

Energy loss by slow electrons in polar gases

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The mean energy loss by slow electrons moving in a gas and rotationally exciting the molecules is proportional to the rotational stopping cross section (RSCS) defined by multiplying the cross section for a rotational transition $\Gamma \rightarrow \Gamma'$ by the transition energy and by summing the product over Γ' . The RSCS for linear and symmetric-top polar molecules are studied in the adiabatic-rotation approximation at scattering angles θ larger than a critical value θ_c and in the first-Born approximation for $\theta < \theta_c$. Formulas independent of θ_c are derived for the RSCS for any Γ as the sum of the RSCS for the ground rotational state $\Gamma=0$ and a term that depends on Γ in a simple analytic form and is proportional to the dipole moment D squared. For a vanishing D , this term vanishes and the formulas reduce to a previously proven theorem for nonpolar molecules that the RSCS is independent of Γ . Useful expressions are also derived for the average of the RSCS over the Boltzmann distribution of Γ .

I. INTRODUCTION

The knowledge of the energy spectra of free electrons in gases, liquids, and solids is indispensable for the studies of radiation physics and chemistry, physics of gas discharges, physics of the upper atmospheres of the Earth and other planets, etc. The energy spectra change as the electrons collide with the molecules in the matter; the fast secondary electrons produced in the matter as a result of ionization slow down in the collisions, first rapidly by electronic excitation, and then gradually by vibrational and rotational excitation after their kinetic energies become insufficient for the lowest electronic excitation.¹

The mean energy loss by electrons with an energy ϵ due to rotational excitation and deexcitation of the molecules is proportional to the stopping cross section¹

$$S(\mu; \epsilon) = \left\langle \sum_{\Gamma'} (\Delta E_{\Gamma, \Gamma'})^\mu \sigma_{\Gamma, \Gamma'} \right\rangle, \quad (1)$$

where $\mu = 1$, $\sigma_{\Gamma, \Gamma'}$ is the integral cross section for a rotational transition $\Gamma \rightarrow \Gamma'$, and $\Delta E_{\Gamma, \Gamma'}$ is the corresponding transition energy. The brackets denote the average over the degenerate initial rotational sublevels.

Rotational excitation often occurs simultaneously with collisional vibrational excitation $v \rightarrow v'$. A convenient definition in this case is

$$S(\mu; \epsilon) = \left\langle \sum_{\Gamma'} (\Delta E_{v\Gamma, v'\Gamma'})^\mu \sigma_{v\Gamma, v'\Gamma'} \right\rangle, \quad (2)$$

which is similar to Eq. (1) but depends on the vibrational states v and v' .

Equations (1) and (2) for general μ (not necessarily equal to 1) define the μ th moment of the rotational structure in the cross section as a function of the transition energy. We may also define the moments $dS(\mu; \epsilon)/d\omega$ by replacing $\sigma_{\Gamma, \Gamma'}$ in Eq. (1) by the differential cross section $d\sigma_{\Gamma, \Gamma'}/d\omega$, or similarly, by replacing $\sigma_{v\Gamma, v'\Gamma'}$ in Eq. (2) by $d\sigma_{v\Gamma, v'\Gamma'}/d\omega$. Such moments were studied previously

in the adiabatic-rotation approximation, which assumes negligible molecular rotation during the electron-molecule collision, and some useful general formulas were found. This approximation is valid except for collision energies close to an excitation threshold, except in extremely narrow resonance regions, and except for extremely forward scattering by polar molecules.

In the calculations of the stopping cross sections $S(1; \epsilon)$ for rotational transitions of polar molecules, forward scattering needs some different treatment without the adiabatic-rotation approximation. The main purpose of the present paper is to derive general formulas for $S(1; \epsilon)$ for polar molecules. Section III is devoted to this derivation for linear-rotator molecules, and Sec. IV for symmetric-top molecules. Prior to them, however, Sec. II reviews the formulas derived previously in the adiabatic-rotation approximation. Section V considers the average of the stopping cross section over the rotational-state distribution. This average should be useful in practical applications to gases consisting of polar molecules. Finally, Sec. VI summarizes the main results of this paper.

