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Effects of permanent dipole moments on the collision-free interaction of a two-level system with a laser and a static electric field

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The consequences of having state-specific diagonal transition matrix elements on the interaction of a two-level system with a laser field and a static electric field are examined within the dipole and rotating-wave approximations. A finite difference between the permanent dipole moments can result in the appearance of subsaturating ancilliary fringes flanking the usual Lorentzian transition resonance. The requisite conditions for a two-level system to exhibit an oscillatory line shape are discussed. These fringes arise from the essential transparency of the system to the field at prescribed intensity-dependent frequencies.

I. INTRODUCTION

The existence of permanent and induced electric dipoles[1] in molecules was first postulated by Debye and the concept is widely used in current theories of dielectrics and molecular structure. For a molecular system consisting of $k=1,2,\ldots,N_n$ nuclei of charges $Z_k e$ at $\mathbf{R}_k$ and $k=1,2,\ldots,N_e$ electrons at $\mathbf{r}_k$, the total electric dipole operator is

$$\boldsymbol{\mu}_m = e\left[\sum_{k=1}^{N_n} Z_k \mathbf{R}_k - \sum_{k=1}^{N_e} \mathbf{r}_k\right],$$

where the R's and r's are referred to a molecule-fixed orthogonal curvilinear coordinate system $\{\hat{\mathbf{e}}_{\alpha,m}\}$, $\alpha=1,2,3$, located at the center of mass of the system. The unit vectors $\hat{\mathbf{e}}_{\alpha,m}$ are parallel to the principal axes of inertia and $\boldsymbol{\mu}_m=\sum_{\alpha=1}^{3}\mu_{\alpha,m}\hat{\mathbf{e}}_{\alpha,m}$, where the $\mu_{\alpha,m}$'s are the components of $\boldsymbol{\mu}_m$ in the molecule-fixed coordinate system. Within the dipole approximation,[2] the interaction potential of the system with a classical field is $-\boldsymbol{\mu}_s\cdot\mathbf{E}(\mathbf{R},t)$, where $\mathbf{E}$ is the electric field vector at the center of mass $\mathbf{R}$ with respect to a laboratory coordinate system and $\boldsymbol{\mu}_s$ is the electric dipole moment operator in a space-fixed orthogonal curvilinear coordinate system $\{\hat{\mathbf{e}}_{\alpha,s}\}$, $\alpha=1,2,3$, located at $\mathbf{R}$. In terms of its components $\mu_{\alpha,s}$ in the space-fixed coordinate system, $\boldsymbol{\mu}_s=\sum_{\alpha=1}^{3}\mu_{\alpha,s}\hat{\mathbf{e}}_{\alpha,s}$. The orthogonal transformation matrix $\mathbf{A}$, whose components are the direction cosines between $\hat{\mathbf{e}}_{\alpha,s}$ and $\hat{\mathbf{e}}_{\alpha,m}$ in terms of the Eulerian angles of orientation, serves to relate the space- and body-fixed dipole moments through $\boldsymbol{\mu}_s=\mathbf{A}\boldsymbol{\mu}_m$. In the stationary state eigenenergy basis, the interaction potential has the general matrix element $\langle i\,|\,\boldsymbol{\mu}_s\cdot\mathbf{E}(\mathbf{R},t)\,|\,j\rangle$ so that $\mathbf{E}$ may couple the nonvanishing permanent electric dipole moment, which is proportional to the diagonal matrix elements $\langle i\,|\,\boldsymbol{\mu}_s\cdot\mathbf{E}\,|\,i\rangle$ when the system is in the state $|\,i\rangle$, in addition to the induced electric dipole moment, which is proportional to the off-diagonal transition matrix elements $\langle i\,|\,\boldsymbol{\mu}_s\cdot\mathbf{E}\,|\,j\rangle$ connecting the states $|\,i\rangle$ and $|\,j\rangle$.

