

Influence of the ac Stark effect on multiphoton transitions in molecules

W. Leo Meerts

Fysisch Laboratorium, Katholieke Universiteit Nijmegen, Toernooiveld 6525 ED Nijmegen, The Netherlands

Irving Ozier

Department of Physics, University of British Columbia 6224 Agriculture Road, Vancouver, BC V6T 2A6 Canada

Jon T. Hougen^{a)}

Division of Molecular Spectroscopy, National Bureau of Standards, Gaithersburg, Maryland 20899

(Received 5 October 1988; accepted 30 December 1988)

A multiphoton mechanism for molecular beam transitions is presented which relies on a large first-order ac Stark effect to modulate the energy separation of the initial and final states of the multiphoton transition, but which does not require the presence of any intermediate level(s). The theoretical formalism uses ideas from the laser multiphoton literature for a two-level system interacting with a monochromatic electromagnetic radiation field, together with a close analog of the rotating wave approximation. The diagonal matrix elements of the Hamiltonian operator corresponding to the large ac Stark effect are removed by a mathematical substitution which in effect transforms appropriate differences of these diagonal elements into transition moments involving higher harmonics of the frequency of the monochromatic radiation field. The electric field strength of the true monochromatic radiation field is "distributed" among the higher harmonics of the effective field according to an expression involving Bessel functions. Because these Bessel functions are bounded, there exists for a given time t of exposure to the radiation, a threshold for the magnitude of the transition dipole matrix element coupling the two levels: Below this threshold, the transition probability in a traditional one-photon molecular beam electric resonance experiment cannot be made unity simply by increasing the amplitude of the radiation field. In fact, if the coupling matrix element is small enough, the molecular beam electric resonance signal cannot be detected within exposure time t . The algebraic formalism described above is checked by computer solution of an initial value problem involving four real coupled linear differential equations. It is then used to explain the multiphoton transitions previously observed in molecular beam electric resonance studies on the two symmetric top molecules OPF_3 and CH_3CF_3 , where the number of photons involved in a given transition varies from 1–40. Application of the analysis to other experiments is briefly discussed.

I. INTRODUCTION

In molecular beam electric resonance (MBER) studies,¹ the intensity of the spectrum is conventionally optimized by first setting the frequency ω of the applied oscillating electric field equal to the molecular transition frequency ω_0 , and then adjusting the amplitude E of the oscillating field. From the standard treatment¹ of the two level problem, it is clear that for a beam of given velocity there exists an optimum value E_{opt} for E at which the transition probability equals unity. Within the assumptions made,¹ the optimum field so defined can always be reached; its value depends only on the time spent in the transition region and on the matrix element μ_{12} of the electric dipole moment operator coupling the states in question. Furthermore, it is impossible to attain unit transition probability at any frequency other than $\omega = \omega_0$.

During a series of MBER studies on avoided crossings in symmetric top molecules,^{2–4} it was observed that in addition to the "normal" signals at $\omega = \omega_0$, resonance signals of

comparable intensity could be observed at $\omega = \omega_0/n$ for integer values of n as large as 40, provided that the amplitude of the oscillating field was increased in proportion to n . That is, if $E_{\text{opt}}^{(n)}$ is the value of E needed to maximize the signal at ω_0/n , then $E_{\text{opt}}^{(n)}/n$ remained approximately constant. In addition, the resonances observed at $\omega = \omega_0/n$ with $E = E_{\text{opt}}^{(n)}$ had half-widths $\Delta\omega_n$ in frequency space equal to $1/n$ times the corresponding half-width observed at ω_0 with $E_{\text{opt}}^{(1)}$. These observations all suggest that multiphoton transitions were being observed in these avoided crossing experiments, in spite of the fact that the systems under study could be treated as two level problems.⁴

While multiphoton transitions are not rare in radio-frequency molecular beam studies,⁵ no treatment could be found in the molecular beam literature to explain our results. In the present paper we therefore adapt ideas from the extensive multiphoton literature associated with high intensity laser experiments,^{6–9} and show that our unusual transitions can be explained by adding terms representing the ac Stark effect to the more conventional treatments^{1,10} of the coherent excitation of a two level system. These terms are normally omitted from MBER analyses because diagonal matrix

^{a)} Nederlandse Organisatie voor Wetenschappelijk Onderzoek Visiting Scientist, Katholieke Universiteit Nijmegen, Spring, 1988.

elements due to the applied oscillating field vanish¹¹ when each of the two levels under consideration has no degeneracy other than the $(2J + 1)$ -fold degeneracy associated with the total angular momentum projection quantum number M_J . For the case of symmetric tops considered here, however, an additional degeneracy is present, associated with the quantum number K , and a significant linear ac Stark effect can therefore arise,¹¹ whose magnitude is large compared with the ac term coupling the initial and final states of the transition. We find that this ac Stark effect, in addition to inducing multiphoton transitions, also modifies the one photon problem, so that for small enough values of $|\mu_{12}|$, the maximum signal at $\omega = \omega_0$ is smaller than that corresponding to unit transition probability.

The terms corresponding to this ac Stark effect can be transformed mathematically^{8,9} into a form equivalent to the introduction of an "effective" oscillating field which contains large numbers of harmonics of the frequency of the monochromatic oscillating field actually being applied. It is the harmonics of this effective field which induce the multiphoton transitions. It is important to note that intermediate states in the energy level diagram of the molecule do not play a role in this mechanism.

In Sec. II below, we give the mathematical details of the treatment⁶⁻⁹ of the ac Stark effect. In Sec. III, we compare the theoretical results obtained with experimental observations from the avoided crossing MBER studies on symmetric top molecules.²⁻⁴ In Sec. IV we briefly discuss other experiments where the ac Stark effect may be important in inducing multiphoton transitions.

II. THEORY

We begin with the standard equations for coherent excitation of a two-level system.^{1,10} We assume a Hamiltonian divided into a time-independent part H_0 and a monochromatic time-dependent part $V(t)$, such that

$$H = H_0 + V(t) \\ = H_0 - \mu E \cos \omega t, \quad (1)$$

where μ is the dipole moment operator of the system being studied, and E and ω are the electric field strength and the angular frequency of the applied radiation, respectively.