II. THEOREMS IN THE ADIABATIC-ROTATION APPROXIMATION

Operator techniques with commutation relations were used in Ref. 2, and a theorem that reads as follows was proved for molecules regarded as linear, spherical-top, symmetric-top, or asymmetric-top rotators: $dS(1; \epsilon)/d\omega$, and hence, also $S(1; \epsilon)$ in the adiabatic-rotation approximation are independent of the initial rotational state. Therefore they remain the same as, say, for the initial ground rotational state even after being averaged over any rotational-state distribution.

This theorem was proved again in Ref. 3 for linear, spherical-top, and symmetric-top molecules, but not for asymmetric-top molecules, by using a different technique that clarifies the physical (or geometrical) meaning of the

theorem. A similar technique is found also in Ref. 4. In the following, J , J' , and J'' denote the quantum numbers of rotational angular momenta, and \tilde{K} , \tilde{K}' , and \tilde{K}'' their projection onto an axis of quantization fixed on the molecule. The latter quantum numbers with a tilde run over both positive and negative values and represent primitive symmetric-top states. Because the energy of a symmetric-top state is independent of the sign of \tilde{K} , the average is taken between \tilde{K} and $-\tilde{K}$ of the initial state in the calculations of moments for symmetric-top molecules. Therefore these moments depend only on J and the absolute value of \tilde{K} , denoted in the following by K without a tilde.

A scaling relation

$$\frac{d\sigma_{J,J'}}{d\omega} = \sum_{J''} \gamma(JJ''J') \frac{d\sigma_{0,J''}}{d\omega} \quad (3)$$

is known, where $\gamma = (2J'+1)/[(2J+1)(2J''+1)]$ for spherical-top molecules^{3,5} and $\gamma = [C(JJ''J';000)]^2$, the square of a Clebsch-Gordan coefficient, for linear-rotator molecules.^{6,7} For symmetric-top molecules the scaling relation reads^{6,7}

$$\frac{d\sigma_{J\tilde{K},J'\tilde{K}'}}{d\omega} = \sum_{J''} \gamma(JJ''J';\tilde{K}\tilde{K}''\tilde{K}') \frac{d\sigma_{00,J''\tilde{K}''}}{d\omega}, \quad (4)$$

where $\gamma = [C(JJ''J';\tilde{K}\tilde{K}''\tilde{K}')]^2$ and $\tilde{K}'' = \tilde{K}' - \tilde{K}$. Use of Eqs. (3) and (4) reveals equivalence of the above theorem for linear and symmetric-top molecules to the second cosine formula $\mathbf{J}'^2 = (\mathbf{J} + \mathbf{J}'')^2 = \mathbf{J}^2 + \mathbf{J}''^2 + 2\mathbf{J} \cdot \mathbf{J}''$.³

The theorem is generalized for higher moments $dS(\mu; \epsilon)/d\omega$ in Ref. 8. The following summarizes the formulas for the lower moments for linear rotators and spherical tops:

$$\begin{aligned} \frac{dS(0;J,\epsilon)}{d\omega} &= \frac{dS(0;0,\epsilon)}{d\omega}, \\ \frac{dS(1;J,\epsilon)}{d\omega} &= \frac{dS(1;0,\epsilon)}{d\omega}, \\ \frac{dS(2;J,\epsilon)}{d\omega} &= \frac{dS(2;0,\epsilon)}{d\omega} + c_{21}E(J) \frac{dS(1;0,\epsilon)}{d\omega}, \\ \frac{dS(3;J,\epsilon)}{d\omega} &= \frac{dS(3;0,\epsilon)}{d\omega} + E(J) \left[c_{32} \frac{dS(2;0,\epsilon)}{d\omega} \right. \\ &\quad \left. - c_{31}E(1) \frac{dS(1;0,\epsilon)}{d\omega} \right], \end{aligned} \quad (5)$$

