electrons in rare earths and we attribute the observed peak to transitions from the $^1S_0$ level.

It is interesting to compare[3] the levels observed for the $4f^2$ configuration of Pr^{3+} in the vapor (E_v) phase with those found in single crystal (E_c). If our value for the $^1S_0$ level in CaF_2 crystals is compared with the calculated[3] value for the vapor, it is found (Fig. 3) that the relation is described by a simple expression: $E_v - E_c \propto E_v^{3/2}$, or $E_c = E_v - 10^{-3.5} E_v^{3/2}$.

Note added in proof. Fortunately, the $^1S_0$ level of Pr^{3+} sits conveniently on the short-wavelength side of the first $4f \rightarrow 5d$ band in fluorides. Otherwise, it might be difficult to distinguish the $^1S_0$ absorption from the zero phonon line of $4f \rightarrow 5d$ transition at low temperature, although the former is a weak and the latter is a strong transition. The absorption spectrum of 0.015% Pr^{3+} in CaF_2 at liquid nitrogen temperature shows a weak $^1S_0$ peak at ~2120 Å and a strong zero phonon peak at ~2240 Å, both being conveniently located on the opposite sides of the $4f \rightarrow 5d$ band with apparent peak at ~2200 Å.

ACKNOWLEDGMENTS

The author wishes to thank G. S. Picus for critical reading of the manuscript, S. Yatsiv for stimulating discussions, M. Robinson for a generous supply of several Pr^{3+}-doped LaF_3 crystals, W. Hargreaves of Optovac, Inc., for a dilute CaF_2:Pr^{3+} crystal, G. Dorosheski for patient construction of several graphs, and M. Himber and J. Montross for frequent assistance. A portion of this study was supported by Air Force Contract AF 33(615)-1999.

PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Theory of Rotational Excitation of Homonuclear Diatomic Molecules by Slow Electrons: Application to N_2 and H_2†

Douglas H. Sampson*
Space Sciences Laboratory, General Electric Company, Valley Forge, Pennsylvania

AND

Raymond C. Mjolsness‡
Space Sciences Laboratory, General Electric Company, Valley Forge, Pennsylvania

and

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

(Received 25 June 1965)

A distorted-wave theory of rotational excitation of homonuclear diatomic molecules with Σ ground states by slow electrons is given. The assumption is made that distortion of only the $l=0$ and $l=1$ partial waves is significant and a simple semiempirical model is used for the potential. Results obtained for H_2 and N_2 using the most recent theoretical and experimental values for the electric quadrupole moments and polarizabilities appear to remove, or very nearly remove, the discrepancies which have existed between theory and the analysis of swarm experiments.

I. INTRODUCTION

It has been well known for many years that for electron energies below vibrational threshold the observed electron energy losses in homonuclear diatomic molecular gases greatly exceed those due to elastic scattering alone. Early theoretical calculations[1,2] of the cross section for rotational excitation considering only the short-range electron-molecule interaction yielded energy loss rates smaller than the observed ones. However, in 1955, Gerjuoy and Stein (G. S.)[3] showed that, for the low energies of interest, the long-range part of the electron-molecule interaction is dominant in determining the rotational excitation cross section. Assuming the electron-molecule interaction to be the r^{-3} pure electric-quadrupole interaction for all r and using the Born approximation, they obtained an expression for the rotation excitation cross section which is proportional to Q^2, where Q is the electric-quadrupole moment of the molecule. Using reasonable values for Q (which was not precisely known in most cases), approximate agreement with observed energy losses was obtained. However, with increase in the precision of the analysis of swarm experiments,[4] some discrepancies became

---

† Work supported primarily under the U. S. Office of Naval Research Contract No. Nonr 4188 (00) and in part for one of us (R. C. M.) by the U. S. Atomic Energy Commission.

* Present address: Astronomy Department, Pennsylvania State University, University Park, Pennsylvania.

‡ Present address: Theoretical Division, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[1] P. M. Morse, Phys. Rev. **90**, 51 (1953).

[2] T. R. Carson, Proc. Phys. Soc. (London) **A67**, 909 (1954).

[3] E. Gerjuoy and S. Stein, Phys. Rev. **97**, 1671 (1955); **98**, 1848 (1955).

