

Rotational Excitation by Slow Electrons*

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Cross sections are calculated for rotational excitation of a homonuclear diatomic molecule by collisions with very slow electrons. The mechanism is assumed to be the long-range quadrupole interaction. The Born approximation is shown to be correct in the low-energy limit. The results are applied to calculation of energy losses in N_2 , and comparison is made with values inferred from swarm and cross-modulation experiments. At energies below 0.29 eV, the threshold for vibrational excitation, losses are \sim twice the experimental values, but many times larger than the value $(2m/M)$ for elastic losses only.

I. INTRODUCTION

AN electron making elastic collisions only as it moves through a gas is expected to lose energy at a rate $\sim(2m/M)\epsilon_a$ per collision,¹ where m is the electron mass, M the molecular mass, and the electron energy ϵ_a is large compared to the mean thermal energy of the molecules. Measurements by swarm experiments² of the rate of energy loss in the noble gases He, Ne, A agree with this theoretical expectation at average electron energies well below the first excitation potential. In molecular gases, on the other hand, the reported energy losses^{1,2} per collision considerably exceed $(2m/M)\epsilon_a$, at average electron energies far below the electronic excitation threshold. In N_2 in particular this excessive energy loss is confirmed by recent experiments in the laboratory^{3,4} and in the ionosphere.^{1,5}

These results obviously suggest that in molecular gases electrons too slow to cause electronic jumps mainly lose energy by rotational and vibrational excitation. Massey⁶ has calculated the cross section for rotational excitation in molecules such as HCl which possess permanent electric dipole moments; he finds the cross section is quite large. In homonuclear diatomic molecules, however, which have no electric dipole moments, Morse⁷ estimated the energy loss by rotational excitation to be of the order of the elastic loss. If this estimate is correct, it is difficult to account for the reported losses at average electron energies much less than the vibrational excitation threshold, under which circumstance vibrational excitation is presumably

negligible. In view of the experimental complications,⁸ and the numerous uncertainties in the interpretation of the swarm experiments,⁹ it cannot be inferred that Morse's estimate of the rotational excitation loss is incorrect. Nonetheless the situation is not satisfactory, and it appears desirable to re-examine the theoretical probability of rotational excitation in homonuclear molecules.

The result that the cross section for rotational excitation by slow electrons is small may be understood as follows. To conserve total angular momentum when the molecule makes a rotational transition, the electron must have some orbital angular momentum either before or after the collision, i.e., it cannot both go in and come out as an s -electron. But at these large wavelengths only s -electrons have an appreciable probability of being found in the vicinity of the molecule. In other words, the electrons possessing the angular momentum to cause rotational transitions are necessarily far from the molecule, interact only weakly with it, and the cross section for rotational excitation is small. This argument, though appealing, proves to be specious⁶ for molecules possessing a dipole moment because the electron-dipole interaction potential, falling off as r^{-2} , is sufficiently strong at long range to permit appreciable interaction with electrons of $l > 0$.

Homonuclear diatomic molecules generally have electric quadrupole moments, so that their interaction with electrons also has a long-range tail, in this case falling off as r^{-3} . In the following section we use a multipole expansion of the molecular field to calculate the cross sections for rotational excitation and de-excitation of homonuclear diatomic molecules by slow electrons. The cross sections, proportional to the square of the quadrupole moment, are smaller than in polar molecules. Nonetheless, in N_2 , at electron energies well below the vibrational threshold, the predicted energy loss by rotational excitation is much larger than the elastic loss and in fact is of the order of magnitude of the observed loss.^{3,4}

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¹ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), pp. 15 and 276-281.

² R. H. Healey and J. W. Reed, *The Behaviour of Slow Electrons in Gases* (Wireless Press, Sydney, 1941), pp. 87-102.

³ R. W. Crompton and D. J. Sutton, Proc. Roy. Soc. (London) **A215**, 467 (1952).

⁴ L. Goldstein (private communication).

⁵ L. G. H. Huxley, *Proceedings of the Conference on Ionospheric Physics (July, 1950) Part A* (Geophysics Research Division, Air Force Cambridge Research Center, 1952), p. 149.

⁶ H. S. W. Massey, Proc. Cambridge Phil. Soc. **28**, 99 (1932).

⁷ P. M. Morse, Phys. Rev. **90**, 51 (1953).

⁸ Crompton, Huxley, and Sutton, Proc. Roy. Soc. (London) **A218**, 507 (1953); L. G. H. Huxley and A. A. Zaazou, Proc. Roy. Soc. (London) **A196**, 402 (1949).

⁹ W. P. Allis and H. W. Allen, Phys. Rev. **52**, 703 (1937).

In our calculation, as in previous calculations^{6,7,10,11} of rotational and vibrational excitation probabilities, Born approximation has been employed despite the fact that the electrons are very slow. Our use of this approximation is defended in the final section of this paper. We argue that the principal contribution to the cross section comes from large distances of the incoming electrons from the molecule, where the wave function is only slightly distorted from its incident form. This argument, which is related to one given by Massey,⁶ leads to the inference that at low energies, because the effective region of interaction is increasingly distant from the molecule, the Born approximation probably improves with decreasing incident electron energy.

We support and justify our argument by evaluating the second Born approximation to the scattering amplitude for a pure quadrupole interaction. We find that the ratio of the second to first Born amplitudes approaches unity with decreasing incident electron energy. Born approximation is much harder to justify when the principal contributions to the cross section come from small distances, as is the case when the quadrupole field of the homonuclear molecule is neglected. The oft-employed assumption that the charge distribution of the molecule is the sum of two spherically symmetric parts, each centered about a nucleus, neglects the quadrupole field, since the potential of such a charge distribution vanishes exponentially at infinity. These remarks amount to a criticism of the use of Born approximation in some previous work, and help account for the fact that we predict a larger energy loss by rotational excitation than does Morse.⁷

It is our conclusion that in N_2 at least, at electron energies below the vibrational threshold, losses significantly exceeding the elastic value are consistent with theory. Our predicted losses are in qualitative agreement with the reported values; as explained in Secs. III and IV, without additional experimental and theoretical work, a more detailed comparison of our predictions with the experiments would not be meaningful. Evidently it would be desirable to have more direct experimental evidence of rotational excitation. A possible means of accomplishing this is described in an accompanying paper¹² on H_2 .

II. FORMULATION

We seek a solution Ψ of the Schrödinger equation:

$$(H-E)\Psi=0, \quad (1)$$

where

$$H=H_0-(\hbar^2/2m)\Delta_r+V, \quad (2)$$

¹⁰ H. S. W. Massey, *Trans. Faraday Soc.* **31**, 556 (1935).

