

Bloch-Siegert shift in giant-dipole molecules

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The resonance-frequency shift and the energy of molecules with a large change in the permanent dipole moments between the ground and the excited levels under an intense oscillating field are investigated. It is found that the higher-order terms with respect to the Rabi frequency of the Bloch-Siegert shift cannot be neglected for molecules with a large permanent-dipole difference. Some perturbational expressions are derived, and numerical calculations are performed for various sets of parameters.

The interaction between molecules (including atoms or ions) and the radiation field is very well represented in terms of electric-dipole transitions. In the theoretical consideration of the interaction, the electric dipole moment of two-level or multilevel molecules is almost always assumed to have no diagonal elements, or in other words, the molecules are assumed to have no permanent dipole moments.¹ However, this assumption is not appropriate to some molecules such as intramolecular weak charge-transfer complexes, which have a large permanent dipole moment in the lowest excited state.²

In the present study the authors will describe the shift of the resonance frequency (Bloch-Siegert shift) and the "dressed-atom" energy of polar molecules interacting with a very intense radiation field with perturbational methods and numerical calculations.

Since the Bloch-Siegert shift³ is an effect which takes place via a counter-rotating wave, permanent dipoles are expected to affect the magnitude of the shift. There are some studies^{4,5} of a system with permanent dipoles in an intense radiation field, or more generally a system where the Hamiltonian has diagonal and off-diagonal oscillating elements, both of which are proportional to the external field amplitude. However, these studies are concerned not with the position of the resonances but only with the transition intensity.

We consider a system which consists of a two-level molecule with large electric dipole moments interacting with a monochromatic radiation field $E(t) = E_0 \cos(\omega t)$. The molecule has two levels $|a\rangle$ (lower level with energy E_a —for example, a level in the electronic ground state) and $|b\rangle$ (upper level with energy E_b —for example, a level in the electronically excited state) which are connected with each other by an electric dipolar interaction $-\mu_{ba}E(t)$.

The levels $|a\rangle$ and $|b\rangle$ have permanent dipole moments μ_{aa} and μ_{bb} , respectively. The elements of the semiclassical Hamiltonian \underline{H}_c are given as follows:

$$\begin{aligned} \underline{H}_{ba} &= -\mu_{ba}E_0 \cos(\omega t) = \underline{H}_{ab}, \\ \underline{H}_{bb} &= E_b - \mu_{bb}E_0 \cos(\omega t), \\ \underline{H}_{aa} &= E_a - \mu_{aa}E_0 \cos(\omega t). \end{aligned} \quad (1)$$

In this study, the transition dipoles and permanent di-

poles of all molecules are assumed to be parallel to the optical field. In the case of freely rotating molecules the effect of reduced transition and permanent dipole moments should be taken into account, and averaged physical quantities will be also reduced to some extent. Even in that case, however, the effect of nonzero permanent dipoles does not vanish, since all the effects treated in this paper are static ones, and, therefore, even functions of dipole moments. The problem of the freely rotating molecules is so complicated to be treated generally that we limited the discussion in the present paper to the case of rigid molecular system with parallel μ_{aa} , μ_{bb} , and μ_{ab} to the incident field.

After a simple unitary transformation, the Hamiltonian can be written in one equation as follows, with $\hbar = 1$,

$$\underline{H}_c = \frac{\omega_0}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - 2b \cos(\omega t) \begin{pmatrix} \alpha & 1 \\ 1 & -\alpha \end{pmatrix}, \quad (2)$$

where $2b = \mu_{ba}E_0$ is the Rabi frequency, $\omega_0 = E_b - E_a$, and $2\alpha = (\mu_{bb} - \mu_{aa})/\mu_{ba}$ is the normalized permanent dipole difference.

We can quantize the field and include the field Hamiltonian in the total system as follows:

$$\underline{H}_q = \omega_0 \hat{J}_z + \omega a^\dagger a - \lambda (\alpha \hat{J}_z + \hat{J}_x) (a^\dagger + a), \quad (3)$$

where a^\dagger and a are the creation and annihilation operators of a photon with frequency ω , \hat{J}_x and \hat{J}_z are the spin operators, and $\lambda = 2b/\sqrt{n}$ is the coupling constant with n being the mean number of photons. For very large n as assumed in the present study, there is no discrepancy between a semiclassical and a wholly quantum treatment of the system.

