

Rotational Excitation of Molecular Ions by Slow Electrons

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The cross section for the excitation of rotation of a molecular ion by low-energy electrons has been calculated using first-order perturbation theory and approximate Coulomb wave functions. For ions with vanishing electric dipole moment, quadrupole moment Q , and rotational quantum number J , the cross section is found to be $2.0 \times 10^{-16} \text{ cm}^2 (Q/ea_0^3) (1 \text{ eV}/E_i) \eta(J)$, where E_i is the incident electron energy and $\frac{1}{4} < \eta(J) < \frac{3}{2}$ for all J . The rate-of-energy loss to molecular ions arising from these inelastic collisions is found to be about 10% of the loss from elastic Coulomb collisions, independent of energy. This mechanism, thus, will result in a slight increase in the energy-transfer collision frequency under conditions where molecular ions are present.

INTRODUCTION

THE rotational excitation of molecules is an important mechanism by which very slow electrons lose energy in gases. In fact, at energies below the threshold for vibrational excitation collisions involving rotational excitation account for most of the energy loss of electrons in neutral molecular gases. The energy exchange in elastic collisions is limited to about $(2m/M)E$, where E is the incident electron energy, whereas the energy exchange in excitation of the rotational state J is of the order $2J(2m/M)$ Ry. Thus, the smaller inelastic cross section is more than offset by its greater energy transfer—especially in the low-energy limit.

In low-temperature partially ionized gases, such as the ionosphere or microwave plasmas, a large fraction of the ions may be molecular in form. Depending upon the fractional ionization, collisions with either neutrals or ions will determine the energy-transfer frequency. The question naturally arises as to the effect of inelastic collisions with molecular ions. Do these inelastic collisions—as in the case of inelastic collisions with neutral molecules—yield larger energy-loss rates than do the elastic collisions?

The rotational excitation of neutral molecules has been widely investigated both theoretically and experimentally, but the excitation of molecular ions apparently has not been studied. In particular, Massey¹ and Altschuler² have calculated the cross section for excitation of neutral polar molecules, while Gerjuoy and Stein³ have found the cross section for excitation of molecules with zero electric dipole moment but nonvanishing quadrupole moment. The calculations are generally in agreement with the experimental measurements^{4,5} to within a factor of 2. In this paper, we calculate the cross section for the excitation of positive molecular ions with zero dipole moment—the case of diatomic homonuclear ions. The cross section is used to find the energy-loss rate which is then

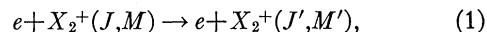
compared to the elastic Coulomb and inelastic neutral loss rates. We will find that the answer to the above question is no—that except when great accuracy is desired the energy loss resulting from the excitation of molecular ions may be neglected.

The theory is straightforward, following to a large extent that given by Gerjuoy and Stein³ for the excitation of neutral molecules. As in their treatment we deal only with Σ states of the molecule so that the rotational wave functions are spherical harmonics. We further neglect the small perturbation of the Σ terms due to the electron spin. Thus, the analysis can be applied reasonably to ground states $\text{N}_2^+(^2\Sigma_g^+)$, $\text{H}_2^+(^2\Sigma_g^+)$, $\text{He}_2^+(^2\Sigma_u^+)$, etc.

Three approximations are made to facilitate the calculation: (1) the use of first-order perturbation theory, (2) the expansion of the perturbing potential in spherical harmonics, and (3) the use of the low-energy approximation to the initial and final Coulomb wave functions. As discussed below, we feel all of these approximations are reasonable and, hence, that the calculated cross section is the right order of magnitude. It is difficult to obtain a more quantitative estimate of the likely error.

