Electric Resonance Transitions in a Tapered Electric Field*

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(Received August 20, 1952)

In this paper we investigate the broadening of the spectral lines produced by small inhomogeneities in the homogeneous C-field of the molecular beam electric resonance apparatus. To do so, we represent the inhomogeneities as an arbitrary function of time because of the flight of the molecules through the field. The transitions which we investigate occur between states which are the instantaneous solutions of the Stark effect problem in which we neglect the effects of nuclear molecular interactions. We obtain a solution for the probability amplitudes for a transition such that $\Delta J=0$ and $\Delta m=\pm 1$ by considering a linear combination of the solutions for the case in which there are no inhomogeneities. As an example, we consider the inhomogeneity of the C-field as represented by a linear taper. In this case the amount of line broadening depends on the ratio of the amplitude of the taper to the amplitude of the radio frequency field which induces the transitions. Because under optimum operating conditions the product of the rf field and the homogeneous field is kept constant, the inhomogeneities have a greater effect in strong than in weak C-fields. The line broadening, however, is considerably smaller than one might estimate from the energy level difference computed for two perfectly hodogeneous fields having respectively field intensities equal to the two extreme values of the tapered field.

IN the electric resonance method of molecular beam spectroscopy,[1] broadening of the spectral lines has been observed in strong fields. This broadening has been attributed to small inhomogeneities in the homogeneous field (C-field) of the molecular beam apparatus.[2] Inasmuch as the determination of the physically interesting parameters of a molecule—electric dipole moment, moment of inertia, nuclear quadrupole moments, etc.—depends on the resolution of the fine and hyperfine structure of the broad lines observed, we have attempted to obtain quantitative information on the degree of broadening of the line profile on account of inhomogeneities in the C-field. In our calculations we have represented this inhomogeneity as a change in the C-field *with time*, because of the flight of the molecule through the field. To simplify matters, we have neglected the effects of the nuclear quadrupole moment; our methods can be modified to include such effects, but the calculations become considerably more laborious. In our opinion, this simplification does not destroy the essentials of the situation.

If a molecule is in a constant electric field $\mathcal{E}$, the separation of its energy levels remains fixed. If we impose an oscillating field $\mathcal{E}_x \cos\omega t$ at right angles to $\mathcal{E}$, such that $\hbar\omega$ is equal to the energy separation of two states with different spatial quantization, transitions will be induced between these states in a regular and predictable manner.[1] If a small inhomogeneity $f(t)$ is added to the constant field, the energy levels will shift adiabatically as long as df/dt is sufficiently small. A molecule exposed to this field for a time τ will no longer be near resonance for the entire time of exposure. Moreover, since the resonance frequency changes in time, the molecule will be near resonance (at least for a small interval of time) over a greater range of frequencies of the oscillating field than is the case in a perfectly homogeneous field. Therefore, one would expect, even without detailed calculations, that the peaks of the spectral lines should be decreased as well as their widths broadened by the presence of a small inhomogeneity.

To show these effects explicitly, we must solve the time dependent Schrödinger equation,

$$[J^2\hbar^2/2I-\mu_z(\mathcal{E}+f(t))-\mu_x\mathcal{E}_x\cos\omega t]\Psi=i\hbar\partial\Psi/\partial t, \quad (1)$$

where J is the total angular momentum, μ is the effective molecular dipole moment, and I is the moment of inertia of the molecule. In the absence of an oscillating field, the last term in the Hamiltonian does not appear. Therefore, transitions will occur between those states which are instantaneous solutions of the Stark effect problem,

$$[J^2\hbar^2/2I-\mu_z(\mathcal{E}+f(t))]\psi_{Jm}=E_{Jm}\psi_{Jm}, \quad (2)$$

provided the selection rules are satisfied. The first index refers to the rotational quantum state and the second to the space quantization of the molecule.

In order to solve the full time dependent problem stated in Eq. (1), we expand Ψ in terms of the ψ_{Jm} with time dependent coefficients:

$$\Psi=\sum_{J'm'} a_{J'm'}(t)\psi_{J'm'}(t)\exp\left[-\frac{i}{\hbar}\int E_{J'm'}dt\right]. \quad (3)$$

By substituting the expansion (3) into Eq. (1), we obtain

* This paper incorporates the major results of a Master's dissertation by one of us (JNG), which was accepted by the Graduate School of Syracuse University in 1950.