and $dS(2n;J,\epsilon)/d\omega$ and $dS(2n+1;J,\epsilon)/d\omega$ are polynomials of integral degree n in $E(J)$, where $E(J)$ is the rotational energy $BJ(J+1)$, B is the rotational constant, and $c_{21}=2$, $c_{32}=6$, and $c_{31}=2$ for linear rotators and $c_{21}=\frac{4}{3}$, $c_{32}=4$, and $c_{31}=\frac{2}{3}$ for spherical-top rotators. Formulas simpler than Eqs. (5) follow from a high- J approximation.⁸ Results similar to Eqs. (3) and (5) are also obtained for collisional transitions of classical rotators in the sudden approximation.⁸

It follows for quantum-mechanical symmetric tops that⁸

$$\begin{aligned} \frac{dS(0;J,K,\epsilon)}{d\omega} &= \frac{dS(0;0,0,\epsilon)}{d\omega}, \\ \frac{dS(1;J,K,\epsilon)}{d\omega} &= \frac{dS(1;0,0,\epsilon)}{d\omega}, \\ \frac{dS(2;J,K,\epsilon)}{d\omega} &= \frac{dS(2;0,0,\epsilon)}{d\omega} + 2[E(J,K) - AK^2] \frac{dS(1;0,0,\epsilon)}{d\omega} - 2[E(J,K) - 3AK^2] \frac{dU(1;0,0,\epsilon)}{d\omega}, \\ \frac{dS(3;J,K,\epsilon)}{d\omega} &= \frac{dS(3;0,0,\epsilon)}{d\omega} + 6[E(J,K) - AK^2] \frac{dS(2;0,0,\epsilon)}{d\omega} - 4B[E(J,K) - AK^2 - BK^2] \frac{dS(1;0,0,\epsilon)}{d\omega} \\ &\quad - 6[E(J,K) - 3AK^2] \frac{dU(2;0,0,\epsilon)}{d\omega} + 4B[(1+B/A)E(J,K) - AK^2 - 5BK^2] \frac{dU(1;0,0,\epsilon)}{d\omega}, \end{aligned} \quad (6)$$

and $dS(2n;J,K,\epsilon)/d\omega$ and $dS(2n+1;J,K,\epsilon)/d\omega$ are polynomials of degree n in $E(J,K)$ and K^2 , where $E(J,K)$ is the rotational energy $BJ(J+1) + (A-B)K^2$, A and B are the rotational constants (where $A > B$ for prolate symmetric tops and $A < B$ for oblate symmetric tops), and another constant parameter $dU/d\omega$ is defined by

$$\frac{dU(\mu;0,0,\epsilon)}{d\omega} = \sum_{J'',\tilde{K}''} AK''^2 [E(J'',K'')]^{\mu-1} \frac{d\sigma_{00,J''\tilde{K}''}}{d\omega}. \quad (6a)$$

Equations (5) and (6) are based on the relations (3) and (4) combined with formulas for the sum⁸

$$\sum_{J'} [J'(J'+1) - J(J+1)]^\mu [C(JJ''J';KK''K')]^2. \quad (7)$$

An approximation slightly better than Eqs. (3) and (4) contains a kinematic factor, or the ratio of the final-channel to initial-channel wave number, on each side of these equations.⁷ This factor may be expanded in terms of powers of $\Delta E_{\Gamma,\Gamma'}/\epsilon$. Retention of the two leading terms in this expansion slightly modifies Eqs. (5) and (6).⁸ Furthermore, the modified formulas may be averaged over the Boltzmann distribution of the rotational states at temperatures T . The averages $d\bar{S}(\mu;T,\epsilon)/d\omega = \langle dS(\mu;\epsilon)/d\omega \rangle_T$ are calculated to be⁸

$$\begin{aligned}\frac{d\bar{S}(0;T,\varepsilon)}{d\omega} &= \frac{d\bar{S}(0;0,\varepsilon)}{d\omega}, \\ \frac{d\bar{S}(1;T,\varepsilon)}{d\omega} &= \frac{d\bar{S}(1;0,\varepsilon)}{d\omega} \left[1 - \frac{kT}{\varepsilon} \right], \\ \frac{d\bar{S}(2;T,\varepsilon)}{d\omega} &= \frac{d\bar{S}(2;0,\varepsilon)}{d\omega} + 2kT \left[\frac{d\bar{S}(1;0,\varepsilon)}{d\omega} \right]\end{aligned}\quad (8)$$

for spherical-top, linear, and symmetric-top rotators for $B \ll kT \ll \varepsilon$, where k is the Boltzmann constant.

