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J. KARLE

U. S. Naval Research Laboratory, Washington, D. C.

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Several formulae have been derived expressing the contribution to the intensity of electron scattering of restricted rotation in the vapors of ethane, ethylene, biphenyl, and their derivatives. The probability distribution of the restricted rotator about its axis of rotation is expressed in terms of the barrier height, V_0. It has, therefore, been possible to evaluate the effect of barriers of known magnitude on scattering patterns. The possibility of evaluating the potential barrier using electron diffraction is discussed.

IT is well known from statistical thermodynamic studies[1] that many molecules exhibit restricted internal rotation at normal temperatures. This type of motion is of interest in the field of electron diffraction by gases because of its effect on the interpretation of scattering patterns in structure determinations, and also because of the possibility of using these patterns for evaluating the magnitude of the restricting potentials. Two methods are commonly used for interpreting the patterns from molecules which may possess restricted internal rotation. In both cases theoretical intensity curves are calculated and are compared to the experimentally observed patterns. These curves are based either on a rigid model (which obviously neglects the internal motion) or on a model undergoing small vibrations according to the theory developed by R. W. James[2] for x-ray diffraction by gas molecules. This theory arises from a normal coordinate treatment which is generally quite unwiedly for polyatomic molecules and so its prescribed effects are introduced into the analysis in an empirical way. Another approach which has been tried[3] is to treat the molecule as a rigid structure with an additional internal librational degree of freedom. In this way the concept of a potential barrier hindering free rotation may be directly introduced and its effect evaluated. This procedure is justified in molecules possessing barriers of the order of 3 kcal., as for instance derivatives of ethane, since in such cases the librational motion is far

more important than the other vibrational degrees of freedom, especially at higher temperatures. On the other hand, some derivatives of ethylene may have barriers as high as 40 kcal. In this case the effect of the librational motion would be negligible at ordinarily attained experimental temperatures. In addition this motion and the energy quantum associated with it would approach the same order of magnitude as that of the other vibrations and could not be readily considered separately.

P. Debye[4] has investigated the effect of the various types of internal motion, namely, vibration and free and hindered rotation, on electron scattering by gas molecules. His theory for hindered rotation concerns 1,2 di-substituted ethanes and does not consider those cases for which classical statistics may not satisfactorily apply. In this article a quantum-mechanical distribution function for the angular distribution of the restricted rotator about its equilibrium position will be developed, and the theory extended to include the more completely substituted ethanes and also the derivatives of biphenyl and ethylene. For molecules undergoing hindered rotation, an increase in temperature may cause profound changes in their electron scattering patterns long before there are any considerable number of them undergoing free rotation, that is in states whose energy is greater than the barrier. This variation with temperature may be used to evaluate the hindering potential.

The theory to be developed will apply to the case in which the molecules of the gas occupy mainly the lower lying levels and the amplitude of the hindered rotation is not too large. The

[1] A discussion of the method and a compilation of the results may be found in G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945).
[2] R. W. James, Physik. Zeits. **33**, 737 (1932).
[3] (a) J. Y. Beach and K. S. Palmer, J. Chem. Phys. **6**, 639 (1938). (b) J. Y. Beach and A. Turkevich, J. Am. Chem. Soc. **61**, 303 (1939).
[4] P. Debye, J. Chem. Phys. **9**, 55 (1941).

other extreme, the case of free rotation, has already been investigated.[4,5]

DEVELOPMENT OF THEORY

The expression for the intensity of coherent molecular scattering from a rigid molecule is

$$\sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j \sin s r_{ij}/s r_{ij}, \quad (i \neq j) \tag{1}$$

where N is the total number of atoms in the molecule, f_i is the atomic scattering factor for electrons for the ith atom, r_{ij} is the distance between the ith and jth atoms and $s = 4\pi \sin(\theta/2)/\lambda$ where θ is the angle of scattering and λ is the wave-length of the electrons. We are concerned with the contribution from varying interatomic distances which may be expressed by integrals of the type

$$\int \sin(s r_{ij}) P(r_{ij}) dr_{ij}/s r_{ij}. \tag{2}$$

The interatomic distances, r_{ij}, affected by the internal rotation and their probability distribution functions, $P(r_{ij})dr_{ij}$, will be expressed in terms of the angle of internal rotation, ϕ. By solving the Schroedinger equation for the restricted rotator undergoing small vibrations, the probability distribution of the rotating group as a function of angle ϕ for each of the lower states can be found. The distribution of the gas molecules among these states is determined by the Boltzmann distribution law. The probability functions $P'(\phi)d\phi = P(r_{ij})dr_{ij}$ may be obtained from multiplying the probability distribution within each of the hindered rotational states, as obtained from the Schroedinger equation, by a factor governing the frequency of occurrence of each of these states, as obtained from the Boltzmann law, and adding these products.