SEPARATION OF THE HAMILTONIAN

We are concerned with the reaction



where J and M are the total and azimuthal rotational quantum numbers of the molecule. All other quantum numbers of the molecule are unchanged in the transition. The total Hamiltonian for the system is

$$H = H_X - \frac{Ze^2}{|\mathbf{r} - \frac{1}{2}\mathbf{s}|} - \frac{Ze^2}{|\mathbf{r} + \frac{1}{2}\mathbf{s}|} + \sum_{j=1}^{2Z-1} \frac{e^2}{|\mathbf{r} - \mathbf{r}_j|} - \frac{\hbar^2}{2m} \nabla_r^2, \quad (2)$$

where H_X is the Hamiltonian for the molecular ion, \mathbf{r} is the coordinate of the incident electron relative to the center of mass of the molecule, \mathbf{s} is the internuclear coordinate, and \mathbf{r}_j the coordinates of the bound electrons. In order to use perturbation theory we write H in the form

$$H = H_0 + H', \quad (3)$$

¹ H. S. W. Massey, Proc. Cambridge Phil. Soc. **28**, 99 (1932).

² S. Altschuler, Phys. Rev. **107**, 114 (1957).

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

⁴ L. S. Frost and A. V. Phelps, Phys. Rev. **127**, 1621 (1962).

⁵ J. L. Pack, R. E. Voshall, and A. V. Phelps, Phys. Rev. **127**, 2084 (1962).

where

$$H_0 = H_X - \frac{e^2}{r} - \frac{\hbar^2}{2m} \nabla_r^2 \quad (4)$$

$$H' = \frac{e^2}{r} - \frac{Ze^2}{|\mathbf{r} - \frac{1}{2}\mathbf{s}|} - \frac{Ze^2}{|\mathbf{r} + \frac{1}{2}\mathbf{s}|} + \sum_{j=1}^{2Z-1} \frac{e^2}{|\mathbf{r} - \mathbf{r}_j|}. \quad (5)$$

The solution to the unperturbed wave equation,

$$H_0\psi = E\psi, \quad (6)$$

separates into the product of a Coulomb wave function for the free electron and a molecular wave function. On restricting our attention to Σ states of the molecule and neglecting the spin-axis interaction (which is usually small for Σ states), the molecular wave function separates further into a vibrational-electronic part⁶ and a spherical harmonic. Thus,

$$H_X[\psi_X(\mathbf{r}_1, \dots, \mathbf{r}_{2Z-1}, \mathbf{s}) Y_{J^M}(\Omega_s)] = (E_X + E_J)\psi_X(\mathbf{r}_1, \dots, \mathbf{s}) Y_{J^M}(\Omega_s), \quad (7)$$

so that the solution to the unperturbed wave equation (6) becomes

$$H_0\psi = H_0[\psi_{\text{Coul}}\psi_X Y_{J^M}] = (E_i + E_X + E_J)\psi_{\text{Coul}}\psi_X Y_{J^M}, \quad (8)$$

where E_i is the energy of the incident electron, E_X the total nonrotational energy of the molecular ion, and E_J is the rotational energy.

COULOMB WAVE FUNCTIONS

The unperturbed Coulomb wave function satisfying the initial boundary condition must have the form of a plane wave plus outgoing spherical waves at infinity. In an attractive field ($Z=1$) this wave function is⁷

$$\psi_{\text{Coul}}^+(\mathbf{r}, \mathbf{k}_i) = e^{\pi/2 k_i a_0} \sum_{l=0}^{\infty} \frac{\Gamma(l+1-i/k_i a_0)}{(2l)!} (2ik_i r)^l e^{ik_i r} \times P_l(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{r}}) F(l+1-i/k_i a_0, 2l+2, -2ik_i r), \quad (9)$$

where

$$k_i = (2mE_i/\hbar^2)^{1/2}, \quad (10)$$

where F is a confluent hypergeometric function, and P_l the usual Legendre function of order l , ($m=0$). ψ_{Coul}^+ is normalized to have flux $\hbar\mathbf{k}_i/m$ at infinity.

The final-state wave function must have the form of a plane wave with ingoing spherical waves at infinity.⁷ Normalized to have flux $\hbar\mathbf{k}_f/m$, it is

$$\psi_{\text{Coul}}^-(\mathbf{r}, \mathbf{k}_f) = e^{\pi/2 k_f a_0} \sum_{l=0}^{\infty} \frac{\Gamma(l+1+i/k_f a_0)}{(2l)!} (2ik_f r)^l e^{-ik_f r} \times P_l(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{r}}) F(l+1+i/k_f a_0, 2l+2, 2ik_f r). \quad (11)$$

⁶ Separation of the vibrational and electronic wave functions is not required in this analysis, and since the rotational wave function separates exactly, no use is made of the Born-Oppenheimer approximation.