¹¹ T. Y. Wu, *Phys. Rev.* **71**, 111 (1947).

¹² E. Gerjuoy and S. Stein (to be published). In H_2 , the only other gas on which there are recent data below the vibrational threshold, the observed losses exceed the expected elastic loss by a rather smaller factor than in N_2 . See Crompton and Sutton, reference 3.

with

$$V=-\sum_j Z_j e^2/|\mathbf{r}-\mathbf{r}_j|. \quad (3)$$

In the above, \mathbf{r} is the coordinate of the incident electron, H_0 is the Hamiltonian of the isolated molecule, and the subscript j indexes the particles, electrons, and nuclei, composing the molecule. The perturbing Coulomb interaction V is summed over the coordinates \mathbf{r}_j of all particles in the molecule. The charge Z_j is -1 for electrons and is $Z=N/2$ for either nucleus, with N the total number of electrons in the molecule. The center of mass of the entire system, molecule plus incident electron, is the origin of coordinates. It may be assumed to coincide with the center of mass of the isolated molecule, since the incident electron mass m is so small. The scattering amplitude $A_{ab}(\mathbf{n}, \mathbf{n}_0)$ for the transition from the initial molecular state φ_a with electron incident along \mathbf{n}_0 to the final molecular state φ_b with electron outgoing along \mathbf{n} is¹³

$$A_{ab}(\mathbf{n}, \mathbf{n}_0) = - (m/2\pi\hbar^2) \int d\mathbf{r} d\mathbf{r}_j \exp[-ik_a\mathbf{n}\cdot\mathbf{r}] \\ \times \varphi_b^*(\mathbf{r}_j) V(\mathbf{r}, \mathbf{r}_j) \Psi_a(\mathbf{r}, \mathbf{r}_j). \quad (4)$$

Here Ψ_a is a solution of Eq. (1) which satisfies the usual boundary conditions, i.e., outgoing at infinity except for its incident part $\varphi_a(\mathbf{r}_j) \exp[ik_a\mathbf{n}_0\cdot\mathbf{r}]$. The integral (and implied spin sum) in Eq. (4) is over the coordinates of the initial electron and of all particles j in the molecule. Since V is independent of spin, the nuclear, molecular electron, and incident electron spins are individually conserved. The initial and final wave numbers of the incident electron, k_a and k_b , respectively, are related by

$$E = (\hbar^2 k_a^2/2m) + E_a = (\hbar^2 k_b^2/2m) + E_b, \quad (5)$$

with E_a and E_b the energies of the corresponding molecular states φ_a and φ_b . The differential cross section for scattering the electron into the direction \mathbf{n} , with the molecule making the transition from state φ_a to φ_b , is

$$\sigma_{ab}(\mathbf{n}) = (k_b/k_a) |A_{ab}|^2. \quad (6)$$

We confine our attention to molecular states which can be classified as ${}^1\Sigma$, in which event¹⁴ the Born-Oppenheimer approximation to φ_a or φ_b is

$$\varphi(\mathbf{r}_j) = w(\mathbf{r}_e, \mathbf{s}) S(s) Y(\Theta, \Phi), \quad (7)$$

where \mathbf{r}_e refer to the molecular electrons only, $w(\mathbf{r}_e, \mathbf{s})$ are the molecular electronic wave functions for fixed

¹³ N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, Chap. VIII.

¹⁴ The ground states of homonuclear diatomic molecules generally have this classification. In particular, H_2 and N_2 have ${}^1\Sigma$ ground states. For O_2 , with a ${}^3\Sigma$ ground state, Eq. (7) requires some modification, but our evaluation of $\sigma(\mathbf{n})$ is not basically invalidated, since the rotational wave functions are still spherical harmonics. Our analysis is not applicable to non- Σ states, the wave functions for which cannot be factored into a product of electronic and rotational wave functions, and for which the rotational wave functions are Jacobi polynomials. R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, Cambridge, 1930), pp. 6 ff.

internuclear coordinate \mathbf{s} , $S(s)$ are vibrational wave functions, and $Y(\Theta, \Phi)$ are spherical harmonics describing the rotational states of the molecule. The coordinates (s, Θ, Φ) of \mathbf{s} are referred to fixed axes in space, and the nuclei are located at $\pm \frac{1}{2}\mathbf{s}$.

In the problem presently at hand, we seek the transition probability for rotational excitation only, with the molecule initially and finally in its ground electronic and vibrational state. In other words, in Eq. (7) we have $w_a = w_b = w_0$, $S_a = S_b = S_0$, where the subscript 0 indicates the ground state. The electronic density distribution in the ground state of the molecule, for fixed \mathbf{s} , is

$$\rho(\mathbf{r}, \mathbf{s}) = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N |w_0(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N, \mathbf{s})|^2. \quad (8)$$

As usual, spin summation is implied in Eq. (8). It can now be concluded from Eqs. (3), (7), and (8), that for rotational excitation only, and in Born approximation, the matrix element A_{ab} of Eq. (4) is

$$A_{ab}(\mathbf{n}, \mathbf{n}_0) = - (m/2\pi\hbar^2) \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \times \int d\Theta d\Phi \sin\Theta Y_b^* Y_a V'(\mathbf{r}, \Theta, \Phi), \quad (9)$$

with $\mathbf{k} = k_a \mathbf{n}_0 - k_b \mathbf{n}$ and

$$V'(\mathbf{r}, \Theta, \Phi) = \int ds s^2 |S_0(s)|^2 V''(\mathbf{r}, \mathbf{s}), \quad (10)$$

$$V''(\mathbf{r}, \mathbf{s}) = -e^2 \left[\frac{Z}{|\mathbf{r} - \frac{1}{2}\mathbf{s}|} + \frac{Z}{|\mathbf{r} + \frac{1}{2}\mathbf{s}|} - \int d\mathbf{r}' \frac{\rho(\mathbf{r}', \mathbf{s})}{|\mathbf{r} - \mathbf{r}'|} \right]. \quad (11)$$

Evidently V' is the electrostatic interaction between the incident electron and molecule, for fixed orientation of the internuclear axis, averaged over the ground state electronic and vibrational wave functions.

