PHYSICAL REVIEW VOLUME 101, NUMBER 2 JANUARY 15, 1956

Resonance Transitions in Molecular Beams Experiments. II. Averages Over the Velocity Distribution

HAROLD SALWEN*
Department of Physics and Watson Scientific Computing Laboratory, Columbia University, New York, New York

(Received August 12, 1955)

General expressions are given for the average, over a v^3 velocity distribution, of the transition probability in a resonance line of an atomic or molecular beams experiment. Explicit expressions are given for multiple quantum transitions which are similar to those of Torrey for "allowed" transitions. The case when the complete velocity distribution is cut off on either the high- or low-velocity side or both is discussed.

IN an earlier paper,[1] we calculated the transition probabilities for an idealization of the usual atomic or molecular beams experiment. The formulas obtained in that paper were applicable to the case when the beam consists of particles all of which have the same velocity. In the present paper we generalize the expressions to the case when the distribution in velocity of the particles is of the form:

$$dn \propto v^3 \exp(-mv^2/2kT)dv, \tag{1}$$

where the velocities may range from zero to infinity or over a portion of that interval. Certain of the present results have been obtained by Torrey.[2] The expressions which we obtain involve integrals of the following form:

$$K(\beta,x_1,x_2)=\int_{x_1}^{x_2} x^3 \exp(-x^2)\sin^2(\beta/2x)dx, \tag{2}$$

which are not expressible in closed form in terms of elementary functions. However, tables of this function are now available.[3] We here present methods for calculating the theoretical shapes of resonance lines observed in molecular beams experiments.

In the earlier paper, the transitions were assumed to be produced by a rotating magnetic field (taken to be in the x,y-plane) in the presence of a constant field perpendicular to the plane of rotation. The amplitude of the rotating field was assumed to be different from zero for a finite "transit time," during which time the amplitude and angular velocity were taken to be constant.

* Now at the University of Syracuse, Syracuse, New York.

[1] H. Salwen, Phys. Rev. **99**, 1274 (1955). This paper shall be referred to as I, and equations shall be noted as (I.24), etc.

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

[3] A brief table of $K(\beta,0,\infty)$ has been given by Torrey.[2] U. E. Kruse and N. F. Ramsey [J. Math. Phys. **30**, 40 (1951)] give a table of $\int_0^\infty x^3 \exp(-x^2)\cos(\beta/x)dx$ from which $K(\beta,0,\infty)$ can be calculated. Extended tables of the functions $K(\beta,0,\infty)$, $K(\beta,1,\infty)$, $K(\beta,0,1)$, and of certain other functions of β and K which are useful in calculating the shapes of resonance lines observed in atomic and molecular beams experiments have been deposited as Document No. 4716 with the American Documentation Institute Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. These latter tables are the ones we cite below as reference 3.

Under the above assumptions it was possible to obtain [Eq. (I.25)] the following general form for the total transition probability from a state of definite J_z (where J is the total angular momentum):

$$P=\sum_{\lambda>\lambda'} A_{\lambda\lambda'}\sin^2[(\tfrac{1}{2}\hbar)(\lambda-\lambda')\tau]. \tag{3}$$

The parameters λ and λ' are eigenvalues of the effective Hamiltonian $\mathcal{H}'$ [Eq. (I.13)] in the rotating frame of reference, and the coefficients $A_{\lambda\lambda'}$ depend only upon the initial stage of the system and upon the eigenstates $|\lambda\rangle$ and $|\lambda'\rangle$. Thus the only dependence of (3) upon the particle velocity is through the transit time, τ.

