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Microwave Double-Photon Transitions in CD_3CN and PF_3

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The microwave double-photon transitions $J=3 \leftarrow\leftarrow 2$ and $J=2 \leftarrow\leftarrow 0$ have been observed for the symmetric-top molecules CD_3CN and PF_3 using high-power microwave double resonance. The pumping of the $J=2 \leftarrow\leftarrow 0$ transition of CD_3CN was so efficient in the low-pressure region that a negative temperature was established between the $J=1$ and the $J=0$ levels, and induced emission $J=1 \rightarrow 0$ was observed. The pressure variation of the efficiency of the double-photon pumping agreed quantitiatively with theoretical values calculated using the Göppert-Mayer formula for the relevant dipole matrix element and Karplus and Schwinger's formula for saturation. The experiment provides interesting information on collision-induced transitions in CD_3CN.

I. INTRODUCTION

Although two-photon processes have been observed in light scattering experiments for many years, the observation of double-photon absorption is relatively recent. It is most easily observed in the radio-frequency (rf) region[1] where the virtual molecular level is fairly close to an actual level and where it is relatively easy to apply a high radiation field. Double-photon absorption has been studied also in the optical region since the advent of lasers. (See Refs. 2 and 3 for summary.) However, no two-photon absorption has so far been observed in the microwave region except for the trivial cases where two resonant photons are used. In this paper, the observation of microwave double-photon absorption in rotational spectra of CD_3CN and PF_3 is reported. These molecules have been chosen since they have intense microwave spectra in a convenient frequency region.

II. FUNDAMENTALS

The energy-level systems considered in this paper are shown in Fig. 1. In the degenerate case [Fig. 1(a)], where each level has a double parity, the double-photon transitions can occur between two levels whereas in the nondegenerate case [Fig. 1(b)], where each level has a single parity, a third level is needed.

The theoretical treatment of the double-photon transition given in the Appendix shows that we can use the Karplus-Schwinger formula for saturation[4] and Javan's formula for the double resonance[5] by replacing $\omega - \omega_0$ and $\langle a | \mu E | b\rangle/\hbar$ in their formula by $2\omega - \omega_0$ and 2γ, respectively, where for the degenerate case

$$\gamma = \langle a | \mu E | b\rangle [\langle b | \mu E | b\rangle - \langle a | \mu E | a\rangle]/4\hbar^2 \omega, \quad (1)$$

and for the nondegenerate case

$$\gamma = \langle c | \mu E | d\rangle \langle d | \mu E | e\rangle /4\hbar^2 \Delta\omega. \quad (2)$$

These dipole matrix elements can also be derived directly from the Göppert-Mayer[6] formula for two-photon processes.

Since $\hbar\omega$ or $\hbar\Delta\omega$ is much greater than μE for practical radiation densities in the microwave region, 2γ is much smaller than the normal dipole matrix element $\langle a | \mu E | b\rangle/\hbar$, and the double-photon transition is extremely weak. However the detection of the transition is possible using the technique of high-power microwave double resonance. We use intense microwave radiation to "pump" the double-photon transition and weak-signal radiation, which is resonant to another transition, to monitor the population change due to the pumping. The effectiveness of this method in observing extremely weak transitions has already been demonstrated on the molecule C_2H_5I, where very weak eq Q-induced $\Delta J = 3$ transitions have been ob-

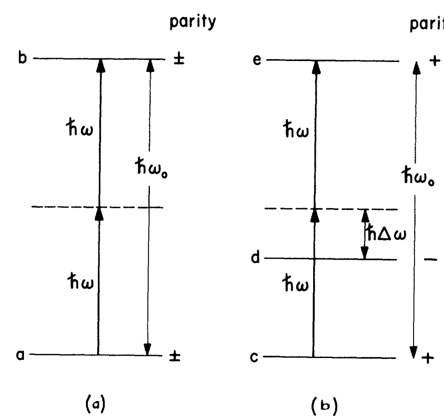

FIG. 1. Double-photon transitions discussed in this paper, (a) degenerate case, (b) nondegenerate case.

