action are different phenomena with different kinds of off-diagonal corrections and there is no *a priori* reason why, for real atoms, $\langle 1/r^3\rangle_{\text{av}}$ of the hyperfine interaction should be equal to $\langle (1/r)(dV/dr)\rangle_{\text{av}}$ of the fine-structure interaction. One can try to account for the non-Coulombic nature of the screened nucleus by the use of an effective charge,[9] but there exist still other corrections to ζ (spin-other orbit, orbit-orbit, spin-spin) which are difficult to evaluate and which do not affect the hyperfine interaction. One should not be surprised then to find that the $\langle 1/r^3\rangle_{\text{av}}$'s estimated in these two different ways differ by 15% or so.

The value of the quadrupole moment Q obtained with the $\langle 1/r^3\rangle_{\text{av}}$ from the corrected a of the $^3P_2$ state has not been corrected for the Sternheimer effect. Sternheimer[14] estimates the angular part of this correction for $4p$ electrons to be $+4.4\%$. The importance of the radial part of this correction is still in doubt. It was decided, because of this uncertainty, to give recognition to the importance of this correction by enlarging the limits of error assigned to Q.

It should be remembered that core polarization was assumed to account for all of the configuration interaction necessary to give the observed a factor of the $^3P_1$ state. The validity of this assumption must be judged upon the basis of its consistency with future developments of theory and experiment.

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We would like to thank Dr. Paul Bagus for performing the self-consistent-field calculations of $\langle 1/r^3\rangle$. We are also grateful to Dr. Brian Wybourne for his help and advice on the theory of hyperfine structure.

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[14] R. Sternheimer, Phys. Rev. 84, 244 (1951).

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Electron Capture by Rotational Excitation of Polar Molecules[*]

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The problem of electron capture by a polar molecule with simultaneous rotational excitation of the molecule is analyzed. Capture cross sections and lifetimes of temporary negative-ion states so formed are calculated on the assumption that the electron interacts primarily at large distances from the molecule by means of the dipole field and forms only loosely bound ionic states. The capture probability is proportional to the ratio $(D/I)^2$, where D is the dipole moment and I the moment of inertia of the molecule about a perpendicular axis passing through the center of the dipole. Electron capture by rotational excitation is most probable for polar molecules that have both a relatively large dipole moment and a small moment of inertia. In order for this process to make effective contributions to momentum-transfer cross sections measured, e. g., in electron-swarm experiments, the spacing of the rotational levels of the molecule must be of the order of thermal energies, so that a relatively large number of electrons can be captured and released. These circumstances, viz., the relatively large value of D/I and the right spacing of rotational levels, appear to offer an explanation of the particular behavior of H_2O, D_2O, and H_2S among a number of polar molecules with which recent swarm experiments have been made. According to the theory, some other molecules (e. g., NH_3, HF, HCl, and H_2O_2) should exhibit a similar behavior. Lifetimes of negative ions formed by this process are estimated to be of the order of 10^{-13} sec.

I. INTRODUCTION

THE interaction of low-energy electrons with molecules has been the subject of many investigations.[1] In particular, a number of theoretical studies have been made on the excitation of rotational motion in molecules by electron impact.[2–4] On the experimental side, it has been found that the drift velocity of electrons in swarm experiments decreases with the addition of a gas having a permanent electric dipole moment[5] and that the amount of decrease is correlated with the magnitude of the dipole moment of the added gas.[6] It has been suggested that the dipole moment provides for the electron-molecule interaction a long-range force, the principal effect of which is to give rise to collisions of relatively long duration during which the electron is scattered from the molecule.[6] The experimental results were interpreted in terms of Altshuler's theory[7] of low-energy electron scattering by polar molecules. Although experiment and theory agree satisfactorily for other polar molecules, a discrepancy was found for H_2O, D_2O, and H_2S. The momentum-transfer cross sections, or diffusion cross sections, for these three molecules were

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[*] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] See E. Gerjuoy, Phys. Today 18, 24 (1965).

[2] H. S. W. Massey, Proc. Cambridge Phil. Soc. 28, 99 (1932).

[3] E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955).

[4] K. Takayanagi and S. Geltman, Phys. Letters 13, 135 (1964).

[5] G. S. Hurst, L. B. O'Kelly, and J. A. Stockdale, Nature 195, 66 (1962).

[6] G. S. Hurst, J. A. Stockdale, and L. B. O'Kelly, J. Chem. Phys. 38, 2572 (1963).