These results are generalized in a few different ways. First, generalization for rotational-vibrational transitions rather than purely rotational transitions is straightforward.^{2,3} Second, generalization for rotational-vibronic transitions needs special considerations. This is because the rotational Hamiltonian for the final vibronic state is often different from that for the initial vibronic state. Reference 3 discusses modifications necessary in this case. Third, many of the above results apply, either directly or with a slight modification, to molecular photoionization and to positron-molecule, ion-molecule, atom-molecule, and molecule-molecule collisions.^{2,3,8}

III. STOPPING CROSS SECTIONS FOR LINEAR POLAR MOLECULES

The interaction between an electron and a polar molecule having a dipole moment $\mathbf{D} = (D, \hat{\mathbf{D}})$ takes an asymptotic form of a dipole potential

$$V_d(r) \sim -\frac{eD}{r^2} \hat{\mathbf{D}} \cdot \hat{\mathbf{r}}, \quad (9)$$

where $-e$ is the charge of an electron, and $\mathbf{r} = (r, \hat{\mathbf{r}})$ is the position vector of the electron relative to the center of mass of the molecule. Because of the long-range nature of the potential (9), the effective collision region for small-angle scattering, which is due dominantly to distant collisions, can be extremely large. Therefore the effective collision time can be extremely long, much longer than the period of the rotational motion of the molecule. This invalidates the adiabatic-rotation approximation for forward scattering by polar molecules.^{7,9,10} Indeed, the integral cross sections for rotational transitions of polar molecules diverge in this approximation because of the divergence of the differential cross sections towards a zero scattering angle. This is pointed out in Ref. 11, which criticizes finite numerical results of previous authors.

$$S_{<}(\mu; J, \varepsilon) = (2B)^\mu \sigma_m^B \left\{ \ln \left[\frac{2\varepsilon}{B} \sin \left[\frac{\theta_c}{2} \right] \right] \left[\frac{(J+1)^{\mu+1} - (-J)^{\mu+1}}{2J+1} - F(\mu; J) + O \left(\frac{B}{\varepsilon} \right) \right] \right\}, \quad (12)$$

where

$$\begin{aligned}F(\mu; J) &= \frac{(J+1)^{\mu+1} \ln(J+1) - (-J)^{\mu+1} \ln J}{2J+1} \quad \text{for } J > 0, \\ F(\mu; 0) &= 0.\end{aligned}\quad (13)$$

For $J=0$ there is no contribution from $J'=J-1$, and

Fortunately, a simple perturbation theory applies to that forward scattering by polar molecules for which the adiabatic-rotation approximation breaks down. This is because, in this case, the electrons interact with the molecules almost only at large distances, and hence, only weakly, although the collision time is long.^{7,9,10} In the first-Born approximation for distant collisions for which the interaction potential is represented accurately by Eq. (9), the differential cross section for a rotational transition $J \rightarrow J'$ of a linear rotator takes a form¹²

$$\frac{d\sigma_{J,J'}}{d\omega} = \delta_{J\pm 1, J'} \frac{4k_f}{3k_i} \left[\frac{emD}{\hbar^2} \right]^2 \frac{J_{>}}{2J+1} |\mathbf{k}_i - \mathbf{k}_f|^{-2}, \quad (10)$$

where \mathbf{k}_i and \mathbf{k}_f are the wave vectors of the initial and final channels, k_i and k_f are their magnitudes, m is the reduced mass of the electron-molecule system, and $J_{>}$ is the larger of J and J' .