Time-dependent solutions of the time-independent Hamiltonian H_0 can be written in the standard manner as

$$\Psi_j(t) = \psi_j(\mathbf{r}) e^{-iE_j t/\hbar}, \quad H_0 \psi_j(\mathbf{r}) = E_j \psi_j(\mathbf{r}), \quad (2)$$

where E_j is the energy of state j , and $\psi_j(\mathbf{r})$ is its spatial wave function. For a two-level problem, $j = 1$ or 2 .

A solution for the complete Hamiltonian $H_0 + V(t)$ can be sought in the standard form

$$\Psi(t) = a_1(t) \Psi_1(t) + a_2(t) \Psi_2(t), \quad (3)$$

with initial conditions

$$a_1(t=0) = 1, \quad a_2(t=0) = 0, \quad (4)$$

corresponding to no population of state 2 at $t = 0$. By substituting Eq. (3) into $H\Psi = i\hbar(\partial\Psi/\partial t)$, multiplying by Ψ_j^* , and integrating over the spatial variables, for $j = 1$ and 2 in turn, we obtain the standard pair of coupled differential equations:

$$i\hbar \frac{da_1}{dt} = V_{11}(t) a_1(t) + V_{12}(t) a_2(t) e^{-i\omega_0 t}, \\ i\hbar \frac{da_2}{dt} = V_{21}(t) a_1(t) e^{+i\omega_0 t} + V_{22}(t) a_2(t), \quad (5)$$

where the $V_{jk}(t)$ are matrix elements of $V(t)$ obtained by integration over the spatial wavefunctions, and $\hbar\omega_0 = E_2 - E_1$. (We assume $\omega_0 > 0$.) When the form of $V(t)$ is introduced explicitly, we have

$$i\hbar \frac{da_1}{dt} = -\mu_{11} E \cos \omega t a_1(t) - \mu_{12} E \cos \omega t a_2(t) e^{-i\omega_0 t}, \\ i\hbar \frac{da_2}{dt} = -\mu_{21} E \cos \omega t a_1(t) e^{+i\omega_0 t} - \mu_{22} E \cos \omega t a_2(t), \quad (6)$$

where μ_{11} and μ_{22} are time-independent diagonal elements of the dipole moment operator μ in the basis set $\psi_j(\mathbf{r})$, which are often associated with the phrase "ac Stark effect" when they are coefficients of a $\cos \omega t$ term; μ_{12} and μ_{21} are the corresponding time-independent off-diagonal elements, i.e., the transition moments.

As mentioned above, it is customary in the molecular beam literature to consider Eqs. (6) with μ_{11} and μ_{22} both zero,^{1,10} or both nearly zero.¹² It is well known,¹³ however, that states of symmetric top molecules for which the K quantum number is greater than zero exhibit a first-order (dc) Stark effect, and that the eigenstates of H_0 remain doubly degenerate. Even though there are then four levels involved in the energy level diagram, it has been shown⁴ that (with the exception of a few special cases) the MBER avoided crossing problem breaks up into a number of separate two-level systems.

Because of the linear Stark effect, μ_{11} and μ_{22} in Eqs. (6) need not be small, and in fact can be large compared to μ_{12} . Thus, rather than discarding these terms,^{1,10} or treating them only in the very small limit,¹² we choose instead to eliminate them through a convenient mathematical substitution^{8,9}

$$a_j(t) = e^{+i(\mu_{jj} E/\hbar\omega) \sin \omega t} X_j(t). \quad (7)$$

Making this substitution in Eqs. (6) yields coupled differential equations for the quantities $X_j(t)$ of the form,

$$i\hbar \frac{dX_1}{dt} = -e^{+i[(\mu_{22} - \mu_{11}) E/\hbar\omega] \sin \omega t} \mu_{12} E \cos \omega t e^{-i\omega_0 t} X_2(t), \\ i\hbar \frac{dX_2}{dt} = -e^{-i[(\mu_{22} - \mu_{11}) E/\hbar\omega] \sin \omega t} \mu_{21} E \cos \omega t e^{+i\omega_0 t} X_1(t), \quad (8)$$

with $X_1(t=0) = 1$ and $X_2(t=0) = 0$. In Eqs. (8), the dependence of dX_j/dt on X_j has been eliminated for $j = 1$ and 2 , and in that sense Eqs. (8) are analogous to the two-level coherent monochromatic excitation equations usually solved.^{1,10} Equations (8) differ from the usual equations, however, since the oscillating electric field term $\mu_{12} E \cos \omega t$, containing a single cosine function, has been replaced by more complicated expressions $F(t)$ and $F(t)^*$, where

$$F(t) \equiv e^{+i[(\mu_{22} - \mu_{11}) E/\hbar\omega] \sin \omega t} \mu_{12} E \cos \omega t. \quad (9)$$

$F(t)$, however, is still periodic in time with a period of

$\Delta t = 2\pi/\omega$, and it can thus be expressed as a Fourier series in harmonics of the fundamental frequency ω

$$F(t) = \sum_{n=-\infty}^{+\infty} n\hbar\omega[\mu_{12}/(\mu_{22} - \mu_{11})] \times J_n[(\mu_{22} - \mu_{11})E/\hbar\omega]e^{+in\omega t}, \quad (10)$$

where J_n is the Bessel function¹⁴ of integer order n .