In nearly all considerations[3] of the dipole interaction of a quantized system with an electromagnetic field it is usually assumed that the diagonal dipole matrix elements are zero since ordinarily atoms, the most common systems of attention, have no permanent dipole moments. Pantell and Puthoff[4] have emphasized how Laporte's rule renders the appearance of only those resonances corresponding to the absorption of an odd number of photons in a two-level system whose states are of definite parity. In contrast, Oka and Shimizu[5] have treated two-photon saturation in a two-level system whose states are of mixed parity. Zon and co-workers[6(a),6(b)] have used second-order perturbation theory to calculate the quasienergy spectra of a dipolar molecule and of an excited-state hydrogen atom, systems with both permanent and induced dipole moments. More recently, Meath and Power[6(c)] investigated the effects of diagonal matrix elements on the multiphoton resonances resulting from the interaction of a two-level system with a static and an oscillating field. Without invoking the rotating-wave approximation (RWA), exact relations were obtained subject to limiting conditions involving the orientations and strengths of the applied fields. Meath and Power[6(d)] have also calculated the rates for multiphoton absorption of plane- and circularly-polarized light by molecules, both rigidly fixed and randomly oriented with respect to the source, and include the contributions from permanent moments. Their analysis involves use of low-order perturbation theory and consequently the results, although applicable to multilevel systems, are limited to relatively short presaturation times where Fermi's golden rule is applicable.

Herein the dipole interaction of a two-level system[7] with a near-resonant applied electromagnetic field is investigated. The system's two states $|\,i\rangle$ and $|\,f\rangle$ are assumed to possess permanent dipole moments. If the field $\mathbf{E}$ has a static component $\mathbf{E}^s$ and an oscillating component $\mathbf{E}^0$ of circular frequency ω each polarized in the direction $\hat{\mathbf{e}}$, i.e., $\mathbf{E}=E\hat{\mathbf{e}}=(E^s+E^0\cos\omega t)\hat{\mathbf{e}}$, we denote the diagonal dipole matrix elements $\langle i\,|\,\boldsymbol{\mu}_s\cdot\hat{\mathbf{e}}\,|\,i\rangle$ and $\langle f\,|\,\boldsymbol{\mu}_s\cdot\hat{\mathbf{e}}\,|\,f\rangle$ by μ_{ii} and μ_{ff}, respectively, while the off-diagonal dipole transition matrix elements $\langle i\,|\,\boldsymbol{\mu}_s\cdot\hat{\mathbf{e}}\,|\,f\rangle$ and $\langle f\,|\,\boldsymbol{\mu}_s\cdot\hat{\mathbf{e}}\,|\,i\rangle$ are denoted by μ_{if} and μ_{fi}, respectively. In Sec. II, the induced transition probability for photoabsorption by a two-level system from an initial state $|\,i\rangle$

with energy ω_i to a final state $|f\rangle$ with energy ω_f in a field $\mathbf{E}$ is calculated, with inclusion of the effects of permanent dipole moments on the line shape. The paper closes in Sec. III with a concluding summary.

Atomic units are used throughout this paper unless otherwise indicated.

II. FORMAL ANALYSIS

Since the analysis in this section is predicted on the diagonal dipole matrix elements $\mu_{ii}=\langle i|\boldsymbol{\mu}_s\cdot\hat{\mathbf{e}}|i\rangle$ and $\mu_{ff}=\langle f|\boldsymbol{\mu}_s\cdot\hat{\mathbf{e}}|f\rangle$ having unique finite values, one must endow the states $|i\rangle$ and $|f\rangle$ with their full complement of quantum numbers and attendant motions in order to establish the condition(s) for the validity of this assumption. For simplicity, take $|i\rangle$ and $|f\rangle$ to be rovibronic states of a polar molecule in a totally symmetrical electronic state. If the polarization axis $\hat{\mathbf{e}}$ is chosen to coincide with the space-fixed axis $\hat{\mathbf{e}}_{3,s}$ and the permanent dipole moment is inclined at an angle θ to $\hat{\mathbf{e}}_{3,s}$ then $\boldsymbol{\mu}_s\cdot\hat{\mathbf{e}}=\mu_{3,m}\cos\theta$ is the projection of the dipole moment operator on $\hat{\mathbf{e}}$. An isolated molecule in a nondegenerate state $|k\rangle$ and free to orientate itself in all directions has a vanishing expectation value $\langle k|\boldsymbol{\mu}_s|k\rangle$ since $|k\rangle$ is of fixed parity and $\boldsymbol{\mu}_s$ is a vector operator. However, in the presence of a static field $\mathbf{E}^s=\hat{\mathbf{e}}E^s$, the projection of the total dipole moment (permanent and induced) operator on $\hat{\mathbf{e}}$ is

$$\mu_{3,m}\cos\theta+(\alpha_{33,m}-\alpha_{11,m})E^s\cos^2\theta+\alpha_{11,m}E^s\ ,$$