⁷ L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press Ltd., London, 1958), pp. 422-3.

In this calculation, we will be concerned with incident electron energies <1 eV. At higher energies, vibrational excitation will take place and make a larger contribution to the energy loss than rotational excitation. In this energy range an expansion of the radial Coulomb wave functions in powers of $k_i a_0$ may be used. The lowest order term yields⁸

$$\psi^+(\mathbf{r}, \mathbf{k}_i) \approx (\pi/k_i r)^{1/2} \sum_{l=0}^{\infty} (2l+1) \times J_{2l+1}[(8r/a_0)^{1/2}] P_l(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{r}}). \quad (12)$$

The final-state Coulomb wave function has the same form in the limit of low k_f . Equation (12) holds only for small r . The maximum value of r for which (12) is a good approximation to ψ may be determined from the radial wave equation for a Coulomb field

$$\frac{d^2(r\psi_r)}{dr^2} + \left[k^2 + \frac{2}{ra_0} - \frac{l(l+1)}{r^2} \right] r\psi_r = 0. \quad (13)$$

Solution (12) results from dropping the k^2 term in the brackets of Eq. (13). This is valid where either

$$kr \ll [l(l+1)]^{1/2} \quad (14)$$

or

$$kr \ll 2/ka_0. \quad (15)$$

It will turn out that the dominant contribution to the radial matrix element comes from $r \sim r_e$ where

$$(8r_e/a_0)^{1/2} \approx 2l+1, \quad \text{or} \quad r_e \approx (2l+1)^2 a_0/8. \quad (16)$$

Thus, for this calculation conditions (14) and (15) both reduce to the condition on k

$$ka_0 \ll \frac{4}{2l+1}. \quad (17)$$

We will find that values of $l > 1$ contribute negligibly to the cross section so that (17) holds fairly well for all incident energies of concern here ($E_i < 1$ eV).

FIRST-ORDER PERTURBATION THEORY

In ordinary first-order time-dependent perturbation theory the probability per unit time, dw , for an electronic transition $\mathbf{k}_i \rightarrow \mathbf{k}_f$ accompanied by a molecular transition $J \rightarrow J'$ is given by

$$dw = \frac{2\pi}{\hbar} \sum_{M, M'} \frac{1}{2J+1} |\langle \psi_f^-, H' \psi_i^+ \rangle|^2 \frac{d^3 k_f}{(2\pi)^3} \times \delta(E_i + E_J - E_f - E_{J'}), \quad (18)$$

where we have averaged over the azimuthal quantum number M of the initial states and summed over M'

⁸ See Ref. 7, p. 127.

of the final states. The total cross section is

$$\begin{aligned} \sigma(J, J') &= \frac{1}{v_i} \int \frac{dw}{d\Omega_f} d\Omega_f \\ &= \left(\frac{m}{2\pi\hbar^2} \right)^2 \frac{v_f}{v_i} \sum_{M, M'} \frac{1}{2J+1} \\ &\quad \times \int |\langle \psi_f^-, H' \psi_i^+ \rangle|^2 d\Omega_f. \quad (19) \end{aligned}$$

We assume that the second and higher order terms are small compared to the first-order contribution. This assumption is difficult to verify without substantial calculations. It is easily seen that the second-order term has the same dependence on k_i as the first-order term. In addition, in the case of the excitation of neutral molecules it has been shown that the numerical coefficient of the second Born approximation is small (=0.15). The only statement that can be made with complete confidence is trivial: The second-order contribution becomes negligible in the limit of small Q (see below).