The effect of hindered rotation on electron scattering will first be developed for substituted ethanes of the type X_3CCY_3. They are symmetric top molecules and therefore lend themselves readily to theoretical treatment. It has been shown[6] that for symmetric top molecules the Schroedinger equation for rotational motion is separable into an equation containing the vari-

ables governing the motion of the molecule as a whole, and one in terms of the variable concerned with the internal motion. We are interested in the latter which is

$$d^2\psi/d\phi^2 + 8\pi^2 I(E-V)\psi/h^2 = 0, \tag{3}$$

where I is the reduced moment of inertia equal to $I_1 I_2/(I_1+I_2)$, where I_1 and I_2 are the moments of inertia about the axis of the molecule of the two ends rotating with respect to each other, and ϕ is the variable of internal rotation. The other quantities have the usual significance. The potential function, V, is assumed to have the form

$$V = V_0(1 - \cos\sigma\phi)/2, \tag{4}$$

where V_0 is the barrier height and σ is the number of minima in the potential function, for instance three for ethane. When ϕ is small, we get

$$V = V_0(\sigma\phi/2)^2. \tag{5}$$

On substituting (5) into (3) the Schroedinger equation for the simple harmonic oscillator is obtained. It is

$$d^2\psi/d\phi^2 + 8\pi^2 I[E - V_0(\sigma\phi/2)^2]\psi/h^2 = 0. \tag{6}$$

The normalized solutions to this equation are[7]

$$\psi_n(\phi) = N_n \exp(-\alpha\phi^2/2) H_n(\alpha^{\frac{1}{2}}\phi), \tag{7}$$

where

$$N_n = \{(\alpha/\pi)^{\frac{1}{2}}/2^n n!\}^{\frac{1}{2}},$$
$$\alpha^2 = 2\sigma^2 \pi^2 I V_0/h^2,$$

and H_n is the Hermite polynomial of order n. Since we are concerned with the situation in which only the first few states are occupied significantly, we may add to the distribution function for these lower states the distributions for the higher harmonic oscillator states since their Boltzmann factors are so small that their contribution is essentially equal to zero. The advantage in including them arises from the fact that the infinite sum may be readily written in compact form.

The probability distribution function in terms

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[5] J. Karle, J. Chem. Phys. **13**, 155 (1945).
[6] H. H. Nielsen, Phys. Rev. **40**, 445 (1932).

[7] There are also vibrations of small amplitude which may be considered as centered not only about $\phi=0$, but also about $\phi=2\pi n/\sigma$ as n goes from 1 to $\sigma-1$. These lead to wave functions and a distribution function which assume significant values in the vicinity of these σ values of ϕ. For our purposes the desired results may be obtained from considering only the distribution about $\phi=0$ since the others make an identical contribution to the scattering problem.

of the contributions from the various states is

$$(\alpha/\pi)^{\frac{1}{2}}(1-\exp[-h\nu/kT]) \exp(-\alpha\phi^2)$$
$$\times \sum_{n=0}^{\infty} H_n^2(\alpha^{\frac{1}{2}}\phi) \exp(-nh\nu/kT)d\phi/2^n n!, \quad (8)$$

where $\nu = \sigma(V_0/2I)^{\frac{1}{2}}/2\pi$, T is the absolute temperature, and k is the gas constant. The quantity $1-\exp[-h\nu/kT]$ normalizes the Boltzmann factors. Mehler[8] in studying the parabolic cylinder function, D, obtained the generating function,

$$\exp[(-[1-t]/[1+t])\rho^2/2]/(1-t^2)^{\frac{1}{2}}$$
$$= \sum_{n=0}^{\infty} t^n D_n^2(\rho)/n!. \quad (9)$$

The following relation exists between the parabolic cylinder function and the Hermite polynomials,

$$D_n^2(\rho) = 2^{-n} H_n^2(\rho/2^{\frac{1}{2}}) \exp(-\rho^2/2). \quad (10)$$

On substituting (10) into (9) it is found that

$$\sum_{n=0}^{\infty} t^n H_n^2(\rho/2^{\frac{1}{2}}) \exp(-\rho^2/2)/2^n n!$$
$$= \exp[-([1-t]/[1+t])\rho^2/2]/(1-t^2)^{\frac{1}{2}}. \quad (11)$$