where the α's are components of the polarizability in the molecule-fixed coordinate system. It is well known[1] that for sufficiently large E^s the orientation-averaged dipole-moment operator is $\mu_{3,m}+\bar{\alpha}_mE^s$, where $\bar{\alpha}_m=\alpha_{33,m}$ is the field-directed polarizability. Thus, the static field aligns the permanent dipole moment along its polarization direction and consequently inhibits the free rotation of the molecule. Under these circumstances one can readily show that the initial state amplitudes $a_i(0)$ and $a_f(0)$ of $|i\rangle$ and $|f\rangle$ evolve under the influence of the static electric field as

$$\begin{bmatrix} a_i(t) \\ a_f(t) \end{bmatrix}=\gamma^{-1}\begin{bmatrix} \exp(-\frac{1}{2}i\bar{\omega}_{fi}t) & 0 \\ 0 & \exp(\frac{1}{2}i\bar{\omega}_{fi}t) \end{bmatrix}\begin{bmatrix} \gamma\cos(\frac{1}{2}\gamma t)+i\bar{\omega}_{fi}\sin(\frac{1}{2}\gamma t) & 2i\mu_{if}E^s\sin(\frac{1}{2}\gamma t) \\ 2i\mu_{fi}E^s\sin(\frac{1}{2}\gamma t) & \gamma\cos(\frac{1}{2}\gamma t)-i\bar{\omega}_{fi}\sin(\frac{1}{2}\gamma t) \end{bmatrix}\begin{bmatrix} a_i(0) \\ a_f(0) \end{bmatrix}\ , \tag{1}$$

where $\bar{\omega}_{fi}=\omega_{fi}-(\mu_{ff}-\mu_{ii})E^s$ is an effective level separation, $\omega_{fi}=\omega_f-\omega_i$ is the isolated system's level separation, $\gamma^2=\bar{\omega}_{fi}^2+4(\mu_{if}E^s)^2$, $\mu_{ii}=\langle i|\mu_{3,m}|i\rangle+\bar{\alpha}_mE^s$, $\mu_{ff}=\langle f|\mu_{3,m}|f\rangle+\bar{\alpha}_mE^s$, $\mu_{if}=\mu_{fi}=\langle i|\mu_{3,m}|f\rangle$, and for simplicity we have taken $\bar{\alpha}_m$ to be independent of the rovibronic state of the system. From Eq. (1) it follows that for $a_i(0)=1$, the field-induced time-resolved transition probability is

$$P_1(0,t)=\frac{4(\mu_{if}E^s)^2}{\gamma^2}\sin^2(\gamma t/2)\ , \tag{2a}$$

which has the steady-state value

$$P_1^\infty(0)=\frac{1}{2}\frac{4(\mu_{if}E^s)^2}{\gamma^2}\ , \tag{2b}$$

where the power-broadening saturation parameter is $2\mu_{if}E^s$. Thus, if $\mu_{ff}>\mu_{ii}$, then E^s effectively decreases the level separation (i.e., $\bar{\omega}_{fi}<\omega_{fi}$), and the nutation period of $P_1(0,t)$ increases, and conversely.

Equation (1) suggests[8] that the static field-oriented two-level system with the Hamiltonian operator

$$H=H_0-(\mu_{3,m}+\bar{\alpha}_mE^s)E^s\ , \tag{3a}$$

where $H_0=\omega_i|i\rangle\langle i|+\omega_f|f\rangle\langle f|$ is the Hamiltonian operator for the *isolated* two-level system, has the nondegenerate stationary states

$$|0\rangle=a|i\rangle+b|f\rangle \tag{3b}$$

and

$$|1\rangle=a'|i\rangle+b'|f\rangle\ , \tag{3c}$$

where the expansion coefficients are given by

$$\begin{aligned} 2a\gamma&=(\gamma+\bar{\omega}_{fi})a_i(0)-2\mu_{if}E^sa_f(0)\ ,\\ 2b\gamma&=(\gamma-\bar{\omega}_{fi})a_f(0)-2\mu_{if}E^sa_i(0)\ ,\\ 2a'\gamma&=(\gamma-\bar{\omega}_{fi})a_i(0)+2\mu_{fi}E^sa_f(0)\ ,\\ 2b'\gamma&=(\gamma+\bar{\omega}_{fi})a_f(0)+2\mu_{fi}E^sa_i(0)\ , \end{aligned} \tag{3d}$$

