ($\sim 10^{-10}$ at $\sim 10^6 \text{ W/cm}^2$). Although the spectrum observed has linewidths determined by the Doppler linewidth (and the laser linewidth), it seems likely that with monomode excitation one will be able to determine the frequency difference between the one-quantum and two-quantum resonances with sub-Doppler accuracy—the intensity of the THG being very sensitively dependent on this difference. This will be explained in Sec. III.

The THG in molecular iodine arises when simultaneous resonant transitions occur from a rotational-vibrational level in the ground electronic state of iodine to a level in the B state and from the same B state level to a level in excited state T . Although

the $X \rightarrow B$ spectrum is exceedingly dense, there being several thousand rotational-vibrational lines above 5000 \AA , the simultaneous coincidence in frequency to within our laser linewidth ($\approx 0.5 \text{ cm}^{-1}$) for the $X \rightarrow B$ and $B \rightarrow T$ transitions with common rotational and vibration quantum numbers in the B state limits the THG spectrum to about 100 lines. This greatly simplifies the analysis of the spectrum.

II. EXPERIMENTAL

The experimental setup is shown schematically in Fig. 1. The light source was a Molelectron DL-300 tunable dye laser pumped by a UV-1000 nitrogen laser, which provided 5-nsec pulses of bandwidth approximately 0.2 \AA at 12 pulses per second. The laser power was approximately $400 \mu\text{J}$ per pulse at 5519 \AA . With a quartz polarizer inside the laser cavity, the beam was nearly 100% linearly polarized. The beam was focused with a $f=20\text{-cm}$ lens to a point approximately 1 cm from the exit window of a 10-cm-long fused quartz cell containing I_2 vapor at room temperature (22°C). The third-harmonic signal was separated from the primary laser beam by means of a fused silica prism and was detected with a solar blind EMR

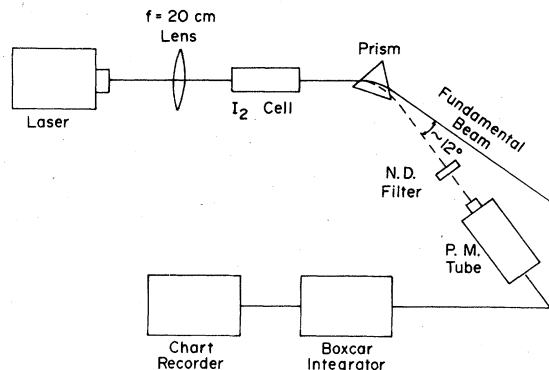


FIG. 1. Schematic diagram of the apparatus.