In order to treat an n -photon transition, we now make the usual rotating wave approximation^{1,10} and near-resonance assumption. We select the term in $F(t)$ oscillating as $e^{+in\omega t}$, with $n\omega \cong \omega_0$, and the term in $F(t)^*$ oscillating as $e^{-in\omega t}$, substitute these terms into the first and second of Eqs. (8), respectively, and solve the resulting coupled differential equations^{1,10} for $X_1(t)$ and $X_2(t)$. Equation (7) then gives immediately $a_1(t)$ and $a_2(t)$, which describe the time dependence of $\Psi(t)$ of Eq. (3) under the influence of the monochromatic oscillating field $V(t)$ of Eqs. (1). For the boundary conditions of interest, and using a notation similar to that of Shimoda¹⁰ we find

$$X_1(t) = \{\cos \Omega t/2 - i[(n\omega - \omega_0)/\Omega]\sin \Omega t/2\} \times e^{+i(n\omega - \omega_0)t/2} \quad (11)$$

$$X_2(t) = (ix/\Omega)\sin \Omega t/2 e^{-i(n\omega - \omega_0)t/2},$$

where

$$x \equiv 2n\omega[\mu_{12}/(\mu_{22} - \mu_{11})]J_n[(\mu_{22} - \mu_{11})E/\hbar\omega], \quad (12)$$

$$\Omega \equiv [(n\omega - \omega_0)^2 + x^2]^{1/2}.$$

Qualitatively speaking, as the electric field strength in $\mu E \cos \omega t$ is increased, the diagonal (ac Stark effect) terms in Eqs. (5) or (6) cause this field strength to be distributed among a number of higher harmonics of the fundamental frequency ω in Eqs. (8). This distribution is governed^{8,9} by Bessel functions, which have extremely small values for high order and small arguments,¹⁴ and Eq. (10) shows that high harmonics are generated only when the oscillating electric field is large enough to induce an ac Stark shift in the transition frequency which is comparable to the photon energy. As a check, we note that in the limit where the ac Stark effect vanishes, i.e., as $(\mu_{22} - \mu_{11}) \rightarrow 0$ in Eq. (9), $F(t) \rightarrow \mu_{12}E \cos \omega t$. $F(t)$ as given in Eq. (10) can also be shown to reduce to $\mu_{12}E \cos \omega t$ in this limit by examination of the Bessel function expansions for small arguments.¹⁴ The very rapid decrease of high-order Bessel functions as their arguments approach zero is in agreement with the results of Torrey,¹² who found that the introduction of small ac Stark effect terms caused no perceptible changes to the molecular beam electric resonance results obtained when the ac Stark effect terms were absent.

Equations (7) and (11) show that the probability of finding a molecule in state 2 at time t , if it is in state 1 at $t = 0$, is given by

$$|a_2(t)|^2 = \{x^2/[(n\omega - \omega_0)^2 + x^2]\} \times \sin^2\{[(n\omega - \omega_0)^2 + x^2]^{1/2}t/2\}. \quad (13)$$

In a coherent excitation experiment, the transition probability is given by Eq. (13) with t being the time the molecule spends in the region containing the applied oscillating field.

In conventional molecular beam electric resonance line shape analyses,^{1,10} $|a_2(t)|^2$ is given by Eq. (13) with $n = 1$, with x equal to $\mu_{12}E/\hbar$, as can be obtained from Eq. (12) in the limit $(\mu_{22} - \mu_{11}) \rightarrow 0$, and with $t = l/v$, where l is the length of the transition region and v is the molecular velocity. The resulting line shape differs from Eq. (13) in two important respects. First, the multiphoton resonances are absent. Second, the value of $|a_2(t)|^2$ can always be made unity, since the first factor equals 1 at $\omega = \omega_0$, and the second can be made unity by setting $x = \mu_{12}E/\hbar = \pi/t$. For fixed t , this can always be done in the conventional case by adjusting E .

By contrast, in the current case with the ac Stark effect present, x is proportional to $J_n(z)$, and z in turn is proportional to E . For any given n , there is still a value of E , denoted here by $E_{\text{opt}}^{(n)}$, which will maximize the n -photon resonance signal, but because $|J_n|$ is bounded, it is possible for given t that the value of $|x|$ will be less than π/t for all values of E , and it will then be impossible to make the transition probability unity. Thus, for small enough values of t and $\mu_{12}/(\mu_{22} - \mu_{11})$, the maximum transition probability can be so low that the resonance signal is lost in the noise. This applies even for $n = 1$.

In the current treatment, there are two parts to the approximation made by considering a single value of n : (a) neglect of the term in $(-n)$, commonly called the rotating wave approximation, and (b) neglect of the terms in $(n+1)$ and $(n-1)$, often called the near-resonance assumption. Errors arising from (b) are expected to be larger than those from (a), since the neighboring frequencies omitted in (b) differ from that retained by about $\delta\omega_n = |(1/n) - [1/(n \pm 1)]|\omega_0 \cong \omega_0/n^2$, while the negative frequency omitted in (a) is off resonance by $2\omega_0/n$. We might expect, however, that the effects of neglecting these off-resonant terms will be mitigated by the reduction in linewidth as n increases. Indeed, if frequency differences are measured as multiples of the line width $\Delta\omega_n$ of the resonance at ω_0/n , then the "distance" from resonance in (a) becomes $(2\omega_0/n)/(\Delta\omega_1/n) = (2\omega_0/\Delta\omega_1)$, which is independent of n . Similarly, the distance from resonance of the $\omega_0/(n \pm 1)$ frequencies becomes $\delta\omega_n/\Delta\omega_n \cong \omega_0/n\Delta\omega_1$, which approaches zero only as $1/n$. Qualitative arguments of this type suggest that the current "single" n approximation will be valid for treating n -photon transitions as long as $\omega_0/n\Delta\omega_1 \gg 1$.

In any case, the validity of the single n approximation was tested by comparing the values for $X_1(t)$ and $X_2(t)$ obtained algebraically from Eqs. (11) with values obtained by direct numerical integration of the coupled differential equations (8). To simplify the computer calculations, the pair of coupled complex differential equations was converted to four coupled real equations, and the resulting initial value problem was solved using the routine DIVPBS from the

IMSL library.¹⁵ For the cases examined, i.e., for the cases of interest in the next section, the values of $|X_2(t)|^2$ from the two methods showed disagreements only in the fourth or fifth decimal places when the multiphoton transition was in exact resonance. For off-resonance calculations, i.e., for line shape calculations, the weak secondary maxima which appear when the frequency is displaced several linewidths from the line center were well reproduced in position, but had errors of 15% or so in their intensity. Nevertheless, the calculations show that the single n approximation applied to the Fourier expansion of Eq. (10) is valid for quantitative treatments of multiphoton transitions near resonance.