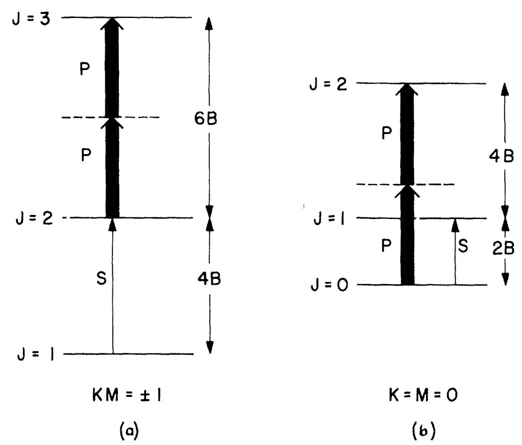

FIG. 2. Three level systems for CD_3CN and PF_3, (a) degenerate case, (b) nondegenerate case.

served.[7]

The energy levels used in the experiment are shown in Fig. 2. In the degenerate case [Fig. 2 (a)], the decrease of molecular population in the $J=2$ level due to the double-photon pumping $J=3 \twoheadleftarrow 2$ increases the absorption signal of the $J=2\leftarrow 1$ transition; in the nondegenerate case [Fig. 2(b)] the decrease of molecular population in the $J=0$ level decreases the absorption signal of the $J=1\leftarrow 0$ transition.

The efficiency of pumping ϕ is given by the Karplus-Schwinger formula as follows[4]:

$$\phi \equiv 1-\frac{n_{pl}-n_{pu}}{n^o_{pl}-n^o_{pu}} = \frac{(2\gamma)^2}{(2\omega-\omega_o)^2+(1/\tau)^2+(2\gamma)^2}, \qquad (3)$$

where n_{pl} and n_{pu} are molecular populations in the lower and the upper levels, respectively, of the double-photon pumped transition and the superscript o denotes values at the thermal equilibrium. The order of magnitude of the relaxation time of saturation τ can be estimated from the pressure-broadening parameter $\Delta\nu$. If the changes of populations in levels other than the pumped levels are neglected, the relative variation of the signal $\Delta I/I$, which is expressed in terms of the molecular populations of the signal levels n_{sl} and n_{su} as $\Delta I/I=(n_{sl}-n_{su})/(n^o_{sl}-n^o_{su})-1$, is given as follows:

Degenerate case [Fig. 2(a)]: $\Delta I/I=\frac{3}{4}\phi$, (4a)

Nondegenerate case [Fig. 2(b)]: $\Delta I/I=-\frac{3}{2}\phi$. (4b)

In the nondegenerate case [Fig. 2(b)], the magnitude of $\Delta I/I$ is larger than 1 if ϕ is more than $\frac{2}{3}$; in such a case a negative temperature is established between the $J=1$ and the $J=0$ levels and induced emission $J=1\rightarrow 0$ is observed.

The values of $2\gamma/2\pi$ are calculated by substituting numerical expressions for the direction cosine matrix element[8] as follows:

Degenerate case [Fig. 2(a)]:

$$\gamma/\pi=\mu^2E^2/27(35)^{1/2}h^2B,$$

Nondegenerate case [Fig. 2(b)]: (5)

$$\gamma/\pi=\mu^2E^2/16(5)^{1/2}h^2B.$$

For a microwave electric field of $E=200$ V/cm, a dipole moment of $\mu=3.92$ D,[8] and a rotational constant of $B=7857.93$ MHz,[8] γ/π is calculated to be 120 kHz for the degenerate case and 550 kHz for the nondegenerate case. Therefore, if we estimate the value of $1/2\pi\tau$ from the pressure broadening parameter of 100 MHz/Torr,[9] we see that a ϕ of 0.5 can be achieved at a pressure of 1.2 mTorr for the degenerate case and at 5.5 mTorr for the nondegenerate case.