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[1] H. K. Hughes, Phys. Rev. **72**, 614 (1947).

[2] J. W. Trischka, Phys. Rev. **74**, 718 (1948).

differential equations for the coefficients a_{Jm}:

$$\dot{a}_{Jm}=\sum_{J'm'}\left\{\langle Jm|\mu_x\mathcal{E}_x|J'm'\rangle\cos\omega t-i\hbar\left\langle Jm\left|\frac{\partial}{\partial t}\right|J'm'\right\rangle\right\}a_{J'm'}\times\exp\left[\frac{i}{\hbar}\int(E_{Jm}-E_{J'm'})dt\right]. \quad (4)$$

The instantaneous Stark effect wave functions, ψ_{Jm}, are linear combinations of ordinary states of a rigid rotator belonging to different values of the quantum number J. If we continue to label stationary levels with a quantum number J, then this quantum number is not quite identical with the usual one describing the total angular momentum of the molecule. As a result, transitions with $\Delta J=0$ and $\Delta m=\pm1$ are permissible. Therefore, we shall consider the case where ψ_{Jm} is the initial state and $\hbar\Omega=E_{Jm}-E_{Jm+1}-\hbar\omega\approx0$. All terms in Eqs. (4) which do not have Ω in the exponent may be neglected as they contribute little to the result. Equations (4) thereby reduce to a pair of simultaneous differential equations. Dropping the subscript J, they are:

$$i\hbar\dot{a}_m=\tfrac{1}{2}h_{10}a_{m+1}\exp\left(i\int\Omega dt\right),$$
$$i\hbar\dot{a}_{m+1}=\tfrac{1}{2}h_{10}a_m\exp\left(-i\int\Omega dt\right), \quad (5)$$

where

$$h_{10}=\langle J, m+1|\mu_x\mathcal{E}_x|Jm\rangle. \quad (6)$$

If the degenerate states with m equal to ±1 are involved, both must be taken into account as transitions can occur to either from the state with $m=0$. The only resulting change in Eqs. (5) is that the right-hand side of the first of these equations is multiplied by 2. Hereafter we shall consider m unequal to zero unless otherwise specified.

If $f(t)$ is sufficiently small, one would not expect the line shape to be seriously affected. Since this condition is satisfied in the experimental set-up, we shall look for a solution as a linear combination of the instantaneous solutions of Eq. (5). These solutions are of the form:

$$a_m\sim c_0\exp\left[\tfrac{1}{2}i\int(\Omega\pm R)dt\right],$$
$$a_{m+1}\sim c_1\exp\left[\tfrac{1}{2}i\int(-\Omega\pm R)dt\right], \quad (7)$$

where $R=(\Omega^2+h_{10}^2/\hbar^2)^{\frac{1}{2}}$. Each probability amplitude, in the homogeneous case, is the sum of two exponential terms, differing by the sign of R in (7). In this case, each exponential would satisfy Eq. (5) separately. However, in the presence of inhomogeneities the two terms will combine. There are two linearly independent solutions of the homogeneous case which separate these different exponentials explicitly:

$$\Psi^+=c_0^+\exp\left[\tfrac{1}{2}i\int(\Omega+R-E_m/\hbar)dt\right]\psi_m+c_1^+\exp\left[\tfrac{1}{2}i\int(-\Omega+R-E_{m+1}/\hbar)dt\right]\psi_{m+1},$$
$$\Psi^-=c_0^-\exp\left[\tfrac{1}{2}i\int(\Omega-R-E_m/\hbar)dt\right]\psi_m+c_1^-\exp\left[-\tfrac{1}{2}i\int(\Omega+R+E_{m+1}/\hbar)dt\right]\psi_{m+1}. \quad (8)$$

The coefficients c_0^+, c_0^-, c_1^+, and c_1^- are determined by Eqs. (5) and the requirement that Ψ^+ and Ψ^- be normalized:

$$c_0^+=h_{10}[h_{10}^2+\hbar^2(\Omega+R)^2]^{-\frac{1}{2}},$$
$$c_0^-=h_{10}[h_{10}^2+\hbar^2(\Omega-R)^2]^{-\frac{1}{2}},$$
$$c_1^+=-\hbar(\Omega+R)[h_{10}^2+\hbar^2(\Omega+R)^2]^{-\frac{1}{2}},$$
$$c_1^-=-\hbar(\Omega-R)[h_{10}^2+\hbar^2(\Omega-R)^2]^{-\frac{1}{2}}. \quad (9)$$