We now make a multipole expansion of V' . The use of this expansion is justified in Sec. IV on the grounds used to defend Born approximation, namely that the principal contribution to the cross section comes from large values of r . In Σ states $\rho(\mathbf{r}', \mathbf{s})$, and, therefore, $V''(\mathbf{r}, \mathbf{s})$, are axially symmetric¹⁵ about \mathbf{s} , so that the expansion has the form at large r

$$V''(\mathbf{r}, \mathbf{s}) = - (e^2/r) \sum_n r^{-n} P_n(\mathbf{r}, \mathbf{s}) B_n(s), \quad (12)$$

$$V'(\mathbf{r}, \Theta, \Phi) = - (e/r) \sum_n r^{-n} P_n(\mathbf{r}, \mathbf{s}) C_n, \quad (13)$$

where we find, for even n ,

$$B_n(s) = 2Z \left(\frac{1}{2}s\right)^n - \int d\mathbf{r}' \rho(\mathbf{r}', \mathbf{s}) r'^n P_n(\mathbf{r}', \mathbf{s}), \quad (14)$$

$$C_n = e \int ds s^2 |S_0(s)|^2 B_n(s). \quad (15)$$

Here $P_n(\mathbf{r}, \mathbf{s})$ is the n th Legendre polynomial in the angle between \mathbf{r} and \mathbf{s} , and e is the absolute value of the electronic charge. $B_n(s)$ is zero for odd n , because $V''(\mathbf{r}, \mathbf{s}) = V''(-\mathbf{r}, \mathbf{s})$. This symmetry follows from the property $\rho(\mathbf{r}, \mathbf{s}) = \rho(-\mathbf{r}, \mathbf{s})$, valid for the gerade or ungerade w_0 of homonuclear molecules.¹⁴ $B_0(s)$ vanishes because, in Eq. (14), $\int d\mathbf{r}' \rho(\mathbf{r}', \mathbf{s}) = N = 2Z$. In fact Eq. (15) makes C_n the n th electric moment of the molecule along the axis of symmetry \mathbf{s} , consistent with the usual definition for an axially symmetric charge distribution $q(\mathbf{r})$:

$$C_n = \langle q(\mathbf{r}) r^n P_n(\mathbf{r}, \mathbf{s}) \rangle. \quad (16)$$

Of course the monopole moment and all odd electric moments must vanish for neutral homonuclear molecules.

The leading term in Eq. (12), proportional to the quadrupole moment, makes the principal contribution to the energy loss. Retaining this term then, and deferring until later the justification for neglecting the higher moments, we find from Eqs. (6), (9), and (13)

$$\sigma_{ab}(\mathbf{n}) = (k_b/k_a) (Qa_0/2\pi)^2 \left| \int d\mathbf{r} r^{-3} e^{i\mathbf{k}\cdot\mathbf{r}} \times \int d\Theta d\Phi \sin\Theta Y_b^* Y_a P_2(\mathbf{r}, \mathbf{s}) \right|^2, \quad (17)$$

where $a_0 = \hbar^2/me^2$, and Q is the measured¹⁶ quadrupole moment of the molecule, in units of ea_0^2 . In Eq. (17) we may interchange the order of integration, whereupon the integral over \mathbf{r} proves to be trivial. Also we now label the states a and b by the initial and final rotational quantum numbers J_a, M_a and J_b, M_b , and perform the sums over the azimuthal quantum numbers M_a and M_b , thereby determining the effective cross section for a transition from rotational level J_a to J_b . There results:

$$\sigma_{ab}(\mathbf{n}) = \frac{k_b}{k_a} \frac{4Q^2 a_0^2}{9} \frac{1}{2J_a + 1} \sum_{M_a} \sum_{M_b} \int d\Omega Y_{J_a}^{M_a}(\mathbf{s}) \times Y_{J_b}^{M_b}(\mathbf{s}) P_2(\mathbf{k}, \mathbf{s}) \int d\Omega' Y_{J_a}^{M_a}(\mathbf{s}') \times Y_{J_b}^{M_b}(\mathbf{s}') P_2(\mathbf{k}, \mathbf{s}'), \quad (18)$$

where \mathbf{s} is specified by the angles Θ, Φ in $d\Omega$ and \mathbf{s}' is similarly specified by Θ', Φ' in $d\Omega'$. The sums over M_a and M_b are immediately evaluated. The effective differential cross section $\sigma_{ab}(\mathbf{n})$ then is seen to be spherically symmetric, so that the total cross section for the transition from level a to level b becomes

$$\sigma_{ab} = \frac{8\pi Q^2 a_0^2}{45} \frac{k_b}{k_a} (2J_b + 1) \int_{-1}^1 dx P_{J_a}(x) P_{J_b}(x) P_2(x). \quad (19)$$

¹⁶ Caution is demanded in using reported values of the quadrupole moment since several different definitions of this quantity are current, differing by numerical factors from the definition Eq. (16) which we adopt.

¹⁵ R. de L. Kronig, reference 14.

The integral in Eq. (19) is known.¹⁷ It vanishes except when $J_b = J_a \pm 2$ or $J_b = J_a$, in agreement with the usual selection rules for electric quadrupole transitions: $|J_a - J_b| \leq 2$ and no change in parity. We are interested in the inelastic processes only, $J_b = J_a \pm 2$. Our final expressions are

$$\begin{aligned} \sigma_{J, J+2} &= \frac{8\pi Q^2 a_0^2 k_b}{15 k_a} \frac{(J+2)(J+1)}{(2J+3)(2J+1)}, \\ \sigma_{J, J-2} &= \frac{8\pi Q^2 a_0^2 k_b}{15 k_a} \frac{J(J-1)}{(2J-1)(2J+1)}, \end{aligned} \quad (20)$$

where $\sigma_{J, J+2}$ refers to a transition from level $J_a = J$ to level $J_b = J+2$, in which the incident electron loses energy to the molecule, and $\sigma_{J, J-2}$ refers to a transition from level J to $J-2$, in which the incident electron gains energy. To very good approximation, the energy levels E_J are

$$E_J = BJ(J+1). \quad (21)$$

Consequently, using Eq. (5), with ϵ_a the incident electron energy, we have in Eq. (20) for

$$\begin{aligned} \sigma_{J, J+2} &: \frac{k_b}{k_a} \left[1 - \frac{B}{\epsilon_a} (4J+6) \right]^{\frac{1}{2}}, \\ \sigma_{J, J-2} &: \frac{k_b}{k_a} \left[1 + \frac{B}{\epsilon_a} (4J-2) \right]^{\frac{1}{2}}. \end{aligned} \quad (22)$$

We conclude this section with the remark that the cross sections, Eq. (20), are not altered by the nuclear spin selection rule which results from the connection between spin and statistics. When the nuclei are identical and the molecule in a 1Σ state, rotational levels with the same total nuclear spin must have the same parity, $(-)^J$. Since the nuclear spin cannot be changed by the potential V of Eq. (3), this implies the selection

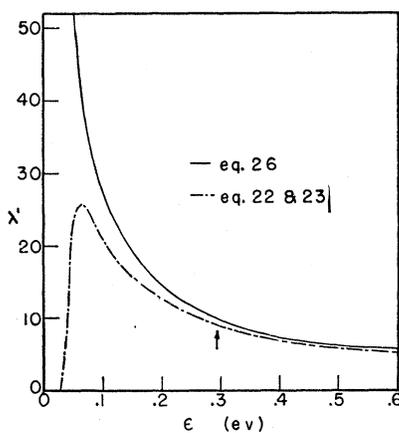


Fig. 1. Comparison of fractional energy losses computed from Eq. (26) or Eqs. (22) and (23).