As a final point, we note that the multiphoton transition mechanism under discussion here does not require any intermediate states in the molecular energy level scheme. It is a two-level mechanism,^{6,8,9} though at least one level must exhibit degeneracy at zero electric field other than that associated with M_J , in order to exhibit a first-order Stark effect when the field is present.

III. COMPARISON WITH MBER AVOIDED CROSSING EXPERIMENTS

The MBER avoided crossing results to be considered here all involve measurements on symmetric top molecules.¹⁶ Thus, it is convenient to consider matrices of H_0 and $V(t)$ of Eq. (1) in a symmetric top basis set $|\gamma_j J_j K_j M_j\rangle$, with $j = a$ or b . (In this section, basis set functions will be labeled by the letters a and b ; eigenfunctions of H_0 will be labeled by the numerals 1 and 2.) The quantum numbers K and M are projections along the molecule-fixed z axis and the laboratory-fixed Z axis, respectively, of the total angular momentum J (exclusive of nuclear spin); γ represents a collection of all other quantum numbers for the molecule.

The matrix of H_0 in the a, b basis set has the form²⁻⁴

$$H_0 = \begin{bmatrix} -\mu[K_a M_a / J(J+1)](E_{ST} - E_c), & (1/2)\hbar\omega_c \\ (1/2)\hbar\omega_c, & -\mu[K_b M_b / J(J+1)](E_{ST} - E_c) \end{bmatrix}, \quad (14)$$

where we have taken μ as the permanent dipole moment of the molecule. As is appropriate for the particular anticrossing experiments to be considered here, $K_a \neq K_b$ and $J_a = J_b = J$. Diagonal elements of this matrix represent the Stark effect of the static (dc) electric field E_{ST} along the laboratory-fixed Z direction, which is used to tune the two levels into energy coincidence at the crossing field E_c . (The origin of energy has arbitrarily been taken to lie at the energy of this crossing.) No off-diagonal elements arise from the permanent moment because its matrix elements obey the selection rule $\Delta K = 0$. The off-diagonal elements in ω_c represent the small interaction ($\omega_c/2\pi \lesssim 250$ kHz) which induces the avoided crossing. These off-diagonal elements may arise from higher order dc Stark effects, from hyperfine interactions, etc., but they do not arise from interaction terms proportional to some power of the ac electric field. It is of interest that the effects of several of these weak off-diagonal interactions can only be seen in the presence of a static electric field of appropriate size to bring the two weakly interacting levels into near resonance.

The matrix of $V(t)$ in the a, b basis set, i.e., the matrix for

an oscillating electric field along the laboratory-fixed Z axis with amplitude E and frequency ω , has the form

$$V(t) = \begin{bmatrix} -\mu[K_a M_a / J(J+1)]E \cos \omega t, & 0 \\ 0, & -\mu[K_b M_b / J(J+1)]E \cos \omega t \end{bmatrix}. \quad (15)$$

The unitary transformation which diagonalizes H_0 of Eq. (14) is given by the matrix

$$U = \begin{bmatrix} +\cos \theta & -\sin \theta \\ -\sin \theta & -\cos \theta \end{bmatrix}, \quad (16)$$

where the rows of U are labeled by the symmetric top basis functions a and b , and the columns are labeled by the eigenfunctions 1 and 2 of H_0 . The angle θ and other quantities to be used below are defined by

$$\begin{aligned} \bar{\mu}_{KM} &\equiv + (1/2)\mu(K_a M_a + K_b M_b) / J(J+1), \\ \Delta\mu_{KM} &\equiv + \mu(K_b M_b - K_a M_a) / J(J+1), \\ \hbar\omega_0 \cos 2\theta &\equiv -\Delta\mu_{KM}(E_{ST} - E_c), \\ \hbar\omega_0 \sin 2\theta &\equiv +\hbar\omega_c \end{aligned} \quad (17)$$

$$\hbar\omega_0 = + [\Delta\mu_{KM}^2 (E_{ST} - E_c)^2 + (\hbar\omega_c)^2]^{1/2}.$$

The quantity $\hbar\omega_0$ is the actual energy difference $E_2 - E_1$ in the molecule at any given static field E_{ST} . The quantity $\Delta\mu_{KM}/h$ is called s_C in Eq. (10) of Ref. 4; it or its negative [depending on the signs of various quantities in Eqs. (17)] represents the Stark tuning rate $\partial(\omega_0/2\pi)/\partial E_{ST}$ of the molecular transition frequency, provided that the static field is far from the crossing.

The diagonalized Hamiltonian $\tilde{H}_0 = U^{-1}H_0U$ has the form

$$\begin{aligned} \tilde{H}_0 &= -\bar{\mu}_{KM}(E_{ST} - E_c) \begin{bmatrix} +1 & 0 \\ 0 & +1 \end{bmatrix} \\ &+ (1/2)\hbar\omega_0 \begin{bmatrix} -1 & 0 \\ 0 & +1 \end{bmatrix}, \end{aligned} \quad (18)$$

and $\tilde{V}(t) = U^{-1}V(t)U$ has the form

$$\begin{aligned} \tilde{V}(t) &= -\bar{\mu}_{KM}E \cos \omega t \begin{bmatrix} +1 & 0 \\ 0 & +1 \end{bmatrix} \\ &- (1/2)\Delta\mu_{KM}E \cos \omega t \begin{bmatrix} -\cos 2\theta & +\sin 2\theta \\ +\sin 2\theta & +\cos 2\theta \end{bmatrix}, \end{aligned} \quad (19)$$

where rows and columns of the matrices in Eqs. (18) and (19) are labeled by the eigenvectors 1 and 2 of H_0 .