By comparing (11) to (8) it is apparent that by setting $t=\exp[-h\nu/kT]$ and $\rho/2^{\frac{1}{2}} = \alpha^{\frac{1}{2}}\phi$ we get for the sum of (8)

$$(\alpha/\pi)^{\frac{1}{2}}[\tanh(h\nu/2kT)]^{\frac{1}{2}}$$
$$\times \exp[-\alpha\phi^2 \tanh(h\nu/2kT)]d\phi. \quad (12)$$

This is the normalized distribution function we have been seeking. The function $b \exp[-b^2\phi^2]d\phi/\pi^{\frac{1}{2}}$, where $b^2 = \alpha \tanh(h\nu/2kT)$, is the probability of finding the rotating group between ϕ and $\phi+d\phi$. Expression (12) is equivalent to the distribution function obtained by Bloch[9] for the linear harmonic oscillator. If $h\nu$ is small with respect to kT we obtain the classical result from (12),

$$(\sigma^2 V_0/4\pi kT)^{\frac{1}{2}} \exp(-\sigma^2 V_0\phi^2/4kT)d\phi. \quad (13)$$

We may proceed now with the scattering problem and the next step is to express the interatomic distances which change with the internal rotation in terms of angle ϕ. The equilibrium distances which occur depend upon whether the molecule, X_3CCY_3, is at equilibrium

in the staggered or eclipsed configuration. The staggered configuration is the more probable one and is considered first. Two types of distances appear,

$$r_1 = (c_1 + c_2 \cos\phi)^{\frac{1}{2}}$$
and $\quad (14)$
$$r_2 = (c_1 - c_2 \cos[\phi - \pi/3])^{\frac{1}{2}},$$

where $c_1 = (l_2^2 + l_1^2)/2$, and $c_2 = (l_2^2 - l_1^2)/2$. The quantity l_1 is the smallest possible distance of approach of atoms X and Y if the rotating groups could rotate freely and l_2 is the largest possible distance between them.

The contribution from small variations in r_1 resulting from hindered rotation is obtained from evaluating the integral,

$$b \int \sin[s(c_1 + c_2 \cos\phi)^{\frac{1}{2}}]$$
$$\times \exp(-b^2\phi^2)d\phi/\pi^{\frac{1}{2}}s(c_1 + c_2 \cos\phi)^{\frac{1}{2}}. \quad (15)$$

We express $\cos\phi$ as $1 - \phi^2/2$ and find that

$$\sin[s(c_1 + c_2 \cos\phi)^{\frac{1}{2}}]$$
$$\sim \text{I.P. } \exp[i(sl_2 - sc_2\phi^2/4l_2)] \quad (16)$$

where I.P. refers to the imaginary part. Integral (15) becomes the imaginary part of

$$b \exp(isl_2) \int_{-\infty}^{\infty} \exp[-(b^2 + iB)\phi^2]d\phi/\pi^{\frac{1}{2}}sl_2, \quad (17)$$

where $B = sc_2/4l_2$. The small variations in r_1 have been omitted in the denominator of the integrand. Integral (17) has the value $b \exp(isl_2)/sl_2(b^2 + iB)^{\frac{1}{2}}$ and the imaginary part is

$$b[\cos(sl_2)\text{I.P.}(b^2 - iB)^{\frac{1}{2}}$$
$$+ \sin(sl_2)\text{R.P.}(b^2 - iB)^{\frac{1}{2}}]/sl_2(b^4 + B^2)^{\frac{1}{2}}, \quad (18)$$

where R.P. refers to the real part. By setting $(b^2 - iB)^{\frac{1}{2}} = \rho^{\frac{1}{2}} \exp(i\xi/2)$ it can be shown that

$$\text{I.P.}(b^2 - iB)^{\frac{1}{2}} = -(b^4 + B^2)^{\frac{1}{4}} \sin(\xi/2)$$
and $\quad (19)$
$$\text{R.P.}(b^2 - iB)^{\frac{1}{2}} = (b^4 + B^2)^{\frac{1}{4}} \cos(\xi/2),$$

where $\tan\xi = B/b^2 = sc_2/4l_2b^2$. We thus obtain for the contribution from r_1

$$(\cos\xi)^{\frac{1}{2}} \sin(sl_2 - \xi/2)/sl_2. \quad (20)$$

There are three r_1 terms occurring for X_3CCY_3. If only a rigid structure was considered, the contribution to the scattered intensity would be,

[8] F. G. Mehler, J. f. reine u. angew. Math. 66, 161 (1866).
[9] F. Bloch, Zeits. f. Physik 74, 295 (1932).