¹⁷ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951), p. 182.

rule ΔJ even, which coincides with the selection rule already derived.

III. NUMERICAL RESULTS

The rate at which an electron of energy ϵ_a loses energy in rotational excitation of the homonuclear gas is

$$\frac{dW_e}{dt} = v_a \sum_J N_J [\sigma_{J, J+2} (E_{J+2} - E_J) - \sigma_{J, J-2} (E_J - E_{J-2})], \quad (23)$$

where N_J is the number of molecules per cc in the J th rotational level, $\sigma_{J, J+2}$ and $\sigma_{J, J-2}$ are given by Eq. (20), and v_a is the electron velocity. Except at the very highest gas temperatures and lowest electron energies, the velocities of the molecules may be and have been neglected in Eq. (23) compared to v_a . Particularly at the higher electron energies, k_b/k_a may be replaced by unity. This approximation yields the very simple result, independent of the relative populations N_J ,

$$dW_e/dt = (32\pi Q^2 a_0^2 / 15) N B v_a, \quad (24)$$

where N is the total number of molecules per cc. According to Eqs. (20) and (22), Eq. (24) always overestimates the energy loss computed from Eq. (23).

In units of $2m/M$, the mean fractional energy loss λ' of the electrons, per collision with the gas molecules, is defined in terms of the total rate of energy loss dW/dt by the relation

$$\lambda' = (M/2m) (N \sigma_t v_a \epsilon_a)^{-1} (dW/dt), \quad (25)$$

where σ_t is the total collision cross section, elastic plus inelastic. λ' equals unity when the elastic cross section is spherically symmetric, the gas velocity negligible compared to the electron velocity, and inelastic losses are unimportant. If the inelastic losses are well approximated by Eq. (24), then

$$\lambda' = 1 + \frac{32\pi Q^2 a_0^2 B \cdot M}{15 \sigma_t \epsilon_a 2m}. \quad (26)$$

Losses in Nitrogen

In nitrogen,^{18,19} $B = 0.249 \times 10^{-8}$ ev, $|Q| = 0.96$. In Fig. 1 are compared λ' from Eq. (26) with λ' computed from Eqs. (22) and (23), for 0.025–0.6 ev electrons incident on N_2 at 290°K, using²⁰ $\sigma_t = 4.8\pi a_0^2$ independent of electron energy and employing a Boltzmann distribution for the populations N_J . The utility of the closed expression Eq. (26) for λ' may be gauged from this figure. In Fig. 2 the exact values of λ' , from Eqs. (22) and (23), again for N_2 at 290°K, are compared with the values of λ' obtained by Crompton and Sutton⁸ (curve C) when they assumed their electrons had a

¹⁸ G. Herzberg, *Molecular Spectra and Molecular Structure I* (D. Van Nostrand, New York, 1950), Table 39.

¹⁹ W. V. Smith and R. Howard, *Phys. Rev.* **79**, 132 (1950).

²⁰ Phelps, Fundingsland, and Brown, *Phys. Rev.* **84**, 559 (1951).

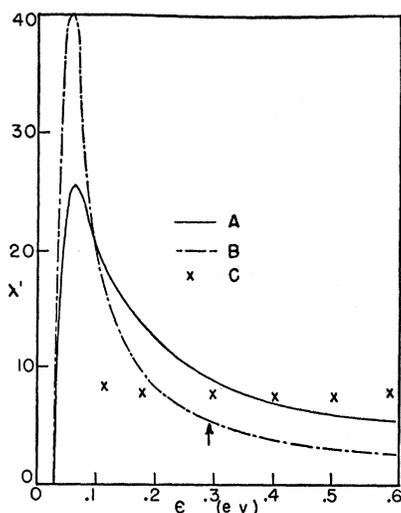


FIG. 2. Theoretical energy losses obtained by assuming various elastic cross sections.

Maxwellian distribution. Since the magnitude and energy dependence of σ_t are uncertain, two "exact" curves are drawn in Fig. 2, curve *A* using the aforementioned constant value of $\sigma_t = 4.8\pi a_0^2$, and curve *B* using an energy dependent σ_t (*B'* of Fig. 3). The various reported values^{3,20-22} of the cross section²³ for electrons in N_2 , in the energy range below 0.8 eV, are summarized in Fig. 3. Curve *A'* in Fig. 3 is the constant value $\sigma_t = 4.8\pi a_0^2$, which is seen to lie below the other reported values, but which lies very close to the theoretical estimate by Fisk²⁴ of the elastic cross section. Curve *B'* is drawn through the experimental points of Crompton and Sutton,³ and extrapolated from their observations. Comparison of curves *A* and *B* in Fig. 2 illustrates the influence on the theoretical estimate of λ' of differing assumptions concerning the magnitude and energy dependence of σ_t . These curves also show that the predicted fractional energy loss by rotational excitation is an order of magnitude greater than the value $\lambda' = 1$ expected for elastic losses only.

The analysis of the raw data of the swarm experiments to get the fractional energy loss as a function of mean energy is complicated and involves numerous assumptions, e.g., the electrons have a specified distribution (Maxwellian or Druyvesteyn) and a mean free path independent of velocity. For this reason the experimental curve *C* (Fig. 2) represents what might be called an effective energy loss *vs* mean energy in the swarm, and is not simply related to the average of curves *A* or *B* over the distribution function. None-

²¹ C. Ramsauer and R. Kollath, *Z. Physik* 4, 91 (1930).

²² J. Townsend and V. A. Bailey, *Phil. Mag.* 42, 873 (1921).

²³ It is not always clear whether the experiments measured σ_t , the total cross section, or merely σ_e , the elastic cross section. The distinction is not important, however, since the inelastic cross sections $\sigma_{J,J+2}$ and $\sigma_{J,J-2}$ of Eq. (20) turn out to be much smaller than the reported values of σ_t .