MULTIPOLE EXPANSION OF H'

The matrix element in Eq. (19) becomes on substitution of the initial and final wave functions from (7):

$$\begin{aligned} A_{fi} &\equiv \langle \psi_f^-, H' \psi_i^+ \rangle \\ &= \int \psi^{*-} \text{Coul}(\mathbf{k}_f, \mathbf{r}) Y_{J', M'}^* \psi_X^* H' \psi_X Y_{J, M} \psi^+ \text{Coul}(\mathbf{k}_i, \mathbf{r}) \\ &\quad \times d^3r d^3s d^3r_1 \cdots d^3r_{2Z-1}. \quad (20) \end{aligned}$$

If we assume, for the moment, that $r > s/2$, r_j (for all j), and define $\langle H' \rangle_X$ to be the integral of H' over $s^2 ds$ and the coordinates of all the bound electrons, we have

$$\begin{aligned} \langle \psi_X, H' \psi_X \rangle_X &= \frac{e^2}{r} - \frac{2Ze^2}{r} \sum_n r^{-n} P_n(\hat{r} \cdot \hat{s}) \langle \psi_X, (s/2)^n \psi_X \rangle \\ &\quad + \frac{e^2}{r} \sum_{j=1}^{2Z-1} \sum_n r^{-n} \langle \psi_X, r_j^n P_n(\hat{r} \cdot \hat{r}_j) \psi_X \rangle \\ &= \frac{e^2}{r} - \frac{e}{r} \sum_n r^{-n} P_n(\hat{r} \cdot \hat{s}) [2Ze \langle \psi_X, (s/2)^n \psi_X \rangle \\ &\quad - (2Z-1) e \langle \psi_X, r^n P_n(\hat{r} \cdot \hat{s}) \psi_X \rangle] \\ &= \frac{e^2}{r} - \frac{e}{r} \sum_n r^{-n} P_n(\hat{r} \cdot \hat{s}) C_n, \quad (21) \end{aligned}$$

where C_n is the n th electric moment of the charge distribution of the molecular ion⁸:

$$C_n \equiv \langle q(\mathbf{r}) r^n P_n(\hat{r} \cdot \hat{s}) \rangle_X. \quad (22)$$

Since $\langle q(\mathbf{r}) \rangle_X = e$ and we are treating molecular ions with a vanishing dipole moment the lowest order term in (21) is $e r^{-3} C_2 P_2(\hat{r} \cdot \hat{s}) \equiv Q e^2 a_0^2 r^{-3} P_2(\hat{r} \cdot \hat{s})$. The contributions to the cross section from $P_4(\hat{r} \cdot \hat{s})$ and higher terms in the multipole expansion are negligible.⁹ Dropping these we are left with

$$\begin{aligned} A_{fi} &= Q e^2 a_0^2 \int \psi_{\text{Coul}}^*(\mathbf{k}_f, \mathbf{r}) Y_{J', M'}^* Y_{J, M} P_2(\hat{r} \cdot \hat{s}) \\ &\quad \times \psi_{\text{Coul}}(\mathbf{k}_i, \mathbf{r}) r^{-3} d^3r d\Omega_s. \quad (23) \end{aligned}$$

The major approximation in (23) clearly is the false assumption that the multipole expansion holds down to $r=0$. This approximation—of a point quadrupole—is good, providing the major contribution to the radial integral arises from values of r greater than the molecular size. In fact, since the S -wave contribution to the cross section will be shown to vanish, this is approximately true [see also Eq. (16)].

EVALUATION OF THE MATRIX ELEMENT

Substituting Eq. (12) for the Coulomb wave functions into Eq. (23) yields

$$\begin{aligned} A_{fi} &= \pi Q e^2 a_0^2 (k_i k_f)^{-1/2} \sum_{l, l'} (2l+1)(2l'+1) \\ &\quad \times \int J_{2l+1}[(8r/a_0)^{1/2}] J_{2l'+1}[(8r/a_0)^{1/2}] P_l(\hat{k}_i \cdot \hat{r}) \\ &\quad \times P_{l'}(\hat{k}_f \cdot \hat{r}) P_2(\hat{s} \cdot \hat{r}) Y_{J', M'}^* Y_{J, M} \frac{dr}{r^2} d\Omega d\Omega_s. \quad (24) \end{aligned}$$