$\sin(sl_2)/sl_2$. The effect of the restricted rotation is to shift the maxima and minima by angle $\xi/2$, which varies with s, and to introduce a damping factor, $(\cos\xi)^{\frac{1}{2}}$. When the same atoms oscillate at each end of the C$-$C bond the relation $l_2^2-l_1^2=4a^2$ holds where a is the radius of rotation. When this relation is substituted into (20) a result similar to Debye's is obtained.

The contribution from small variations in r_2 resulting from hindered rotation is obtained from the integral

$$b\int \sin[s(c_1-c_2\cos[\phi-\pi/3])^{\frac{1}{2}}]$$
$$\times\exp(-b^2\phi^2)d\phi/\pi^{\frac{1}{2}}s(c_1-c_2[\phi-\pi/3])^{\frac{1}{2}}. \quad (21)$$

For small values of ϕ we have $\cos(\phi-\pi/3)\sim 0.5+(3^{\frac{1}{2}}\phi)/2-0.25\phi^2$. If we define

$$\tau_1=s(c_1-c_2/2)^{\frac{1}{2}},$$
$$\beta=c_2/8(c_1-c_2/2)-3(c_2/[c_1-c_2/2])^2/32,$$

and

$$\gamma=3^{\frac{1}{2}}c_2/4(c_1-c_2/2)$$

(21) becomes

$$b\int_{-\infty}^{\infty}\sin[\tau_1(1-\gamma\phi+\beta\phi^2)]$$
$$\times\exp(-b^2\phi^2)d\phi/\pi^{\frac{1}{2}}\tau_1. \quad (22)$$

As in (17) the variation of r_2 about its equilibrium value is omitted from the denominator. Integral (22) may be expressed as

$$b\left[\sin\tau_1\int_{-\infty}^{\infty}\cos(\gamma\tau_1\phi-\beta\tau_1\phi^2)\exp(-b^2\phi^2)d\phi\right.$$
$$-\cos\tau_1\int_{-\infty}^{\infty}\sin(\gamma\tau_1\phi-\beta\tau_1\phi^2)$$
$$\left.\times\exp(-b^2\phi^2)d\phi\right]/\pi^{\frac{1}{2}}\tau_1. \quad (23)$$

After further expanding the integrands and bearing in mind that odd integrands do not contribute to the values of the integrals, it is found that the problem reduces to evaluating

$$\int_{-\infty}^{\infty}\cos(\gamma\tau_1\phi)\exp[-(b^2+i\beta\tau_1)\phi^2]d\phi. \quad (24)$$

The real part of the integrand of (24) is the contributing portion of the integrand of the first integral in (23), and the imaginary part is the contributing portion of the integrand of the second integral in (23). Integral (24) has the value

$$\pi^{\frac{1}{2}}\exp[-\gamma^2\tau_1^2/4(b^2+i\beta\tau_1)]/(b^2+i\beta\tau_1)^{\frac{1}{2}}. \quad (25)$$

By defining $(b^2-i\beta\tau_1)^{\frac{1}{2}}=\rho^{\frac{1}{2}}\exp(-i\theta/2)$ we find that the real part of (25) is

$$\pi^{\frac{1}{2}}\cos[(\gamma^2\beta\tau_1^3/4[b^4+\beta^2\tau_1^2])-\theta/2]$$
$$\times\exp[-\gamma^2b^2\tau_1^2/4(b^4+\beta^2\tau_1^2)]/(b^4+\beta^2\tau_1^2)^{\frac{1}{4}}, \quad (26)$$

and the imaginary part of (25) is

$$\pi^{\frac{1}{2}}\sin[(\gamma^2\beta\tau_1^3/4[b^4+\beta^2\tau_1^2])-\theta/2]$$
$$\times\exp[-\gamma^2b^2\tau_1^2/4(b^4+\beta^2\tau_1^2)]/(b^4+\beta^2\tau_1^2)^{\frac{1}{4}} \quad (27)$$

where $\tan\theta=\beta\tau_1/b^2$. By combining (26) with the coefficient of the first integral in (23), and (27) with the coefficient of the second, we get the desired result, the contribution from r_2,

$$(\cos\theta)^{\frac{1}{2}}\sin[\tau_1-(\gamma^2\tau_1\sin^2\theta/4\beta)+\theta/2]$$
$$\times\exp[-\gamma^2\tau_1^2\cos^2\theta/4b^2]/\tau_1. \quad (28)$$

If distance r_2 were fixed at the equilibrium point, the contribution to the scattering would be $\sin\tau_1/\tau_1$. The hindered rotation introduces not only a shifting in the maxima and minima and a damping term, $(\cos\theta)^{\frac{1}{2}}$, but also an exponential damping term dependent upon s^2. There are six distances of the type r_2 in X_3CCY_3.