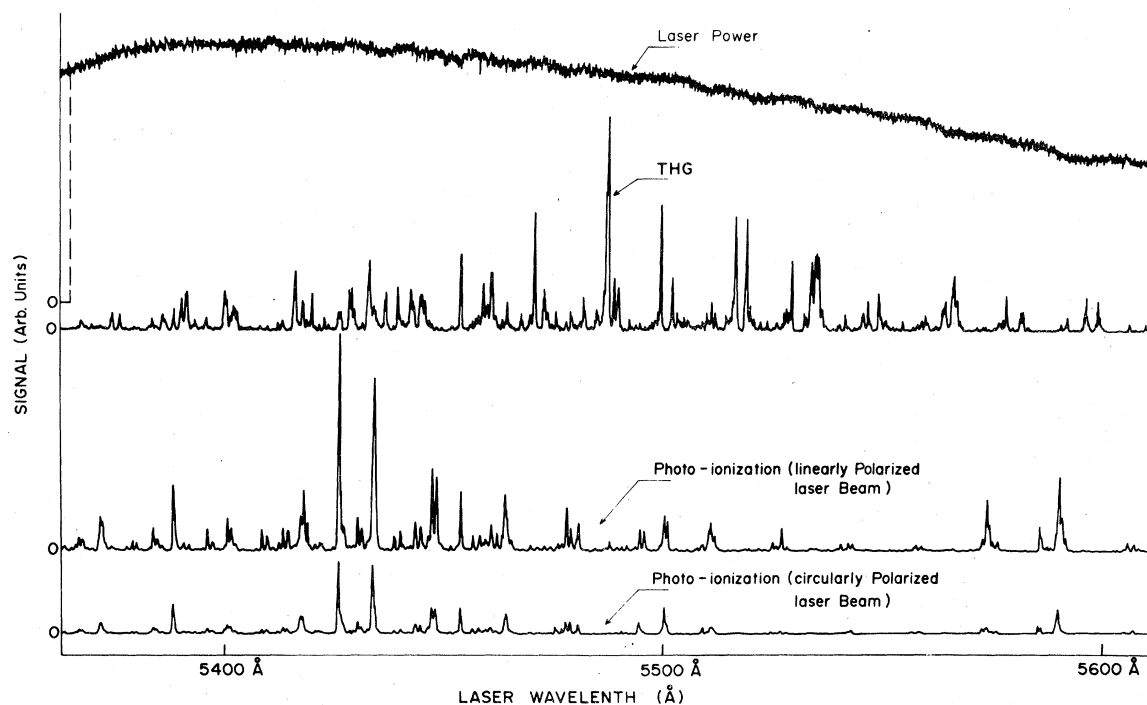


FIG. 2. THG and the photoionization spectrum of I_2 . No THG signal was detected with circularly polarized light.

G-08-18 PM tube which had a quantum efficiency of approximately 0.5% at 1850 Å. The PM tube was placed approximately 15 cm from the exit window of the cell. Neutral density filters were placed in front of the tube to avoid saturation. The output of the tube was fed into a boxcar integrator and was recorded on a chart recorder. The gate width of the boxcar was 25 μ sec and the integrating time constant was 0.3 msec, effectively averaging over 12 laser pulses. Strong THG signals, shown in Fig. 2, were recorded as the laser wavelength was scanned. The off-resonant signal was negligible. The third-harmonic signal generated at the laser wavelength 5753 Å was measured to have a linewidth less than 0.3 Å, the resolution of our monochromator. A photoionization experiment in this region (a five-photon process), based on the method reported in earlier papers,^{22,23} indicated that the photoionization signal was small and the photoionization spectrum was quite different from that of the THG, as is also shown in Fig. 2. Note that the photoionization signal decreased and the spectrum changed slightly when the polarization of the laser was changed from linearly to circularly polarized. The photoionization spectrum is due mainly to simultaneous resonances in the one- and in the three- or four-quantum states. With a circularly polarized laser beam no THG was detected. The laser power dependence of the THG at laser

wavelength 5535 Å, as shown in Fig. 3, varied with a power index from 2.2 to 1.5 as the laser power varied from 20 μ J/pulse to 400 μ J/pulse. The resonance at laser wavelength 5489 Å had an in-

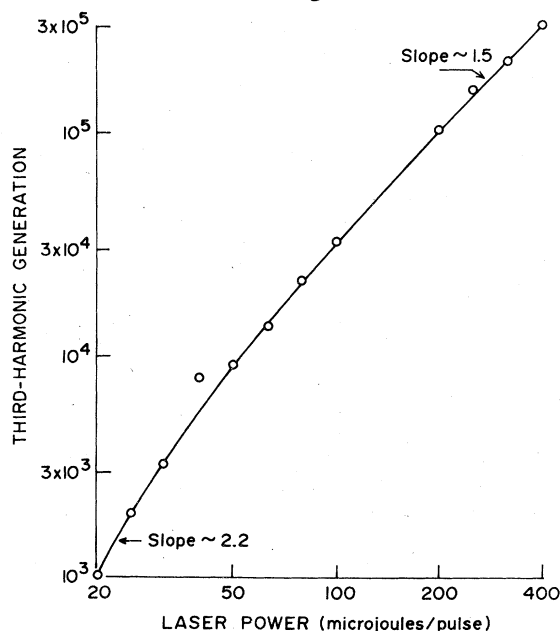


FIG. 3. THG signal as a function of laser power at laser wavelength 5535 Å. The THG signal is expressed in photons generated per pulse.

tensity corresponding to 1.0×10^6 third-harmonic photons generated per pulse, an energy conversion ratio of 3.0×10^{-9} . Possible losses due to the absorption by the window, prism, and air were not corrected for and the real conversion efficiency could be somewhat higher.