²⁴ J. B. Fisk, *Phys. Rev.* 49, 167 (1936).

theless we may conclude from curves *A* or *B* and *C*, as they stand, that rotational excitation, occurring through the coupling between the electron and the molecular quadrupole field, is of the right order of magnitude²⁵ to account for the observed energy losses in N_2 , at energies below the vibrational threshold (0.29 eV, indicated by the arrow on the energy scale in Fig. 2). If vibrational excitation is in fact negligible, the electron distribution function can be computed by numerical integration of the Boltzmann equation, using some assumed elastic cross section and the theoretical inelastic cross sections of Eq. (20). From the distribution function there can be determined, again using Eq. (20), the expected drift velocities and diffusion coefficients which are the raw data of the swarm experiments. Thus it is possible in principle to make a detailed comparison of our theory with the experimental results. In view of the previously mentioned experimental and theoretical uncertainties in the swarm experiments, and our present inaccurate knowledge of the elastic cross section σ_t and quadrupole moment²⁶ Q , such a comparison probably would be no more than qualitatively significant. However, with any reasonable assumptions concerning the errors in the swarm experiments, and the values of σ_t and Q , it is unlikely that such a comparison would not bear out an obvious inference from Fig. 2—namely that rotational excitation becomes relatively unimportant at energies above the vibrational threshold, and consequently that vibrational excitation becomes important. As explained in Sec. IV the approximations leading to Eq. (20) are increasingly inaccurate in N_2 as the incident energy increases above the vibrational threshold, so that the foregoing inference may not stand up. Nonetheless it appears worthwhile to re-examine the theoretical predictions of only small energy loss by vibrational excitation,^{7,10,11} particularly since the similar theoretical estimates of the rotational loss appear to have been too small.

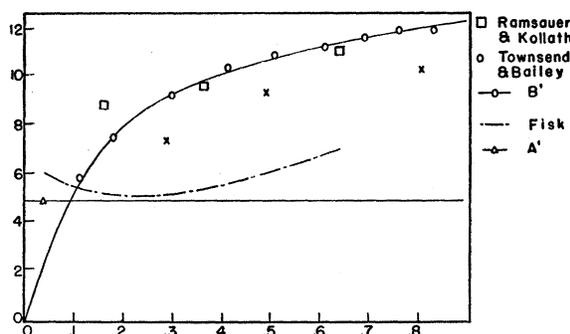


FIG. 3. Elastic cross section data.

²⁵ We remark that curves *A* or *B* are indistinguishable from computed curves taking into account corrections to the rotational spacing, i.e., using $E_J = BJ(J+1) - DJ^2(J+1)^2$ with $D = 0.72 \times 10^{-9}$ eV. See Herzberg, reference 18.

²⁶ Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), p. 294.

Laboratory cross modulation experiments provide further data. When the average electron energy $\bar{\epsilon}_a$ is very nearly equal to the mean kinetic energy ϵ_0 of the molecules, the rate of loss of energy per electron usually is taken to be

$$(dW/dt) = G\nu(\bar{\epsilon}_a - \epsilon_0), \quad (27)$$

where ν is the collision frequency and G a numerical factor. For a Maxwellian distribution of electrons, making elastic collisions only,²⁷ $G = 8m/3M$. Goldstein⁴ finds $G\nu = 6.4 \times 10^5 \text{ sec}^{-1}$. In the cross-modulation experiment the electron distribution presumably is Maxwellian, at a temperature nearly equal to the gas temperature. Averaging Eq. (23) over a Maxwellian distribution, and dividing by $(\bar{\epsilon}_a - \epsilon_0)$, we can compute the theoretical value of $G\nu$ implied by our rotational excitation cross sections. We find $G\nu = 13 \times 10^5 \text{ sec}^{-1}$, independent of σ_t [which does not appear in Eq. (23)], for an electron temperature of 290°K, equal to the gas temperature. Using $\sigma_t = 4.8\pi a_0^2$, Goldstein's value of $G\nu$ corresponds to $G = 51(2m/M)$, and our value to $G = 100(2m/M)$. These results again demonstrate that rotational excitation can account for observed losses much larger than elastic.

IV. VALIDITY OF APPROXIMATIONS

The following approximations employed in Sec. II require discussion: (i) Born approximation; (ii) the multipole expansion of V' , Eq. (13); (iii) the neglect of moments higher than quadrupole in obtaining Eq. (20). Granting (i) and (ii), justification of (iii) is not difficult. Retaining the higher moments in Eq. (13) we find, by the same procedure as was used to obtain Eq. (19), that the differential cross section for transitions from rotational level J_a to J_b is

$$\sigma_{ab}(\mathbf{n}) = \frac{k_b}{k_a} (2a_0^2) (2J_b + 1) \sum_n \frac{(ka_0)^{2n-4} Q_n^2}{[1 \cdot 3 \cdots (2n-1)]^2 (2n+1)} \times \int_{-1}^1 dx P_{J_a}(x) P_{J_b}(x) P_n(x), \quad (28)$$

where the sum is over even n only, of course, and we have introduced

$$C_n = Q_n e a_0^n; \quad (29)$$

i.e., Q_n is the n th electric moment of the molecule, in units of $e a_0^n$. In these units, for N_2 or any likely homonuclear diatomic molecule, Q_n is a number at most of order unity, and probably decreases rapidly with increasing n . The maximum magnitude of \mathbf{k} is $k_a + k_b$, attained when \mathbf{n} is antiparallel to \mathbf{n}_0 . As k_b is always nearly equal to k_a , we estimate that for 0.6-eV electrons incident, at which energy in N_2 our computed rotational losses become about equal to elastic (Fig. 2), the maximum value of ka_0 in Eq. (28) is 0.42. Since the series in Eq. (28) is an expansion in powers of (ka_0) ,⁴

²⁷ A. M. Cravath, Phys. Rev. 36, 248 (1930).

it is apparent that at the low energies in which we are interested, the moments higher than quadrupole will make a small or negligible contribution to the cross sections Eq. (20).