From the integration over $d\Omega$ we see that A_{fi} vanishes except when $l=l'$ or $|l-l'|=2$. It also vanishes for $l=l'=0$. But the radial integral is just¹⁰

$$\begin{aligned} &\int \frac{dr}{r^2} J_{2l+1}[(8r/a_0)^{1/2}] J_{2l'+1}[(8r/a_0)^{1/2}] \\ &= \frac{16}{a_0} \int_0^\infty \frac{dz}{z^3} J_{2l+1}(z) J_{2l'+1}(z) \\ &= \frac{4}{a_0} \frac{(l+l'-1)!}{(l-l'+1)!(l'+l+1)!(l+l'+2)!}. \quad (25) \end{aligned}$$

The denominator of the right-hand side of Eq. (25) becomes infinite for l, l' integral and $|l-l'| > 1$.¹¹ We are left with the selection rule that $l=l'$ which yields

$$\begin{aligned} A_{fi} &= \frac{\pi Q e^2 a_0}{(k_i k_f)^{1/2}} \sum_{l=1}^\infty \frac{2l+1}{l(l+1)} \int P_l(\hat{k}_i \cdot \hat{r}) P_l(\hat{k}_f \cdot \hat{r}) \\ &\quad \times P_2(\hat{s} \cdot \hat{r}) Y_{J', M'}^* Y_{J, M} d\Omega d\Omega_s. \quad (26) \end{aligned}$$

⁹ The lowest order transition arising from the P_4 coupling is the $l=l'=2$ transition which we find is already very small in the case of the P_2 coupling due to the rapid falloff of the radial integral with l .

¹⁰ G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, London, 1944), 2nd ed., p. 403.

¹¹ The selection rule $|\Delta l| \leq 1$ arising from the radial integration is not exact if allowance is made for the finite size of the quadrupole; however, the $|\Delta l|=2$ contribution to the cross section will be small in any case.

Using the addition theorem to expand $P_2(\hat{s} \cdot \hat{r})$ and $P_l(\hat{k}_f \cdot \hat{r})$ in terms of $x \equiv \hat{r} \cdot \hat{k}_i$ and integrating over $d\varphi$ yields

$$A_{fi} = \frac{2\pi^2 Q e^2 a_0}{(k_i k_f)^{1/2}} \sum_{l=1}^{\infty} \frac{2l+1}{l(l+1)} \sum_{m=0}^2 \frac{\epsilon_m (2-m)!(l-m)!}{(2+m)!(l+m)!} \\ \times P_l^m(\hat{k}_i \cdot \hat{k}_f) \int Y_{J, M'} Y_{J, M} P_2^m(\hat{s} \cdot \hat{k}_i) \\ \times \cos m(\Phi - \varphi_f) \int_{-1}^1 dx P_2^m(x) P_l^m(x) P_l(x). \quad (27)$$

The last integral in Eq. (27) results in a sum of terms [cf., Eq. (c.14) of Ref. 7] which may be reduced to

$$\frac{(-1)^{m+1} 2(l+1)! [2l(m^2-1) + 3m^2]}{(4l^2-1)(2l+3)(2-m)!(l-m)!}.$$

The sums over M and M' are greatly simplified by considering only the total cross section. We square (27) and integrate over $d\Omega_f$ to obtain:

$$\int |A_{fi}|^2 d\Omega_f = \frac{64\pi^5 Q^2 e^4 a_0^2}{k_i k_f} \\ \times \sum_l \frac{(l-1)!^2}{(2l-1)^2 (2l+3)^2 (2l+1)} \\ \times \sum_{m=0}^2 \frac{\epsilon_m [2l(m^2-1) + 3m^2]^2}{(2+m)!^2 (l+m)!(l-m)!} \\ \times \int Y_{J, M'}(s) Y_{J, M}(s) P_2^m(\hat{s} \cdot \hat{k}_i) \cos m(\Phi - \Phi') \\ \times Y_{J, M'}(s') Y_{J, M}(s') P_2^m(\hat{s}' \cdot \hat{k}_i) d\Omega d\Omega'. \quad (28)$$