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

apparent. Furthermore, an inadequacy in the G.S. theory results from the fact that a slow electron polarizes the molecule. An account of the resulting r^{-4} polarization interaction was first included by Dalgarno and Moffett in a Born-approximation calculation of the cross section.[5] This failed to account completely for the discrepancies between theory and experiment. However, the central part of the polarization potential is large enough for one to expect distortion of the electron wave function to be of some importance. Moreover, although the long-range r^{-3} and r^{-4} interactions are dominant in determining the cross section, some account should be taken of the proper short-range part of the interaction. This is especially important in determining the effect of distortion. Recently, several authors have reported work along these lines.[6–10] In Ref. 7, it was found that for N_2, using the now fairly well-established value $Q=-1.1$ (in units of ea_0^2), and a reasonable approximate form for the short-range interaction, a distorted-wave calculation yielded essentially perfect agreement between theory and experiment.

In the present paper, the theory used in Ref. 7 is given in more detail[11] and application is made to N_2 and H_2. In the case of N_2, use is made of the new experimental values for the polarizabilities recently reported by Bridge and Buckingham.[12] The results do not alter the conclusions reached in Ref. 7. For H_2, using the recent theoretical value $Q\simeq 0.49$ of Kolos and Wolniewicz[13] and the values $\alpha_0=2.75$ and $\alpha_2=0.69$ based on recent theoretical[13] and experimental[12] values for the polarizabilities, we obtain results for the case of one short-range form for the interaction [Eq. (13) below] which appear to be very nearly in complete agreement with the analysis of swarm experiments.[4,14] However, the computed cross section is still too small when another form [Eq. (11) below] is used for the interaction at small distances. Additional reasons are given for preferring use of the former, Eq. (13), in the case of H_2. Some discrepancies between the results obtained by us and those obtained by Takayanagi and Geltman[10] are discussed.

II. EFFECTIVE ELECTRON-MOLECULE INTERACTION

In the case of homonuclear diatomic molecules, such as H_2, N_2, and O_2, which have Σ ground states, the molecular wave functions separate approximately into a product of electronic-vibrational states $\psi_m(\mathbf{r}_1\cdots\mathbf{r}_n, s)$ and spherical harmonic rotator states $Y_j^m(\hat{s})$. Then, for the calculation of the cross section for rotational excitation by low-energy ($\lesssim 1$ eV) electrons when no change in electronic-vibrational state occurs, the molecule behaves approximately as a rigid rotator, with states $Y_j^m(\hat{s})$ and effective electron-molecule interaction energy $V(\mathbf{r},\mathbf{s})$ given by the total electron-molecule interaction $V_t(\mathbf{r},\mathbf{r}_1\cdots\mathbf{r}_n,\mathbf{s})$ averaged over the electronic-vibrational state

$$V(\mathbf{r},\mathbf{s})=\int\psi_m^*(\mathbf{r}_1\cdots\mathbf{r}_n,s)V_t(\mathbf{r},\mathbf{r}_1\cdots\mathbf{r}_n,\mathbf{s})\times\psi_m(\mathbf{r}_1\cdots\mathbf{r}_n,s)d^3r_1\cdots d^3r_n\,s^2ds\,. \quad (1)$$

Here $\mathbf{r}_1\cdots\mathbf{r}_n$ are the positions of the n bound electrons, $\mathbf{r}$ is the position of the free electron relative to the center of mass of the molecule, and $\mathbf{s}$ is the internuclear separation. For the conditions that rotational excitation is of importance, "m" generally refers to the electronic-vibrational ground state. If the electronic-vibrational wave function $\psi_m^0(\mathbf{r}_1\cdots\mathbf{r}_n,s)$ for the isolated molecule is used in Eq. (1), one obtains the effective static interaction[3]

$$V_s(\mathbf{r},\mathbf{s})=\int\psi_m^{0*}V_t\psi_m^0d^3r_1\cdots d^3r_ns^2ds=\sum_{l=0}^{\infty}f_l(r)P_l(\hat{r}\cdot\hat{s})\,, \quad (2)$$

$$f_l(r)=-eC_l/r^{l+1};\quad r>R\,, \quad (3)$$

where C_l is the lth electric moment of the molecule and R is the approximate radius of the molecular charge cloud. For neutral homonuclear diatomic molecules, $C_0=0$ and $C_{2l+1}=0$ for all l. Hence, to good approximation,

$$V_s(\mathbf{r},\mathbf{s})\simeq-\frac{Qe^2a_0^2}{r^3}P_2(\hat{r}\cdot\hat{s})\,,\quad Q=\frac{C_2}{ea_0^2};\quad r>R. \quad (4)$$

As required for the validity of our approach, the principal electron-molecule interaction takes place in a time short compared with the rotational period. On the other hand, the free electron moves very slowly relative to the bound electrons of the molecule. Hence, the bound electrons adjust almost completely to the instantaneous position of the free electron as though it were stationary. Thus, one should not use the isolated molecular electronic-vibrational states ψ_m^0 in Eq. (1)

---

[5] A. Dalgarno and R. J. Moffett, Proc. Natl. Acad. Sci. India **A33**, 511 (1963).