In order to examine the validity of (i) and (ii), we write the matrix element, Eq. (4), as the sum of two amplitudes:

$$A_{ab}(\mathbf{n}, \mathbf{n}_0) = A_1 + A_2, \quad (30)$$

where the "near-field" amplitude is

$$A_1 = - (m/2\pi\hbar^2) \int_{r < r_0} d\mathbf{r} \int d\mathbf{r}_j \exp[-ik_b \mathbf{n} \cdot \mathbf{r}] \varphi_b^*(\mathbf{r}_j) \times V(\mathbf{r}, \mathbf{r}_j) \Psi_a(\mathbf{r}, \mathbf{r}_j), \quad (31)$$

and the "far-field" amplitude is

$$A_2 = - (m/2\pi\hbar^2) \int_{r > r_0} d\mathbf{r} \int d\mathbf{r}_j \exp[-ik_b \mathbf{n} \cdot \mathbf{r}] \varphi_b^*(\mathbf{r}_j) \times V(\mathbf{r}, \mathbf{r}_j) \Psi_a(\mathbf{r}, \mathbf{r}_j). \quad (32)$$

The distance r_0 is so chosen that only a negligible fraction of the molecular charge distribution lies outside r_0 . In other words, the integral in A_1 extends over the interior of the molecule, and that in A_2 over the exterior of the molecule. A_2 , but not A_1 , can be correctly evaluated using the multipole expansion.

We assume for the moment that A_1 is negligible in Eq. (30), and that Born approximation is valid in Eq. (32). We are thereby led to the cross section

$$\sigma_{ab}(\mathbf{n}) = \frac{k_b}{k_a} (2a_0^2) (2J_b + 1) \sum_n (ka_0)^{2n-4} Q_n^2 \left[\frac{j_{n-1}(kr_0)}{(kr_0)^{n-1}} \right]^2 \times \frac{1}{2n+1} \int_{-1}^1 dx P_{J_a}(x) P_{J_b}(x) P_n(x). \quad (33)$$

In deriving Eq. (28), (i) and (ii) were assumed valid for all r , i.e., r_0 was assumed equal to zero in Eqs. (31) and (32), which made A_1 identically zero. Thus as r_0 approaches zero in Eq. (33), that equation becomes identical with Eq. (28). At $\rho = 1$ the functions $j_{n-1}(\rho)/\rho^{n-1}$ appearing in Eq. (33) are only ten percent different from their values²⁸ at $\rho = 0$. If kr_0 does not exceed unity, therefore, $\sigma_{ab}(\mathbf{n})$ of Eq. (33) will differ from $\sigma_{ab}(\mathbf{n})$ of Eq. (28) by at most twenty percent. Also the quadrupole contribution in Eq. (33) will be as dominant as in Eq. (28). We thereby have reduced the problem of justifying Eq. (20) to demonstrating (a) $kr_0 \leq 1$; (b) (i) is valid in Eq. (32); and (c) A_1 of Eq. (31) is negligible.

In N_2 , the internuclear distance in the ground vibrational state¹⁸ is $2.1a_0$. The atomic radius of nitrogen is²⁹ close to $1.0a_0$. Consequently, it is reasonable to assume that in N_2 the charge distribution is mainly confined to

²⁸ *Tables of Spherical Bessel Functions* (Columbia University Press, New York, 1947).

²⁹ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

the interior of a sphere of radius $r_0 = 2.1a_0$, centered at the origin midway between the two nuclei. Thus in N_2 , for 0.6-ev electrons incident, the maximum value of kr_0 is 0.88. Moreover since k_b is nearly equal to k_a , and the differential cross sections leading to Eq. (20) are spherically symmetric, a mean value of $k = |k_b \mathbf{n} - k_a \mathbf{n}_0|$ is $\sqrt{2}k_a$, which makes $kr_0 = 0.62$ in N_2 , for 0.6-ev electrons incident. We infer that in N_2 , for incident electron energies < 0.6 ev, condition (a), $kr_0 \leq 1$, is satisfied, and in fact so well that the differences between cross sections computed from Eqs. (20) and (33) are not significant, especially at the lower incident electron energies.

It is more difficult to demonstrate condition (b). An indication of the order of magnitude of the distance r_1 beyond which the distortion of the incident wave function is small is provided by the criterion:

$$Qe^2 a_0^2 / r_1^3 = \hbar^2 k_a^2 / 2m, \quad (34)$$

which makes r_1 the distance at which the incident electron energy equals its interaction energy with the molecule. This estimate of r_1 is based on the conventional view that Born approximation is valid when the interaction energy is small compared to the kinetic energy, as is the case at distances $r > r_1$. From Eq. (34) we obtain, with $k = \sqrt{2}k_a$,

$$kr_1 = \sqrt{2}(2Qk_a a_0)^{\frac{1}{2}}. \quad (35)$$

Equation (35) makes kr_1 just about equal to unity for 0.6-ev electrons in N_2 . As the incident energy decreases, kr_1 approaches zero, though r_1 increases and becomes infinite at zero incident energy. We have already seen, from comparison of Eqs. (20), (28), and (33), that the principal contribution to the scattering amplitude of Eq. (9), or to A_2 of Eq. (32), comes from distances r such that $kr > 1$. Equation (35) suggests therefore that for N_2 , with incident electron energies < 0.6 ev, Born approximation is valid, increasingly so as the incident energy is decreased, since at these low energies the principal contribution to Eq. (32) appears to arise from distances r at which the wave function is only slightly distorted from its incident form.

The criterion Eq. (34) is not theoretically sound because at any distance r the distortion of the wave function from its incident form depends not merely on the value of the interaction at that r , but also on the values of the interaction at all other distances, in particular at smaller distances, where the interaction is larger. Moreover the distortion of the wave function at small distances may be so great as to result in an appreciable contribution to the scattering amplitude from distances $kr \leq 1$, even though these distances are not significant in first Born approximation. We have further examined this question by evaluating the second Born approximation to the scattering amplitude for a pure quadrupole interaction, i.e., in Eq. (13) $V' = -eC_2 r^{-3} P_2(\mathbf{r}, \mathbf{s})$ for all r . The difference between the

first and second Born approximations is a first estimate of the error made in Eq. (4) by neglecting the distortion from $\varphi_a(\mathbf{r}_j) \exp(i\mathbf{k}_a \mathbf{n}_0 \cdot \mathbf{r})$ of Ψ_a . Details of the calculation (which involves some approximations) are given elsewhere,³⁰ and it is found that

$$A_{ab}^{(2)} \sim (1 + 0.15Qk_a a_0) A_{ab}^{(1)}, \quad (36)$$

where $A_{ab}^{(1)}$ and $A_{ab}^{(2)}$ are respectively the first and second Born approximations to A of Eq. (4), using a pure quadrupole interaction. From Eq. (36), $A_{ab}^{(2)} / A_{ab}^{(1)}$ approaches unity as $k_a \rightarrow 0$, and in N_2 , for 0.6-ev electrons, equals 1.03. Thus we conclude that our qualitative argument based on Eqs. (34) and (35) did not lead us astray; that in computing the "far-field" amplitude A_2 of Eq. (32) (first) Born approximation is increasingly valid as the incident energy decreases; and that in N_2 , for incident electron energies < 0.6 ev, the error in first Born approximation to A_2 probably is not appreciable, although since the factor in Eq. (36) is admittedly approximate, an error of 10 percent or more in $|A_2|^2$ cannot be ruled out at energies close to 0.6 ev.