III. OBSERVATIONS

A. Experimental

The apparatus used is similar to the one used for other high-power microwave double-resonance experiments.[7,10] The K-band microwave power of about 20 W generated by an Elliot-Litton 12 TFK2 klystron was used as the pumping radiation. This power gave an average microwave field of the order of 200 V/cm in the K-band Stark modulation cell. OKI 30 V 10 and 17 V 10 klystrons were used for signals and the signal was observed by a 125-KHz Stark modulation and phase-sensitive detection. The pressure of the gas was measured by a MKS Baratron pressure meter.

B. $J=3\twoheadleftarrow 2$ Double-Photon Transition in CD_3CN

The $J=3\twoheadleftarrow 2$ double-photon transition is observed as shown in Fig. 3. The observation was made by fixing the frequency of the signal radiation at the maximum of the absorption for the $J=2\leftarrow 1$ transition (at 31 431.50 MHz) and sweeping the frequency of the pumping klystron. The possibility that the second harmonics of the pumping microwave radiation might be pumping the transition was checked by inserting a low-pass filter at various points of the microwave circuit.[10] A low Stark-modulation field (of the order of 2–10 V/cm) was applied so that only those lines corresponding to KM = ± 1 were observed. An increase of the signal was observed when the frequency of the pumping power was 23 573.6 MHz which is exactly $\frac{1}{2}$ of the frequency of the $J=3\leftarrow 2$ transition. The double-photon transition was observable only at low pressure, i.e., a few mTorr. From the observed

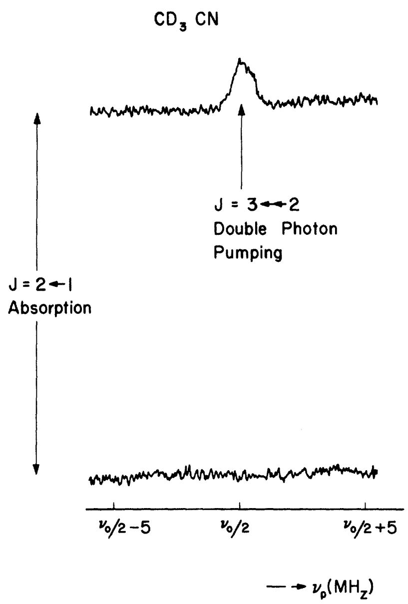

FIG. 3. Observed increase of the $J=2\leftarrow 1$ absorption (31 431.50 MHz) due to the $J=3\leftarrow\leftarrow 2$ double-photon pumping in CD_3CN. $\frac{1}{2}\nu_0=23\,573.6$ MHz. Pressure of the sample is 3 mTorr.

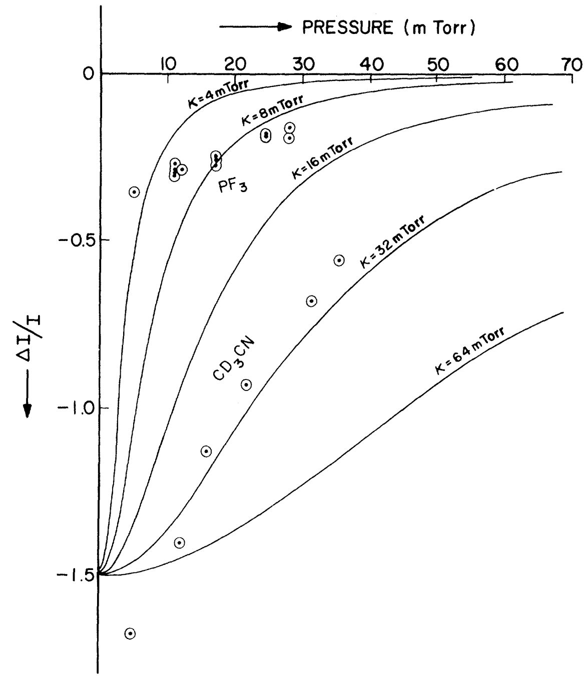

FIG. 5. $\Delta I/I$ versus pressure. Curves are drawn according to Eq. (6).

relative change of the signal $\Delta I/I=13.6\%$, Eqs. (3) and (4), and calculated values of γ/π, the relaxation time of the saturation, is determined to be $\tau\simeq 6\times 10^{-7}$ sec for a pressure of 3 mTorr which corresponds to the value of $1/2\pi\tau_0 \sim 85$ MHz/Torr. Since the pressure was so low, this value must also contain the effect of wall collisions.