Note that this system is equivalent to a spin- $\frac{1}{2}$ system under static magnetic field $-\omega_0/\gamma$ and oscillating magnetic field which has a component perpendicular to the static field $(-2b/\gamma)\cos(\omega t)$, and a parallel component $(-2\alpha b/\gamma)\cos(\omega t)$, where γ is the gyromagnetic ratio.

For weak radiation field, i.e., $b, \alpha b \ll \omega, \omega_0$, the energy of the system can be obtained using a perturbational method similar to the one described by Cohen-Tannoudji *et al.*⁶ Regarding the last term of \underline{H}_q in Eq. (3) as perturbation, the resonance condition was obtained to the fourth order of b/ω for the case of $\omega_0 \simeq \omega$:

$$\omega_0 = \omega - b^2/\omega + \left(-\frac{5}{4} + \frac{28}{3}\alpha^2\right)b^4/\omega^3. \quad (4)$$

The last term of the right-hand side of Eq. (4) becomes comparable to the second term when $b/\omega \simeq 0.3/\alpha$ is satisfied. Therefore, when considering the Bloch-Siegert shift of molecules with large permanent dipole moments, terms higher than second order cannot be neglected even for rather small Rabi frequency.

We can also easily obtain the expressions for the positions and the widths of the multiple quantum resonances to the lowest order of b/ω . Resonances occur when the following relation is satisfied:

$$\omega_0 = p\omega - \frac{4p}{p^2-1} \frac{b^2}{\omega}, \quad (5)$$

with p being an integer greater than unity. Note here that multiple photon resonances of both odd and even quantum numbers occur when $\alpha \neq 0$. In the case of $\alpha = 0$, multiple photon resonances take place only when p is odd. The above result is in agreement with the result of other works with $\alpha = 0$ when p is odd.⁷

The widths of two-, three-, and four-photon resonance transitions are also obtained as follows:

$$4\alpha b^2/\omega \quad \text{for } p=2, \quad (6a)$$

$$\left(\frac{1}{2} - 4\alpha^2\right)b^3/\omega^2 \quad \text{for } p=3, \quad (6b)$$

$$\frac{8}{9}\alpha(1-3\alpha^2)b^4/\omega^3 \quad \text{for } p=4. \quad (6c)$$

When ω_0 is much smaller than ω , then the Hamiltonian is transformed by the following unitary operator:

$$S_2 = \left[\frac{[\alpha + (\alpha^2 + 1)^{1/2}]}{2(\alpha^2 + 1)^{1/2}} \right]^{1/2} \\ \times \exp[-(\lambda/\omega)(\alpha^2 + 1)^{1/2} \hat{J}_z (a^\dagger - a)] \\ \times \{1 + 2i[(\alpha^2 + 1)^{1/2} - \alpha] \hat{J}_y\} \quad (7)$$

and we obtain the following equation for $n \gg 1$:

$$S_2 \underline{H}_q S_2^{-1} \\ = \omega a^\dagger a + \omega_0 (\alpha^2 + 1)^{1/2} \\ \times \{ \alpha \hat{J}_z - \hat{J}_x \exp[(2\lambda/\omega)(\alpha^2 + 1)^{1/2}] \\ \times \hat{J}_z (a^\dagger - a) \}. \quad (8)$$

With this transformed Hamiltonian, the eigenvalues q 's to the third order of ω_0/ω are obtained as follows, by regarding the last term in Eq. (8) as a perturbation:

$$q = \pm \frac{\omega_0}{2} (\alpha^2 + 1)^{-1/2} (\alpha^2 + J_0^2)^{1/2} \\ \mp \frac{\omega_0^3}{2\omega^2} (\alpha^2 + 1)^{-3/2} S, \quad (9)$$

with

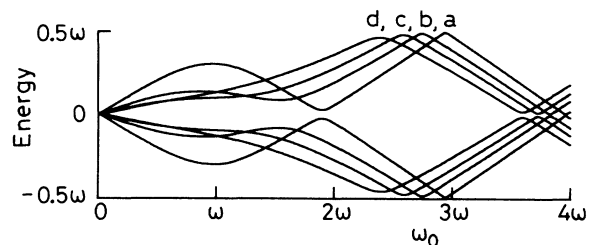


FIG. 1. Energies of the system consisting of the radiation field and a two-level molecule with permanent dipole moments as a function of ω_0 , plotted for $\alpha=0.3$, and b/ω is equal to (a) 0.2, (b) 0.4, (c) 0.5, and (d) 0.6.