with corresponding eigenenergies

$$\omega_0=\tfrac{1}{2}(\omega_i+\omega_f)-\tfrac{1}{2}\gamma \tag{3e}$$

and

$$\omega_1=\tfrac{1}{2}(\omega_i+\omega_f)+\tfrac{1}{2}\gamma\ , \tag{3f}$$

respectively. If $E^s=0$, one notes that $|0\rangle=a_i(0)|i\rangle$, $\omega_0=\omega_i$ and $|1\rangle=a_f(0)|f\rangle$, $\omega_1=\omega_f$. Thus, the initially isolated two-level system is rotationally polarized by the static field and adopts the stationary states $|0\rangle$ and $|1\rangle$ with energies ω_0 and ω_1, respectively. We now proceed to explore the photodynamics of the aligned two-level system in a classical time-varying field. The equation of motion for the state amplitudes of this nondegenerate two-level system dipole interacting with an oscillating field $\mathbf{E}^0=\hat{\mathbf{e}}E^0\cos\omega t$ is

$$i\,\frac{d}{dt}\begin{bmatrix}a_0\\a_1\end{bmatrix}=\begin{bmatrix}\omega_0-\mu_{00}E^0\cos(\omega t) & -\mu_{01}E^0\cos(\omega t)\\ -\mu_{10}E^0\cos(\omega t) & \omega_1-\mu_{11}E^0\cos(\omega t)\end{bmatrix}\begin{bmatrix}a_0\\a_1\end{bmatrix}, \tag{4}$$

where a_k is the probability amplitude of the state $|k\rangle$, $k=0$ or 1, $\mu_{00}=\langle 0|\mu_{3,m}|0\rangle+\bar{\alpha}_m E^s=2ab\mu_{if}+\bar{\alpha}_m E^s$, $\mu_{11}=\langle 1|\mu_{3,m}|1\rangle+\bar{\alpha}_m E^s=2a'b'\mu_{fi}+\bar{\alpha}_m E^s$, and $\mu=\mu_{01}=\mu_{10}=\langle 0|\mu_{3,m}|1\rangle=(ab'+a'b)\mu_{if}$. We denote the difference in the permanent dipole moments of the field-orientated two-level system by $d=\mu_{11}-\mu_{00}$. Using Eq. (3d) one can easily show that $|d|\leq|\mu_{if}|$ and $d=0$ if $E^s=0$; otherwise d is finite, even if $\mu_{ff}-\mu_{ii}=0$ in the isolated molecule eigenenergy basis. Also, $\gamma^2\geq 4(\mu_{if}E^s)^2$. Transforming to an interaction picture defined by

$$a_k(t)=b_k(t)\exp\left[-i\left[\omega_k t-\frac{\mu_{kk}E^0}{\omega}\sin(\omega t)\right]\right],\quad k=0 \text{ or } 1 \tag{5}$$

Eq. (4) becomes

$$i\frac{d}{dt}\begin{bmatrix}b_0\\b_1\end{bmatrix}=-\mu E^0\cos(\omega t)\begin{bmatrix}0 & \exp\{-i[\omega_{10}t-\eta\sin(\omega t)]\}\\ \exp\{i[\omega_{10}t-\eta\sin(\omega t)]\} & 0\end{bmatrix}\begin{bmatrix}b_0\\b_1\end{bmatrix}, \tag{6}$$

where $\omega_{10}=\omega_1-\omega_0$ is the level separation, and the dimensionless parameter η is defined by

$$\eta=dE^0/\omega\;. \tag{7}$$

Using the identity

$$\exp[i\eta\sin(\omega t)]=J_0(\eta)+\sum_{k=1}^{\infty}J_k(\eta)[\exp(ik\omega t)+(-1)^k\exp(-ik\omega t)]\;, \tag{8}$$

where the J's are Bessel functions[9] of the first kind, and invoking the RWA wherein one discards all rapidly oscillating terms that make negligible contribution to the transition rates, Eq. (6) reduces to

$$i\frac{d}{dt}\begin{bmatrix}b_0\\b_1\end{bmatrix}=-\tfrac{1}{2}\mu E^0\alpha_1(d,E^0,\omega)\begin{bmatrix}0 & \exp(-i\tilde{\omega}_{10}t)\\ \exp(i\tilde{\omega}_{10}t) & 0\end{bmatrix}\begin{bmatrix}b_0\\b_1\end{bmatrix}, \tag{9}$$

where the time-independent parameter $\alpha_1(d,E^0,\omega)$ is defined by

$$\alpha_1(d,E^0,\omega)=(2/\eta)J_1(\eta)\;, \tag{10}$$

and $\tilde{\omega}_{10}=\omega_{10}-\omega$ is the detuning frequency. Further transforming to an interaction picture defined by

$$c_k(t)=b_k(t)\exp(-\tfrac{1}{2}i\tilde{\omega}_{10}t),\quad k=0 \text{ or } 1 \tag{11}$$