In the particular case of resonance transition $a\leftrightarrow b$ we obtained the explicit formula (I.85):

$$P=\frac{b_{ab}^2}{(\nu_{ab}^*-\nu)^2+b_{ab}^2} \times\sin^2\{\pi|m_a-m_b|[(\nu_{ab}^*-\nu)^2+b_{ab}^2]^{\frac{1}{2}}\tau\}. \tag{4}$$

where

$$b_{ab}\propto|\text{rotating field amplitude}|^{|m_a-m_b|} \tag{5}$$

and ν_{ab}^* is the corrected resonance frequency.[4] The parameters m_a and m_b are the magnetic quantum numbers of the initial and final states. Aside from the factor $|m_a-m_b|$ in the argument of the $\sin^2$, Eq. (4) above is the same as Torrey's Eq. (4).[2]

If we assume that the velocity distribution of the particles in the beam is given by Eq. (1), we may average the transition probability over the velocity distribution.

For the general case [Eq. (3)] we obtain as the average over the entire velocity distribution

$$\bar{P}=2\sum_{\lambda>\lambda'} A_{\lambda\lambda'}K[(1/\hbar)(\lambda-\lambda')L/v_0], \tag{6}$$

where

$$K(\beta)\equiv K(\beta,0,\infty), \tag{7}$$

$$v_0=(2KT/m)^{\frac{1}{2}}. \tag{8}$$

The quantity v_0 is the most probable velocity of a Maxwell distribution of particles of mass m at a temperature T.

[4] ν_{ab}^* and b_{ab} are given by Eq. (I.104) and (I.105) respectively.

In the particular case where Eq. (4) is applicable, the average is

$$\bar{P}=2(\beta_0^2/\beta^2)K(\beta), \quad (9)$$

where

$$\begin{aligned}\beta_0&=2\pi|m_a-m_b|b_{ab}L/v_0,\\ \beta&=2\pi|m_a-m_b|[(\nu_{ab}^*-\nu)^2+b_{ab}^2]^{\frac{1}{2}}L/v_0 \quad (10)\\ &=\{[(\nu_{ab}^*-\nu)^2+b_{ab}^2]^{\frac{1}{2}}/b_{ab}\}\beta_0.\end{aligned}$$

At the resonant frequency, ν_{ab}^*, β is equal to β_0 so that

$$\bar{P}(\nu_{ab}^*)=2K(\beta_0) \quad (11)$$

gives the peak intensity for the transition.

In certain experiments, the geometry of the system eliminates a whole range of velocities. In these cases the results are similar to those given above except that the integration must be limited to the velocities of those particles which actually reach the detector.

If all particles of velocities less than v_1 or greater than v_2 have been eliminated, we must replace $K(\beta)$ by $\frac{1}{2}K(\beta,x_1,x_2)/N$, where

$$x_1=v_1/v_0;\quad x_2=v_2/v_0,$$

$$N=\int_{x_1}^{x_2}x^3\exp(-x^2)dx. \quad (12)$$

Equations (6) through (11) will then carry over to this case.

In Table I, of reference 3, $K(\beta)$ and $(1/\beta^2)K(\beta)$ are given as functions of β. This table, with the help of Eqs. (7) through (11), enables one to calculate the peak intensity and the shape of a given line as a function of rf amplitude.

For a resonance transition at a given rf amplitude, the intensity varies with the frequency as $(1/\beta^2)K(\beta)$. The half-intensity point, therefore, occurs at $\beta=\beta_{\frac{1}{2}}$, where $\beta_{\frac{1}{2}}(\beta_0)$ is defined by

$$(1/\beta_{\frac{1}{2}})^2K(\beta_{\frac{1}{2}})=\tfrac{1}{2}(1/\beta_0)^2K(\beta_0). \quad (13)$$

Table II of reference 3 lists $\beta_{\frac{1}{2}}$ and $(\beta_{\frac{1}{2}}^2-\beta_0^2)^{\frac{1}{2}}$ as functions of β_0.

Perhaps the easiest way of applying the table is to make use of the relation

$$(\beta_{\frac{1}{2}}^2-\beta_0^2)^{\frac{1}{2}}/\beta_0=|\nu_{\frac{1}{2}}-\nu_{ab}^*|/b_{ab}. \quad (14)$$

This ratio approaches unity only for quite large rf amplitudes. For somewhat smaller amplitudes it oscillates about the value 1, while for low rf amplitudes the width is relatively independent of the power and is governed by the uncertainty principle.