[7] Saul Altshuler, Phys. Rev. 107, 114 (1957).

found to be larger by about a factor of 2 than the values predicted by Altshuler's theory.

To account for the discrepancy, it was suggested that electrons, in addition to being scattered, might also be captured, or at least momentarily held, by the molecules.[6] A passing electron can exert a torque on the molecular dipole and might excite the molecule to a higher rotational state. The electron might lose enough energy in doing this to form a bound ionic or quasi-trapped state in the field of the dipole. The natural decay of this temporary state would supply electrons back into the swarm, thus introducing a contribution to the momentum-transfer cross section not included in Altshuler's theory. Since spacing between rotational states is of the order of thermal energies (kT), stabilized negative ions are not formed by this mechanism.

The present investigation was prompted by the picture just described. Cross sections for capture and lifetimes of the states formed are calculated below. Such a calculation shows the details of electron capture by the mechanism described. The theoretical results substantiate the hypothesis that short-lived ions can be formed by the permanent dipole-electron interaction and appear to offer an explanation of the particular behavior of H_2O, D_2O, and H_2S in swarm experiments.

II. GENERAL FORMULAS

The calculation of the cross section for the transition of a free electron to a bound state in the field of a polar molecule with the simultaneous rotational excitation of the dipole can be carried out along the lines of an earlier theory employed for unimolecular electron capture with vibrational excitation.[8,9] As shown in Fig. 1, we represent the molecule as a rigid dipole with charges $\pm Q$ separated by a distance b. We choose the center of the dipole as the origin of a set of axes XYZ which are fixed in space and which we shall call the laboratory system. The polar and azimuthal angles of the dipole relative to XYZ are denoted by (μ,ν) and the spherical coordinates of the electron relative to XYZ are denoted by (r,θ,φ). We shall also employ polar and azimuthal angles $(\bar{\theta},\bar{\varphi})$ of the electron relative to the dipole. In terms of the separations r_1 and r_2 of the electron from the charges $\pm Q$, the complete Hamiltonian of the system, molecule plus electron, is

$$H=H_M+H_e=-\frac{\hbar^2}{2I}\Theta^2-\frac{\hbar^2}{2m}\nabla^2-\frac{Qe}{r_1}+\frac{Qe}{r_2}. \tag{1}$$

Here $H_M=-\hbar^2\Theta^2/2I$ is the Hamiltonian of a rigid rotator representing the polar molecule with moment of inertia I, and H_e is the Hamiltonian of the electron in the field of the dipole. The operator ∇^2 depends on the coordinates (r,θ,φ) of the electron, whose mass is m. The operator Θ^2 is the square of the total angular momentum of the dipole (in units of $\hbar$) and depends on the coordinates (μ,ν) of the dipole in the laboratory system.

We represent an eigenfunction Ψ of H as a product of an eigenfunction $\psi(r,\bar{\theta},\bar{\varphi})$ of H_e calculated for fixed dipole coordinates and an angular momentum eigenfunction $\mathcal{Y}_{LM}(\mu,\nu)$ of H_M: $\Psi=\psi(r,\bar{\theta},\bar{\varphi})\mathcal{Y}_{LM}(\mu,\nu)$. It is assumed that the functions ψ and $\mathcal{Y}_{LM}$ are related adiabatically.[10] The quantity $-\hbar^2\Theta^2/2I$ representing the rotational kinetic energy of the molecule can be treated as a perturbation that couples the motion of the molecule and the motion of an electron in its field.[9]

Consider an electron swarm moving through a gas consisting of N identical, randomly oriented polar molecules per unit volume. If initially an electron is in a positive-energy eigenstate ψ_i normalized to unit volume and the molecule is in an angular-momentum eigenstate $\mathcal{Y}_{L_iM_i}$, then the transition probability for capture of the electron to state ψ_f with simultaneous excitation of the molecule to a rotational state $\mathcal{Y}_{L_fM_f}$ is given by

$$\begin{aligned} w&=\frac{2\pi}{\hbar}|T_{fi}|^2Nf(E)\\ &=\frac{2\pi}{\hbar}\left|\langle\psi_f\mathcal{Y}_{L_fM_f}|\left(-\frac{\hbar^2}{2I}\Theta^2\right)|\psi_i\mathcal{Y}_{L_iM_i}\rangle\right|^2Nf(E). \end{aligned} \tag{2}$$