[6] R. C. Mjolsness and D. H. Sampson, Bull. Am. Phys. Soc. **9**, 187 (1964).

[7] R. C. Mjolsness and D. H. Sampson, Phys. Rev. Letters **13**, 812 (1964).

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

[9] A. Dalgarno and R. J. W. Henry, Proc. Phys. Soc. (London) **85**, 679 (1965), and (private communication).

[10] K. Takayanagi and S. Geltman, Phys. Rev. **138**, A1003 (1965).

[11] This theoretical model was first presented by the authors at the Sixteenth Gaseous Electronics Conference in October, 1963 (unpublished).

[12] N. J. Bridge and A. D. Buckingham, J. Chem. Phys. **40**, 2733 (1964). They recommend (private communication from A. D. Buckingham) that the results for the asymmetrical polarizabilities ($\alpha_{\parallel}-\alpha_{\perp}$) be lowered about 1%.

[13] W. Kolos and L. Wolniewicz, Bull. Am. Phys. Soc. **9**, 103 (1964); L. Wolniewicz (private communication).

[14] A. G. Engelhardt and A. V. Phelps, Phys. Rev. **131**, 2115 (1963).

but rather should use those corresponding to the molecule in the presence of the free electron, i.e., the ψ_m should depend parametrically on $\mathbf{r}$. The result of this can be written

$$V(\mathbf{r},\mathbf{s})\simeq V_p(\mathbf{r},\mathbf{s})+V_s(\mathbf{r},\mathbf{s})\,, \tag{5}$$

where $V_p(\mathbf{r},\mathbf{s})$, called the polarization interaction, is the result of polarization of the molecular charge cloud and exchange effects. For large distances for which the effect of exchange is insignificant,

$$V_p(\mathbf{r},\mathbf{s})=-\frac{e^2a_0{}^3\alpha_0}{r^4}-\frac{e^2a_0{}^3\alpha_2}{r^4}P_2(\hat{r}\cdot\hat{s})\,;\quad r\gtrsim 2R\,, \tag{6}$$

$$\alpha_0=\tfrac{1}{6}(\alpha_{\shortparallel}+2\alpha_{\perp})\,,\quad \alpha_2=\tfrac{1}{3}(\alpha_{\shortparallel}-\alpha_{\perp})\,. \tag{7}$$

Here $\alpha_{\shortparallel}$ and $\alpha_{\perp}$ are the polarizabilities, in units of $a_0{}^3$, of the molecule along the direction $\mathbf{s}$ and a direction perpendicular to $\mathbf{s}$, respectively. Note that our α_0 and α_2 have half the values used by some authors.

In the present paper, the form adopted for the potential is

$$V(\mathbf{r},\mathbf{s})=V_0(r)+V_2(r)P_2(\hat{r}\cdot\hat{s})\,, \tag{8}$$

$$V_0(r)=-\frac{e^2a_0{}^3\alpha_0}{r^4}G(r)\,,\quad V_2(r)=-\frac{e^2a_0{}^2Q}{r^3}D(r)\,, \tag{9}$$

where

$$D(r)=\theta(r)+(\alpha_2a_0/Qr)G(r)\,, \tag{10}$$

$$G(r)=r^4/(r_0{}^2+r^2)^2\,,\quad \text{nonexponential cutoff}\,, \tag{11}$$

and

$$\begin{aligned}\theta(r)&=1\,,\quad r\geq r_c\\ &=0\,,\quad r<r_c\,.\end{aligned} \tag{12}$$

The factor $G(r)$, Eq. (11), is familiar from atomic scattering theory[15] and is expected to take into account approximately (at least for $r\gtrsim R$) the weakening of the polarization attraction, Eq. (6), due to exchange effects and the change in the response of the bound electrons for intermediate and small r. We also make calculations using the form[16]

$$G(r)=\{1-\exp[-(r/r_0)^4]\} \tag{13}$$

(exponential cutoff). The free parameter r_0 is chosen to match experimental elastic scattering data, as described more fully in Sec. V, and does not have the same value for the nonexponential cutoff, Eq. (11), and the exponential cutoff, Eq. (13). The value chosen for r_c, the abrupt cutoff in the static interaction, is based on the approximate knowledge available to us on the particular molecules being studied.