Table III of reference 3 gives $K(\beta,0,1)$ and $K(\beta,1,\infty)$ as functions of β. These functions are useful if the beam is restricted entirely to particles with $v\geqslant v_0$ or to particles with $v\leqslant v_0$.

Table IV of reference 3 is a table of $(1/\beta^2)K(\beta,0,1)$ and $(1/\beta^4)K(\beta,0,1)$. It was calculated for application to a system with $j=1$ and a normal Zeeman effect.[5] In this case the problem is complicated by the superposition of several transitions. In this case Eq. (6) becomes[6]:

$$\begin{aligned}P_{1\rightarrow}&=P_{-1\rightarrow}\\ &=\left[2-\frac{b^2}{(\nu-\nu_0)^2+b^2}\right]\frac{b^2}{(\nu-\nu_0)^2+b^2}\\ &\quad\times\sin^2\{\pi[(\nu-\nu_0)^2+b^2]^{\frac{1}{2}}\tau\}+\frac{1}{4}\left[\frac{b^2}{(\nu-\nu_0)^2+b^2}\right]^2\\ &\quad\times\sin^2\{2\pi[(\nu-\nu_0)^2+b^2]^{\frac{1}{2}}\tau\}, \quad (15)\\ P_0&=4\left[1-\frac{b^2}{(\nu-\nu_0)^2+b^2}\right]\frac{b^2}{(\nu-\nu_0)^2+b^2}\\ &\quad\times\sin^2\{\pi[(\nu-\nu_0)^2+b^2]^{\frac{1}{2}}\tau\}+\left[\frac{b^2}{(\nu-\nu_0)^2+b^2}\right]\\ &\quad\times\sin^2\{2\pi[(\nu-\nu_0)^2+b^2]^{\frac{1}{2}}\tau\},\end{aligned}$$

where

$$\nu_0=g_J\mu_0H_z/h;\quad b=g_J\mu_0H_r/h. \quad (16)$$

The notation $P_{m\rightarrow}$ indicates the total probability for a transition from the state with $J_z=m\hbar$ to one of the other two states.

The average of Eq. (15) over a velocity distribution from v_1 to v_2 is

$$\begin{aligned}\bar{P}_{1\rightarrow}&=\bar{P}_{2\rightarrow}\\ &=(1/N)\{2(\beta_0/\beta)^2K(\beta,x_1,x_2)-(\beta_0/\beta)^4K(\beta,x_1,x_2)\\ &\qquad+4(\beta_0/2\beta)^4K(2\beta,x_1,x_2)\}, \quad (17)\\ \bar{P}_{0\rightarrow}&=(1/N)\{4(\beta_0/\beta)^2K(\beta,x_1,x_2)-4(\beta_0/\beta)^4\\ &\qquad\times K(\beta,x_1,x_2)+16(\beta_0/2\beta)^4K(2\beta,x_1,x_2)\},\end{aligned}$$

where N, x_1, and x_2 are defined in Eq. (12) and the parameters β_0 and β are defined by equation (10) with ν_0 and b substituted for ν_{ab}^* and b_{ab}. Table IV may thus be used in a simple manner to compute the line shape for this case.

It should be noted that, though $(1/\beta^2)K(\beta)$ is a monotonically decreasing function of β, $(1/\beta^2)K(\beta,0,1)$ is not. This means that in some cases (e.g., for $\beta_0=5.6$) the intensity will *increase* as we move *away* from the center of the line. This makes it possible with such a velocity distribution to observe a line with a dip in the middle and peaks on either side. Such an effect has, in fact, been observed by Hughes *et al.*[5]

[5] Hughes, Tucker, Rhoderick, and Weinreich, Phys. Rev. 91, 828 (1953), Appendix 2.

[6] This result is obtained by substituting (I.113) and (I.36) into (I.41). ν_0 and b as defined here differ from a and b of Eq. (I.36) by a factor of $(1/2\pi)$.