Perturbation in I_2 levels studied by nonlinear coherent spectroscopy

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The technique of harmonic generation with circularly polarized light is applied to study the Landé g factor of the two-quantum excited states of I_2 molecules. Systematic and abrupt changes in the g factor are observed. The large change in the g factor is interpreted in terms of perturbation by a level that has no bound state. Enhancement of harmonic generation in a high magnetic field with linearly polarized light is also observed in some resonances that have a small g factor in the two-quantum state. The enhancement is interpreted in terms of constructive interference of resonances originating from the ground state and the first thermally excited vibrational state.

I. INTRODUCTION

The development of the laser has stimulated the development of many new techniques in the investigating of atoms and molecules. Multiphoton excitation which was first observed in the radio-frequency range[1–6] was soon extended into the visible and ultraviolet regions[7] after the advent of the laser in 1960. Fast progress in multiphoton processes[8–15] followed the development of the dye laser.

The spectroscopic properties of multiphoton transitions are very interesting because it is possible to use them to eliminate the Doppler broadening.[16–19] Because of the high resolution and the ability of studying the detailed dynamics of the interaction of radiation and matter, the coherent spectroscopic techniques such as the two-photon absorption in a standing wave,[18–20] the coherent Raman spectroscopy,[21–24] and the various photon-echo techniques[25–28] and optical coherent transient effects[29–31] have been widely applied to study the energy or collision cross section associated with the various atomic and molecular states.

It may be interesting to compare the technique of coherent spectroscopy with classical Doppler-free methods such as the double-resonance method,[32] the Hanle[33] and level-crossing methods,[34] and quantum beats.[35,36] The classical methods can measure small structures such as the hyperfine structure and the Landé-g factor in a small magnetic field with a precision which is only limited by the natural width of the level under consideration. The classical methods are probably more convenient than the coherent spectroscopy. However, these methods cannot give any information about isotope shifts and absolute measurements of wavelength. For the study of atomic or molecular structure and the properties of the resonant states, these two approaches may give complementary results in many respects.

It may also be interesting to see that the two methods—the classical spectroscopy and the nonlinear coherent processes—can actually be combined to give many interesting new physics. Recently developed techniques in classical spectroscopy such as the level crossing and the photon echo have been applied to the resonant harmonic generation[37–39] in I_2.[40,41] Polarization rotation of third-harmonic generation[42] (THG) with asynchronous pulses[43] have also been studied. The techniques of nonlinear ellipsometry[44] may also be based on the same scheme. The preliminary results of work done with this approach are very encouraging. The detailed dynamics of the various coherent processes and the mechanism of saturation as well as the properties of the resonant states may be studied. Because of the coherent nature of wave mixing, work with this approach very often generates results that are strikingly different from their counterparts in the conventional spectroscopy. In addition, because the processes studied usually involve several photons, it is possible to develop new techniques in coherent spectroscopy that may not have a counterpart in conventional spectroscopy. A recent example is provided by the technique of harmonic generation with circularly polarized light[45] in a magnetic field which is based on the angular momentum nonconservation in a broken symmetry geometry.

In this work the technique of THG with circularly polarized light in a magnetic field is further applied to study the Landé g factor of the two-quantum states of I_2. Both systematic and abrupt changes in the g value are observed. The change in the g factor may be interpreted in terms of perturbation by an electronic state that seems to have no resonance in the spectrum of THG. Observation of the perturbation may provide the only way of studying the perturbing level which has no bound state. The g value of one-quantum state (state B) is reported in Refs. 46–48.

In this work the magnetic field dependence of the THG is also studied with the laser beam polarized parallel to the magnetic field. High-field level-crossing-type enhancement in THG is also observed in some resonances. The enhancement may be interpreted in terms of constructive interference of resonances originating from the ground state and the first thermally excited vibrational state. This is similar to a level-crossing experiment[33,34] in conventional spectroscopy. However, in coherent spectroscopy, level crossing is not necessary and only the coincidence of the transition frequency is required. The tech-

nique of coherent enhancement is a general technique that should have wide application. Isotope shift and isotope concentration may be measured directly by this technique which is based on the interference between different molecules.