$$S = \frac{1}{4} \left[-J_0(\alpha^2 + J_0^2)^{-1/2} \sum_{r,s \neq 0} \frac{J_r J_{-s} J_{r-s}}{rs} \right. \\ \left. + (\alpha^2 + J_0^2)^{1/2} \sum_{r \neq 0} \frac{J_r^2}{r^2} \right]. \quad (10)$$

Here the arguments of all Bessel functions are $4b(\alpha^2 + 1)^{1/2}/\omega$. The g factor of this system is proportional to the slope of the right-hand side of Eq. (9) at $\omega_0=0$, which is a function of the field amplitude. When $\alpha=0$, the g factor is $g_0 J_0(4b/\omega)$ which oscillates between positive and negative values as the field amplitude grows

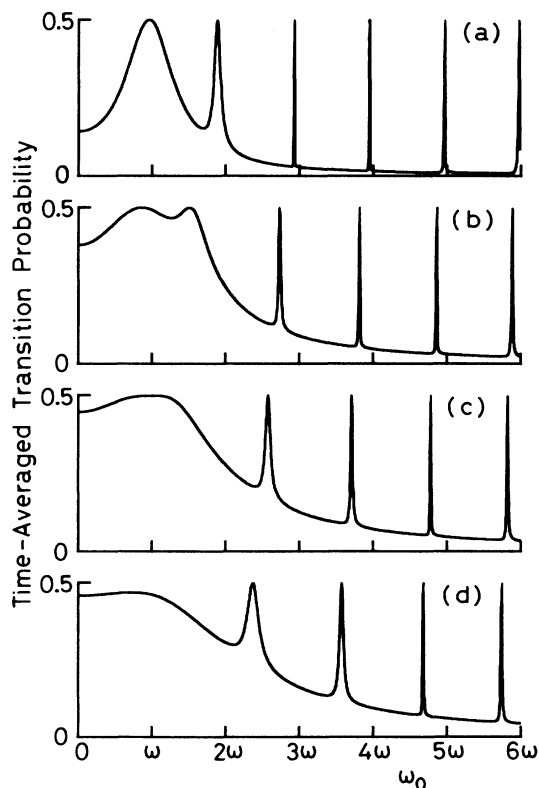


FIG. 2. Time-averaged transition probabilities for the same value of α as Fig. 1. The values of b/ω are (a) 0.2, (b) 0.4, (c) 0.5, and (d) 0.6.

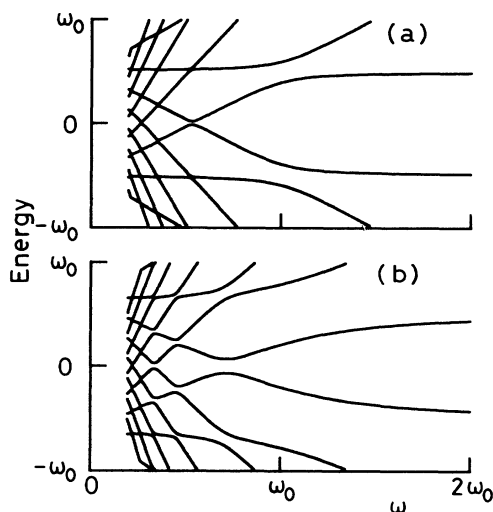


FIG. 3. Energy of the system as a function of ω , plotted for $\alpha=0.3$, and b/ω_0 is equal to (a) 0.1 and (b) 0.3.

strong, whereas when $\alpha \neq 0$, the g factor also oscillates but is always positive (or negative).

When $\alpha=0$, Eq. (9) is also used to obtain the resonance frequency near $\omega_0=0$. It takes place when $4b/\omega \simeq j_{0,1}$, where $j_{0,1}=2.405$ is the first zero of J_0 . However, Eq. (9) cannot be used to obtain the resonance condition when $\alpha \neq 0$, as is explained below. The following condition for resonance is obtained by equating $\partial q/\partial \omega_0=0$:

$$\omega_0 = \omega \left[\frac{\alpha^2 + 1}{3} \right]^{1/2} \frac{(\alpha^2 + J_0^2)^{1/4}}{\sqrt{S}}. \quad (11)$$

The right-hand side of Eq. (11) becomes smallest when $J_0=0$ or $4b(\alpha^2+1)^{1/2}/\omega=2.40483$, and the minimum value of ω_0 is 0.83ω . This is of the same order as ω , so the approximation made for the case $\omega_0 \ll \omega$ cannot be applied to the calculation of the resonance frequency. The situation will be explained in the following.