Eq. (9) yields

$$\ddot{c}_0(t)+\tfrac{1}{4}[\tilde{\omega}_{10}^2+(\mu E^0\alpha_1)^2]c_0(t)=0\;, \tag{12}$$

with a similar equation for c_1. So within the RWA, the two-level system dipole interacting with a classical field is dynamically equivalent to a unit mass oscillator with a Rabi frequency of oscillation

$$\Omega_R=\tfrac{1}{2}[\tilde{\omega}_{10}^2+(\mu E^0\alpha_1)^2]^{1/2}\;. \tag{13}$$

The solutions of Eq. (12) are of the form $\dot{c}_0^2+\Omega_R^2c_0^2=A$, A an arbitrary constant, and represent a family of ellipses in the $c_0\dot{c}_0$ plane so that all solutions are $2\pi/\Omega_R$ periodic in time. The most interesting solution is that corresponding to the situation in which the two-level system is initially in the lower state $|0\rangle$ with the oscillating field inducing Rabi nutations between $|0\rangle$ and the upper state $|1\rangle$. In the c picture the initial conditions are $c_0(0)=1$ and $\dot{c}_0(0)=-(i/2)\tilde{\omega}_{10}$ so that the induced transition probability for excitation from $|0\rangle$ to $|1\rangle$ is $P_1(\omega,t)=1-|c_0(t)|^2$ and is given by

$$P_1(\omega,t)=\frac{(\mu E^0\alpha_1)^2}{\tilde{\omega}_{10}^2+(\mu E^0\alpha_1)^2}\sin^2(\Omega_R t)\;. \tag{14a}$$

If the oscillating field executes many optical cycles throughout its duration then the long-time averaged value of $P_1(\omega,t)$ is

$$P_1^{\infty}(\omega)=\frac{1}{2}\frac{(\mu E^0\alpha_1)^2}{\tilde{\omega}_{10}^2+(\mu E^0\alpha_1)^2}\;. \tag{14b}$$

Whenever $d\neq 0$, the power-broadening saturation parameter $\mu E^0\alpha_1(d,E^0,\omega)$ is frequency dependent and, from Eq. (10), it clearly vanishes at frequencies

$$\omega_1^{(k)}=dE^0/j_{1,k},\quad k=1,2,\ldots \tag{15}$$

where $j_{1,k}$ is the kth zero of J_1. At frequencies approaching $\omega_1^{(k)}$, the Rabi nutation period increases, especially if $\omega_1^{(k)}$ is near resonant with ω_{10}. Further, the long-time averaged transition probability vanishes at these prescribed frequencies so that the usual Lorentzian line shape is flanked at the saturating central frequency $\omega=\omega_{10}$ by subsaturating oscillatory fringes. However, if $d=0$ so that[9] $\alpha_1(0,E^0,\omega)=1$, then Eq. (14a) and Eq. (14b) reduce to the well-known Rabi expressions[10(a)] for the time-resolved and time-averaged induced transition probabilities, respectively. Torrey[10(b)] claims that if $E^0\ll\omega_{10}$

then the diagonal matrix elements μ_{00} and μ_{11} do not appear in the approximate solution of Eq. (4) valid near resonance.

As is well known, the composite two-level molecule-field system may be described in terms of dressed states[11] with eigenenergies

$$\omega_0^D=\omega_0-\tfrac{1}{2}\tilde{\omega}_{10}+\Omega_R \tag{16a}$$

and

$$\omega_1^D=\omega_1+\tfrac{1}{2}\tilde{\omega}_{10}-\Omega_R \ , \tag{16b}$$

where, because of the periodicity of the oscillating field, $\pm\Omega_R$ are the Floquet quasienergies. When $E^0=0$, ω_0^D and ω_1^D reduce to the undressed stationary states of the static field-orientated two-level system. However, when $d\neq0$ and in an electric field oscillating at $\omega=\omega_1^{(k)}$, $\Omega_R=\frac{1}{2}\tilde{\omega}_{10}$ and the dressed eigenenergies ω_0^D and ω_1^D coincide with ω_0 and ω_1, respectively. Further, if for finite d, E^0 becomes arbitrarily large then[9] again $\Omega_R=\frac{1}{2}\tilde{\omega}_{10}$. Thus it would appear that a finite difference d in permanent dipole moments between the states in an aligned two-level system can allow such a system to be essentially transparent to the laser field, irrespective of the strength of that field.