It is assumed that the electron swarm is characterized by an energy distribution for which $f(E)dE$ represents the probability of finding an electron with energy be-

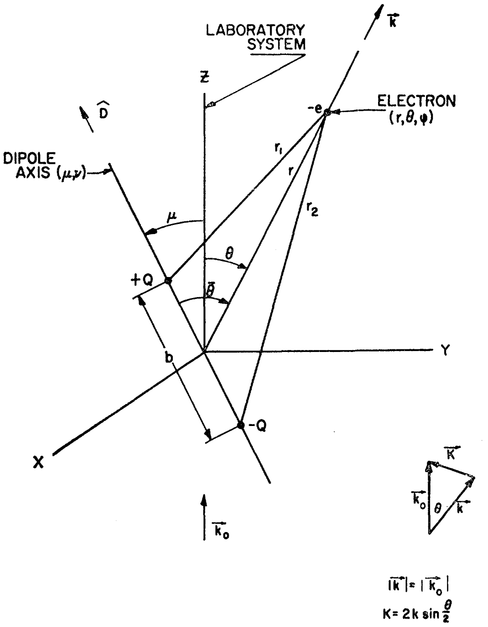

FIG. 1. Reference axes and coordinates used in calculation.

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[8] Felix Bloch and Norris E. Bradbury, Phys. Rev. 48, 689 (1935).

[9] H. S. W. Massey, *Negative Ions* (University Press, Cambridge, England 1938).

[10] M. Born and J. R. Oppenheimer, Ann. Physik 84, 457 (1927).

tween E and $E+dE$. It is understood that the energy E to be used in Eq. (2) is the particular value of the electron kinetic energy for which energy is conserved in the transition $\psi_i\mathcal{Y}_{L_iM_i}\rightarrow\psi_f\mathcal{Y}_{L_fM_f}$. Transitions to a definite final state thus select electrons from the swarm in a narrow energy interval dE, the breadth of which is determined by the lifetime of the final state.

The capture cross section σ_c is defined in terms of the average speed v_0 of electrons as

$$\sigma_c=w/v_0N=(2\pi/\hbar v_0)|T_{fi}|^2f(E) \tag{3}$$

with

$$v_0=\int_0^\infty\left(\frac{2E}{m}\right)^{1/2}f(E)dE. \tag{4}$$

To a good approximation, electrons in the swarm experiments to be considered are in thermal equilibrium and can be characterized by a normalized Maxwellian distribution,[11]

$$f(E)=\frac{2}{\pi^{1/2}(kT)^{3/2}}E^{1/2}e^{-E/kT}. \tag{5}$$

The quantity σ_c is measured experimentally provided the negative ions formed by capture are stabilized before they have a chance to decay, i.e., provided the lifetime of the ion is long compared with the time needed for transfer of the excitation energy to another molecule by collision. When the ions are stabilized, the expression (3) should be multiplied by a pressure factor $p/(p+p')$, where p is the gas pressure and p' is the "critical pressure" at which the lifetime of the negative ion is equal to the time needed for transfer of the excitation energy.[8] The estimates below show that stable ions are not formed; hence we make no use of the pressure factor.

The intrinsic lifetimes of negative ions can be estimated from the matrix element T_{fi}. For decay of the state $\psi_f\mathcal{Y}_{L_fM_f}\rightarrow\psi_i\mathcal{Y}_{L_iM_i}$, the lifetime is given by

$$\tau=\frac{\hbar}{2\pi|T_{fi}|^2dn/dE}, \tag{6}$$

in which dn/dE is the density of final states. For the free electron and neutral molecule, $dn/dE=k^2/2\pi^2\hbar v$, where $\hbar k$ is the magnitude of the momentum of the electron, and so

$$\tau=\pi\hbar^4/m(2Em)^{1/2}|T_{fi}|^2. \tag{7}$$

III. WAVE FUNCTIONS

To calculate the transition probability (2) for electron capture explicitly, we next determine the wave functions involved. For the initial and final rotational eigenstates of the molecule, $\mathcal{Y}_{L_iM_i}$ and $\mathcal{Y}_{L_fM_f}$, we choose the normalized spherical harmonics as defined by Bethe and Salpeter.[12] For the electronic wave functions we assume that the wavelength of an electron in a swarm at thermal energies is long compared with the extension b of the molecular dipole and that in the trapped state the electron is only loosely bound over a volume with dimensions large compared to b. We then approximate the interaction of the electron with the molecule by the interaction of the electron with a point dipole. Expanding the potential energy part of H_e in terms of Legendre polynomials involving the orientation $\bar{\theta}$ of the position of the electron with respect to the dipole axis and keeping only the lowest order terms, we obtain from Eq. (1)