To complete the justification of Eq. (20) we must demonstrate (c) A_1 of Eq. (31) is negligible. This we do by evaluating A_1 in Born approximation, although we recognize that in the region $r < r_0$ Born approximation is not valid. In default of a better way to estimate A_1 , however, we trust that Born approximation does give a measure of the magnitude of A_1 . It turns out, as we shall show, that in Born approximation, for incident electron energies < 0.6 ev in N_2 , A_1 is small, though perhaps not negligibly so at 0.6 ev. We conclude therefore, that our theoretical estimates of the energy losses in N_2 , especially at energies below the vibrational threshold, probably would not be significantly altered by including in $A_{ab}(\mathbf{n}, \mathbf{n}_0)$ of Eq. (32), along with A_2 , the correct "near-field" amplitude A_1 somehow arduously computed from Eq. (31).

Our conclusion that A_1 is small is supported and made understandable by the argument of Sec. I, indicating that for a short-range interaction, because the electron cannot both go in and come out as an s -wave, the cross section for rotational excitation by slow electrons is small. To elaborate somewhat, at distances $r < r_0$ the multipole expansion is not legitimate. However, the effective interaction always can be expanded in spherical harmonics. In Born approximation, for all r ,

$$V'(\mathbf{r}, \Theta, \Phi) = -e \sum_n f_n(r) P_n(\mathbf{r}, \mathbf{s}), \quad (37)$$

where V' is defined by Eqs. (10) and (11), the sum is over even n only, and $f_n(r) = C_n r^{-n-1}$ for large r . As we have seen, at the low energies of interest, even when the multipole expansion is assumed valid all the way to $r=0$, which makes $f_n(r)$ highly divergent at the origin, the contribution to the inelastic amplitude A_{ab} from distances $r < r_0$ is small. Thus we expect A_1 to be

³⁰ S. Stein, thesis, University of Pittsburgh, 1955 (unpublished).

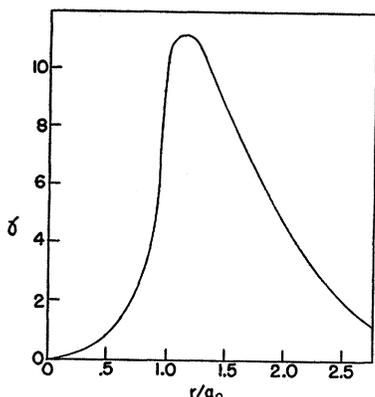


FIG. 4. Ratio of P_2 terms used in computing the near-far-field amplitudes. $\gamma = ef_2 / (Qa_0^2 e^2 / r^3)$.

small for small kr_0 ; still A_1 may not be negligible as kr_0 nears unity if there is a region $r < r_0$ in which the terms $f_n(r)$ are appreciably larger than their corresponding asymptotic forms $C_n r^{-n-1}$. Of course the contribution to A_1 from the spherically symmetric term $n=0$ in Eq. (37) has not been assessed by extending the multipole expansion to $r=0$, since the molecule has no monopole moment. But a spherically symmetric interaction cannot of itself cause a rotational transition. Consequently the short-range term $f_0(r)$ has to cause rotational transitions not only through incident and outgoing waves which, with decreasing incident energy, have a vanishingly small probability of being found at $r < r_0$, but also only in higher approximation, through waves which have already been scattered by the long-range non-spherically symmetric part of the interaction.

An estimate of the magnitude of A_1 is obtained on the assumption that the charge distribution is composed of two spherically symmetric parts, each centered about a nucleus. Such a charge distribution has vanishing multipole moments of all orders, so that A_2 is zero in Eq. (32), and A_1 becomes precisely the total inelastic amplitude A_{ab} computed, in Born approximation, by Morse.⁷ We have, extending now r_0 to ∞ in Eq. (31),

$$A_1 = - (m/2\pi\hbar^2) \int dr ds e^{i\mathbf{k}\cdot\mathbf{r}} |S_0(s)|^2 \times Y_{J_a M_a}(\mathbf{s}) Y_{J_b M_b^*}(\mathbf{s}) V''(\mathbf{r}, \mathbf{s}), \quad (38)$$

where V'' is identical with V'' of Eq. (11) but is now specifically assumed to have the form

$$V''(\mathbf{r}, \mathbf{s}) = U(|\mathbf{r} - \frac{1}{2}\mathbf{s}|) + U(|\mathbf{r} + \frac{1}{2}\mathbf{s}|). \quad (39)$$

Then, following Morse,

$$A_1 = 2f_a(\theta) \int ds |S_0(s)|^2 Y_{J_a M_a}(\mathbf{s}) \times Y_{J_b M_b^*}(\mathbf{s}) \cos(\frac{1}{2}\mathbf{k}\cdot\mathbf{s}), \quad (40)$$

with

$$f_a(\theta) = - (m/2\pi\hbar^2) \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} U(r) = - (2m/\hbar^2) \int_0^\infty dr r^2 j_0(kr) U(r). \quad (41)$$

In N_2 at low energies, recalling that r_0 is the internuclear distance in the ground vibrational state, the leading term in Eq. (40) is, since $J_b = J_a \pm 2$,

$$A_1 = -10 f_a(\theta) j_2(\frac{1}{2}kr_0) \int d\Omega Y_{J_a M_a}(\mathbf{s}) \times Y_{J_b M_b^*}(\mathbf{s}) P_2(\mathbf{k}, \mathbf{s}). \quad (42)$$

The inelastic amplitude A_2 for this transition, from J_a, M_a to J_b, M_b is, as can be verified from Eq. (18)

$$A_2 = -\frac{2}{3} Q a_0 \int d\Omega Y_{J_a M_a}(\mathbf{s}) Y_{J_b M_b^*}(\mathbf{s}) P_2(\mathbf{k}, \mathbf{s}). \quad (43)$$

Thus, for small k ,

$$A_1/A_2 = f_a(\theta) (\frac{1}{2}kr_0)^2 / Q a_0. \quad (44)$$

In nitrogen, if we use the parameters of Duncanson and Coulson,³¹ the effective charge density $\rho(r)$ contributing in the low-energy limit to $f_a(\theta)$ of Eq. (41) arises almost entirely from the $2s$ and $2p$ electrons, and is very closely represented, in atomic units, by

$$\rho(r) = -\frac{5\mu^5}{3\pi} r^{-2} e^{-2\mu r}, \quad (45)$$

with $\mu = 1.95$. We find $f_a(\theta) = 3.5a_0$, so that from Eq. (44), with $k = \sqrt{2}k_a$,

$$A_1 = 8(k_a a_0)^2 A_2. \quad (46)$$

At 0.6 ev, Eq. (46) yields $A_1/A_2 = 0.35$ which, though small, is not negligible. Because it is proportional to k_a^2 , A_1/A_2 does become negligible at lower energies, below the vibrational threshold.