II. THEORY

Third-harmonic generation in I_2 is enhanced with simultaneous resonances in one- and two-quantum resonances.[49] A theory of doubly resonant third-harmonic generation in molecules with nearly degenerate states as presented in Ref. 42 can explain the level crossing of THG as well as THG with circularly polarized light. The ensemble-averaged macroscopic (total) nonlinear dipole moment responsible for the wave mixing in a unit volume in the sample may be written as

$$\vec{P}=\sum{}'\left[\sum_{g,n}\rho_{ng}\vec{d}_{gn}\right]. \tag{1}$$

Here the prime indicates summation over all molecules in a unit volume. $\vec{d}_{gn}$ is the matrix element of $\vec{d}$, the dipole moment operator between the ground state $|g\rangle$ and the virtual three-quantum state $|n\rangle$. ρ_{ng} is the density matrix between states $|n\rangle$ and $|g\rangle$. The intensity of the harmonic generated is proportional to the square of the macroscopic nonlinear dipole moment or

$$I\propto\sum_{g,n,g',n'}(\vec{u}\cdot\vec{d})_{gn}\rho_{ng}\rho_{g'n'}(\vec{u}^{*}\cdot\vec{d})_{n'g'}. \tag{2}$$

Here $\vec{u}$ is the polarization vector of the mixed wave. In order to simplify the calculation of the intensity I, one may neglect the effect of the homogeneous linewidth. With the laser wavelength in the visible spectrum range, the homogeneous linewidth (which is determined by the natural lifetime, the collision cross section, etc.) is usually much narrower than the inhomogeneous linewidth (which is closely related to the coherent lifetime) and the simplification may be justified. With a laser of broad line profile and a pulse duration ($\sim$10 ns) much longer than the coherent lifetime ($1/kv_b\leq 1$ ns), one has[42]

$$\rho_{ng}\rho_{g'n'}=\sum_{\substack{e,d,\\ e',d'}}\left\{\frac{C_sC_{s'}^{*}}{\theta_1-\theta_2}\left[\frac{2}{\sqrt{\pi}}\left[e^{-\theta_1^2}\int_0^{\theta_1}e^{t^2}dt-e^{-\theta_2^2}\int_0^{\theta_2}e^{t^2}dt\right]-i(e^{-\theta_1^2}-e^{-\theta_2^2})\right]+\text{c.c.}\right\}. \tag{3}$$

Here $\theta_1=\Omega_{ee'}/\sqrt{2}kv_B$, $\theta_2=\Omega_{dd'}/2\sqrt{2}kv_B$, $\Omega_{ee'}=\Omega_{eg}-\Omega_{e'g'}$, $\Omega_{dd'}=\Omega_{dg}-\Omega_{d'g'}$, and $v_B=(2k_BT/m)^{1/2}$. k_B is the Boltzmann constant, T is the temperature, and m is the molecular weight. Ω_{dg} and Ω_{eg} are defined as $(E_d-E_g)/\hbar$ and $(E_e-E_g)/\hbar$. C_s is proportional to $d_{eg}d_{de}d_{nd}$. It is also assumed that there is no saturation in the calculation of the intensity I.

The intensity of the harmonic generated with a circularly polarized laser pulse may be calculated from the above equations. Since the process of THG with circularly polarized light has been discussed before,[45] the theory in this paper will be devoted to level-crossing-type high field enhancement in THG. For simplicity, consider THG in a cell containing molecules that have no hyperfine structure and the THG is enhanced only in the two-quantum transitions. One may further assume that the two independent transitions $|g,J\rangle\rightarrow|d,J+2\rangle$ and $|g',J'\rangle\rightarrow|d',J'+2\rangle$ are nearly coincident in their transition frequency. The two transitions may be associated with two isotopes of an element, the ground and thermally excited rotational-vibrational states of a molecular or different hyperfine states of atoms or molecules. A special case where the total angular momentum quantum number of the ground state $J=J'=\frac{1}{2}$ is particularly easy to analyze. In Fig. 1 the transition frequencies $\Omega_{dg},\Omega_{d'g'}$ are plotted as a function of the magnetic field H. Here it is assumed that the magnetic field is applied in a direction parallel to the polarization direction of the light. The selection rule is $\Delta m=0$. The transition frequency difference between the resonances is assumed to be less than the laser linewidth but larger than the Doppler linewidth so that the two transitions are independently and simultaneously excited. At zero field, the transition frequencies of sublevels of $|g\rangle$ and $|e\rangle$ ($|g'\rangle$ and $|e'\rangle$) with $m=\frac{1}{2}$ and $-\frac{1}{2}$ as indicated by 1 and 2 (1′ and 2′) are equal. The total intensity of the harmonic generated is given by $I\propto(n_g\sum_{i=1,2}\vec{P}_i)^2+(n_{g'}\sum_{i'=1',2'}\vec{P}_{i'})^2$. Here n_g ($n_{g'}$) is the density of molecules in the state $|g\rangle$ ($|g'\rangle$). $\vec{P}_i$ is the nonlinear dipole moment of the transition i. As the magnetic field increases, dipole moments associated with the Zeeman sublevels gradually lose coherence and the intensity of the harmonic generated decreases to one-half of its value at zero field with a linewidth determined by the Doppler linewidth. When the H field is increased to H_0 as shown in the diagram, the transition frequency associated with transitions 1′ and 2′ coincides and the intensity of the harmonic generated,