C. $J=2\leftarrow\leftarrow 0$ Double-Photon Transition in CD_3CN

Since an efficient pumping can be achieved for the $J=2\leftarrow\leftarrow 0$ double-photon transition, this transition was easily observed on an oscilloscope for a sample at relatively high pressures. The observed changes of the signal corresponding to the $J=1\leftarrow 0$ transition (at 15 715.9 MHz) at various pressures are shown in Fig. 4. In each picture, the upper trace gives the normal absorption of the $J=1\leftarrow 0$ transition ($\Delta M=0$), while the lower trace shows the absorption under the double-photon pumping. In the lower-pressure region ($p<20$ mTorr) the pumping is so efficient that emission is observed. The expected splitting of about 500 kHz in the signal was not observed because of a large line width due to pressure broadening (0.94 MHz at 10 mTorr)[9] and to the inhomogeneity of the microwave electric field along the waveguide. The latter broadens the line through the inhomogeneous second-order Stark shift of the line.

The pressure dependence of the observed $\Delta I/I$ is plotted in Fig. 5, together with the calculated

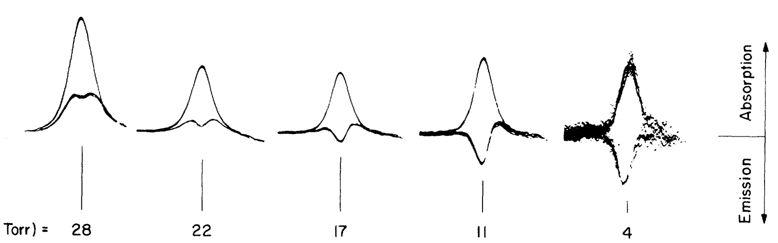

FIG. 4. Comparisons of the normal signal (upper trace) with double-photon pumped signals (lower trace) for various pressures of CD_3CN. $J=2\leftarrow\leftarrow 0$ $K=M=0$ transition was pumped while the $J=1\leftarrow 0$ $K=M=0$ transition is monitored. Note that emissions are observed for lower pressures of the sample.

values using Eqs. (3) and (4). Equation (4b) exact resonance $2\omega = \omega_0$ is written

$$\Delta I/I = -\tfrac{3}{2}\,\kappa^2/(p^2+\kappa^2). \qquad (6)$$

Here p is the pressure of sample and $\kappa = 2\gamma\,\tau_0$ (in Torr), where τ_0 is the relaxation time of saturation in sec Torr. It is seen that the observed values of $\Delta I/I$ agree with the calculated values when $\kappa \sim 30$ mTorr. If we use the value $\gamma/\pi = 550$ kHz, τ_0 is determined to be $\tau_0 \sim 8.8\times10^{-9}$ sec Torr or $1/2\pi\tau_0 \sim 18$ Mc/Torr. The disagreement between this value and the pressure-broadening parameter and between the observed and calculated values in the low-pressure region in Fig. 5 will be discussed in Sec. IV.

The double-photon transition $J=2 \twoheadleftarrow 0$ can also be monitored by the absorption of the $J = 2 \leftarrow 1$ transition. In this case by using a suitable Stark-modulation voltage we can choose any of the four different lines corresponding to (a) $(K=M=0)$, (b) $(K=0,\ M=\pm1)$, (c) $(K=\pm1,\ M=0)$, (d) $(K=M=\pm1)$, and (e) $(K=-\ M=\pm1)$ as the signals. The first line changes its intensity by about − 75% since this transition is directly connected to the pumped transition. The lines (c), (d), and (e) are not affected by the pumping since they are not connected to the double-photon pumping either directly or indirectly through collision-induced transitions.[11] However, the line (b) corresponding to $J=2\leftarrow1$ $K=0$, $M=\pm1$ decreased its intensity by about 4% when the double-photon pumping was made. This change is interpreted as partly due to the inhomogeneity of the Stark field in the waveguide which causes $\Delta M=\pm1$ pumping and partly due to the collision-induced effect. However, in view of results of other experiments on M selection rules in OCS and NH_3,[12] the former effect cannot be so large as to change the sign of the latter. Therefore, it is concluded that collision-induced transitions produce negative $\Delta I/I$. The implication of this result is discussed in Sec. IV.