We note that when r_0 and r_c are set equal to zero, Eq. (8) reduces to Eq. (5) with the long-range forms, Eqs. (4) and (6), for $V_s(\mathbf{r},\mathbf{s})$ and $V_p(\mathbf{r},\mathbf{s})$ being used for all r. This is the interaction used by Dalgarno and Moffett.[5] When r_c, $\alpha_{\perp}$, and $\alpha_{\shortparallel}$ are set equal to zero, Eq. (8) reduces to the interaction used by Gerjuoy and Stein[3] [Eq. (4) for all r].

For $r<R$, the terms proportional to higher order Legendre polynomials in the true expression for $V(\mathbf{r},\mathbf{s})$ are not completely negligible. However, they are expected to be large only for a fairly narrow range of r near $s/2$. Moreover, they contribute to different rotational transitions than $V_2(r)P_2(\hat{r}\cdot\hat{s})$ does. Thus, we expect that use of the form given by Eq. (8) is a good approximation. (This is born out by the recent calculations for H_2 in Ref. 9.) However, the correct $V_0(r)$ and $V_2(r)$ also differ from our choice, Eqs. (9)–(13), for $r<R$. They are large in magnitude [especially $V_2(r)$] for $r\sim s/2$, while $\lim_{r\to 0}V_2(r)=0$ and $\lim_{r\to 0}V_0(r)=\text{const}$. Nevertheless, with our choice we have eliminated the singularities in the interaction at $r=0$ resulting from use of the long-range forms, Eqs. (4) and (6), for all r. Also, by choosing r_0 by matching to the elastic scattering, we can hope with some justification that the interaction is fairly well represented for the important range of r. The fact that the main contribution to rotational excitation comes from $l=l'=1$ scattering and $l=l'=0$ scattering gives no contribution, where $l\hbar$ and $l'\hbar$ are the initial and final electron orbital momentum, reduces the importance of the small r region. For these reasons, we expect that our choice of interaction is probably good enough to enable us to obtain fairly accurate results for $\epsilon_a\lesssim 0.4$ or 0.5 eV, where ϵ_a is the initial free-electron energy. However, the importance of the region $r<R$ increases rapidly with ϵ_a, so that results obtained for $\epsilon_a\gtrsim 1$ eV, without use of the approximately correct interaction for $r\lesssim R$, are of little value. The work done and being done by Dalgarno and Henry[9] should lead eventually to fairly good results for these higher energies, at least for H_2 where they are most likely to be important.

III. GENERAL METHOD OF CALCULATION AND VALIDITY CRITERIA

The method used to calculate the cross section in this paper can be regarded as an approximation to the method of distorted waves. Recall that the inelastic differential scattering cross section according to the method of distorted waves is given by[17,18]

$$I(a,\mathbf{k}_a\to b,\mathbf{k}_b)=\frac{k_b}{k_a}\left(\frac{m}{2\pi\hbar^2}\right)^2 \times\left|\int d^3rF_b(-\mathbf{k}_b,\mathbf{r})V_{ba}(\mathbf{r})F_a(\mathbf{k}_a,\mathbf{r})\right|^2. \tag{14}$$

---

[15] M. N. Klein and K. A. Brueckner, Phys. Rev. **111**, 1115 (1958).

[16] This form was suggested to us by C. F. Curtiss.

[17] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1933), 2nd ed., p. 146.

[18] M. J. Seaton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 386.

Here $F_a(\mathbf{k}_a,\mathbf{r})$ and $F_b(\mathbf{k}_b,\mathbf{r})$ are the solutions of the differential equations

$$[\nabla_r^2+k_i^2-(2m/\hbar^2)V_{ii}(\mathbf{r})]F_i(\mathbf{k}_i,\mathbf{r})=0\,,\quad i=a,\,b\,, \tag{15}$$

with asymptotic forms for large r of plane waves plus outgoing waves. V_{ba} is the matrix element of the electron-molecule interaction energy taken between initial and final molecular states a and b. In the present problem, where the effective electron-molecule interaction energy $V(\mathbf{r},\mathbf{s})$ is given by Eq. (8) and the molecule behaves as a rigid rotator with states $Y_j{}^m(\hat{s})$,

$$V_{ba}(\mathbf{r})=V_0(r)\delta_{j_bj_a}\delta_{m_bm_a}+V_2(r)\langle j_b,m_b|P_2(\hat{r}\cdot\hat{s})|j_a,m_a\rangle\,. \tag{16}$$