The detected signal decreased by a factor of 23 when the cell was cooled from 22 to 0°C, effectively changing the I_2 pressure from 230 to 30 μ m. The signal is also sensitive to the focal length f of the focusing lens. When f is changed from ∞ to 2 cm, the THG varied by a factor of 300 with the measured maximum output given at $f=20$ cm. All these results may indicate that the density of I_2 was so low that the phase matching was automatically satisfied.

III. THEORY

A mechanism that seems to explain at least qualitatively most of the observations is shown in Fig. 4. A molecule is excited resonantly to the level B of symmetry u and then excited resonantly to the state T of symmetry g . Finally, a third excitation leads to a virtual level F of symmetry u and from there the I_2 molecule "radiates" back to the original level X . Note that the whole process is coherent and the third harmonic is radiated

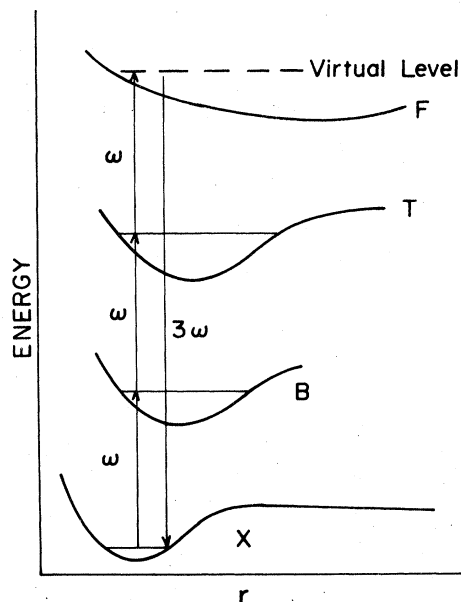


FIG. 4. Schematic diagram of the THG process.

coherently by all the molecules. The spectrum of Fig. 2 is best understood by examining Fig. 5, where the transition frequency of $(B-X)$ and half the frequency of $(T-X)$ of the various bands are plot-