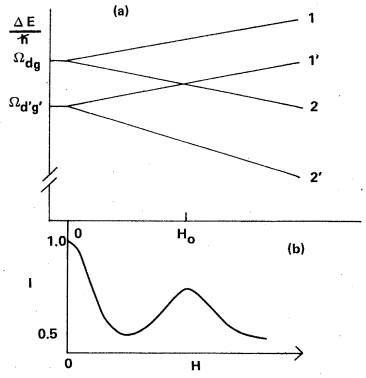

FIG. 1. Enhancement of the intensity of THG, I, caused by coincidence of transition frequency 1′ and 2 occurs at $H=H_0$. The transition is assumed to be $|g,J=\frac{1}{2}\rangle\rightarrow|d,J=\frac{5}{2}\rangle$ and $|g',J=\frac{1}{2}\rangle\rightarrow|d',J=\frac{5}{2}\rangle$. The light is polarized parallel to the magnetic field. $|g\rangle$ is the ground state and $|d\rangle$ is the resonant two-quantum state. It is assumed that $n_g|\vec{P}_i|=n_g'|P_{i'}|$ for $i=1$ and 2.

$$I \propto n_g^2 \sum_{i=1,2} (\vec{P}_i)^2 + n_{g'}^2 \sum_{i'=1',2'} (\vec{P}_{i'})^2 + 2n_g n_{g'} \vec{P}_{1'} \cdot \vec{P}_2 ,$$

increases to a maximum with a linewidth determined again by the Doppler broadening. If J is larger than $\frac{1}{2}$, the linewidth will be reduced by a factor of approximately $2J$ (Ref. 42) and the Zeeman sublevels will start to have transition frequency coincidence at $H \approx \Delta E/(Jg + J'g')\mu_n$. Here ΔE is the resonant energy difference between the two resonances at $H=0$. g $(=g_d - g_g)$ and g' $(=d_{d'} - g_{m'})$ are "effective g factors" of the two transitions and μ_n is the nuclear magneton. Notice that maximum high field enhancement will occur if $|n_g P_i| = |n_{g'} P_{i'}|$. If $|n_g P_i|$ is much smaller than $n_{g'} P_{i'}$, the relative enhancement will be $2n_g P_i / n_{g'} P_{i'} \sim 2n_g / n_{g'}$ which is twice the value of $n_g / n_{g'}$ obtained with the techniques of the conventional spectroscopy.

III. EXPERIMENT

The experimental setup is shown in Fig. 2. The light source is a Molectron DL-II tunable dye laser pumped by a Molectron MY-32 pulsed Nd:YAG (neodymium-doped yttrium aluminum garnet) laser which provides approximately 8-ns pulses of bandwidth approximately 0.1 Å at ten pulses per second. A smooth pulse assembly is put inside the Nd:YAG laser cavity to give temporarily smooth pulses. Filters are used to reduce the power of the laser to approximately 200 μJ/pulse. The beam is collimated by an $f=100$ cm lens and then passes through a 1-cm-long fused quartz cell containing I_2 vapor at room temperature ($\sim$25 °C). The peak laser power density is estimated to be less than 10^9 W/cm^2. A Glan prism is put between the lens and the cell to ensure that the light is close to 100% linearly polarized in a direction parallel to the magnetic field. A Soleil-Babinet compensator may be put between the Glan prism and the I_2 cell and adjusted for quarter-wave retardation to produce circularly polarized light. Third-harmonic generation in the cell is separated from the primary beam by means of a fused-silica prism and is detected by an EMI G-26G-315 rubidium telluride ultraviolet tube protected by two narrow-band ultraviolet interference filters. The output of the tube is recorded on a chart recorder. Strong third-harmonic signals, as reported in Ref. 42, are recorded as the laser-beam wavelength is scanned. Sharp and strong resonances are observed approximately every 55 cm^{-1}. The spectrum may be interpreted in terms of simultaneous resonances in one- and two-quantum transitions.[49]