When equilibrium occurs in an X_3CCY_3 molecule in the eclipsed position, there are again two different types of interatomic distances affected by the hindered rotation,

$$r_3=(c_1-c_2\cos\phi)^{\frac{1}{2}}$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad (29)$

$$r_4=(c_1-c_2[\phi-2\pi/3])^{\frac{1}{2}}.$$

The contribution to the scattered intensity may be obtained in precisely the same fashion as for the molecule in a staggered configuration at equilibrium. The contribution from r_3 is

$$(\cos\zeta)^{\frac{1}{2}}\sin(sl_1+\zeta/2)/sl_1 \quad (30)$$

where $\tan\zeta=sc_2/4b^2l_1$. The contribution from r_4 is

$$(\cos\delta)^{\frac{1}{2}}\sin[\tau_2+(\mu^2\tau_2\sin^2\delta/4\omega)-\delta/2]$$
$$\times\exp[-\mu^2\tau_2^2\cos^2\delta/4b^2]/\tau_2, \quad (31)$$

where

$$\tan\delta = \omega\tau_2/b^2,$$
$$\omega = c_2/8(c_1+c_2/2)+3(c_2/[c_1+c_2/2])^2/32,$$
$$\tau_2 = s(c_1+c_2/2)^{\frac{1}{2}},$$

and

$$\mu = 3^{\frac{1}{2}}c_2/4(c_1+c_2/2).$$

Molecules of biphenyl and its derivatives, ethylene and its derivatives, and partially substituted ethanes also exhibit hindered rotation. In general those molecules are not symmetric tops and therefore the internal rotational motion cannot be separated from the over-all rotational motion to give Eq. (3). If the coupling is not too strong, and this may be determined by comparing the values of the principal moments of inertia, it is still legitimate to consider (12) as the correct distribution function arising from the lower lying levels.

For many biphenyl derivatives the equilibrium position probably occurs with the planes of the benzene rings at right angles. In this case the formula to be used is

$$\sin(sc_1^{\frac{1}{2}}) \exp[-s^2c_2^2/16c_1b^2]/sc_1^{\frac{1}{2}}. \quad (32)$$

If the planar configuration is correct for some biphenyl derivatives as it is for ethylene derivatives, formulae (20) and (30) apply. It should be born in mind that the two potential minima may not be the same.

In substituted ethanes the structure problem is rather complicated owing to the existence of a threefold potential which does not have identical minima.[10] For the case of H_2XCCXH_2, the *trans*-configuration has been found to be the more stable one.[3] The restricted rotation formula which applies to this model is (20). It is probably more nearly correct in using (20) to set $\sigma=3$ instead of one, even though it does not have identical minima. The potential barrier V_0 would still signify the energy required to break out of the *trans*-position, but its value might be different than that of the potential barrier at the *cis*-position.

The formulae for hindered rotation occasionally may not be reliable for V_0/RT less than 5 but often may be used for V_0/RT as low as 3. This estimate is based on the requirement that the

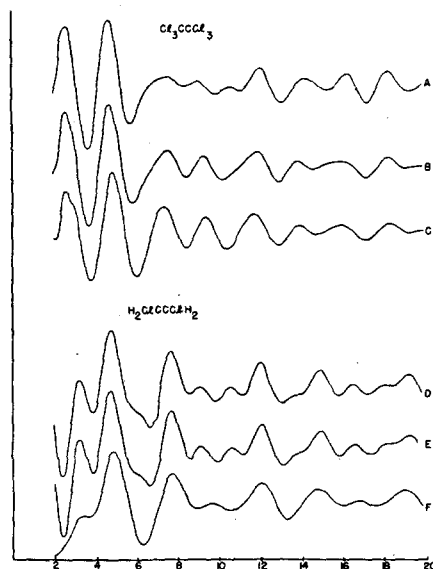[10] For an excellent discussion of this problem see reference 1, p. 346.