D. $J=2\twoheadleftarrow0$ Double-Photon Transition in PF_3

Since the dipole moment of PF_3 (1.025 D[8]) is about $\frac{1}{4}$ of that of CD_3CN, the value of γ for PF_3 is about $\frac{1}{15}$ of that of CD_3CN. Therefore, the relative change of the signal is much smaller than in CD_3CN. An example of the observed signal is shown in Fig. 6. The pressure dependence of $\Delta I/I$ is plotted in Fig. 5. The value of κ was determined at the higher pressure region to be $\kappa \sim 10$ mTorr. The deviation of the observed values from the calculated at lower pressures must be due to the wall collision. If we use the value $\gamma/\pi = 120$ kHz, τ_0 is determined to be 1.3×10^{-8} sec Torr or $1/2\pi\tau_0 \sim 12$ MHz/Torr.

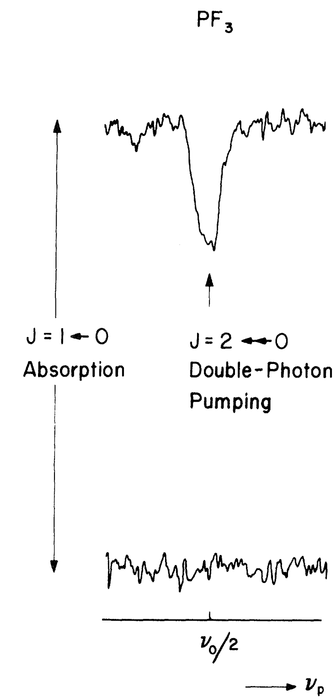

FIG. 6. Observed decrease of the $J=1\leftarrow0$ absorption (15 639.8 MHz) due to the $J=2\twoheadleftarrow0$ double-photon pumping in PF_3. $\nu_0/2 = 23\,459.7$ MHz. Pressure of the sample is 25 mTorr.

IV. DISCUSSIONS

The observed intensities of the double-photon transitions agree quantitatively with the theoretical values. Although only symmetric-top molecules have been studied in this paper, similar experiments can be performed with linear molecules or with asymmetric-top molecules. Also the two pumping photons do not need to have the same frequency. We can pump a transition by using two radiations of frequency ν_1 and ν_2 provided that they are sufficiently intense and that $\nu_1+\nu_2=\nu_0$.

An interesting use of the microwave double photon transitions for the study of collision-induced rotational transitions[11,13,14] is that we can establish by this method a non-Boltzmannian rotational distribution which cannot be established by the normal single-photon pumping, as for example the negative temperature between the $J=1$ and the $J=0$ levels. Among various results described in Sec. III, there are three results which provide interesting information on collision-induced transitions in CD_3CN; they are (a) the negative change of the $J=2\leftarrow1$, $M=1$ signal due to the $J=2\twoheadleftarrow0$, $M=0$ double photon pumping, (b) the fact that the value of $\Delta I/I$ is less than − 1.5 in the low-pressure region in

Fig. 5, and (c) the observed value of $\kappa(=2\gamma\tau_0)\sim 30$ mTorr which is much larger than the value expected from the pressure-broadening parameter.