The Laplace collisional time-averaged value of $P_1(\omega,t)$, i.e.,

$$P_1^\tau(\omega)=\tau^{-1}\int_0^\infty \exp(-t/\tau)P_1(\omega,t)dt \ ,$$

is given by

$$P_1^\tau(\omega)=\frac{1}{2}\frac{4(\mu E^0\alpha_1)^2}{\tau^{-2}+\Omega_R^2} \ , \tag{17}$$

where τ is a mean collisional relaxation time. Off resonance and when dE^0 is arbitrarily large so that[9] $\eta\rightarrow\infty$, $\alpha_1\rightarrow0$ and consequently $P_1^\tau(\omega)\rightarrow0$. Similarly, as $\tau\rightarrow0^+$, $P_1^\tau(\omega)\rightarrow0$ at on- and off-resonance frequencies. Thus, excitation processes induced by a near-resonant oscillating field will be ineffective if dE^0 is arbitrarily large or if the collisional relaxation time is very short.

An interesting consequence of the power broadening parameter's dependence on both d and ω is that $P_1^\infty(\omega)$ will be asymmetrically skewed with respect to the one-photon resonance or the central frequencies of the ancillary fringes. This asymmetry is independent of the sign of d and $P_1^\infty(\omega)$'s one-photon resonance and attendant fringes will be skewed towards higher frequencies.

The foregoing formulas were derived within the RWA on the tacit assumption that the oscillating field is near resonant with the level separation. Since d and the $j_{l,k}$'s are unalterable, appropriate choice of E^0 will ensure that the $\omega_1^{(k)}$'s, for some k's, will cluster close to $\omega=\omega_{10}$. If this is so then use of the fact that $|d|\leq|\mu_{if}|$ and $\gamma^2\geq(2\mu_{if}E^s)^2$ in Eq. (7) allows one to show that $E^0\gtrsim2j_{l,k}E^s$. Thus, provided E^s is strong enough to orientate the molecule along a fixed direction, a near-resonant laser field of frequency $\omega_1^{(k)}\sim\omega_{10}$ and of strength $E^0\gtrsim2j_{l,k}E^s$ and polarized in this direction will ensure the appearance of a line shape with satellite fringes. The estimates $\omega_1^{(k)}\sim\omega_{10}$ and $E^0\gtrsim2j_{l,k}E^s$ on the requisite laser frequency, and field strength for an oscillatory line shape are sufficiently flexible to embrace the bandwidth uncertainty in the former and the inherent modulation of the latter from its peak value. The conditions for the validity of the RWA are

$$|\omega-\omega_{10}|\simeq0 \ , \tag{18a}$$

and

$$\omega^2\gg[(\mu E^0/\eta)J_1(\eta)]^2 \ , \tag{18b}$$

which physically correspond to the requirements for a small detuning and a small coupling-strength parameter, respectively. When $E^s=0$ and hence $d=0$, Eq. (18) reduce to the usual criteria,[12] viz., $\omega_{10}\simeq\omega\gg|\frac{1}{2}\mu E^0|$. It is well known[13] that the antiresonant terms omitted when invoking the RWA introduce intensity-dependent shifts in the energy levels. The first-order Bloch-Siegert shifted one-photon resonance is

$$\omega_{\text{res}}=\omega_{10}\{1+[\mu E^0J_1(\eta_{\text{res}})/\omega_{10}\eta_{\text{res}}]^2\} \ , \tag{19}$$