Comparison of various equations in this and the preceding section shows that the matrix elements $V_{jk}(t)$ of Eqs. (5) correspond to the matrix elements $\tilde{V}_{jk}(t)$ of Eq. (19). The quantities μ_{jk} in Eqs. (6) thus become

$$\begin{aligned} \mu_{jj} &= \bar{\mu}_{KM} + (-1)^j (1/2)\Delta\mu_{KM} \cos 2\theta, \\ \mu_{12} &= \mu_{21} = + (1/2)\Delta\mu_{KM} \sin 2\theta. \end{aligned} \quad (20)$$

In the avoided crossing experiments, the n photon transition probability is given by Eq. (13) with ω_0 given by the last of Eqs. (17) and

$$x = n\omega \tan 2\theta J_n(\Delta\mu_{KM} \cos 2\theta E / \hbar\omega). \quad (21)$$

There are two limiting cases of interest here for x . For transitions far from the avoided crossing, i.e., when $\omega_0 \gg \omega_c$ in Eqs. (17), $\sin 2\theta$ is very small and $|\cos 2\theta|$ is near unity. This represents the case for most of the measurements in the avoided crossing studies.²⁻⁴ On the other hand, for transi-

tions very close to the avoided crossing, i.e., when $E_{ST} \cong E_c$ in Eqs. (17), $\cos 2\theta$ is very small and $\sin 2\theta$ is near unity. Since both the Stark tuning rate $\partial(\omega_0/2\pi)/\partial E_{ST}$ and the ac Stark effect of the molecular transition (though not of the individual energy levels) approach zero in this limit, the values $\cos 2\theta = 0$ and $\sin 2\theta = 1$ correspond to the more traditional two-level coherent excitation treatments.^{1,10} This can also be seen from the fact that this limit leads to a value for x in Eq. (21) which agrees with the matrix element given in Eq. (12) of Ref. 4. In this connection we note that the present mechanism requires all multiphoton transitions to vanish right at the avoided crossing.

Table I gives a summary of the experimental measurements and some theoretical quantities for the molecule OPF₃. The first column of the table gives the quantum numbers (J', K', M')–(J'', K'', M'') of the two rotational states participating in the avoided crossing, and the Stark tuning rate $|\Delta\mu_{KM}/h|$ in kHz/(V/cm). The second, third, and fourth columns in Table I give the integer number n of photons required for resonant absorption, the applied radio oscillator frequency $\nu = \omega/2\pi$ in MHz, and the molecular transition frequency $\nu_0 = \omega_0/2\pi$ in MHz, respectively. The fifth column gives the value of the static electric field E_{ST} in V/cm at which the molecular transition assumes a frequency of ν_0 .

It can be seen from columns 2–5 that two types of measurements were carried out. In one type of measurements, the molecular transition frequency ν_0 was held constant (by keeping E_{ST} constant) and the applied radio-frequency ν was varied. In the other type of measurements, the applied radio-frequency ν was held constant and the molecular transition frequency was varied (by adjusting E_{ST}).

Column 6 gives the amplitude of the radio-frequency field $E_{opt}^{(n)}$ required to maximize the molecular beam flop-out signal¹ for each n -photon transition. The experimental uncertainty in $E_{opt}^{(n)}$ is 10% to 20%, since its measurement involves determining the top of a rather flat and somewhat noisy intensity maximum. The half-width $\Delta\nu_n$ for an n -photon transition observed with $E_{opt}^{(n)}$ was approximately $1/n$ times the width $\Delta\nu_1$ for the corresponding one-photon transition observed with $E_{opt}^{(1)}$.

Column 7 gives an unsigned value for the argument z appearing in the Bessel function $J_n(z)$ of Eq. (21), i.e., gives

$$z = |\Delta\mu_{KM} \cos 2\theta E_{opt}^{(n)} / \hbar\omega|. \quad (22)$$

For preliminary calculations, $|\cos 2\theta|$ was set equal to unity. This approximation is reasonably well satisfied, since $\sin 2\theta$ in Eqs. (17) has a value of ω_c/ω_0 , and this latter ratio does not exceed 0.1 for the measurements reported in Table I. Column 8 gives the value of $J_n(z)$ for each measurement, as taken from tables¹⁴ or from the computer program DBSINS of the IMSL library.¹⁵

The present interpretation of the multiphoton absorptions indicates that the observed values of $E_{opt}^{(n)}$ can be used to determine $\nu_c = \omega_c/2\pi$ as follows. In the experiments reported here, the length l of the transition region is 6.2 cm, and the molecular velocity v is 550 m/s. These parameters determine the optimum value for $x = \pi v/l$, which when used together with Eq. (21) and n , ω , and $J_n(z)$ from Table I,

leads to a value for $\tan 2\theta$. This latter quantity, used together with the definitions in Eqs. (17) then gives a value for the parameter $\nu_c = \omega_c/2\pi$. It is necessary, however, to carry out this procedure in an iterative fashion: (i) set the magnitude of $\cos 2\theta$ equal to unity in Eq. (22) for the argument z of J_n , (ii) use Eq. (21) to determine a value for $\tan 2\theta$, (iii) use this value of $\tan 2\theta$ to obtain an improved value for $\cos 2\theta$ in the argument of J_n , (iv) continue the iteration procedure. It is the converged values of z , obtained after several iterations, that are actually given in column 7 of Table I.

Column 9 of Table I gives the values for the minimum energy spacing ν_c (right at the avoided crossing) obtained from this iterative procedure. These values can be compared with the more accurate values in column 10, which are obtained from Eqs. (13) and (23) of Ref. 4

$$\nu_c = \mu_D E_c m_J [(J-1)(J+2)]^{1/2}, \quad (23)$$

together with the values for μ_D and E_c given there. While the agreement is not outstanding, it is probably as good as can be expected, since the values of ν_c in column 9 are determined from intensity, rather than frequency, measurements and are thus subject to the large experimental errors mentioned above. Comparison of columns 9 and 10 indicates that intensity measurements of the present type can be used to determine ν_c to about a factor of 2. This method could thus be useful in cases where ν_c is too small to be determined by the direct frequency measurement technique.⁴

The reasonable agreement between ν_c values in columns 9 and 10, as well as the approximate constancy of the values of $J_n(z)$ within each group of multiphoton transitions, provides good evidence that the present explanation for these observed multiphoton results is correct.