Let θ_c be a scattering angle such that the dipole-Born approximation (10) is valid for $\theta \leq \theta_c$ and such that the adiabatic-rotation approximation is valid for $\theta \geq \theta_c$. We may assume an overlap between the angular regions of the validity of the two approximations, and the choice of θ_c is arbitrary, provided that it lies in this overlap region. Note that Eq. (10) satisfies the theorems summarized in Sec. II, if we make a further approximation that $k_i = k_f$, which is equivalent to the application of the first-order perturbation theory to the adiabatic-rotation expression with the dipole potential (9). This fact is consistent with the assumption of the overlap of the two angular regions.

The momentum-transfer cross section in the adiabatic-rotation dipole-Born approximation is

$$\sigma_m^B = \frac{8\pi}{3} \left[\frac{meD}{k_i \hbar^2} \right]^2. \quad (11)$$

This quantity often appears in later derivations, although it is not employed as an approximation to the true momentum-transfer cross section; Eq. (11) is to be understood merely to define a notation for the quantity on the right-hand side.

The contribution $S_{<}(\mu; J, \varepsilon)$ from the angular region $0 \leq \theta \leq \theta_c$ to the moment $S(\mu; J, \varepsilon)$ may be easily calculated by multiplying Eq. (10) by $(\Delta E_{J,J'})^\mu = (\pm 2BJ_{>})^\mu$, by integrating it over this angular region, and by summing over $J' = J \pm 1$, as

$S_{<}$ takes a simple form

$$S_{<}(\mu; 0, \varepsilon) = (2B)^\mu \sigma_m^B \left\{ \ln \left[\frac{2\varepsilon}{B} \sin \left[\frac{\theta_c}{2} \right] \right] + O \left(\frac{B}{\varepsilon} \right) \right\}. \quad (14)$$

Take an example of $\mu=0$. Combining Eq. (14) with an equation

$$S_{<}(0;J,\varepsilon)=\sigma_m^B \left\{ \ln \left[\frac{2\varepsilon}{B} \sin \left(\frac{\theta_c}{2} \right) \right] - F(0;J) + O \left(\frac{B}{\varepsilon} \right) \right\} \quad (15)$$

that follows from Eq. (12), we find that

$$S_{<}(0;J,\varepsilon)=S_{<}(0;0,\varepsilon)-\sigma_m^B F(0;J)+O \left(\frac{B}{\varepsilon} \right). \quad (16)$$

We have assumed the validity of the adiabatic-rotation approximation for $\theta \geq \theta_c$. Therefore the contribution $S_{>}(0;J,\varepsilon)$ from the region $\theta \geq \theta_c$ to $S(0;J,\varepsilon)$ satisfies the relation

$$S_{>}(0;J,\varepsilon)=S_{>}(0;0,\varepsilon) \quad (17)$$

according to the first of Eqs. (5). Because $S(0;J,\varepsilon)=S_{<}(0;J,\varepsilon)+S_{>}(0;J,\varepsilon)$, summation of Eqs. (16) and (17) leads to a relation for $S(0;J,\varepsilon)$ that has the same form as Eq. (16) for $S_{<}(0;J,\varepsilon)$. This relation is a sum rule for the cross section for electron scattering by a polar molecule.

Similar procedures also apply to higher moments. In summary it follows for the lower moments that

$$S(0;J,\varepsilon)=S(0;0,\varepsilon)-\sigma_m^B F(0;J), \quad (18a)$$

$$S(1;J,\varepsilon)=S(1;0,\varepsilon)-(2B)\sigma_m^B F(1;J), \quad (18b)$$

$$S(2;J,\varepsilon)=S(2;0,\varepsilon)+2E(J)S(1;0,\varepsilon)-(2B)^2\sigma_m^B F(2;J), \quad (18c)$$

$$S(3;J,\varepsilon)=S(3;0,\varepsilon)+2E(J)[3S(2;0,\varepsilon)-(2B)S(1;0,\varepsilon)] - (2B)^3\sigma_m^B F(3;J), \quad (18d)$$

where terms of order $(B/\varepsilon)\ln(B/\varepsilon)$ are omitted. Note that these equations are independent of the choice of the critical angle θ_c , as is natural from the definition of θ_c ; only the assumption of the *existence* of θ_c suffices for the proof of these equations.