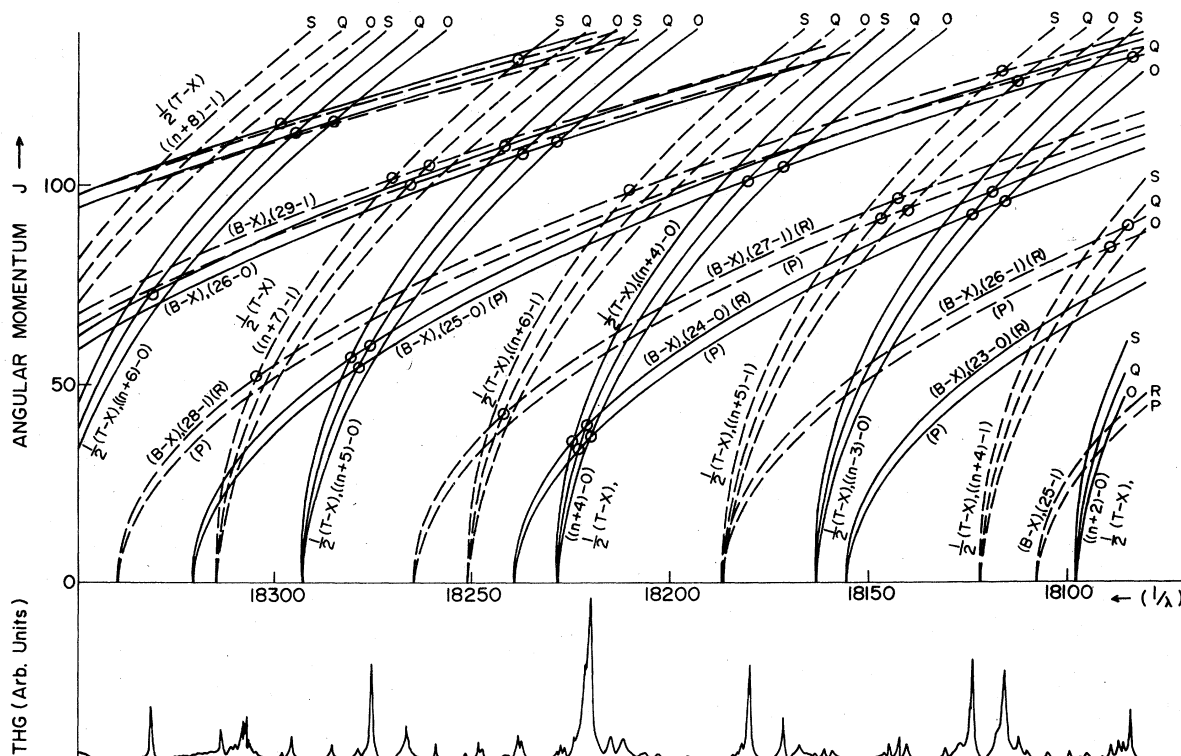


FIG. 5. Interpretation of the THG spectrum in terms of Fortrat parabolas for the $B-X$ and $\frac{1}{2}(T-X)$ transition. Circles indicate those intersections of the $(B-X)$ and $\frac{1}{2}(T-X)$ curves with J close to an integer.

ted as abscissa and the angular momentum J of the molecule in its ground level X is plotted as ordinate. The condition of simultaneous resonances in the $(B-X)$ and $(T-B)$ transitions is satisfied at the intersection of the $(B-X)$ and $\frac{1}{2}(T-X)$ curves. Since J must be an integer, only intersections close to an integer J yield THG.

The resonances may be conveniently derived in

$$\left| \sum_{\text{phase matched molecules}} E^3 \sum_F \frac{\langle X | \vec{\mu} \cdot \vec{\epsilon}_3 | F \rangle \langle F | \vec{\mu} \cdot \vec{\epsilon} | T \rangle \langle T | \vec{\mu} \cdot \vec{\epsilon} | B \rangle \langle B | \vec{\mu} \cdot \vec{\epsilon} | X \rangle}{[\Omega_{FX} - 3\omega(1 - v/c) + i\Gamma_F][\Omega_{TX} - 2\omega(1 - v/c) + i\Gamma_T][\Omega_{BX} - \omega(1 - v/c) + i\Gamma_B]} \right|^2, \quad (1)$$

where the various electronic vibrational-rotational states of the molecule are denoted by $|X\rangle$, $|B\rangle$, $|T\rangle$, and $|F\rangle$ and the Γ 's represent the corresponding natural linewidths. v is the molecular velocity. Ω_{FX} , Ω_{TX} , and Ω_{BX} represent the energy difference between the various levels. Although here the laser is assumed to be coherent and monochroma-

tic, such properties as the resonant frequencies and symmetry selection rules between the various levels remain valid for a laser of finite linewidth. Write $\Omega_{TX} = 2\Omega_{BX} + \delta$. It is easy to see that the THG, $I(\omega)$, at laser frequency ω , where ω is within the Doppler linewidth of the $(B-X)$ transition, is for a monochromatic laser beam proportional to

$$\int \frac{W(v) dv}{\{[2\Omega_{BX} - 2\omega(1 - v/c) + \delta]^2 + \Gamma_T^2\} \{[\Omega_{BX} - \omega(1 - v/c)]^2 + \Gamma_B^2\}}, \quad (2)$$

where $W(v)$ represents the statistical distribution of the molecular velocities. Since the major contribution to the integral is from molecules with such a velocity that $\Omega_{BX} - (1 - v/c)\omega \approx 0$, we may approximate (2) by

$$I(\omega) \propto \int \frac{W(v) dv}{(\delta^2 + \Gamma_T^2) \{[\Omega_{BX} - \omega(1 - v/c)]^2 + \Gamma_B^2\}} = \frac{1}{(\delta^2 + \Gamma_T^2)} \int \frac{W(v) dv}{[\Omega_{BX} - \omega(1 - v/c)]^2 + \Gamma_B^2}. \quad (3)$$

Equation (3) is nothing but the ordinary Doppler profile multiplied by the factor $1/(\delta^2 + \Gamma_T^2)$. If the laser frequency is tuned to within the Doppler linewidth of the $(B-X)$ transition and then the "one- and two-quantum resonance difference δ " is scanned by an external field, we will get a "Doppler-free" spectrum with a linewidth determined by the natural linewidth, the laser linewidth, and the various homogeneous broadenings. Power broadening is expected to be the main limitation of such an experiment. The above argument can be easily generalized to the situation where two lasers of frequency Ω_{BX} and Ω_{TB} are used to generate the wave mixing. Such an arrangement will greatly increase the applicability of the technique.