where $\eta_{\text{res}}=dE^0/\omega_{\text{res}}$. The shift, which depends on both the intensity of the field and on the difference in permanent dipole moments between the levels, is towards the blue but will be small if $\omega\simeq\omega_1^{(k)}$. If $d=0$, Eq. (19) reduces[9] to the usual expression[13] for the shift caused by the counter-rotating phasor of the oscillating field. Notwithstanding the possible fulfillment of the RWA and the attainment of a negligible Block-Siegert shift, there are two other major implicit requirements of our treatment that must be met, viz., validity of the resonance approximation and the absence of field ionization. The resonance approximation,[7] in which all but two of the quantized system's energy levels are ignored, provides a convenient starting point for analyzing the response of atomic or molecular systems undergoing interactions with an oscillating field which is nearly resonant with only two states of the system. Berman,[14(a)] by evaluating the polarization of an atomic system both exactly and within the two-level approximation, has given an interesting account of the assumptions necessary to justify the resonance approximation; only when one includes the lowest-order contributions from states outside the two-level manifold will the resonance approximation be generally applicable. Wong *et al.*[14(b)] and Burrows and Salzman[14(c)] have shown that neighboring nonresonant states cause a shift in the frequency of the resonance profile of the two resonant levels. The prevailing paradigm[15] of infrared laser-induced multiphoton dissociation of many polyatomic molecules suggests that the ascent up the low-energy harmonic stack of discrete states proceeds through the sequential near-resonant absorption of single photons, each photon being absorbed by a two-level system in accordance with the resonance approximation. It would appear that the resonance approximation and the concept of a two-level system are well based provided field ionization does not jeopardize the integrity of the two-level system. Field ionization[16] usually refers to the ionization of an atomic or molecular system by a static electric field which renders possible the tunneling of one or more electrons to unbound states. Normally, field ionization requires either large field strengths $E^s\sim e/a_0^2$ so that the electron-field interaction $\sim eE^s a_0 \sim e^2/a_0$ is comparable to the Coulombic electron-nucleus interaction, or that the atom or molecule be in a high Rydberg state. In the present context the requirement for a static electric field is merely to orientate the polar molecule in a fixed direction and can be accomplished by relatively low-field strengths $E^s \ll e/a_0^2$ so that the likelihood of inducing field ionization is small. Both theoretical[17(a),17(b)] and experimental[17(c)] evidence suggest that such a weak static field results in an enhancement in intense laser-induced multiphoton processes in atomic and molecular systems. Even if the static field is relatively weak it is possible for the laser field to cause the system to ionize. However, the moderately intense infrared lasers used[15] for the deposition of many photons delivered in short duration pulses to polyatomics do not generally result in the photo-ionization of such systems but, at best, give rise to photodissociation through desirable channels. In many cases the deposited energy is randomized throughout the molecule via intramode coupling. Such a thermalization mechanism is not possible in diatomics and one must resort to the use of ultraintense laser fields with $E^0 \sim e/a_0^2$ in order to induce dissociation or possibly ionization. In such circumstances one should legitimately work[3(b)] with the field-dressed Hamiltonian operator of the system and in terms of the field-dressed eigenstate basis. Herein we are restricted to the use of laser field strengths that, on the one hand, are large enough to induce single photon (and multiphoton, see the discussion to follow) absorption in molecules but, on the other hand, are not so large as to undermine the validity of the resonance approximation through allowing for the possibility of photo-ionization. Also, since we are considering the photodynamics of a single molecule orientated in a static electric field under collision-free conditions, the possibility of dielectric breakdown is not an issue since the usual cascade processes cannot take place.

For single-photon processes considered above, use of Eq. (8) in Eq. (6) coupled with the RWA amounts operationally to the retention of only those terms evolving slowly enough to make an appreciable contribution to the state transition rates, subject to the proviso of Eq. (18). Extension to multiphoton processes occurring at integer fractions of the level separation is straightforward. The generalization of Eq. (10) is easily shown to be

$$\alpha_n(d,E^0,\omega)=(2n/\eta)J_n(\eta)\ , \tag{20}$$

where $n=1,2,\ldots$ refers to the photon multiplicity of the process. Since[9] $\alpha_n(0,E^0,\omega)=\delta_{n,1}$, it follows that when $d\neq 0$ the RWA treatment adequately accounts for unshifted multiphoton resonances at $\omega=\omega_{10}/n$, $n=2,3,\ldots$, in a two-level system. Thus, the absorption of n photons by the two-level system involves the participation of $(n-1)$ virtual intermediate states. This ability to absorb many photons rescues the concept of a two-level system from the derisive claims that it is a mere artifice with an apparent life of its own, especially if the interleaving levels correspond to stationary eigenstates bracketed by the initial $|i\rangle$ and final $|f\rangle$ states of the isolated molecule. As in the single-photon case, if $E^0 \simeq j_{n,k}\omega_{10}/nd$ so that $E^0 \gtrsim 2j_{n,k}E^s/n$ for some integer k, where $J_n(j_{n,k})=0$, the n-photon resonance exhibits an oscillatory line shape that is asymmetrically skewed towards higher frequencies although the "degree" of asymmetry and the "widths" of the resonance decrease as n increases. Thus, with multiphoton resonances essentially no new features emerge over those revealed in the consideration of single-photon processes.