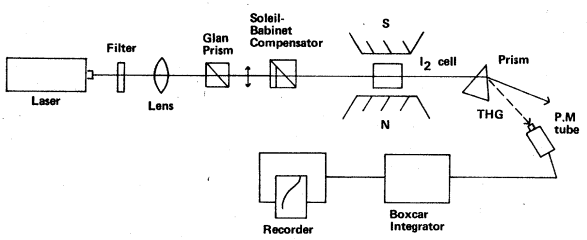

FIG. 2. Schematic diagram of the experimental apparatus of THG with circularly polarized light. Laser beam is converted by a combination of a polarizer (Glan prism) and a compensator to circularly polarized beam and is focused with an $f=1$ m lens to a cell containing I_2 vapor. The generated THG is separated from the primary beam by a prism and is detected by a photomultiplier tube. Signal is averaged by a boxcar integrator and is recorded on a chart recorder. Magnetic field is applied in a direction perpendicular to the direction of propagation of the light.

Before discussing the experimental results, a few words should be said about saturation. Since the coherent lifetime in resonant harmonic generation which is determined mainly by the Doppler broadening is less than 0.5 ns for the two quantum states as compared to a typical lifetime of 10^{-7} s in conventional spectroscopy, effects of saturation are negligible under the present experimental conditions. As reported earlier,[42] "line broadening" in a Hanle-type level-crossing experiment is measured to be less than 15% of the linewidth when the laser powered is increased by a factor of 50 from the present power level. For the same reason, homogeneous linewidth including contributions of collision and predissociation of the B state (one-quantum state) may also be neglected in explaining the experimental results if the total homogeneous linewidth is much narrower than the inhomogeneous linewidth.

The rate of dissociation of the two-quantum state, however, is unknown and may not be neglected. Effects of the dissociation rate of the two-quantum state on the experimental results will be discussed later.

A. THG with circularly polarized light

In this work THG with circularly polarized light is studied with the laser wavelength changing from 5600 to 5900 Å. The value of I_c/I_l, the ratio of THG with circularly polarized light to THG with linearly polarized light, of the various resonances at $H=9000$ G is shown in Fig. 3. The most interesting feature of the data is the large and abrupt change in the value of I_c/I_l at laser wavelength $\lambda_L \approx 5753$ Å. The value of I_c/I_l decreases systematically from a value of approximately 0.04 to approximately 0.001 as the laser wavelength is increased from 5600 to 5753 Å, abruptly jumps to 0.06, and then decreases gradually to approximately 0.04 when the laser

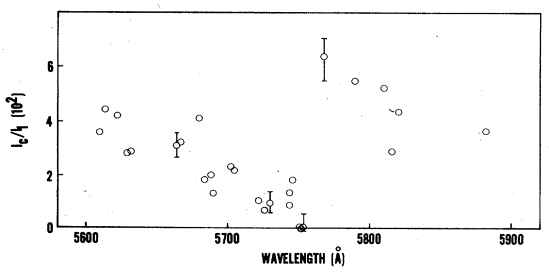

FIG. 3. The value if I_c/I_l, the ratio of THG with the light circularly polarized to that with the light linearly polarized, for the resonances measured at $H=9000$ G. Systematic and abrupt change in the value of I_c/I_l at $\lambda \approx 5753$ Å indicates perturbation by a level that has no bound state.