$$H_e\psi_i=(-(\hbar^2/2m)\nabla^2-(De/r^2)\cos\bar{\theta})\psi_i=E_c\psi_i, \tag{8}$$

where $D=bQ$ is the dipole moment of the molecule and E_c is the electron energy in the captured state ($E_c<0$). In terms of the initial kinetic energy E of the electron and the rotational excitation energy ΔE of the molecule, the conservation of energy requires that $\Delta E=E-E_c$.

We regard the initial electron state as consisting of the sum of a plane wave e^{ikz}, with the wave number $k=(2mE/\hbar^2)^{1/2}$, incident along the positive Z axis in the laboratory system and an outgoing spherical wave $f(\theta,\varphi)e^{ikr}/r$ of relatively small amplitude that represents elastic scattering[13] from the dipole with a fixed orientation (μ,ν) in space (Fig. 1):

$$\psi_i=e^{ikz}+f(\theta,\varphi)(e^{ikr}/r). \tag{9}$$

Substituting Eq. (9) into (8) and neglecting terms of order Df and higher, we obtain[14]

$$f(\theta,\varphi)=\frac{Dem}{2\pi\hbar^2}\int\frac{\cos\theta'}{r'^2}e^{i\mathbf{K}\cdot\mathbf{r}'}d^3r', \tag{10}$$

in which $\mathbf{K}=\mathbf{k}_0-\mathbf{k}$ is the momentum change of the scattered electron in units of $\hbar$ and $|\mathbf{k}|=|\mathbf{k}_0|$. Carrying out the integration in Eq. (10) gives

$$f(\theta,\varphi)=2iDem\gamma'/\hbar^2K, \tag{11}$$

where γ' is the direction cosine of the axis of the dipole with respect to the direction of $\mathbf{K}$. To write Eq. (11) explicitly in terms of (μ,ν) and (θ,φ), we form the scalar product of $\mathbf{K}$ with the unit vector $\hat{D}$ along the dipole axis in the direction from the origin to the charge $+Q$

$$\mathbf{K}\cdot\hat{D}=K\gamma'=\alpha K_x+\beta K_y+\gamma K_z. \tag{12}$$

Here K_x, K_y, and K_z are the components of $\mathbf{K}$ in the laboratory system (Fig. 1) and α, β, and γ are the

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[11] Here, as later, the symbol k appearing with the absolute temperature T denotes Boltzman's constant; k used by itself will denote the wave number of an electron.

[12] H. A. Bethe and E. E. Salpteter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press Inc., New York, 1957).

[13] See D. M. Chase, Phys. Rev. **104**, 838 (1956). Note that Altshuler's theory, which rests on the adiabatic approximation as discussed by Chase, explicitly leaves out transitions to bound or quasibound states, such as those considered here.

[14] See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 165.

direction cosines of $\hat{D}$ in this system:

$$\begin{aligned}\alpha &= \sin\mu\,\cos\nu\,,\\ \beta &= \sin\mu\,\sin\nu\,,\\ \gamma &= \cos\mu\,.\end{aligned}\tag{13}$$

The initial momentum $\mathbf{k}_0$ of the electron is directed along the positive Z axis, and so

$$\begin{aligned}K_x &= K_{0x}-k_x=-k\,\sin\theta\,\cos\varphi\,,\\ K_y &= k_{0y}-k_y=-k\,\sin\theta\,\sin\varphi\,,\\ K_z &= k_{0z}-k_z=k(1-\cos\theta)\,.\end{aligned}\tag{14}$$

As indicated in Fig. 1, $K=2k\,\sin(\frac{1}{2}\theta)$, and so we write in place of Eq. (11)

$$f(\theta,\varphi)=\frac{iDem}{2\hbar^2k}\times\frac{-\alpha\,\sin\theta\,\cos\varphi-\beta\,\sin\theta\,\sin\varphi+\gamma(1-\cos\theta)}{\sin^2(\frac{1}{2}\theta)}\,.\tag{15}$$

This expression, combined with (9), gives the initial-state electron wave function. Note that f depends on the coordinates of the dipole in the laboratory system through α, β, γ and Eq. (13).