In obtaining Eqs. (14) and (15), i.e., in using the method of distorted waves, one truncates and decouples the infinite set of coupled differential equations for the free-electron wave functions by neglecting all off-diagonal matrix elements of the interaction energy, except the one connecting the final state to the initial state. Thus, in the present problem where Eq. (16) applies, a criterion for the validity of the method is

$$\begin{aligned}|V_0(r)+V_2(r)\langle j_a,m_a|P_2(\hat{r}\cdot\hat{s})|j_a,m_a\rangle|\\ \gg|V_2(r)\langle j_b,m_b|P_2(r\cdot\hat{s})|j_a,m_a\rangle|\,;\\ j_b,\,m_b\neq j_a,\,m_a\,.\end{aligned} \tag{17}$$

In our calculations, we make the additional approximation

$$V_{aa}(\mathbf{r})\simeq V_{bb}(\mathbf{r})\simeq V_0(r)\,. \tag{18}$$

As seen from Eq. (16), the criterion for the validity of this approximation is

$$|V_0(r)|\gg|V_2(r)\langle j_a,m_a|P_2(\hat{r}\cdot\hat{s})|j_a,m_a\rangle|\,. \tag{19}$$

The utility of this latter approximation is that the potential entering Eqs. (15) is then spherically symmetric and independent of molecular states. This simplifies the calculation and shortens the required computing-machine time. Condition (17) may tend to be an overly severe criterion for the validity of the method of distorted waves, because the coupling terms neglected in obtaining Eqs. (14) and (15) involve products of the off-diagonal matrix elements of $V(\mathbf{r},\mathbf{s})$ with electron wave functions which are either small in amplitude or out of phase with the wave functions entering the retained part. A more precise criterion which takes the approximate average over r effect of this into account can be obtained from S-matrix theory.[19,20] The true S matrix is unitary and symmetric, while in the method of distorted waves the diagonal elements of the S matrix have an absolute value of unity. Thus, the sum of the squares of the nondiagonal elements must be small if the method of distorted waves is to be valid,[20] i.e.,

$$\textstyle\sum_{j'l'\neq jl}|S^J(j,l;\,j',l')|^2\ll1\,, \tag{20}$$

where $\mathbf{J}\hbar$ is the total angular momentum of the system, electron plus rotator (molecule), compounded out of electron orbital momentum $\mathbf{l}\hbar$ and rotator angular momentum $\mathbf{j}\hbar$.

It is interesting to note that, when approximation (18) is made, Eqs. (14) and (15) can be regarded as giving the inelastic scattering cross section according to first-order perturbation theory with $V_0(r)$ included in H_0. We have preferred to regard the method as an approximation to the method of distorted waves because then the above criteria are readily available for the validity of the approach. Application of these criteria is made in Sec. VI.

Since the potential entering Eqs. (15) is spherically symmetric when approximation (18) is made, there is no azimuthal dependence in the decomposition of $F_a(\mathbf{k}_a,\mathbf{r})$ and $F_b(\mathbf{k}_b,\mathbf{r})$ into partial waves. Thus, we make the expansion

$$F_a(\mathbf{k}_a,\mathbf{r})=\sum_{l=0}^{\infty}(2l+1)i^lu_{al}'(r)P_l(\hat{k}_a\cdot\hat{r})\,, \tag{21}$$

where $u_{al}'(r)$ satisfies the equation

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+k_a{}^2-\frac{2m}{\hbar^2}V_0(r)-\frac{l(l+1)}{r^2}\right]u_{al}'(r)=0\,, \tag{22}$$

and has the asymptotic form for large r

$$\lim_{r\to\infty}u_{al}'(r)=\frac{e^{i\delta_l}}{kr}\sin\left(k_ar-\frac{\pi l}{2}+\delta_l\right). \tag{23}$$

Since the plane-wave decomposition is

$$e^{i\mathbf{k}_a\cdot\mathbf{r}}=\sum_{l=0}^{\infty}(2l+1)i^lj_l(k_ar)P_l(\hat{k}_a\cdot\hat{r})\,, \tag{24}$$

we can write

$$F_a(\mathbf{k}_a,\mathbf{r})=e^{i\mathbf{k}_a\cdot\mathbf{r}}+\sum_{l=0}^{\infty}(2l+1)i^lu_{al}(r)P_l(\hat{k}_a\cdot\hat{r})\,, \tag{25}$$

where

$$u_{al}(r)=u_{al}'(r)-j_l(k_ar)\,. \tag{26}$$

Similar expressions apply for $F_b(\mathbf{k}_b,\mathbf{r})$ with b replacing a everywhere. The separation in Eq. (25) is convenient because it leads to the Born approximation to the cross section plus corrective terms due to distortion involving various products of the u_l.