wavelength is further increased to 5900 Å. Since I_c/I_l is determined mainly by the g factor of the excited states[41] (or gT if T, the lifetime including dissociation, is less than the coherent lifetime), an abrupt change in I_c/I_l implies an abrupt change in the g value (or gT) of one of the resonant states. Since the reported work[46–48] on the measurement of g_e (state B) gives a small value that showed no abrupt change as a function of energy in this spectrum region, it is logical to attribute the sudden change in the value of g (or gT) to the two-quantum state $|d\rangle$. The sudden change in the value of g (or gT) implies a change in the property of the $|d\rangle$ state caused by a perturbation. The perturbing state appears to have no resonance in the THG spectrum. The perturbation which extended a wavelength range of approximately 200 Å and has only one abrupt change in I_c/I_l (g_d, or g_dT) may indicate that the perturbing level has no bound state. Consequently, the perturbed state $|d\rangle$ may be predissociated through the perturbation. Some of the properties of the perturbing state may be studied by the coherent spectroscopy. With the rotational constant of the $|d\rangle$ state, $B\approx 0.0286$ cm^{-1},[49] one has $r_0\approx 3.05$ Å. Here r_0 is the equilibrium separation between the two nuclei. With the vibrational constant $\omega_0\approx 110$ cm^{-1} estimated from the spectrum and assume the vibrational quantum number n approximately 10, the perturbing state is estimated to be approximately 34 800 cm^{-1} above the ground state when it intersects the potential curve of the two quantum states $|d\rangle$ at the internuclear distance $r=3.05\pm 0.25$ Å. A comparison of this conclusion with the calculation of Mulliken[50] may identify the perturbing state as a $^1\Sigma_g$ state that will dissociate into two atoms in state $^2P_{1/2}+{}^2P_{1/2}$. As shown in Fig. 4, the two potential curves intersect at r not far from 2.8 Å. As is discussed before, the state $|d\rangle$ is also believed to have symmetry $^1\Sigma_g$. The nature of the perturbation that decreases the value of g (gT) by a factor of approximately 4 is unclear and should be of interest to theoretical molecular physicists.

Figure 5 shows the experimental data on the measurement of THG with the laser beam linearly and circularly polarized. The laser wavelength in Fig. 5(a) is 5668 Å and the resonance has a relatively large value of I_c/I_l at high magnetic field. The resonances at laser wavelength $\lambda_L=5753$ Å as shown in Fig. 5(b) shows no evidence of increasing in THG with increasing magnetic field.

Figure 6(a) shows a comparison of the theoretical calculation of I_c/I_l with the experimental data at $\lambda_l=5614$ Å. The theoretical calculation with $J_g=83$, $J_e=84$, $J_d=85$, $g_d=-11$, $g_e=0$, and $g_g=-2$ fits the experimental data well at low magnetic field. Figure 6(b) shows a comparison of the experimental data at $\lambda_L=5668$ Å with the theoretical curve calculated with $J_g=75$, $J_e=76$, $J_d=77$, $g_d=-6$, $g_e=0$, and $g_g=-2$. Again the theoretical curve fits the experimental data well except at high magnetic field where the experimental data are systematically higher than the theoretical value. For resonances in the vicinity of $\lambda_L=5753$ Å where I_c/I_L is minimum, g_d is determined to be -3 ± 3. In the calculation of THG with circularly polarized light, effects due to the hyperfine structure are neglected. At low magnetic field, the calculated THG is mainly circularly polarized in the same direction of the laser beam. As the magnetic field increases, components of calculated THG which is oppositely circularly polarized increase to approximately 25% of the total intensity at $H=10\,000$ G at $\lambda_L=5614$ Å.

In the theoretical calculation of I_c/I_l, the homogeneous

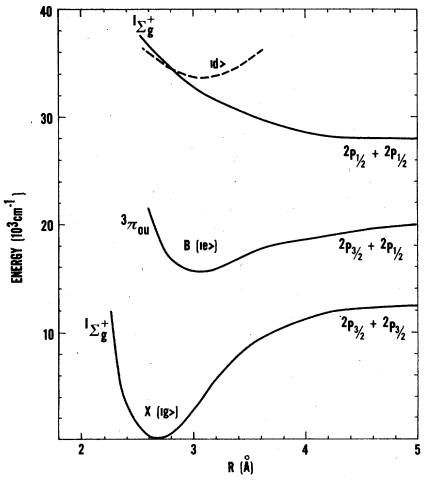

FIG. 4. Potential curves of the resonant states as well as the perturbing state in the harmonic generation in I_2. Changes in the value of the Landé g factor (or gT) of state $|d\rangle$ is believed to be caused by the presence of the perturbing level. The potential curves of the two states cross at $r\approx 2.7$ Å. r is the internuclear distance.