Our THG spectrum of I_2 consisting of about 100 lines is due to simultaneous resonances in the one- and two-quantum transitions, i.e., the laser frequency ω satisfies the relation

$$\omega \approx \Omega_{BX} = T_B - T_X$$

and

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Write $\Omega_{TX} = 2\Omega_{BX} + \delta$. It is easy to see that the THG, $I(\omega)$, at laser frequency ω , where ω is within the Doppler linewidth of the $(B-X)$ transition, is for a monochromatic laser beam proportional to

$$\omega \approx \Omega_{TB} \approx \frac{1}{2} \Omega_{TX}.$$

It is clear that since the analysis of the $X \rightarrow B$ transition is well known,^{24,25} one can use our spectrum to obtain constants for the T state if a correct assignment of the observed resonances can be made. Before we discuss further the determination of the constants of the T state it is convenient to point out that the other possible assignment of the THG spectrum of I_2 —simultaneous resonances in the one and three quantum transitions—does not play a significant role in the present work. The Cordes^{26,27} band system does fall in the region of the three-quantum states. However, both the spacing of our THG lines and the absolute frequencies correspond poorly to those expected for a three-quantum resonance to the upper state of the Cordes bands. Moreover, a characteristic feature of our spectrum is pairs of lines separated by approximately 100 cm^{-1} , about half the ground-state vibrational separation. This is difficult to account for if resonances occur in the three quantum transition, but is just what is expected for two-quantum resonances arising from the hot band structure of the ground state.

The constants of the two-quantum state T are uniquely and accurately determined from a correct assignment of the rotational-vibrational quantum numbers of the $B-X$ transition. Once the rotational quantum number J is determined for several resonances originating from a particular vibrational level of T , the B value and vibrational origin of this vibrational band can be easily determined. Virtually all of the observed resonances, listed

ν_L	I	T	B	X	J	Remarks	ν_L	I	T	B	X	J	Remarks
17 911.5	0.6	0	22	0	110	(P.Q)	18 313.7	1.4					
17 913.1	0.6						18 331.1	2.3	6	26	0	73	(R.Q)
17 914.3	0.4						18 357.9	0.9	7	28	0	119	(R.S)
17 924.1	1.0	2	25	1	116	(P.O)			8	29	1	64	(R.Q)
17 959.6	0.95	0	21	0	41	(P.Q)	18 361.6	1.1	8	29	1	59	(P.Q)
		0	21	0	45	(R.S)	18 366.5	1.1	10	33	2	85	(S.R)
17 962.3	1.7	4	28	2	107	(P.Q)	18 369.3	1.2					
17 968.3	0.9	2	24	1	64, 65	(P, O)	18 379.2	1.3	9	31	1	107	(P.O)
17 971.2	0.7	2	24	1	67	(R.Q)			9	31	1	109	(Q.R)
		1	23	0	121	(R.S)			11	36	2	131	(R.S)
18 017.3	1.0	5	29	2	115	(R.Q)	18 388.1	1.2	7	27	0	82	(R.Q)
18 018.3	1.2	2	24	0	131	(R.Q)	18 389.2	1.0	7	27	0	77	(P.Q)
									9	31	1	106	(R.S)
18 060.3	0.7	5	28	2	71	(R.O)	18 397.8	0.7	11	35	2	110	(P.Q)
		2	23	0	84	(P.O)	18 400.1	2.15	8	29	0	123	(P.O)
18 062.5	2.25	2	23	0	87	(R.Q)	18 406.8	2.0	8	29	0	125	(R.Q)
18 063.8	2.35	2	23	0	86	(R.Q)	18 410.7	0.2	10	33	1	135	(R.Q)
18 065.1	2.30						18 412.6	0.6	8	29	0	120	(P.Q)
18 067.5	2.1	2	23	0	81	(P.Q)	18 415.0	1.3	9	30	1	67	(P.O)
18 080.8	2.1	6	30	2	116	(R.Q)			10	33	1	131	(P.Q)
		3	35	0	132	(P.Q)	18 416.9	1.2	9	30	1	70	(P.Q)
18 086.1	0.7	4	26	1	89	(P.Q)			8	29	0	122	(R.S)
18 088.4	0.6	4	26	1	83	(R.Q)	18 422.9	0.2	9	30	1	66	(R.S)
18 115.5	3.4	3	24	0	95	(P.O)			9	30	1	64	(P.Q)
		5	28	1	128	(R, S)	18 435.8	0.4	12	37	2	130	(R.Q)
18 117.0	0.7	3	24	0	98	(R, Q)	18 441.3	0.2	8	28	0	87	(P.O)
18 123.9	3.5	3	24	0	92	(P.Q)			10	32	1	109	(R.Q)
18 140.5	0.5	4	26	0	136	(P.Q)	18 445.1	1.2	8	28	0	89	(R.Q)
18 142.2	0.9	5	27	1	96	(R.Q)	18 452.9	0.9	8	28	0	86	(R.S)
18 145.1	0.5	5	27	1	91	(P.Q)			10	32	1	106	(R.S)
		4	26	0	138	(R.S)	18 458.2	1.8	11	33	2	33	(R.S)
18 171.5	1.6	4	25	0	104	(P.O)			12	36	2	111	(R.Q)
18 179.8	3.8	4	25	0	101	(P.Q)	18 467.7	0.3	9	30	0	127	(R.Q)
18 211.5	1.3	8	32	2	113	(P.Q)	18 469.6	0.3	9	30	0	123	(P.Q)
		6	28	1	98	(R.S)	18 502.8	0.6	9	29	0	94	(R.Q)
		8	32	2	115	(R.S)	18 504.6	0.7	11	33	1	110	(R.Q)
18 215.1	1.6						18 506.2	0.7	9	29	0	89	(P.Q)
18 219.3													