Equations (18) are extensions of the integral-cross-section version of Eqs. (5) for polar linear-rotator molecules. In fact, Eqs. (18) are general in the sense that they also apply to nonpolar molecules, because σ_m^B vanishes for these molecules.

$$S(2;J,K,\varepsilon)=S(2;0,0,\varepsilon)+2[E(J,K)-AK^2]S(1;0,0,\varepsilon)-2[E(J,K)-3AK^2]U(1;0,0,\varepsilon) - (2B)^2\sigma_m^B [F(2;J)-K^2F(0;J)], \quad (21b)$$

where terms of order $(B/\varepsilon)\ln(B/\varepsilon)$ are neglected. The quantity U is defined by the integral of Eq. (6a) over the whole angular region, and has no contribution from the region $0 \leq \theta \leq \theta_c$ because of the conservation of the \tilde{K} quantum number in the dipole-Born approximation (19), which means that $K''=|\tilde{K}''|=0$ in Eq. (6a).

IV. STOPPING CROSS SECTIONS FOR SYMMETRIC-TOP POLAR MOLECULES

In the first-Born approximation with the potential (9), the differential cross section for a rotational transition $J\tilde{K} \rightarrow J'\tilde{K}'$ of a symmetric-top rotator vanishes if $|J-J'| \geq 2$ or $\tilde{K} \neq \tilde{K}'$. The differential cross section for $J'=J \pm 1$ and $\tilde{K}'=\tilde{K}$ is¹³

$$\frac{d\sigma_{J\tilde{K},(J\pm 1)\tilde{K}}}{d\omega} = \frac{4k_f}{3k_i} \left[\frac{emD}{\hbar^2} \right]^2 \frac{1}{2J+1} \left[J_{>} - \frac{K^2}{J_{>}} \right] \times |\mathbf{k}_i - \mathbf{k}_f|^{-2}, \quad (19a)$$

and that for elastic scattering (J',\tilde{K}')=(J,\tilde{K}) is

$$\frac{d\sigma_{J\tilde{K},J\tilde{K}}}{d\omega} = \frac{4}{3} \left[\frac{emD}{\hbar^2} \right]^2 \frac{K^2}{J(J+1)} |\mathbf{k}_i - \mathbf{k}_f|^{-2}, \quad (19b)$$

where the definition of the quantities \mathbf{k}_i , \mathbf{k}_f , and $J_{>}$ is similar to that in Eq. (10).

The cross section (19b) diverges as θ^{-2} for forward scattering, because $k_i=k_f$ and $|\mathbf{k}_i - \mathbf{k}_f|=2k_i \sin(\theta/2)$ for elastic scattering. Therefore the integral cross section for elastic scattering with $K \neq 0$ diverges logarithmically. This means that the zeroth moment $S(0;J,K,\varepsilon)$, or the summed cross section, for any polar symmetric-top molecule with $K \neq 0$ (and hence, $J \neq 0$) is infinitely large. The moments of the first and higher orders, however, are finite, because the summation over the final state for these moments excludes elastic scattering, for which the transition energy is zero.