For the final bound state we choose a function for the electron which is a sum of S and P states referred to angles $(\bar{\theta},\bar{\varphi})$ of the electron's position relative to the dipole axis. These angular-momentum values are coupled by the dipole operator and tend to concentrate the probability density for the electron in the region of space on the side of the perpendicular plane bisecting the dipole axis that contains the positive charge $+Q$. We form a trial function for the electron with a hydrogenic radial dependence corresponding to a principal quantum number $n=1$ and write

$$\psi_f=2(Z/a)^{3/2}e^{-Zr/a}[C_0Y_{00}(\bar{\theta},\bar{\varphi})+C_1Y_{10}(\bar{\theta},\bar{\varphi})]\,.\tag{16}$$

Here $a=\hbar^2/me^2$ is the Bohr radius for hydrogen and Y_{00} and Y_{10} are normalized spherical harmonics[12] depending on the electron coordinates relative to the dipole. The quantity Z plays the role of an "effective charge" that serves as a scaling factor in the expression for the expectation value of the electron energy. For the moment we leave the value of Z unspecified. The function ψ_f is normalized by requring that

$$|C_0|^2+|C_1|^2=1\,.\tag{17}$$

In order to test the suitability of (16) as a trial function, we demonstrate that it can provide a negative expectation value, which we can minimize afterwards by adjusting C_0 and C_1, for the energy of the electron $\langle H_e\rangle$. The calculation of $\langle H_e\rangle$ using (16) is straightforward and yields

$$\langle H_e\rangle=Z^2\left[\frac{e^2}{2a}(|C_0|^2+5|C_1|^2)-\frac{4De\,\mathrm{Re}(C_0C_1^*)}{\sqrt{3}a^2}\right].\tag{18}$$

The first term in the bracket represents the kinetic-energy operator in (8) averaged over the wave function (16). The factor 5 multiplying $|C_1|^2$ in this term arises from the use of a hydrogenic radial state with $n=1$ together with the angular-momentum eigenstate Y_{10} in (16). Under the condition (17) relating C_0 and C_1, the value of $\langle H_e\rangle$ as given by (18) will be a minimum when the phases of C_0 and C_1 are the same, so that the second term will have its maximum magnitude. For real C_0 and C_1, combining (17) and (18) gives

$$\langle H_e\rangle=Z^2[(e^2/2a)(1+4C_1^2)-(4De/\sqrt{3}a^2)C_1(1-C_1^2)^{1/2}]\,.\tag{19}$$

For a fixed value of C_1 the electron energy will be negative provided the dipole moment D is large enough. The minimum value of the dipole moment that will give bound states can be found by setting $\langle H_e\rangle=0$, solving for D, and then setting $\partial D/\partial C_1=0$.[15] This occurs when $C_1=1/\sqrt{6}$, and the minimum value of the energy is given by

$$\langle H_e\rangle_{\min}=(5Z^2/3)\,\mathrm{Ry}(1-(4D/ea\sqrt{15}))\,,\tag{20}$$

where $\mathrm{Ry}=e^2/2a$ is the Rydberg energy. This result implies that there is a bound state for an electron in the field of a point dipole for a dipole moment $D>ea\times\frac{1}{4}\sqrt{15}=2.46\times10^{-18}$ esu cm. This value of the dipole moment is somewhat larger than that of H_2O (1.85×10^{-18} esu cm).[16] The smallest value of dipole moment for which numerical calculations have apparently been made is 2.14×10^{-18} esu-cm; the binding energy in this case is 6.3×10^{-4} eV.[17]

The binding energy itself is not given until the quantity Z^2 in Eq. (20) is evaluated. A plot of the numerical values[17] of the electron ground-state binding energies $-E_c$ shows an almost linear dependence on dipole moment over a wide range in the region $D\sim2$ to 8×10^{-18} esu-cm. The linear function (20) of D can, accordingly, be adjusted to give the correct binding energies over this range. For $D=ea=2.54\times10^{-18}$ esu cm Wallis *et al.* find $E_c=-2.05\times10^{-3}$ Ry. Using these values in Eq. (20) gives $Z^2\sim0.04$, which we shall use below in making numerical estimates.

Finally, we express the angular variables in the trial function (16) in terms of the coordinates (μ,ν) and

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[15] Because of the linear dependence of $\langle H_e\rangle$ on D in Eq. (19), this procedure gives the same result (with less algebraic work) as that obtained by first taking $\partial\langle H_e\rangle/\partial C_1=0$.