For most of the n -photon experiments reported in Table I, the one-photon signal intensity could be fully recovered. For the sequence of measurements with superscripts j in Table I, however, the intensity was observed to fall off with increasing n . From a theoretical point of view, the values of $J_n(z)$ calculated from the measured values of $E_{opt}^{(n)}$ were actually the maximum allowed for each Bessel function, implying that while the transition probability was maximized, it was probably *not* unity. Thus, if l/v could have been made larger, then even stronger MBER signals could probably have been achieved. This statement applies even to the one-photon case in this sequence of measurements.

Better evidence for this effect is given in Table II, where we present a series of relative intensity measurements for multiphoton transitions in CH₃CF₃ with n ranging from 1–40. The experimental intensities were normalized such that the $n = 1, 2$, and 3 photon transitions, which were observed to be equally strong, all correspond to 100%. The theoretical intensities were normalized by assuming that the “true” value of J_n for unit transition probability in the MBER apparatus is $(J_1 + J_2 + J_3)/3 = 0.46$. (The 25% spread in the values of J_1, J_2 and J_3 gives a measure of the experimental uncertainty.) Theoretical intensities were thus calculated from the expression $\sin^2[(J_n/0.46)(\pi/2)]$. It can be seen that the experimental and theoretical intensities are in very good agreement.

From the discussion above, it is clear that a threshold

TABLE I. Comparison of multiphoton theory and experiment for OPF_3 .

Transition ^a	n^b	ν^b	ν_0^c	E_{ST}^c	$E_{\text{opt}}^{(n)d}$	z^e	$J_n(z)^e$	ν_c^f	ν_c^g
$(3, \pm 2, \pm 3)-(3, \mp 1, \pm 3)$ $s_C = 704.5 \text{ kHz cm/V}$	1	2236	2236	922.633 ^h	1.729	0.545	0.26	17	26
	2	1118	2236	922.633	2.554	1.609	0.26	17	
	3	745	2236	922.633	3.300	3.121	0.33	13	
$(3, \pm 2, \pm 2)-(3, \mp 1, \pm 2)$ $s_C = 472.3 \text{ kHz cm/V}$	1	250	250	926.161 ⁱ	0.216	0.608	0.29	15	
	2	250	500	926.518	0.550	1.549	0.24	18	
	4	250	1000	927.228	1.572	4.430	0.34	13	
	1	250	250	926.117 ⁱ	0.236	0.664	0.31	14	
	2	250	500	926.468	0.629	1.772	0.30	15	
	4	250	1000	927.176	1.768	4.982	0.39	11	
	8	250	2000	928.595	3.143	8.857	0.30	15	
	4	250	1000	1386.789	1.886	3.562	0.21	21	
$(2, \pm 2, \pm 2)-(2, \mp 1, \pm 2)$ $s_C = 938.4 \text{ kHz cm/V}$	1	250	250	695.003	0.236	0.885	0.40	11	8
	2	250	500	695.270	0.629	2.361	0.43	10	
	4	250	1000	695.803	1.336	5.015	0.39	11	
$(2, \pm 2, \pm 1)-(2, \mp 1, \pm 1)$ $s_C = 483.8 \text{ kHz cm/V}$	1	250	250	1368.687	0.943	1.824	0.58 ^j	8	8
	2	250	500	1369.204	1.572	3.041	0.49 ^j	9	
	4	250	1000	1370.237	2.357	4.561	0.36 ^j	12	
$(4, \pm 2, \pm 4)-(4, \mp 1, \pm 4)$ $s_C = 563.9 \text{ kHz cm/V}$	1	1875	1875	1153.566	0.707	0.213	0.106	42	58
	2	938	1875	1153.566	1.572	0.945	0.104	43	
	3	625	1875	1153.566	2.357	2.127	0.150	30	
$(5, \pm 2, \pm 5)-(5, \mp 1, \pm 5)$ $s_C = 470.0 \text{ kHz cm/V}$	1	2050	2050	1383.615	0.471	0.108	0.054	82	108
	2	1025	2050	1383.615	1.572	0.721	0.062	72	
	3	683	2050	1383.615	2.200	1.513	0.062	72	

^a $(J', K', M')-(J'', K'', M'')$ are quantum numbers for the two states involved in the avoided crossing. The quantity $s_C = |\Delta\mu_{KM}/h|$ is the Stark tuning rate from Eqs. (17).

^bThe number of photons n of the radio-frequency $\nu = \omega/2\pi$ in MHz absorbed at resonance.

^cThe molecular transition frequency $\nu_0 = \omega_0/2\pi$ in MHz, from Eqs. (17), and the corresponding dc Stark field E_{ST} in V/cm.

^dThe radio-frequency electric field amplitude in V/cm necessary to maximize the MBER signal. Errors in these amplitudes are estimated to be from 10% to 20%.

^eThe argument z from Eq. (22) of the n th-order Bessel function in Eq. (21), and the value of that Bessel function.

^fThe value of ν_c , as obtained from Eqs. (17) and (21). The value of ν_c should be a constant for all measurements on a given $(J', K', M')-(J'', K'', M'')$ transition.

^gA much more accurate value of ν_c from Eqs. (13) and (23) of Ref. 4.

^hTransitions studied below the avoided crossing.

ⁱTransitions studied above the avoided crossing. These two sets were studied on different days with different polarities, and the $\sim 50 \text{ mV/cm}$ differences in corresponding E_{ST} values reflect a small contact potential. The small correction is not relevant here and has not been made.

^jMaximum (or near maximum) value of $J_n(z)$, implying that these Bessel functions cannot achieve a large enough value to make the MBER transition probability unity.

exists for ν_c below which the transition probability cannot be made unity, even for a one-photon transition. In order that $|a_2(t)|^2 = 1$ at $E_{\text{opt}}^{(n)}$, it is necessary that $|x|l/v = \pi$. Far from the crossing, this condition can be rewritten as $2\nu_c J_n l/v = 1$. The smallest value of ν_c for which the $n = 1$ transition probability can be made unity is thus

$$(\nu_c)_{\min} = v/2l(J_1)_{\max} \cong 7.6 \text{ kHz.} \quad (24)$$

For values of ν_c significantly smaller than $(\nu_c)_{\min}$, the one-photon MBER signal may disappear into the noise. As mentioned in Sec. II, this cutoff does not arise in the conventional line shape analysis, which does not take into account the ac Stark effect. It is hoped that this cutoff phenomenon can be used to explain the failure to observe a number of expected

avoided crossing signals in symmetric top molecules exhibiting internal rotation splittings.¹⁸⁻²⁰

IV. APPLICATION TO OTHER EXPERIMENTS

It is of interest to ask whether the multiphoton mechanism discussed in the present paper plays a role in other two-level coherent excitation problems.