Oka and Shimizu[5] have shown that the two-photon transition probability is given approximately by

$$P_1^{\infty}(\omega)=\frac{1}{2}\frac{[\mu d(E^0)^2/\omega_{10}]^2}{[\mu d(E^0)^2/\omega_{10}]^2+[\omega-\frac{1}{2}\omega_{10}-\frac{2}{3}(\mu E^0)^2/\omega_{10}]^2}\ . \tag{21a}$$

This was derived[18] within the RWA and under the assumption that the state amplitudes can be written as the sum of high- and low-frequency parts. Equation (21a) gives $P_1^{\infty}(\omega)$ as a Lorentzian exhibiting a two-photon resonance at $\omega=\frac{1}{2}\omega_{10}[1+\frac{4}{3}(\mu E^0/\omega_{10})^2]$, which has been shifted towards the blue with respect to $\frac{1}{2}\omega_{10}$. In contrast, from Eq. (20) one obtains

$$P_1^{\infty}(\omega)=\frac{1}{2}\frac{[4\mu E^0 J_2(\eta)/\eta]^2}{[4\mu E^0 J_2(\eta)/\eta]^2+(2\omega-\omega_{10})^2}\ , \tag{21b}$$

where η is given by Eq. (7). If we set $\omega \simeq \frac{1}{2}\omega_{10}$ in Eq. (7), then for sufficiently small dE^0 so that[9] $\eta \sim 0$, $P_1^{\infty}(\omega)$ in Eq. (21b) is equivalent to Eq. (21a) provided that we neglect the shift in the resonance.

III. CONCLUSIONS

Within the RWA, a difference between the permanent dipole moments in the states of a two-level system dipole interacting with an oscillating electric field and a static electric field was shown to result in a carrier frequency-dependent Rabi-flopping frequency and power-broadening saturation parameter. This power-broadening parameter vanishes at prescribed frequencies so that the usual Lorentzian time-averaged transition probability is flanked by subsaturating oscillatory fringes. The first-order shift in the saturating resonance is towards the blue and is dependent on both the strength of the oscillating field and the difference in permanent dipole moments between the levels. The steady-state transition probability and its attendant fringes will be asymmetrically skewed towards higher frequencies, with the widths of the fringes becoming smaller as the detuning frequency increases. If the difference between the permanent dipole moments in the states is sufficiently large, then an off-resonance field will be ineffective in inducing transitions between the levels. A short collisional relaxation time will suppress all excitation of the system. Both necessary (validity of the RWA, negligible Block-Siegert shift) and sufficient (moderate laser field strength E^0, relatively weak static field strength E^s, $\omega \sim \omega_{10}/n$ and $E^0 \gtrsim 2j_{n,k}E^s/n$ for $n=1,2,3\ldots$, validity of the resonance approximation, absence of field ionization) conditions, that delineate the validity of the analysis presented on the possibility of a polar molecule exhibiting a line shape with satellite fringes, were discussed.

The essential reason why the time-averaged transition probability is accompanied by oscillatory fringes is that at certain near-resonant frequencies consistent with the validity of the RWA, the two-level system is transparent to the field. Indeed, at such frequencies the dressed states of the molecule-field system coincide with the undressed stationary states of the static field-aligned two-level system.

Generalization of the formulas presented herein to account for induced multiphoton absorption in a two-level system allows for the recovery of an early result of Oka and Shimizu[5] for the two-photon transition probability in a system with state-specific permanent dipole moments.

We mention the resemblance of the oscillatory line shape discussed here with the appearance of Ramsey fringes[19] in beam experiments. Whereas the oscillatory fringes we have discussed originate with the finite difference between the permanent dipole moments of a pair of states near resonant with a laser field, Ramsey fringes arise from the phase relation between two magnetic fields experienced by an atom and/or molecule in a beam apparatus.

Finally, apart from allowing a uniform collisional relaxation mechanism to compete with the power-broadening effects, the treatment presented here relates to an isolated two-level system. Elsewhere[20] we examine the effects of permanent dipole moments on the response of a Doppler-broadened two-level medium to a single-mode standing wave.

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