[16] A separate calculation by Dr. K. Fox and the author with a trial function having a radial dependence of the form $\exp(-\alpha r^n)$, where α and n are positive real numbers, gives a bound state for $D\sim1.65\times10^{-18}$ esu-cm when n becomes large. Some results from a study of electronic bound states in the field of a permanent electric dipole appear in Oak Ridge National Laboratory Report No. ORNL-3895 (unpublished). Note that for a trial function utilizing only S- and P-state wave functions for the electron, Eq. (8) is equivalent to the *complete* Hamiltonian for the point dipole. The matrix elements of the third and higher order Legendre polynomials in the potential energy haveero valve with this trial z function.

[17] R. F. Wallis, R. Herman, and H. W. Milnes, J. Mol. Spectroscopy **4**, 51 (1960).

(θ,φ) of the dipole and the electron in the laboratory system. With $Y_{00}=1/(4\pi)^{1/2}$, $C_0=\sqrt{\tfrac{5}{6}}$, and $C_1=1/\sqrt{6}$, we obtain from the addition theorem for spherical harmonics

$$\psi_f=\frac{2}{\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}e^{-Zr/a}\biggl[\left(\frac{5}{4\pi}\right)^{1/2}+\left(\frac{4\pi}{3}\right)^{1/2} \times(\mathcal{Y}_{1-1}{}^*Y_{1-1}+\mathcal{Y}_{10}{}^*Y_{10}+\mathcal{Y}_{11}{}^*Y_{11})\biggr]. \tag{21}$$

The functions $\mathcal{Y}$ depend on (μ,ν) and Y on (θ,φ).

IV. EVALUATION OF THE MATRIX ELEMENT FOR TRANSITION PROBABILITY

The matrix element in (2) can now be written with the help of Eqs. (9) and (21) in the form

$$\begin{aligned}T_{fi}&=-\frac{\hbar^2}{2I}\langle\psi_f\mathcal{Y}_{L_fM_f}|\Theta^2|\psi_i\mathcal{Y}_{L_iM_i}\rangle\\&=-\frac{\hbar^2}{I\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\int\int e^{-Zr/a}\biggl[\left(\frac{5}{4\pi}\right)^{1/2}+\left(\frac{4\pi}{3}\right)^{1/2}\\&\quad\times(\mathcal{Y}_{1-1}Y_{1-1}{}^*+\mathcal{Y}_{10}Y_{10}{}^*+\mathcal{Y}_{11}Y_{11}{}^*)\biggr]\mathcal{Y}_{L_fM_f}{}^*\\&\quad\times\Theta^2\left[e^{ikz}+f(\theta,\varphi)\frac{e^{ikr}}{r}\right]\mathcal{Y}_{L_iM_i}\,d^3r\,d\Omega\end{aligned}\tag{22}$$

in which $d\Omega=d(\cos\mu)d\nu$, and $f(\theta,\varphi)$ is understood to depend on μ and ν through the relationships (15) and (13). The molecular rotational states $\mathcal{Y}_{L_fM_f}$ and $\mathcal{Y}_{L_iM_i}$ are orthogonal and hence Eq. (22) can be written as the sum of three integrals

$$T_{fi}=-(\hbar^2/I\sqrt{6})(Z/a)^{3/2}(I_1+I_2+I_3), \tag{23}$$

with

$$I_1=\left(\frac{5}{4\pi}\right)^{1/2}\int\int e^{-Zr/a}\mathcal{Y}_{L_fM_f}{}^*\times\Theta^2 f(\theta,\varphi)\frac{e^{ikr}}{r}\mathcal{Y}_{L_iM_i}d^3r d\Omega, \tag{24}$$

$$I_2=\left(\frac{4\pi}{3}\right)^{1/2}\int\int e^{-Zr/a}\times(\mathcal{Y}_{1-1}Y_{1-1}{}^*+\mathcal{Y}_{10}Y_{10}{}^*+\mathcal{Y}_{11}Y_{11}{}^*)\mathcal{Y}_{L_fM_f}{}^*\times\Theta^2 e^{ikz}\mathcal{Y}_{L_iM_i}d^3r d\Omega, \tag{25}$$

$$I_3=\left(\frac{4\pi}{3}\right)^{1/2}\int\int e^{-Zr/a}\times(\mathcal{Y}_{1-1}Y_{1-1}{}^*+\mathcal{Y}_{10}Y_{10}{}^*+\mathcal{Y}_{11}Y_{11}{}^*)\mathcal{Y}_{L_fM_f}{}^*\times\Theta^2 f(\theta,\varphi)\frac{e^{ikr}}{r}\mathcal{Y}_{L_iM_i}d^3r d\Omega. \tag{26}$$

I_1 represents coupling between the scattered wave and the bound S state; I_2, coupling between the incident plane wave and the P state; and I_3, coupling between the scattered wave and the P state.