The collision-induced transitions which contribute to the results (a) and (b) mentioned above are shown in Figs. 7(a) and 7(b), respectively. The transitions α_1 and α_2 are of dipole type (parity $+\leftrightarrow-$) while γ_1 and γ_2 are of quadrupole type (parity $+\leftrightarrow+$, $-\leftrightarrow-$). The fact that the signal decreases by the double-photon pumping [result (a)] indicates that

$$k_{\alpha_1}+k_{\gamma_2}>k_{\alpha_2}+k_{\gamma_1}\ , \tag{7}$$

where k's represent the rate constants of the collision-induced transitions. It is known that the rate constants for the dipole-type transitions are larger than those for the quadrupole-type transitions[12–14]; therefore, Eq. (7) indicates

$$k_{\alpha_1}>k_{\alpha_2}\ . \tag{8}$$

This can be explained from the fact that the dipole matrix element for the α_1 transition $\mu/\sqrt{6}$ is larger than that for the α_2 transition $\mu/(30)^{1/2}$. [8]

The fact that $\Delta I/I$ is less than -1.5 [result (b)] in the system described in Fig. 7 (b) indicates that not only the pumped levels $J=2$ and $J=0$ but also the level $J=1$ now has different molecular population from that in the equilibrium state. The three collision-induced transitions shown in Fig. 7(b) contribute directly in establishing the steady state under the strong double-photon pumping radiation. The transition α_2' makes the value of $\Delta I/I$ more negative whereas the transition α_1' makes the value of $\Delta I/I$ less negative. The observed result (b) suggests that

$$k_{\alpha_2'}>k_{\alpha_1'}\ . \tag{9}$$

Since the dipole matrix element for the transitions α_1' and α_2' are nearly equal [$\mu/\sqrt{3}$ and $2\mu/(15)^{1/2}$, respectively], a detailed analysis will be needed to explain Eq. (9).

The result (c) provides direct experimental evidence that the relaxation time of saturation is different from the relaxation time determined from the pressure broadening.[8, 15] As discussed in Sec. III C, the observed value of $\kappa=30$ mTorr when combined with the calculated value of γ gives a value of $1/2\pi\tau_0 = 18$ MHz/Torr, which is very much smaller than the pressure-broadening parameter $\Delta\nu = 94$ MHz/Torr [9] measured for the $J=1\leftarrow 0$ transition. The absolute value of $1/2\pi\tau_0$ determined may not be accurate because it depends on the estimation of the microwave electric field in the waveguide; however the agreement between the pressure-broadening parameter and the value of $1/2\pi\tau_0$ determined for the $J=3\leftarrow\leftarrow 2$ double-photon pumping (Sec. III B) convinces us that the relaxation time for saturation for the $J=2\leftarrow\leftarrow 0$ transition is appreciably smaller than that for the $3\leftarrow 2$ transition. Presumably, this is due to the fact that the two levels are connected directly by a dipole-type transition in the latter transition while they are not in the former transition. Pressure broadening would not differentiate between these two cases since it is the simple sum of uncertainties in the two levels and does not depend on whether the two levels are directly connected by a collision-induced transition or not.

The results of this paper suggest that if we can measure the microwave electric field accurately,

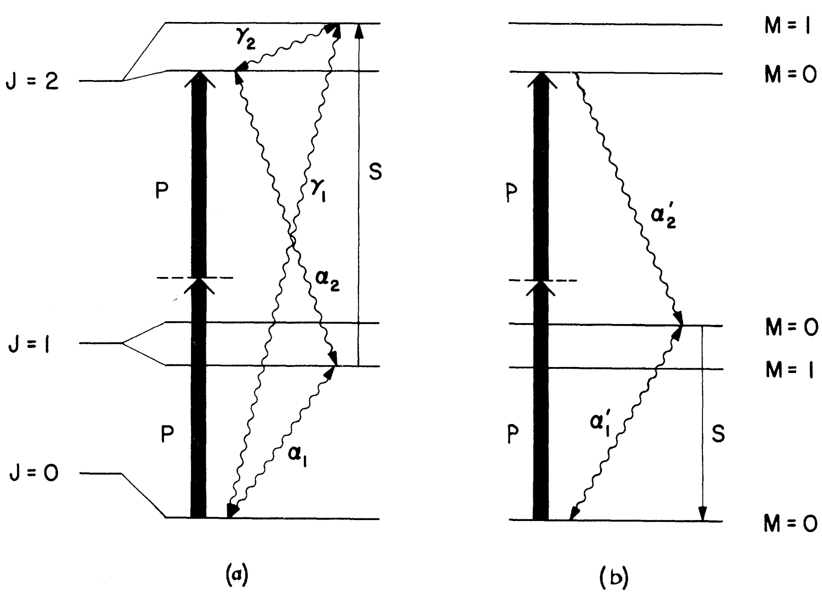

FIG. 7. Collision-induced transitions discussed in the text. Wavy arrows indicate collision-induced transitions. Energy levels are only schematic.

a saturation experiment such as those described provides useful quantitative information on collision-induced transitions which cannot be obtained otherwise.