The approximations leading to Eq. (42) are such that A_1 therein depends only on the coefficient of $P_2(\mathbf{r}, \mathbf{s})$ in the expansion of $V''(\mathbf{r}, \mathbf{s})$, Eq. (39). The coefficient $ef_2(r)$ of Eq. (37) can be computed for the potential $U(r)$ resulting from the charge distribution of Eq. (45), by fixing the nuclei at $\frac{1}{2}\mathbf{s} = \pm 1.05a_0$, and making use of the expansion³² in Legendre polynomials of $\exp(-2\mu|\mathbf{r} - \frac{1}{2}\mathbf{s}|)/|\mathbf{r} - \frac{1}{2}\mathbf{s}|$. In Fig. 4 we plot the ratio γ for N_2 of the thereby determined $ef_2(r)$ to $Qe^2 a_0^2 r^{-3}$. It is seen that $ef_2(r)$ greatly exceeds the pure quadrupole interaction in an extended region about $r = r_0/2$. This makes reasonable the fact that A_1/A_2 turns out to be non-negligible at energies near 0.6 ev, where $kr_0 = 0.62$.

³¹ W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. Edinburgh A62, 37 (1944).

³² G. N. Watson, Treatise on the Theory of Bessel Functions (Cambridge University Press, London, 1952), pp. 80 and 366.

It also is possible to estimate A_1 as does Morse⁷ in a semiempirical fashion from the known elastic scattering cross section σ_i , noting that in the same approximation as Eq. (40) the elastic scattering amplitude is $2f_a(\theta)j_0(\frac{1}{2}kr_0)$. With $\sigma_i = 4.8\pi a_0^2$ we obtain $f_a(\theta) = 0.55a_0$, which, substituted in Eq. (44), implies A_1/A_2 is about 0.05 at 0.6 eV in N_2 . Hence this method of estimating A_1 indicates it is in fact negligibly small even at 0.6 eV; in any event it supports the view that Eq. (46) is not a gross underestimate of A_1/A_2 .

Finally, we mention some other "near-field" effects which, like A_1 , depend on details of the short-range interaction and are decreasingly important as the incident energy approaches zero. These effects include: (1) distortion of the wave function by a very large $ef_2(r)P_2(r,s)$ interaction, such as was inferred (Fig. 4) from the parameters of Duncanson and Coulson,³¹ thereby possibly modifying the estimate from Eq. (36) of the ratio of the second to first Born approximation; (2) the contribution, appearing in second Born

approximation, which the short-range spherically symmetric $f_0(r)$ term of Eq. (37) makes to the inelastic amplitude A_{ab} ; (3) electron exchange, which plays no role in the "far field," where the incident and atomic electron wave functions do not overlap. To sum it up, our approximations are of such a character that for any homonuclear gas, not merely N_2 , the cross sections of Eq. (20) are increasingly reliable as the incident electron energy decreases to zero, because with diminishing energy the long-range tail of the interaction becomes increasingly important.

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Nuclear Spin Exchange in Solids: Tl^{203} and Tl^{205} Magnetic Resonance in Thallium and Thallic Oxide*

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The line width of the Tl^{203} and Tl^{205} nuclear magnetic resonance in thallium and thallium oxide greatly exceeds the dipolar width, and is a function of the abundance of the other isotope. The results can be interpreted in terms of an exchange interaction $A\mathbf{I}_1 \cdot \mathbf{I}_2$ between a pair of nuclear spins which exceeds the normal dipolar interaction. The exchange between different isotopes leads to broadening. Exchange between like nuclei should lead to narrowing, but it was found that samples containing 98.7 percent Tl^{205} still exhibit lines broader than the dipolar interaction. Two causes are shown to exist: anisotropy of the chemical shift and pseudo-dipolar exchange interaction. Analysis with the method of the moments gives for the exchange interaction constant $Ah^{-1} = 17.5$ kc/sec with a 30 percent anisotropic pseudo-dipolar character in the hexagonal metal, and $Ah^{-1} = 12$ kc/sec with less than 10

percent pseudo-dipolar character in thallic oxide. The oxide has a chemical shift of +0.55 percent with an anisotropy of 34 percent of this amount. The metal exhibits a shift of 1.56 percent with 16 percent anisotropy.

Ramsey's theory of the nuclear spin exchange via excited electron states in molecules, is extended to solids. Most heavy isotopes in metals and insulators should exhibit exchange effects. From the anisotropy of the exchange, information about the relative amount of p or d character of the electron wave function in the solid can be obtained.

It is predicted that thallic oxide has a nuclear Curie point at 3.5×10^{-6} °K. Whether it will become nuclear ferromagnetic or antiferromagnetic depends on details of the electronic band structure.

I. INTRODUCTION

IN an earlier paper¹ an anomalous behavior of the Tl^{203} and Tl^{205} magnetic resonance lines in metallic thallium had been noted, but no satisfactory explanation was given at that time. It was found that the width of the Tl^{205} resonance was about 10 times as large as could be expected from the dipolar broadening, but even more anomalous was the fact that the Tl^{203}

resonance was again much broader than the Tl^{205} resonance. The two isotopes both have a spin $I = \frac{1}{2}$, and the magnetic moment of Tl^{203} is only one percent smaller than that of Tl^{205} . Quadrupolar effects are thus excluded. The only reason why the two isotopes could behave differently seemed to be contained in the fact that they occur in unequal abundance. Natural thallium contains 29.5 percent Tl^{203} and 70.5 percent Tl^{205} . Consequently a Tl^{203} nucleus has fewer identical neighbors than a Tl^{205} nucleus. The dipolar width of the Tl^{203} resonance should therefore be smaller than that of Tl^{205} . An exchange interaction of the type $A_{12}\mathbf{I}_1 \cdot \mathbf{I}_2$ between the nuclear spins would act in the opposite direction.

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¹ N. Bloembergen and T. J. Rowland, *Acta Metallurgica* **1**, 731 (1953).