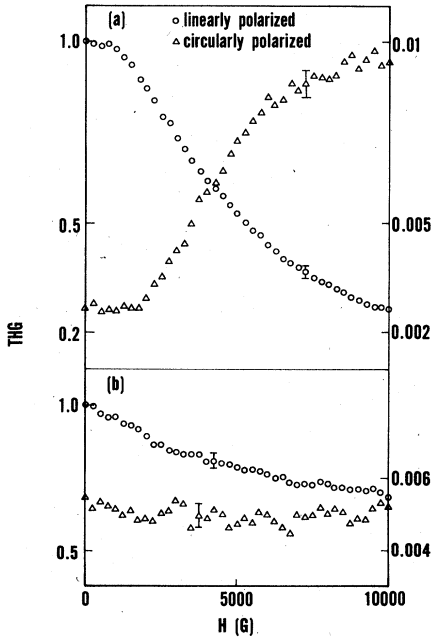

FIG. 5. Experimental data on the measurement of THG with the laser beam linearly polarized as well as circularly polarized. (a) wavelength of the laser beam is $\lambda_L=5668$ Å. (b) $\lambda_L=5753$ Å. The value of I_c/I_l depends on the g factors (or gT) of the resonant states.

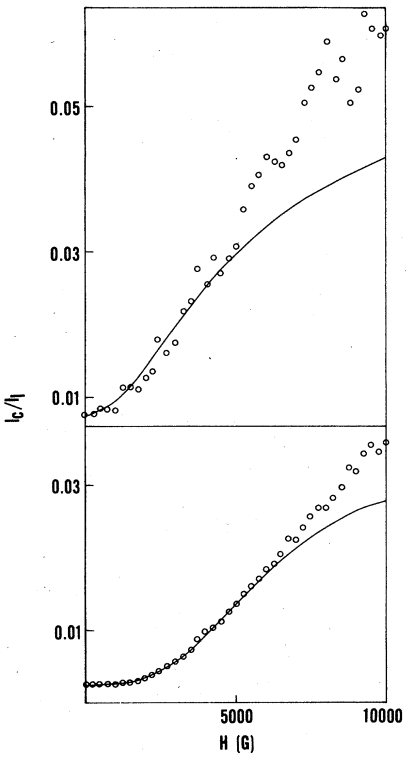

FIG. 6. Comparison of the theoretical calculation of I_c/I_l with the experimental data. (a) $\lambda_L=5614$ Å. The theoretical curve is calculated with $J_g=83$, $J_e=84$, $J_d=85$, $g_g=-2$, $g_e=0$, and $g_d=-11$. (b) $\lambda_L=5668$ Å. Theoretical curve is calculated with $J_g=75$, $J_e=76$, $J_d=77$, $g_g=-2$, $g_e=0$, and $g_d=-6$. Homogeneous linewidth of the $|d\rangle$ state is neglected in the calculation.

linewidth of the $|d\rangle$ state is neglected. With the strong perturbation, a few words should be said about the dissociation rate of state $|d\rangle$. An effort trying to detect the fluorescence of the transition $|d\rangle$-$|e\rangle$ with laser excitation failed. This may indicate that the dissociation rate of level $|d\rangle$ must be much greater than any radiative decay rate. This is consistent with the theory of perturbation discussed above. On the other hand, there is also no sign of decreasing of the intensity of THG in the region close to $\lambda=5753$ Å. Since the intensity of THG is related to the effective population of state $|d\rangle$, it may indicate that the lifetime (corresponding to the homogeneous linewidth) of the $|d\rangle$ state may not be much shorter than the corresponding coherent lifetime and the calculation may not be too wrong. Nevertheless, the deviation between the theoretical curve and the experimental data may be caused by the neglected "homogeneous linewidth" and the real value of g_d and g_g may be somewhat larger than the value used in the calculation.