The evaluation of these integrals is straightforward but lengthy. The results are

$$I_1=-\frac{2i(5\pi)^{1/2}Dem}{\hbar^2k}\left(\frac{Za}{Z^2+a^2k^2}\right)^2\times\left[1-\left(\frac{ak}{Z}\right)^2+2i\left(\frac{ak}{Z}\right)\right]S_{fi}{}^{(1)}, \tag{27}$$

$$I_2=-\frac{2i(3\pi)^{1/2}a^2}{k(Z^2+a^2k^2)}\left\{1-\frac{Z^2}{Z^2+a^2k^2}\times\left[1-\left(\frac{ak}{Z}\right)^2\right]\right\}S_{fi}{}^{(2)}, \tag{28}$$

$$I_3=-\frac{i(3\pi)^{1/2}Dem}{\hbar^2k}\left(\frac{Za}{Z^2+a^2k^2}\right)^2\times\left[1-\left(\frac{ak}{Z}\right)^2+2i\left(\frac{ak}{Z}\right)\right]S_{fi}{}^{(3)}. \tag{29}$$

The quantities S_{fi} are given by

$$S_{fi}{}^{(1)}=L_f(L_f+1)[\alpha(L_iM_i)\delta_{L_f,L_i+1}+\beta(L_iM_i)\delta_{L_f,L_i-1}]\delta_{M_fM_i}, \tag{30}$$

$$S_{fi}{}^{(2)}=L_i(L_i+1)[\alpha(L_iM_i)\delta_{L_f,L_i+1}+\beta(L_iM_i)\delta_{L_f,L_i-1}]\delta_{M_fM_i}, \tag{31}$$

$$\begin{aligned}S_{fi}{}^{(3)}=\{&L_i(L_i-1)[\gamma(L_fM_f)\eta(L_iM_i)\\&+\epsilon(L_fM_f)\zeta(L_iM_i)]\delta_{L_f+1,L_i-1}\\&+(L_i+1)(L_i+2)[\gamma(L_iM_i)\eta(L_fM_f)\\&+\epsilon(L_iM_i)\zeta(L_fM_f)]\delta_{L_f-1,L_i+1}\}\delta_{M_fM_i}.\end{aligned}\tag{32}$$

Here δ_{ij} represents the Kronecker δ; the angular-momentum coupling coefficients are given by[12]

$$\alpha(LM)=\beta(L+1,M)=\left[\frac{(L+M+1)(L-M+1)}{(2L+1)(2L+3)}\right]^{1/2}, \tag{33}$$

$$\gamma(LM)=\eta(L+1,-M+1)=\left[\frac{(L-M+1)(L-M+2)}{(2L+1)(2L+3)}\right]^{1/2}, \tag{34}$$

$$\epsilon(LM)=\zeta(L+1,-M-1)=\left[\frac{(L+M+1)(L+M+2)}{(2L+1)(2L+3)}\right]^{1/2}. \tag{35}$$

The selection rules for transitions in the molecule are $\Delta L=\pm1$, ±2, and $\Delta M=0$.

To make numerical estimates for electron capture in swarm experiments, we evaluate the leading terms in the above expressions at low energies, $ak \to 0$. In this case, $I_2 \to 0$, I_1 and I_3 can be combined, and the matrix element (23) becomes

$$T_{fi} = \frac{iDem}{Ik\sqrt{6}}\left(\frac{a}{Z}\right)^{1/2}(2(5\pi)^{1/2}S_{fi}^{(1)} + (3\pi)^{1/2}S_{fi}^{(3)}). \quad (36)$$

V. NUMERICAL ESTIMATES AND COMPARISON WITH EXPERIMENT

In this section we present a few quantitative estimates based on the theory described above. To be specific, we consider an experiment at room temperature ($kT \sim 0.025$ eV) with molecules for which $D \sim 2\times10^{-18}$ esu-cm and $I \sim 10^{-40}$ g cm^2. These values approximate, at least, conditions for swarm experiments with H_2O, D_2O, and H_2S.[6]