We now write the solution of Eq. (1) as a linear combination of Ψ^+ and Ψ^- with time dependent coefficients:

$$\Psi=b_1(t)\Psi^++b_2(t)\Psi^-. \quad (10)$$

A comparison of Eqs. (10) and (8) with Eq. (3) shows that the probability amplitudes a_m and a_{m+1} are related to the coefficients b_1 and b_2 as follows:

$$a_m=b_1c_0^+\exp\left[\tfrac{1}{2}i\int(\Omega+R)dt\right]+b_2c_0^-\exp\left[\tfrac{1}{2}i\int(\Omega-R)dt\right],$$
$$a_{m+1}=b_1c_1^+\exp\left[\tfrac{1}{2}i\int(-\Omega+R)dt\right]+b_2c_1^-\exp\left[-\tfrac{1}{2}i\int(\Omega+R)dt\right]. \quad (11)$$

Substituting Eq. (10) into (1), we obtain a pair of differential equations for b_1 and b_2:[3]

$$\dot{b}_1=-b_2(c_0^+\dot{c}_0^-+c_1^+\dot{c}_1^-)\exp\left(-i\int Rdt\right),$$
$$\dot{b}_2=b_1(c_0^+\dot{c}_0^-+c_1^+\dot{c}_1^-)\exp\left(i\int Rdt\right). \quad (12)$$

[3] These equations have been simplified by means of the orthonormality conditions of Ψ^+ and Ψ^-. These conditions result in the following relations for the coefficients:

$$(c_0^+)^2+(c_1^+)^2=1,$$
$$(c_0^-)^2+(c_1^-)^2=1,$$
$$c_0^+c_0^-+c_1^+c_1^-=0.$$

The above equations show clearly that when $f(t)$ is identically zero $\dot{b}_1$ and $\dot{b}_2$ do indeed vanish. That is, the solution would reduce to that for a constant field, as it should. Since $f(t)$ is much smaller than the steady field, we say that b_1 and b_2 will not differ much from the homogeneous field solution. Therefore, we can apply the method of successive approximations to obtain a solution of Eqs. (12). We shall let $b_1(0)=b_2(0)=1$ and apply the initial conditions later. Thus we obtain:

$$b_1(t)=1-\int_0^t RA\exp\left(-i\int_0^{t'}Rdt''\right)dt',$$
$$b_2(t)=1+\int_0^t RA\exp\left(i\int_0^{t'}Rdt''\right)dt', \tag{13}$$

where

$$A=(c_0^+\dot{c}_0^-+c_1^+\dot{c}_1^-)/R.$$

To evaluate the integrals which appear in the above equations, we hold A fixed and so obtain:

$$b_1(t)=1-iA\left[\exp\left(-i\int_0^t Rdt'\right)-1\right],$$
$$b_2(t)=1-iA\left[\exp\left(i\int Rdt'\right)-1\right]. \tag{14}$$

This solution will be valid only if $A\ll 1$. A should be evaluated at the mean value of the static field, so that as little asymmetry as possible will be introduced by means of the approximation method.

Applying the initial conditions $a_m(0)=1$ and $a_{m+1}(0)=0$ in Eqs. (10), we find for the probability amplitudes the following expressions:[3]

$$\begin{aligned}a_m(t)=&\left[1-iA\left\{\exp\left(-i\int Rdt\right)-1\right\}\right]\\&\times c_0^+(0)c_0^+(t)\exp\left[\tfrac{1}{2}i\int(\Omega+R)dt\right]\\&+\left[1-iA\left\{\exp\left(i\int Rdt\right)-1\right\}\right]\\&\times c_0^-(0)c_0^-(t)\exp\left[\tfrac{1}{2}i\int(\Omega-R)dt\right],\\ a_{m+1}(t)=&\left[1-iA\left\{\exp\left(-i\int Rdt\right)-1\right\}\right]\\&\times c_0^+(0)c_1^+(t)\exp\left[\tfrac{1}{2}i\int(-\Omega+R)dt\right]\\&+\left[1-iA\left\{\exp\left(i\int Rdt\right)-1\right\}\right]\\&\times c_0^-(0)c_1^-(t)\exp\left[-\tfrac{1}{2}i\int(\Omega+R)dt\right].\end{aligned} \tag{15}$$