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APPENDIX

We consider the time-dependent Schrödinger equation in a strong microwave field E,[5, 16]

$$i\hbar\frac{\partial\Psi}{\partial t} = (H_0 - \mu E\cos\omega t)\Psi\ , \tag{A1}$$

where $2\omega \sim \omega_0$.

A. Degenerate Case [Fig. 1(a)]

Under the influence of the pumping radiation, the wave function for the molecules in the pumped levels is expressed as a linear combination of the stationary wave functions of levels a and b:

$$\Psi = a(t)\Psi_a + b(t)\Psi_b. \tag{A2}$$

Substituting this expression into Eq. (A1), we obtain the following equations for $a(t)$ and $b(t)$:

$$\dot{a}(t) = i\ \cos\omega t[a(t)x_{aa} + b(t)x_{ab}\,e^{-i\omega_0 t}]\ , \tag{A3a}$$

$$\dot{b}(t) = i\ \cos\omega t[b(t)x_{bb} + a(t)x_{ba}e^{i\omega_0 t}]\ , \tag{A3b}$$

where

$$x_{ij} = \langle i\,|\,\mu E|\,j\rangle/\hbar.$$

Contrary to the single-photon case where $\omega \sim \omega_0$, we have $2\omega \sim \omega_0$ and therefore the right-hand sides of Eqs. (A3) do not have any explicit low-frequency term. The low-frequency terms are supplied by high-frequency parts of $a(t)$ and $b(t)$. We shall divide $a(t)$ and $b(t)$ into the sum of the low-frequency part $a_l(t)$ and $b_l(t)$ and the high-frequency part $a_h(t)$ and $b_h(t)$:

$$a(t) = a_l(t) + a_h(t)\ , \tag{A4a}$$

$$b(t) = b_l(t) + b_h(t)\ . \tag{A4b}$$

The magnitudes of $a_h(t)$ and $b_h(t)$ are much smaller than those of $a_l(t)$ and $b_l(t)$, but the magnitude of $\dot{a}_h(t)$ and $\dot{b}_h(t)$ are of the same order as those of $\dot{a}_l(t)$ and $\dot{b}_l(t)$.

We can derive the high-frequency parts of $a(t)$ and $b(t)$ by integration of Eqs. (A3) to be as follows:

$$a_h(t) = \tfrac{1}{2}\left[2ia_l(t)x_{aa}\ \sin\omega t/\omega + b_l(t)\left(\frac{e^{i(\omega-\omega_0)t}}{\omega-\omega_0} - \frac{e^{-i(\omega+\omega_0)t}}{\omega+\omega_0}\right)x_{ab}\right]\ , \tag{A5a}$$

$$b_h(t) = \tfrac{1}{2}\left[2ib_l(t)x_{bb}\ \sin\omega t/\omega + a_l(t)\left(\frac{e^{i(\omega+\omega_0)t}}{\omega-\omega_0} + \frac{e^{i(\omega_0-\omega)t}}{\omega_0-\omega}\right)x_{ba}\right]\ . \tag{A5b}$$

Substituting these equations into Eqs. (A3) and retaining only low-frequency terms we obtain the following equations:

$$\dot{a}(t) = i\ [a(t)\delta + b(t)\gamma e^{i(2\omega-\omega_0)t}]\ , \tag{A6a}$$

$$\dot{b}(t) = i[-bt)\delta + a(t)\gamma^* e^{-i(2\omega-\omega_0)t}]\ , \tag{A6b}$$

where we have

$$\delta = 2|x_{ab}|^2/3\omega_0\ ,\quad \gamma = x_{ab}(x_{bb}-x_{aa})/2\omega_0, \tag{A7}$$

when ω is approximated by $1/2\omega_0$. The subscript l is omitted in Eqs. (A6).