The g factor of the resonant states calculated in this work is smaller than that calculated with a simplified model in Ref. 45 which neglects the Zeeman splitting of the $|g\rangle$ state. Under an external magnetic field perpendicular to the propagation direction of the light, the state $|g,m\rangle$ is also not an eigenstate and will be developed into a combination of states $|g,m'\rangle$ with $m'=-J,\ldots,J$ at a later time. As a result, even molecules with $g_e=g_d=0$ but $g_d\neq 0$ will generate THG when $B\neq 0$. The fast decreasing of the intensity of THG in a quantum-beat experiment with nonsynchronous circularly polarized light[45] is also due to the development of state $|g,m\rangle$ in a symmetry-breaking geometry.

B. High field enhanced THG

A careful study of Fig. 3 shows that the value of I_c/I_l associated with resonances at $\lambda_L=5743$ and 5746 Å are not nearly as small as that of other resonances in the vicinity. The measurement of the intensity of THG at $\lambda_L=5743$ Å as a function of the magnetic field with the laser beam linearly as well circularly polarized is shown in Fig. 7. A most striking feature of the data in Fig. 7 is the apparent high field enhancement in the intensity of THG with the laser beam linearly polarized. Of over 30 resonances studied, only two resonances with the laser wavelength in the vicinity of 5745 Å have high field enhancement in THG which is clearly observed. The resonance at $\chi_L=5743$ Å is believed to be due to interference between the transitions $|X;v=0,J=35\rangle\rightarrow|B;v=15,J=36\rangle\rightarrow|d,v=n,J=35\rangle$ and $|X;v=1,J=89\rangle\rightarrow B;v=18,J=90\rangle\rightarrow|d;v=n+2,J=91\rangle$. Here n is an unknown integer, v is the vibrational quantum number, and J is the rotational quantum number. Those two resonances are believed to be within the laser linewidth but outside the coherent linewidth at $H=0$. As the H field increases, transition frequencies of some of the Zeeman sublevels start to coincide with each other within the coherent linewidth and the intensity of THG increases due to constructive interference. The populations of molecules in states $|X;v=0,J=35\rangle$ and $|X;v=1,J=89\rangle$ are in a ratio of approximately 3:1. Because of the thermal energy, the two-quantum state originating from the $v=1$ state

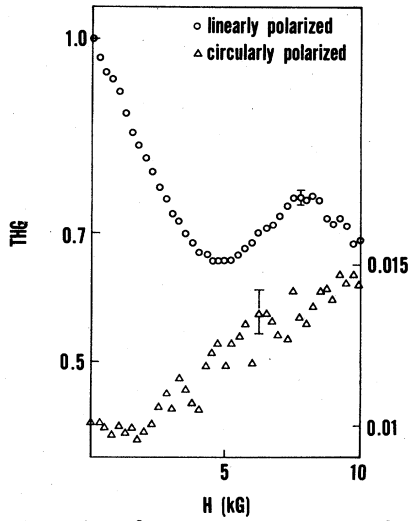

FIG. 7. Intensity of THG measured as a function of the magnetic field. Wavelength of the laser light is 5743 Å. Note the increase of the intensity of THG at high field, when the light is linearly polarized. The high field enhancement in THG, like the Hanle-type enhancement at $H=0$, is believed to be caused by the constructive interference between two independent transitions.

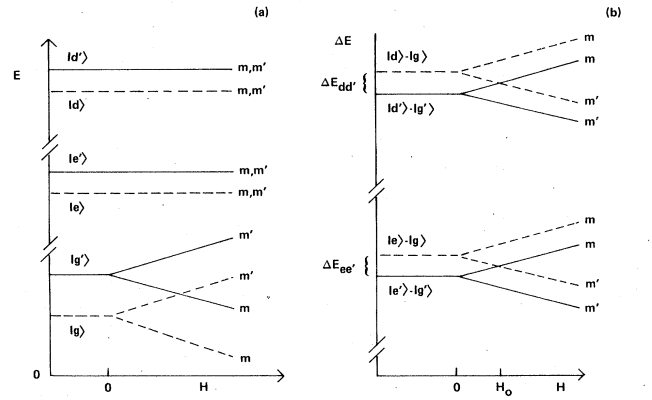

FIG. 8. (a) Energy level of the molecule plotted as a function of the magnetic field H. m (m') is the magnetic quantum number of a particular Zeeman sublevel. (b) Simultaneous coincidence in one- and two-quantum transitions $|g,m'\rangle \rightarrow e,m'\rangle \rightarrow |d,m'\rangle$ and $|g',m\rangle \rightarrow |e',m\rangle \rightarrow |d',m\rangle$ occur at H_0. The light is polarized parallel to the magnetic field and the selection rule is $\Delta m = 0$. It is assumed that $g_e = g_{e'} = g_d = g_{d'} = 0$, $g_{g'} = g_g \neq 0$, and $\Delta E_{dd'} = \Delta E_{dd'}$.

is in fact approximately 300 cm^{-1} above where it appears to be in Fig. 3.