Thus, the probability $P(m, m+1)$ of a transition from the state ψ_m to the state ψ_{m+1} after a time τ is given by[4]

$$\begin{aligned}P(m,\dot{m}+1)=&\tfrac{1}{2}[(1+\delta^2(0))(1+\delta^2(\tau))]^{-\frac{1}{2}}\\&\times\Big\{[(1+\delta^2(0))(1+\delta^2(\tau))]^{\frac{1}{2}}-\delta(0)\delta(\tau)\\&-\cos\int_0^\tau Rdt-2A[\delta(\tau)(1+\delta^2(0))^{\frac{1}{2}}\\&-\delta(0)(1+\delta^2(\tau))^{\frac{1}{2}}]\sin\int_0^\tau Rdt\Big\},\end{aligned} \tag{16}$$

where we have used the abbreviation

$$\delta(t)=\hbar\Omega(t)/h_{10}. \tag{17}$$

It is evident that if $f(t)$ vanishes, Eq. (16) reduces to the usual expression for the transition probability,[5]

$$P_0(m, m+1)=(1+\delta^2)^{-1}\sin^2(\tfrac{1}{2}R\tau). \tag{18}$$

If we evaluate the matrix elements involved and neglect second-order terms in $f(t)$, we find that

$$\Omega(t)=\omega_0-\omega+2K\mathcal{E}f(t), \tag{19}$$

where

$$K=3(2m+1)/[J(J+1)(2J-1)(2J+3)],$$

and $\omega_0=K\mathcal{E}^2$ is the frequency separation of the energy levels at the mean field value. We also have

$$h_{10}=-\tfrac{1}{2}K\hbar\mathcal{E}\mathcal{E}_x[(J-m)(J+m+1)]^{\frac{1}{2}}. \tag{20}$$

For optimum operating conditions, one chooses

$$h_{10}/\hbar=-\pi/\tau. \tag{21}$$

Hence, one can write[6]

$$\delta(t)=\frac{(\omega-\omega_0)\tau}{\pi}-\frac{4f(t)}{\mathcal{E}_x[(J-m)(J+m+1)]^{\frac{1}{2}}}. \tag{22}$$

Up to now we have represented the inhomogeneity of the C-field as an arbitrary function $f(t)$. For most functions, however, the integration over R cannot be carried out easily. A particularly simple example for which this integration can be carried out in closed form is that in which the inhomogeneity is represented as a linear taper:

$$f(t)=\Delta\mathcal{E}(t/\tau-\tfrac{1}{2}). \tag{23}$$

In this case we have

$$\delta(t)=\frac{(\omega-\omega_0)\tau}{\pi}-\frac{4\Delta\mathcal{E}(t/\tau-\tfrac{1}{2})}{\mathcal{E}_x[(J-m)(J+m+1)]^{\frac{1}{2}}}, \tag{24}$$

[4] When $m=0$, $P(0, 1)$ is equal to one-half the expression given in Eq. (16) and $\delta(t)=\hbar\Omega/\sqrt{2}h_{10}$. Similarly for $P(0, -1)$.

[5] H. C. Torrey, Phys. Rev. **59**, 293 (1941).

[6] If the initial state is one with $m=0$, the fact that the transition can take place to either of the two states with $m=\pm 1$ introduces a factor of 2 multiplying h_{10}^2 in R. The definition of optimum operating conditions is then altered by a factor of $\sqrt{2}$. Thus

$$\delta(t)=\frac{(\omega-\omega_0)\tau}{\pi}-\frac{2\sqrt{2}f(t)}{\mathcal{E}_x[J(J+1)]^{\frac{1}{2}}}.$$

and[7]

$$\int_0^\tau R dt = -\frac{\pi \mathcal{E}_x[(J-m)(J+m)]^{\frac{1}{2}}}{8\Delta\mathcal{E}}\left\{\delta(\tau)[1+\delta^2(\tau)]^{\frac{1}{2}} - \delta(0)[1+\delta^2(0)]^{\frac{1}{2}} + \ln\frac{\delta(\tau)+[1+\delta^2(\tau)]^{\frac{1}{2}}}{\delta(0)+[1+\delta^2(0)]^{\frac{1}{2}}}\right\}. \quad (25)$$