In the preceding part, we have described two extreme cases where one parameter is small and the expressions for the resonance frequency and the energy can be obtained using perturbation theory. However, the perturbation method cannot be used for systems with parameters having general values. In this case we can calculate the eigenvalues of the system by integrating the Schrödinger equation numerically.⁸

Time-averaged transition probability P_{av} is also calculated using Shirley's formula:⁷

$$P_{av} = \frac{1}{2} [1 - 4(dq/d\omega_0)^2]. \quad (12)$$

This offers a measure of the degree of resonance, and takes the maximum value of $\frac{1}{2}$ when the external field frequency is in exact resonance with the molecular system.

In Figs. 1 and 2 the energy of the system and the time-

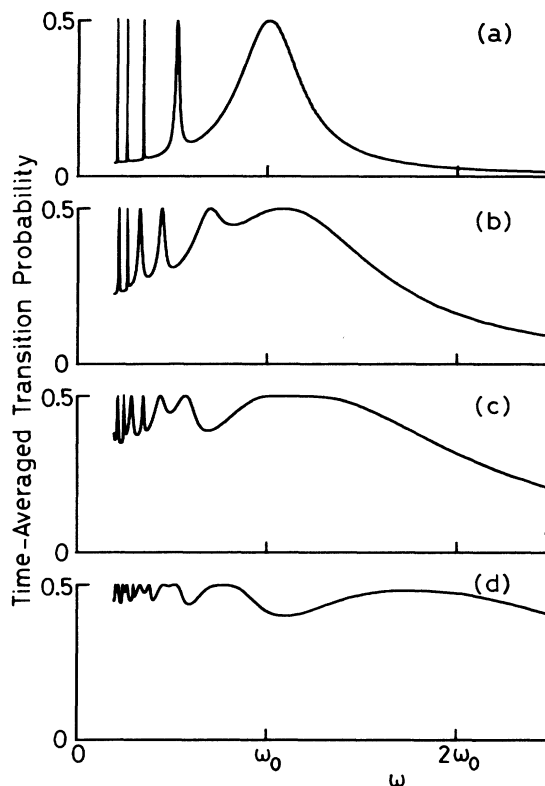


FIG. 4. Time-averaged transition probabilities as a function of ω , plotted for $\alpha=0.3$, and b/ω_0 is equal to (a) 0.1, (b) 0.3, (c) 0.5, and (d) 0.9.

averaged transition probability are plotted for $\alpha=0.3$ as a function of ω_0 for several values of b/ω . When the field becomes more intense and increases up to about 0.5, the first and the second peaks, which correspond to one-photon and two-photon resonances, respectively, become broader and shift towards smaller values, and at the same time get closer to each other. The two peaks are originally located at ω and 2ω for smaller values of b/ω . When $b \simeq 0.5$ they combine to form a broad peak, of which intensity decreases with increase in b . The first peak near ω does not shift appreciably, and it disappears at a point near $\omega_0=\omega$, whereas when $\alpha=0$, all peaks shift to smaller values and then vanish at the point $\omega_0=0$.^{7,9} This corresponds to the fact that the perturbation method cannot be applied to calculate the resonance frequency for the small ω_0 for $\alpha \neq 0$ systems as mentioned above.

The energy is also plotted in Fig. 3 as a function of ω with fixed values of α and b/ω_0 . By applying weak probe light to the system, the energy of the system can be experimentally determined. Figure 4 shows the plots of the time-averaged transition probability as a function of ω . Distances between all two neighboring peaks decrease with increase in b/ω_0 . The neighboring peaks are then combined to form one peak and then the intensity is decreased, while, when $\alpha=0$, all peaks move to greater values of ω infinitely.⁹

Finally the authors estimate the experimental condition for the effect of permanent dipole moments on the Bloch-Siegert shift to be observed. Parameters are chosen as: $\mu_{ba} = 10$ D, $\mu_{bb} - \mu_{aa} = 30$ D, and the central wave-

length is $1 \mu\text{m}$. Then the fourth-order term in Eq. (4) becomes comparable to the second-order term if the power density is $1 \text{ TW}/\text{cm}^2$, which is available with the use of conventional pulsed lasers.

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