It is clear that it will play a role in some MBER experiments in which $\Delta M = \pm 1$ transitions are studied, since in many cases the oscillating rf field is not applied exactly perpendicular to the axis of quantization Z , but is instead generated²¹ by using a "split C field," which leads to a large component of the rf field in the Z direction in addition to the desired component in the X direction. In those cases, for

TABLE II. Comparison of theory and experiment^a for multiphoton intensities in CH₃CF₃.

Transition	<i>n</i>	<i>v</i>	<i>v</i> ₀	<i>E</i> _{ST}	<i>E</i> _{opt} ^(<i>n</i>)	<i>z</i>	<i>J_n</i> (<i>z</i>) ^b	Int ^c	Int ^d
(3, ±2, ±3)–(3, ∓1, ±3)	1	227	227	1062.969	0.346	1.347	0.53	1.00	0.94
<i>s_c</i> = 884.5 kHz cm/V	2	227	454	1063.225	0.605	2.356	0.42	1.00	0.98
	3	227	681	1063.486	1.037	4.041	0.43	1.00	0.99
<i>v_c</i> ^e = 10 kHz	4	227	908	1063.742	1.241	4.836	0.38	0.94	0.93
	5	227	1135	1064.000	1.454	5.665	0.34	0.83	0.84
<i>v_c</i> ^f = 16 kHz	10	227	2270	1065.282	2.852	11.113	0.29	0.67	0.70
	20	227	4540	1067.848	5.359	20.881	0.21	0.46	0.43
	40	227	9080	1072.986	10.372	40.414	0.15	0.27	0.24

^aSee the footnotes to Table I for an explanation of the column headings.

^bThe experimentally determined value of each *n*th-order Bessel function *J_n* in this column is equal or nearly equal to the maximum value for that Bessel function.

^cExperimental relative intensity measurements.

^dTheoretical relative intensity estimates, obtained from $\sin^2\{[J_n(z)/0.46](\pi/2)\}$, where the value 0.46 in the denominator is equal to the average $(J_1 + J_2 + J_3)/3$.

^eValue of the minimum separation *v_c*, as obtained from Eqs. (17) and (21).

^fMore accurate value of *v_c* from Eq. (23) of Ref. 4 and molecular parameters of Ref. 17.

molecules with a first order Stark effect, multiphoton transitions can be induced via a mechanism essentially identical to that described above.

In a similar manner, a large ac Zeeman effect can lead to the observation of multiphoton magnetic dipole transitions in a molecular beam. Typically, ± 1 transitions are studied in a large static magnetic field **H**₀ taken to be in the *Z* direction. The rf coil used to drive the transitions is oriented so that the oscillating magnetic field **H**₁ produced is perpendicular to **H**₀. Although ideally **H**₁ lies in the *XY* plane, in practice it can have a significant *Z* component. This produces the diagonal matrix elements which can lead to multiphoton transitions by means of the mechanism described above. A case in point is a recent study²² of O₂. While this system presents other theoretical complexities because of the presence of sets of (2*J* + 1) equally spaced levels,²³ multiphoton transitions with the properties discussed above can be clearly observed for *n* = 2 and 3 when the rf power is raised above the level required for the single photon case.

Two-photon magnetic-dipole transitions have been reported recently in electron-spin resonance experiments²⁴ and in electron-nuclear spin double resonance studies.²⁵ In the former, the oscillating field **H**₁ was set at $\pi/4$ to the *Z* axis in the *XZ* plane, while in the latter the internal field rotated the effective static field so that it had a significant component along **H**₁. The possibility of such multiphoton transitions associated with the parallel component of **H**₁ was first pointed out by Winter.²⁶ An analysis using a doubly rotating frame and Bloch-like equations has been developed.²⁷ The alternative approach used here and in the analysis of high-intensity laser experiments⁶⁻⁹ may be useful in these magnetic resonance studies as well.

It is also of interest to ask to what extent the two-level mechanism described above contributes to vibrational multiphoton transitions in the infrared region. For that purpose we consider the quantity

$$\sin^2(xt/2) = \sin^2\{(\omega t)[\mu_{12}/(\mu_{22} - \mu_{11})] \times J_n[(\mu_{22} - \mu_{11})E/\hbar\omega]\}, \quad (25)$$

which gives the probability as a function of time *t* that a system initially in state 1 was pumped into state 2 by resonant absorption of *n* photons.

To obtain a numerical estimate for a favorable case of this probability for an infrared multiphoton transition in a molecule with no permanent dipole moment, we can set $\omega/2\pi \sim 3 \times 10^{13} \text{ s}^{-1}$ (CO₂ laser radiation), and $\mu_{11} = 0$. If we further make the reasonable assumptions that: (i) the (*v* = *n*) – (*v* = 0) overtone transition dipole moment μ_{12} is approximately given by $10^{-n/2} \text{ D}$, (ii) the vibrationally induced^{28,29} dipole moment μ_{22} of the (degenerate) excited vibrational state is $\sim 10^{-2} \text{ D}$, (iii) the infrared laser power is $\sim 10 \text{ GW/cm}^2$, corresponding to $\mu_{22}E/\hbar \sim 10^{13} \mu_{22} [\text{s}^{-1} \text{ D}^{-1}]$, and (iv) the laser pulse duration *t* is 10^{-7} s , then, using also the approximate expression¹⁴ for a Bessel function *J_n*(*z*) for small values of its argument *z*, we find that

$$\sin^2(xt/2) \sim \sin^2[10^{9-4n}/(n-1)!]. \quad (26)$$

From this expression we see that the probability of a two-photon transition would be unity for even lower laser powers or even shorter laser pulses, but that the probability of a three-photon transition drops dramatically to 10^{-7} . Since a vibrationally induced dipole moment cannot occur in molecules with a center of symmetry,^{28,29} Eq. (26) cannot be applied at all to the extensively studied class of molecules like SF₆ belonging to the point group O_h. Even for molecules like SiF₄, belonging to the point group T_d, it seems unlikely that the present mechanism will be of general importance for inducing three or more photon transitions in the infrared region.