The energy of a transition $J\tilde{K} \rightarrow J'\tilde{K}$ without change in the \tilde{K} value is the same as that of a transition $J \rightarrow J'$ of a linear-rotator molecule. The only essential difference between the derivation of the moments for symmetric tops and for linear rotators arises from the second term $K^2/J_{>}$ in large parentheses in Eq. (19a). Introducing a critical angle θ_c as in the preceding section, we may express the contribution $S_{<}(\mu;J,K,\varepsilon)$ from the angular region $0 \leq \theta \leq \theta_c$ to the moment $S(\mu;J,K,\varepsilon)$ in terms of the quantity $S_{<}(\mu;J,\varepsilon)$ of Eq. (12) as

$$S_{<}(\mu;J,K,\varepsilon)=S_{<}(\mu;J,\varepsilon)-K^2(2B)^2S_{<}(\mu-2;J,\varepsilon). \quad (20)$$

This result combined with Eqs. (6), (12), and (14) yields relations independent of θ_c as

$$S(1;J,K,\varepsilon)=S(1;0,0,\varepsilon) - (2B)\sigma_m^B [F(1;J)-K^2F(-1;J)] \quad (21a)$$

and

V. AVERAGE OVER THE BOLTZMANN DISTRIBUTION

If the molecular gas is in rotational equilibrium at a temperature T , the normalized Boltzmann distribution $N(J;T)$ for polar linear-rotator molecules is expressible

as

$$N(J;T) \propto (2J+1)\exp[-E(J)/kT], \quad (22)$$

because the statistical weight due to the nuclear spins is independent of J for these molecules. At high temperatures the summation over J in taking the Boltzmann average may be replaced by integration, and hence the average of $[E(J)]^n$, for example, may be approximated by⁸

$$\begin{aligned} \langle [E(J)]^n \rangle_T &= \sum_J N(J;T)[E(J)]^n \\ &\sim (n!)(kT)^n \text{ for } kT \gg B. \end{aligned} \quad (23)$$

This formula was used previously to derive Eqs. (8).⁸ In the present paper, however, this high- T approximation is avoided, and the following procedure is taken. First, analytic forms of the sum over J at high T and at low T are studied, and are compared with accurate numerical values of the sum at various T . If the analytic expressions are inaccurate at intermediate T , another approximate expression is proposed for this temperature region. In this way an approximation that applies in the whole

temperature region is derived.

For the rotational average of $E(J)$ the high- T and low- T expressions

$$\langle E(J) \rangle_T = \begin{cases} \frac{6B\alpha(1+5\alpha^2)}{(1+3\alpha+5\alpha^3)} & \text{for } \tau < 1.4, \\ B(\tau - \frac{1}{3} - 1/45\tau) & \text{for } \tau \geq 1.4, \end{cases} \quad (24)$$

suffice for approximate representation in the whole region of temperature; the relative error of Eq. (24) is 0.78% at most, and is much smaller than that of Eq. (23) even at high T . In Eq. (24) τ and α are defined by

$$\tau = kT/B \quad (25a)$$

and

$$\alpha = \exp(-2/\tau). \quad (25b)$$

For the calculations of the Boltzmann average of the moments for polar molecules, $F(\mu;J)$ of Eq. (13) must be averaged. For example, approximate formulas necessary for calculating the summed cross section are

$$\langle F(0;J) \rangle_T = \begin{cases} \frac{\alpha[2\ln 2 + (3\ln 3 + 2\ln 2)\alpha^2]}{1+3\alpha+5\alpha^3} & \text{for } \tau \leq 2.2, \\ 0.393\ln\tau + 0.031 & \text{for } 2.2 < \tau < 20, \\ (\ln\tau - \gamma)/2 & \text{for } 20 \leq \tau, \end{cases} \quad (26)$$

where γ is Euler's constant and is 0.5772. The maximum relative error of Eq. (26) is 3.2%. Formulas necessary for calculating the stopping cross section are

$$\langle F(1;J) \rangle_T = \begin{cases} \frac{\alpha[4\ln 2 + (9\ln 3 - 4\ln 2)\alpha^2]}{1+3\alpha+5\alpha^3} & \text{for } \tau < 1.6, \\ 0.48\ln\tau + 0.261 & \text{for } 1.6 \leq \tau < 12, \\ (\ln\tau + 1 - \gamma)/2 & \text{for } 12 \leq \tau. \end{cases} \quad (27)$$

The maximum relative error of Eq. (27) is 0.47%.