Substituting (28) into (19), writing the molecular spherical harmonics with respect to the axis \hat{k}_i , and integrating over $d\Phi$ and $d\Phi'$ we have

$$\sigma(J, J') = \frac{\pi Q^2}{k_i^2} (2J'+1) \\ \times \sum_{l=1}^{\infty} \frac{(l-1)!^2}{(2l-1)^2 (2l+3)^2 (2l+1)} \\ \times \sum_{m=0}^2 \frac{\epsilon_m [2l(m^2-1) + 3m^2]^2}{(2+m)!^2 (l+m)!(l-m)!} \\ \times \sum_{M=0}^J \sum_{M'=0}^{J'} \frac{\epsilon_M \epsilon_{M'}}{(J+M)!(J'+M')} \\ \times \left[\int_{-1}^1 P_J^M(x) P_{J, M'}(x) P_2^m(x) dx \right]^2 \\ \times \pi^2 [\delta_{M+M'+m} + \delta_{M-M'+m} + \delta_{M+M'-m} + \delta_{M-M'-m}]. \quad (29)$$

Due to the restrictions on the azimuthal quantum numbers through the Kronecker deltas the remaining integral in Eq. (29) is seen to vanish unless $|J-J'|=0, 2$. The case $J=J'$ just yields a correction to the elastic Coulomb scattering cross section due to the quadrupole moment. Integrating and summing over all the azimuthal quantum numbers we finally obtain

$$\sigma(J, J \pm 2) = \frac{96\pi^3 Q^2}{5k_i^2} \eta^{\pm}(J) \sum_{l=1}^{\infty} \frac{(2l-2)!}{(2l+3)!}, \quad (30)$$

where

$$\eta^+(J) \equiv \frac{(J+1)(J+2)}{(2J+1)(2J+3)}, \quad (31) \\ \eta^-(J) \equiv \frac{J(J-1)}{(2J-1)(2J+1)}.$$

The sum over l in Eq. (30) may be evaluated in closed form:

$$\sum_{l=1}^{\infty} \frac{(2l-2)!}{(2l+3)!} = \frac{1}{3} \left(\ln 2 - \frac{2}{3} \right). \quad (32)$$

Note that about 95% of the cross section arises from the $l=1$ partial wave, and thus that Eq. (17) is readily satisfied.¹² Numerically the cross section is

$$\sigma(J, J \pm 2) = \frac{32(\ln 2 - \frac{2}{3})\pi^3 Q^2}{5k_i^2} \eta^{\pm}(J) \\ = 2.0 \times 10^{-15} \text{ cm}^2 Q^2 (1 \text{ eV}/E_i) \eta^{\pm}(J) \quad (33)$$

with

$$\sigma(J, J+2) = 0, \quad E_i < E_{J+2} - E_J, \quad (34)$$

where Q , being the quadrupole moment of the molecular ion in units of ea_0^2 , is of order unity, and where $\frac{1}{4} < \eta^+ \leq \frac{2}{3}$, $0 \leq \eta^- < \frac{1}{4}$. The threshold behavior of the excitation cross section is similar to that of the photoelectric cross section—zero below threshold and rising discontinuously to a finite value above threshold in agreement with Wigner's laws.¹³

As would be expected, the cross section for the excitation or de-excitation of positive molecular ions is large compared to that for neutral homonuclear molecules. The ratio of (33) to the neutral cross section, σ_0 , obtained by Gerjuoy and Stein³ is

$$\frac{\sigma^+(J, J \pm 2)}{\sigma_0(J, J \pm 2)} = \frac{12\pi^2 (\ln 2 - \frac{2}{3})}{k_i k_f a_0^2} \\ \approx \frac{3}{k_i k_f a_0^2}, \quad (35)$$

which becomes infinite near threshold.

¹² It should be noted that in the excitation of neutral molecules also, a large fraction (27/40) of the cross section arises from the $l=1 \rightarrow l=1$ transition. Thus, the quadrupole field despite its "long-range tail" does not interact strongly with partial waves $l > 2$.