FIG. 1. Variation of scattering pattern with changes in V_0/RT for Cl_3CCCl_3 and $H_2ClCCClH_2$. V_0/RT is equal to ∞ in A and D, 5 in B and E, and zero in C and F. The hydrogen distances in $H_2ClCCClH_2$ were not included in the calculations. The abscissa is given in s units.

distribution function $P'(\phi)$ should damp out fast enough to justify the replacement of $1-\cos\sigma\phi$ by $(\sigma\phi)^2/2$ in (4), and also damp out fast enough to allow the approximated interatomic distances as in (16) and (22) to yield valid results when s becomes as large as 20.

It is interesting to compare the effects of restricted rotation on distances whose equilibrium positions are *trans*, *cis* or intermediate. *Trans*- and *cis*- formulae are represented by (20) and (30), respectively, whereas (28), (31), and (32) represent various intermediate positions. The exponential damping factor in the latter three formulae should be noted. Owing to this term the contribution to the scattering from intermediate distances affected by hindered rotation is largely damped out, whereas that from the *cis*- and *trans*-positions is relatively unchanged. This may be related to the case of free rotation in which the contributions to the scattering arise from the vicinity of the *cis*- and *trans*-positions.

APPLICATION OF THEORY

Electron diffraction offers the possibility of determining the height of the potential barrier restricting rotation in certain molecules. One method, which is probably the least promising,

involves treating the barrier as an additional unknown in fitting theoretical intensity curves of assumed models to observed data. The difficulty with this method is that the number of variables ordinarily involved is too great to permit the establishment of a unique solution. Another method which is based on the radial distribution function has been suggested by Debye.[4] He has shown how the values of the radial distribution function in the vicinity of an equilibrium distance can be related to the probability distribution for that distance, e.g., (12).

Another approach to the problem of evaluating the barrier, which obviates to a large extent the ambiguity which arises in the first method suggested, is to study the changes introduced into the diffraction patterns when the sample of vapor is heated to successively higher temperatures. In favorable cases the ambiguity may be resolved owing to the fact that only a unique combination of structural parameters and potential barrier can fit the diffraction data over a range of temperatures.

Theoretical intensity curves for various values of V_0/RT are plotted for Cl_3CCCl_3 and $H_2ClCCClH_2$ in Fig. 1. Curves A, B, and C refer to Cl_3CCCl_3 and were based on an assumed model in which $C-C=1.54A$, $C-Cl=1.76A$ and angle $Cl-C-Cl$ was given the regular tetrahedral value. Curves D, E, and F refer to $H_2ClCCClH_2$ and were based on the same model as hexachloroethane by giving angle $Cl-C-H$ the same value as was given to angle $Cl-C-Cl$. Curves A and D were calculated from the scattering formula for a rigid molecule, (1), the atomic scattering factors being set equal to the corresponding atomic numbers. Curve A was based on a staggered configuration and curve D on a *trans*-configuration. These curves represent the scat-

tered intensity when the barrier is very large or the temperature is very low. Curves B and E were calculated for V_0/RT equal to 5. The contribution from the rigid portion of the molecules was calculated using formula (1). The contribution from the hindered rotation was obtained using formulae (19) and (27) multiplied by the atomic number of chlorine squared, and the proper frequency of occurrence of these terms for the molecules considered. The quantum correction was not introduced and σ was set equal to three. Curves C and F represent free rotation in the molecules. Formula (1) was used to calculate the contribution from the rigid portions of the molecules and the contribution from the freely rotating portions was calculated from the formulae in reference (5). Additional correction terms to the asymptotic formula of Debye were found to be negligible.

The effect of the internal motion on the scattering patterns of hexachloroethane and 1,2-dichloroethylene is vastly different. A great change in pattern has occurred in the range ∞ to 5 for V_0/RT in hexachloroethane whereas practically no change has occurred for dichloroethylene. If T is about room temperature then V_0/RT equal to 5 means that V_0 is equal to 3 kcal./mole. This is a customary order of magnitude.

We may conclude that electron scattering from some molecules may be sufficiently sensitive to changes in V_0/RT to permit an evaluation of their potential barriers. The possibility of a useful experiment depends upon the magnitude of the barrier, the vapor pressure and the heat stability of the substance as well as the pattern sensitivity. It is perhaps well to emphasize that the determination of the structure of some molecules may be greatly dependent upon proper evaluation of their hindered internal rotations.