It is clear from Eq. (23) that the effect of the taper is completely determined by $\Delta\mathcal{E}/\mathcal{E}_x$. By choosing optimum operating conditions the product $\mathcal{E}\mathcal{E}_x$ was set equal to a constant. Hence, if $\mathcal{E}$ is increased $\mathcal{E}_x$ must be decreased in order to maintain optimum operating conditions. Therefore, the inhomogeneities will have the greatest effect on the line shape in strong C-fields where they were first observed by Trischka.[2] The fact that a given ratio $\Delta\mathcal{E}/\mathcal{E}$ has a greater effect when the C-field is relatively strong than when it is weak may seem paradoxical. However, it is well known[1,8] that the line width is proportional to the product $\mathcal{E}\mathcal{E}_x$. On the other hand, the energy level perturbation due to the taper is proportional to $\mathcal{E}\Delta\mathcal{E}$. Thus the shift in energy levels due to the inhomogeneities is small in weak and large in strong C-fields, compared with the line width in a homogeneous field. Therefore, one should expect the inhomogeneities of the C-field to produce greater broadening of the line profile in strong fields.

In Fig. 1(a) we have plotted the probability that a molecule initially in a state with $J=1$ and $m=0$ will undergo a transition to a state with $J=1$ and $m=\pm 1$. The curves are drawn for both a homogeneous field and a field with a linear taper. (In both of these cases the specific molecular parameters drop out of the expression for the transition probability.) The field values represented by the curves are such that $\Delta\mathcal{E}/\mathcal{E}_x=0.625$. For such field values we have:[9]

$$A=(\Delta\mathcal{E}/\pi\mathcal{E}_x)[1+\delta^2(\tau/2)]^{-\frac{1}{2}}\leqslant 0.20.$$

[7] For $m=0$, the factor outside the brackets becomes

$$-\pi\mathcal{E}_x[J(J+1)]^{\frac{1}{2}}/(4\sqrt{2}\Delta\mathcal{E}).$$

[8] The dependence of the line width on the product $\mathcal{E}\mathcal{E}_x$ can easily be verified if one examines the transition probability for the homogeneous case, Eq. (18), using the fact that $\mathcal{E}\mathcal{E}_x\sim 1/\tau$.

[9] The general relation is

$$A=\frac{4\dot{f}(t)}{K\mathcal{E}\mathcal{E}_x^2(J-m)(J+m+1)}[1+\delta^2(\tau/2)]^{-\frac{1}{2}}.$$

For the case $m=0$, the numerator is divided by 2.

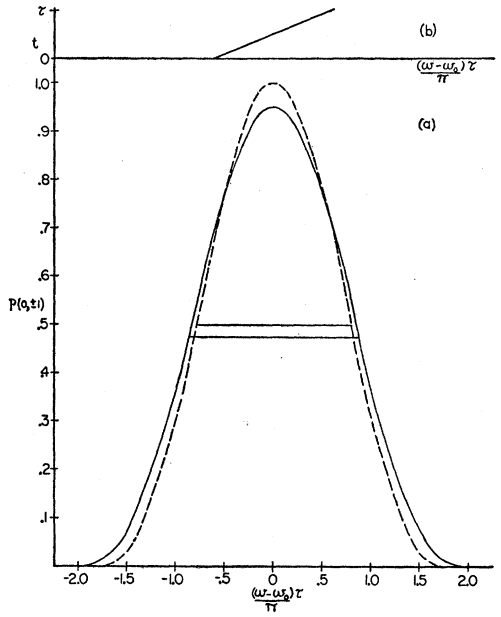

FIG. 1. (a) compares the line profiles for a transition occurring from the state $J=1$, $m=0$ to the state $J=1$, $m=\pm 1$ in a homogeneous field (broken curve) and in a field with a linear taper (solid curve). The taper has produced a 13 percent increase in half-width and a 5 percent decrease in peak. (b) shows the instantaneous resonance position as a function of time.

Thus, these field values represent the limit of our approximation method. Figure 1(b) shows that the instantaneous resonance frequency sweeps over nearly the entire range of frequencies included within the half-width of the homogeneous field curve. Following the, conservative method of estimating the broadening,[2] one would expect the half-width to be nearly doubled. However, the taper increases the half-width by only 13 percent and decreases the peak by 5 percent.

If one attempts to use a larger ratio of $\Delta\mathcal{E}/\mathcal{E}_x$, the curve becomes double peaked, dipping at resonance. Because the approximation breaks down first in the immediate vicinity of resonance (since A achieves its maximum value at resonance), this result may well be spurious. For points off resonance, however, one should still get a reasonable picture of the broadening as long as $A\leqslant 0.20$.