¹³ E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

ENERGY-LOSS RATE

The net rate of energy loss of an electron due to the excitation and de-excitation of rotational levels of a molecular ion is given by

$$\frac{-dW_{\text{inel}}}{dt} = v_i \sum_J N_J \sigma(J, J+2)(E_{J+2} - E_J) - \sigma(J, J-2)(E_J - E_{J-2}), \quad (36)$$

where N_J is the number density of molecules with rotational quantum number J . Setting $E_J = J(J+1)B$, and noting that the threshold for excitation by an electron of energy E_i occurs at the level J_1 given by

$$J_1 = \frac{E_i}{4B} - \frac{3}{2},$$

we find

$$\frac{-dW_{\text{inel}}}{dt} = \frac{128\pi^3}{5} (\ln 2 - \frac{2}{3}) Q^2 B \left(\frac{\hbar}{mk_i} \right) \times \left[\sum_{J \leq J_1} N_J - \sum_{J > J_1} N_J \frac{J(J-1)}{2(2J+1)} \right]. \quad (37)$$

The second term in the brackets is negligible when the rotational temperature, T_r , is small compared to $k^{-1}E_{J_1}$. This condition is equivalent to the condition that

$$E_i \gg 4(kT_r B)^{1/2}, \quad (38)$$

which is satisfied for almost all cases of interest.

The rate of energy loss from inelastic collisions given by (37) must be compared with the energy loss from elastic Coulomb collisions. Neglecting the kinetic energy of the ions, the latter quantity is about¹⁴

$$\frac{-dW_{\text{el}}}{dt} = \frac{8\pi\hbar}{Mk_i} \text{Ry}(\ln\Lambda)N, \quad (39)$$

where $R_y = 13.6$ eV and Λ is a cutoff factor¹⁴ ($\ln\Lambda \sim 10$ for low electron temperature). Thus,

$$\frac{dW_{\text{inel}}/dt}{dW_{\text{el}}/dt} = \frac{16\pi^2 (\ln 2 - \frac{2}{3}) Q^2}{5 \ln\Lambda} \left(\frac{B}{R_y} \right) \left(\frac{M}{m} \right) \approx \frac{Q^2}{\ln\Lambda} \left(\frac{B}{B_0} \right), \quad (40)$$

where $B \lesssim B_0 \equiv (m/M) \text{Ry}$ and as noted above $Q \lesssim 1$.

¹⁴ L. Spitzer, Jr., *Physics of Fully Ionized Gases* (Interscience Publishers, Inc., New York, 1956), pp. 72-3 gives a definition and a table of values of $\ln\Lambda$. For a discussion of the various expressions for the Coulomb energy loss see Ref. 16.

The result given by (40) is quite general, showing that over 80% of the total rate of energy transfer to homonuclear molecular ions is accounted for by the elastic losses below the threshold for vibrational excitation. The comparison of the elastic and inelastic losses differs markedly from the case of scattering from neutral molecules due to the different energy dependences of the relevant cross sections.

DISCUSSION

We have calculated an approximate cross section for the excitation and de-excitation of molecular ions by electron impact. The result is very large—being of the order of 10^{-14} cm² for electron energies ~ 0.1 eV [see Eq. (33)]. About 95% of the total inelastic cross section arises from the p -wave scattering. This partial cross section is

$$\sigma_{l=1}(J \gg 1, J+2) = (\pi^2 Q^2 / 25) (3\pi / k_i^2), \quad (41)$$

where $3\pi/k_i^2$ is the theoretical limit imposed by flux conservation.¹⁵ It is clear from Eq. (41) that first-order perturbation theory breaks down for $Q^2 > 2.5$. In the limit of Q and $k_i a_0 \ll 1$, however, the derived cross sections should be reasonably accurate.

The rate of energy exchange due to inelastic collisions between low-energy electrons and molecular ions will range from 1 to 20% of the elastic exchange rate, depending on the values of Q and B and on the electron temperature and density [see Eq. (40)]. The only experimental measurements of this quantity are those of Dougal and Goldstein¹⁶ who have measured the energy-transfer rate between electron and ions in low-temperature weakly ionized gases. They find order-of-magnitude agreement between their observations and various theories for the elastic exchange rate. Since, as they point out, there are many indeterminacies in the analysis (in particular, the mean ion mass), no information can be obtained relating to the inelastic cross sections obtained here.

ACKNOWLEDGMENTS

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¹⁵ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1933), 2nd ed., p. 135.

¹⁶ A. A. Dougal and L. Goldstein, *Phys. Rev.* **109**, 615 (1957).