As was discussed before, THG in I_2 is enhanced by simultaneous resonances in one- and two-quantum transitions. In Sec. II, formula (3) shows that the constructive interference between nonlinear dipole moments associated with two independent transitions will give a maximum contribution to the harmonic generation when the frequency coincidence in one- and two-quantum transitions happens at the same magnetic field. A special case where $g_e = g_{e'} = 0$, $g_{g'} = g_g \neq 0$, and $g_d = g_{d'} = 0$ is shown in Fig. 8. If the energy difference in one- and two-quantum transitions, $\Delta E_{ee'}$ and $\Delta E_{dd'}$, are equal at $H = 0$, transitions $|g,m'\rangle \rightarrow |e,m'\rangle \rightarrow |d,m'\rangle$ and $|g',m\rangle \rightarrow |e',m\rangle \rightarrow |d',m\rangle$ will coincide in one- and two-quantum transition frequencies simultaneously at magnetic field H_0 as shown in the diagram. As discussed before, it is assumed that $\vec{H}$ is parallel to the polarization direction of the light and the selection rule is $\Delta m = 0$.

In I_2 it is found that the value of g_d of most of the resonant states studied has the same sign and is much larger than g_g. With such a set of g values ($|g_d| \gg |g_g| \gg |g_e| \approx 0$), the rate of change with respect to H of the transition frequency in one- and two-quantum transitions, $(\Delta\Omega_{eg})_{m,m}/\Delta H$ and $(\Delta\Omega_{de})_{m,m}/\Delta H$, have opposite signs. Coincidence in the transition frequency in one- and two-quantum transition is unlikely to happen at the same magnetic field (within the coherent linewidth) if g_d/g_g is much larger than 1. As is discussed before, high field enhancement in THG is observed only in two resonances that have small values of g_d. This is in good agreement with the theory given above. Since the level-crossing-type enhancement in THG of the resonance at $\lambda_L = 5743$ Å starts at $H \approx 4000$ G, one has $\Delta E_{ee'} \approx (Jg_{eg} + J'g_{e'g'})\mu_n H \approx 1$ GHz, $\Delta E_{dd'} \approx (Jg_{dg} + J'g_{d'g'})\mu_n H \approx 2$ GHz.

IV. CONCLUSION

Techniques of coherent spectroscopy have been applied to study the g factor of the excited states of the I_2 molecule. A very large perturbation on the Landé factor (by a factor of approximately 4) is observed and the perturbing state is identified. Since the perturbing state has no bound level, the perturbed state may predissociate through this perturbation. The predissociation may be dominant over the decay of the molecule and thus make it difficult to be studied with conventional spectroscopy which is based on the observation of the fluorescence from the excited state. With the short coherent lifetime, techniques of coherent spectroscopy have been proved to be suitable to study the strongly perturbed states. In view of the existence of many kinds of perturbations in most molecules, the technique of coherent spectroscopy should have wide application in molecular physics. The coherent spectroscopic techniques may also be applied to study the electric and magnetic properties of the excited states of molecules besides the energy. Measurements of the electric and magnetic properties as well as the collision cross section are important in understanding the molecular structure.

In this work level-crossing-type high field enhancement in THG is also observed. The enhancement is interpreted in terms of constructive interference between radiation of nonlinear dipole moments associated with transitions originating from the ground level and the thermally excited vibrational levels of I_2 molecules. Since coherent spectroscopy is based on the interference between different molecules, level crossing in wave mixing provides a particularly simple method to measure the isotope shift and isotope concentration directly.

Because of the simplicity of the techniques described above it is likely that they will have practical application for studying properties of molecular states and for the measurement of isotopic concentration. Combination of these techniques with Doppler-free spectroscopic methods will be particularly interesting and may lead to exciting progress in molecular physics.

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