It follows from the result of the numerical calculation discussed after Eq. (20) that the binding energy $-E_c$ of an electron in the field of a dipole with $D \sim 2\times10^{-18}$ esu-cm is less than 6.3×10^{-4} eV. We shall neglect, therefore, the binding energy of the electron in comparison with the energies needed for excitation of the molecule. For $I \sim 10^{-40}$ g cm^2, the rotational eigenstates $L=1, 2, 3$, for example, have energies 0.006, 0.019, and 0.038 eV. Typically, then, with $E_c \sim 0$, a neutral molecule in the state $L=2$ can capture an electron with kinetic energy E equal to the difference in energies of the states $L=3$ and $L=2$, i.e., with energy $E=0.019$ eV. The importance of this transition in a swarm experiment depends, of course, on the availability of electrons having energies close to this value. Apart from the dependence of the transition probability on the ratio $(D/I)^2$ through Eq. (36), it is important that I be small so that the spacing of rotational levels in the molecule is of the order of kT.

We shall give explicit results for the transition between the states $L=2$ and $L=3$ with $M=0$. Using the numerical values just discussed and remembering that $Z \sim 0.20$, we find from Eq. (36) that $|T_{fi}|^2 \sim 3.6\times10^{-48}$ erg^2. The capture cross section (3) for the transition $L=2 \to L=3(M=0)$ is $\sigma_c \sim 2.4\times10^{-14}$ cm^2. For the negative ion formed in the state $L=3$, $M=0$, Eq. (7) gives for the lifetime $\tau \sim 1.3\times10^{-13}$ sec. By comparison, the rotational period of the state $L=3$ is $\sim 1.8\times10^{-13}$ sec. The theory thus indicates that electrons in a swarm can, by means of rotational excitation of the dipole, become attached to a polar molecule for times less than or comparable to the rotational periods of the molecule. The ions do not live long enough, however, to become stabilized, and their decay returns electrons to the swarm.

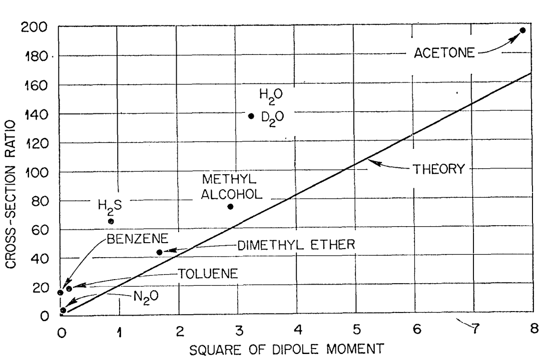

FIG. 2. Summary of data from Hurst, Stockdale, and O'Kelly (Ref. 6), compared with Altshuler's theory. The ordinate gives the momentum transfer cross section ratio for various polar molecules and ethylene.

In effect, the two-step process of capture and loss serves as a mechanism for scattering electrons elastically from the molecules. This process should, therefore, contribute to the momentum transfer cross section.[18] The experimental results of Hurst, Stockdale, and O'Kelly, which are interpreted in terms of Altshuler's theory, are shown in Fig. 2. Except for H_2O, D_2O, and H_2S, which have small polarizabilities, the departures of the experimental results from theory can be attributed to induced polarization of the molecules. From among the molecules shown, H_2O, D_2O, and H_2S appear to be the only ones that satisfy the criteria of having relatively large values of D/I and level spacings comparable to kT.

A search through molecular data tables shows that relatively few molecules meet both these criteria. For all but the lightest molecules, rotational energy level spacings are much less than kT. From among other compounds, the theory given here predicts behavior similar to that of H_2O, D_2O, and H_2S for the molecules NH_3, HF, HCl, and H_2O_2.

Note added in proof. A recent calculation of elastic scattering of electrons on a dipole has been done by M. H. Mittleman and R. E. von Holdt [Phys. Rev. **140**, A726 (1965)]. The newer theory gives a curved line lying somewhat above that in Fig. 2. As in the older theory, however, there is no indication that the observed momentum-transfer cross sections of H_2O, D_2O, and H_2S should be so large compared with those of other molecules having approximately the same dipole moment.

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[18] This suggestion was made by Dr. G. S. Hurst (private communication).