The temperature dependence of the Boltzmann average of the first two moments for polar linear-rotator molecules may then be written in terms of the quantities given by Eqs. (26) and (27) as

$$\bar{S}(0;T,\varepsilon) = \bar{S}(0;0,\varepsilon) - \sigma_m^B \langle F(0;J) \rangle_T \quad (28a)$$

and

$$\bar{S}(1;T,\varepsilon) = \bar{S}(1;0,\varepsilon) - (2B)\sigma_m^B \langle F(1;J) \rangle_T, \quad (28b)$$

where $\bar{S}(\mu;0,\varepsilon) = S(\mu;J=0,\varepsilon)$. Terms of the order of $(kT/\varepsilon)\bar{S}(1;0,\varepsilon)$ and higher have been omitted in Eq. (28b).

The Boltzmann distribution $N(J,K;T)$ for symmetric-top molecules involves a statistical weight that depends on the rotational quantum numbers and on the molecule. The following arguments neglect this factor, which is a good approximation at high temperatures. It then follows that

$$N(J,K;T) \propto (2J+1)\exp[-E(J,K)/kT]. \quad (29)$$

The average of the quantity $F(1;J) - K^2F(-1;J)$ in Eq. (21a) over $N(J,K;T)$ at high T is approximately

$$\langle F(1;J) - K^2F(-1;J) \rangle_T = \frac{1}{2}\ln\tau + C_1. \quad (30)$$

If the constant C_1 is chosen to be

$$\begin{aligned} C_1 &= (1-\gamma)/2 + (\frac{5}{6} - \ln 2)(B/A)^{3/4} \\ &= 0.2114 + 0.1402(B/A)^{3/4} \end{aligned} \quad (31a)$$

for prolate symmetric tops (for which $B/A < 1$), the relative error is less than 1% for $\tau \geq 10$. If the expression

$$C_1 = 0.03 + 0.32(B/A)^{1/3} \quad (31b)$$

is used for oblate symmetric tops (for which $B/A > 1$), the relative error for $\tau \geq 10$ is less than 2% for $B/A \leq 30$, less than 5% for $B/A \leq 50$, and less than 12% for $B/A \leq 100$.

The average stopping cross section for polar symmetric-top molecules may be expressed in terms of Eq. (30) as

$$\bar{S}(1; T, \epsilon) = \bar{S}(1; 0, \epsilon) - (2B)\sigma_m^B \langle F(1; J) - K^2 F(-1; J) \rangle_T, \quad (32)$$

where $\bar{S}(1; 0, \epsilon) = S(1; 0, 0, \epsilon)$. Here again, terms of the order of $(kT/\epsilon)\bar{S}(1; 0, \epsilon)$ and higher have been omitted.

VI. SUMMARY

The theorems, proved previously in the adiabatic-rotation approximation and summarized in Sec. II, for the moments of the rotational structure of the cross sections for electron scattering by nonpolar molecules, have been generalized for polar molecules. The main results are Eqs. (18a)–(18d) for linear-rotator molecules, in which the definition of Eqs. (11) and (13) is used, and Eqs. (21a) and (21b) for symmetric-top molecules, in which the

definition of Eqs. (6a), (11), and (13) is used. The rotational-state-independence theorem for the stopping cross sections that applies to nonpolar molecules does not apply to polar molecules. However, the dependence on the rotational state is weak and is expressible in a simple analytic form; both the stopping cross sections and other moments are expressed as the sum of a constant term and a term depending on the rotational state and proportional to the cross section σ_m^B . Because σ_m^B contains a factor D^2 , as is defined in Eq. (11), the latter term vanishes for nonpolar molecules, and the previously proven theorems are recovered.

Practically useful results for molecular gases in rotational equilibrium at temperature T are Eqs. (28a) and (28b) with Eqs. (26) and (27) for linear-rotator molecules, and Eq. (32) with Eqs. (30), (31a), and (31b) for symmetric-top molecules.

This paper has considered purely rotational transitions only. Generalization for vibrational-rotational transitions is straightforward as is explained in Refs. 2 and 3.

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