Proceeding as in Ref. 16 and imposing the initial condition that $a(0) = 1$ and $b(0) = 0$, we obtain the following solutions:

$$a(t) = e^{i(\epsilon+\delta)t}[\cos\Omega t - i\epsilon/\Omega\ \sin\Omega t], \tag{A8a}$$

$$b(t) = i\gamma^*/\Omega e^{-i(\epsilon+\delta)t}\ \sin\Omega t, \tag{A8b}$$

where we have

$$\epsilon = \tfrac{1}{2}(2\omega-\omega_0-2\delta)\ ,\quad \Omega = [\epsilon^2 + |\gamma|^2]^{1/2}.$$

If we place the second-order Stark shift $\delta\hbar$ into the energy term in the stationary-state wave functions, we see that the solutions above are exactly analogous to the case of the single-photon transition if $\omega-\omega_0$ and $\langle a|\mu E|b\rangle/\hbar$ in the latter are replaced by $2\omega-\omega_0-2\delta$ and 2γ, respectively.

B. Nondegenerate Case [Fig. 1(b)]

The wave function is expressed as a linear combination of the stationary wave functions of levels c, d, and e:

$$\Psi = c(t)\Psi_c + d(t)\Psi_d + e(t)\Psi_e. \tag{A9}$$

Proceeding as in Sec. A of the Appendix, we obtain the following equations for the time-dependent coefficients:

$$\begin{aligned}\dot{c}(t) &= -i[c(t)\delta_c + e(t)\gamma e^{i(2\omega-\omega_0)t}],\\ \dot{d}(t) &= i(\delta_c+\delta_d)d(t),\\ \dot{e}(t) &= -i[e(t)\delta_e + c(t)\gamma^* e^{-i(2\omega-\omega_0)t}],\end{aligned} \tag{A10}$$

where

$$\begin{aligned}\delta_c &= |x_{cd}|^2(\omega-\Delta\omega)/2\Delta\omega(\omega_0-\Delta\omega),\\ \delta_e &= |x_{de}|^2(\omega+\Delta\omega)/2\Delta\omega(\omega_0+\Delta\omega),\\ \gamma &= x_{cd}x_{de}/4\Delta\omega.\end{aligned} \tag{A11}$$

It is seen that the level d is merely shifted by the second-order Stark effect but no time modulation is introduced. The similarity of the equations of $c(t)$ and $e(t)$ in Eq. (A9) with those of $a(t)$ and $b(t)$ in Eqs. (A6) shows that we have similar results as Eqs. (A7) except that the expression of γ is different as shown above and

$$\epsilon = \tfrac{1}{2}(2\omega - \omega_0 - \delta_c + \delta_e).$$

The expressions of γ in Eqs. (A7) and (A11) are used in the text.

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Correlation Effects on Hyperfine-Structure Expectation Values for the Boron ^2P Ground State*

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Pure correlation effects on the hyperfine structure of atomic boron were investigated and found to be important. A natural spin-orbital expansion of the well-correlated 187-term wave function of Schaefer and Harris was used. Pure correlation effects are those contributions to an expectation value obtained when the wave function is improved beyond the best possible Slater determinant (the best overlap determinant). Our results indicate that the unrestricted Hartree-Fock method yields valuable information about the orbital and spin magnetic dipolar and electric quadrupolar terms, but gives unreliable results for the Fermi contact term. Utilizing both experimental and theoretical results, the Fermi contact term f was estimated as $0.096a_0^{-3}$, and the quadrupolar nuclear-shielding factor γ as 0.093.

INTRODUCTION

Correlation effects have proven to be important in some cases for the explanation of experimental atomic hyperfine-structure parameters. Calculations of hyperfine structure for the boron atom have been made by Schaefer, Klemm, and Harris. Their two wave functions, the polarization wave