Investigation of a molecule with a permanent dipole moment, however, might permit experimental observation in the midinfrared region of the mechanism described in this paper. For example, if ($\mu_{22} - \mu_{11}$) takes on a value of 1 D, instead of 10^{-2} D , then Eq. (25) becomes

$$\sin^2(xt/2) \sim \sin^2[10^{7-2n}/(n-1)!]. \quad (27)$$

Under these circumstances, a three-photon transition would

have a high probability, while a four-photon transition would have a probability of 10^{-4} .

Fourier transform microwave spectroscopy³⁰ offers another possibility for observing multiphoton transitions arising from the mechanism discussed above. For the instrument described by Campbell *et al.*,³¹ a power R of 1.5 mW put into the Fabry–Perot cavity with a Q of 6300 at 10 GHz leads to an amplitude of 1 V/cm for the electric field. For the transition $(J = 2, K = 1, M = 1) \leftarrow (J = 1, K = 1, M = 1)$ in a molecule with a dipole moment of 1 D, a power R of about 240 W with an excitation pulse length of 2 μ s is required to make the two-photon transition probability equal to unity. By raising the Q by a factor of 3, the power required is reduced to < 30 W. Thus, by putting in pulses at 10 GHz, it should be possible to observe molecular emission at 20 GHz. Among other things, this technique would extend the frequency range of the spectrometer for molecules with large first order Stark effects by a factor of 2.

ACKNOWLEDGMENTS

The authors are greatly indebted to Dr. Liwen Pan for introducing them to a number of two-level multiphoton treatments in the high-intensity laser–atom interaction literature, and to Dr. A. Schweiger and Dr. D. W. Pratt for helpful discussions of the ESR/ENDOR literature. The authors also wish to express their appreciation to Dr. J. Reuss for bringing his O₂ magnetic dipole multiphoton observations to their attention, and to Dr. A. Bauder for fruitful discussions concerning the application of the multiphoton mechanism to Fourier transform microwave experiments. One of the authors (I.O.) expresses his appreciation to the Natural Sciences and Engineering Research Council of Canada for its support.

¹N. F. Ramsey, *Molecular Beams* (Oxford University, London, 1956).

²I. Ozier and W. L. Meerts, *Phys. Rev. Lett.* **40**, 226 (1978).

³W. L. Meerts and I. Ozier, *Phys. Rev. Lett.* **41**, 1109 (1978).

⁴I. Ozier and W. L. Meerts, *Can. J. Phys.* **59**, 150 (1981).

⁵T. C. English and J. C. Zorn, in *Methods of Experimental Physics*, Vol. 3, Part B, edited by Dudley Williams (Academic, New York, 1974).

⁶D. R. Dion and J. O. Hirschfelder, *Adv. Chem. Phys.* **35**, 265 (1976).

⁷J. E. Bayfield, *Phys. Rep.* **51**, 317 (1979).

⁸B. A. Zon and E. I. Sholokhov, *Sov. Phys. JETP* **43**, 461 (1976).

⁹W. J. Meath and E. A. Power, *Mol. Phys.* **51**, 585 (1984).

¹⁰K. Shimoda, *Introduction to Laser Physics*, 2nd ed. (Springer, Berlin, 1986).

¹¹J. K. G. Watson, *J. Mol. Spectrosc.* **50**, 281 (1974).

¹²H. C. Torrey, *Phys. Rev.* **59**, 293 (1941).

¹³C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

¹⁴M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).

¹⁵Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental and theoretical procedures. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards of the United States, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

¹⁶G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, Princeton, 1945).

¹⁷N. Moazzen-Ahmadi and I. Ozier, *J. Mol. Spectrosc.* **126**, 99 (1987); W. L. Meerts and I. Ozier, Symposium on Molecular Spectroscopy, The Ohio State University, Paper MG6, June, 1978.

¹⁸W. L. Meerts and I. Ozier, *Chem. Phys.* **71**, 401 (1982).

¹⁹W. L. Meerts and I. Ozier, *J. Mol. Spectrosc.* **94**, 38 (1982).

²⁰I. Ozier and W. L. Meerts, *Can. J. Phys.* **62**, 1844 (1984); **63**, 1375 (1985).

²¹F. H. de Leeuw and A. Dymanus, *J. Mol. Spectrosc.* **48**, 427 (1973).

²²J. Reuss (private communication); P. Verhoeve, Doctoral thesis, (Katholieke Universiteit Nijmegen, 1985) (unpublished).

²³A. Amirav, U. Even, J. Jortner, and L. Kleinman, *J. Chem. Phys.* **73**, 4217 (1980).

²⁴R. Boscaino, F. M. Gelardi, and G. Messina, *Phys. Rev. A* **28**, 495 (1983).

²⁵P. F. Brode III and D. W. Pratt, *Chem. Phys. Lett.* **59**, 334 (1978).

²⁶J. M. Winter, *J. Phys. Rad.* **19**, 802 (1958).

²⁷R. Boscaino and G. Messina, *Physica C* **138**, 179 (1986).

²⁸M. Mizushima and P. Venkateswarlu, *J. Chem. Phys.* **21**, 705 (1953).

²⁹I. M. Mills, J. K. G. Watson, and W. L. Smith, *Mol. Phys.* **16**, 329 (1969).

³⁰J. Ekkers and W. H. Flygare, *Rev. Sci. Instrum.* **47**, 448 (1976).

³¹E. J. Campbell, L. W. Buxton, T. J. Balle, M. R. Keenan, and W. H. Flygare, *J. Chem. Phys.* **74**, 829 (1981).