in Table I, except for some minor features, can be accounted for in terms of the five constants of the excited state T . Thirteen vibrational bands are observed. Their energy, in cm^{-1} , is found to be

$$E_T(n, J) = (35\,972.4 \pm 0.5) + (132.9 \pm 0.2)(n + \tfrac{1}{2}) \\ - (0.34 \pm 0.02)(n + \tfrac{1}{2})^2 + [(0.028\,57 \pm 0.000\,15) \\ - (0.000\,15 \pm 0.000\,02)n](J)(J+1).$$

Since the origin of the band system is not fully determined, the band parameter n is different from the vibrational quantum number v by an undetermined integer.

The rotational selection rules for the $X \rightarrow B$ transition are well known; $J \rightarrow J+1$ and $J-1$. The selection rules for the transition $B \rightarrow T$ are $J \rightarrow J$, $J+1$, and $J-1$ if T state is electronically 1_g , and $J \rightarrow J+1$ and $J-1$ if it is 0_g^+ . Since there is no evidence of the $J \rightarrow J \pm 1$ resonances in the observed ($T-X$) transition, the T state must have the symmetry of 0_g^+ . There is also a possibility that this level may be the level designated as $E(\sum_g^+)^{28}$ with origin given by $41\,407\text{ cm}^{-1}$, ω_g by 102.2 cm^{-1} , and $\omega_g x_g$ by 0.34 cm^{-1} . If we assume that the origin of the E level is incorrectly assigned and that the E state is actually a continuation of the T state, the vibrational constants of the E state would be ω_g

$= 133.3\text{ cm}^{-1}$ and $\omega_g x_g = 0.33\text{ cm}^{-1}$, in good agreement with our values for the T state.

The photoionization spectra, mainly due to the simultaneous resonances to the B level and the Cordes bands, can also be easily analyzed and agree very well with previous work.^{27,29} The preliminary B value of the $v=15$ Cordes band is determined to be $(0.0338 \pm 0.0010)\text{ cm}^{-1}$.

IV. CONCLUSION

Because of the simplicity and sensitivity of this experiment it may have further applications. The high conversion efficiency of the THG may provide a basis for generation of continuous coherent vacuum ultraviolet radiation if a gas cell was put into the laser cavity of a narrow band continuous laser. The fact that the precision of this technique is not limited by the Doppler broadening is also interesting and may be valuable in investigating fine and hyperfine structure of molecules in external fields.

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²¹The THG, at 1849 Å , in Hg was detected with a setup similar to that described in this paper. The third-harmonic signal generated is approximately 10^{-4} times that of I_2 at room temperature. The signal increased by approximately a factor of 3 when the temperature was reduced to 0°C .

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