IV. REDUCTION OF THE CROSS SECTION

We consider now the explicit form taken by Eq. (14) in the present problem. For homonuclear diatomic molecules, the rotational cross section is generally small in comparison to the elastic cross section and makes

---

[19] A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. (London) **A256**, 540 (1960).

[20] C. S. Roberts, Phys. Rev. **131**, 209 (1963).

little contribution to the momentum transport cross section. For this reason, rotational excitation of such molecules is of practical importance only in determining the electron-molecule energy exchange rate. This depends on the total rotational cross section $\sigma(j_a \rightarrow j_b)$ for the transition $j_a \rightarrow j_b$ averaged over initial and summed over final azimuthal quantum numbers m_a and m_b. Hence, we calculate only $\sigma(j_a \rightarrow j_b)$:

$$\sigma(j_a \rightarrow j_b) = \frac{1}{2j_a+1} \sum_{m_a} \sum_{m_b} \int d\Omega I(a, j_a \rightarrow b, j_b) , \quad (27)$$

which is somewhat easier than calculating $I(a, j_a \rightarrow b, j_b)$. This is done using Eqs. (8), (14), (16), and (25) and making the approximation that distortion of the partial waves with $l > 1$ can be neglected. Appropriate ordering of the angular integrations, use of the identities satisfied by the spherical harmonics,[21,22] and replacement of the $d\Omega$ integration by an integration over k, where $k = |\mathbf{k}_a - \mathbf{k}_b|$, leads to the final expression for the cross section after a long but straightforward calculation. Details are given in Ref. 23. The result is conveniently expressed in terms of the Gerjuoy-Stein value[3] for the cross section

$$\sigma_{GS}(j_a \rightarrow j_b) = \frac{8\pi Q^2 a_0^2}{15} \frac{k_b}{k_a} \frac{(j_a+2)(j_a+1)}{(2j_a+3)(2j_a+1)} \quad \text{for} \quad j_b = j_a + 2 ,$$

$$= \frac{8\pi Q^2 a_0^2}{15} \frac{k_b}{k_a} \frac{j_a(j_a-1)}{(2j_a-1)(2j_a+1)} \quad \text{for} \quad j_b = j_a - 2 , \quad (28)$$

and the auxiliary quantities

$$f_u(a,b) = 2 - \frac{r_c^2}{5a_0^2} K_a^2 - \frac{3(K_a^2+K_b^2)}{4K_a^2} + \frac{3(K_a^2-K_b^2)^2}{8K_a^3 K_b} \ln\left|\frac{K_a+K_b}{K_a-K_b}\right| , \quad (29)$$

$$g_u(a,b) = h_1 - h_3 K_b^2 - cpK_a^2 + dp^2[h_2 - K_b^2 h_4] , \quad (30)$$

$$f_v(a,b) = -\frac{2r_c^2}{5a_0^2} K_a K_b + \frac{9}{10}\left[\frac{K_a^2+K_b^2}{K_a K_b} - \frac{(K_a^2-K_b^2)^2}{2K_a^2 K_b^2} \ln\left|\frac{K_a+K_b}{K_a-K_b}\right|\right] , \quad (31)$$

$$g_v(a,b) = \frac{12K_a K_b}{5}\left[\tfrac{2}{3}h_3 - \tfrac{5}{6}cp + dp^2 h_4\right] , \quad (32)$$

$$f_w(a,b) = \frac{3}{40}\left[\frac{-3K_a^4+22K_a^2K_b^2-15K_b^4}{K_a^3 K_b} + \frac{3(K_a^2+5K_b^2)(K_a^2-K_b^2)^2}{2K_a^4 K_b^2} \times \ln\left|\frac{K_a+K_b}{K_a-K_b}\right|\right] , \quad (33)$$

$$g_w(a,b) = \frac{3K_b}{10K_a}\{-(3K_a^2+5K_b^2)h_3 + 5h_4 + dp^2[-(7K_a^2+5K_b^2)h_4 + h_5]\} , \quad (34)$$

in which

$$h_1 = \frac{3K_1^2+K_2^2}{3K_1} , \quad h_2 = \frac{5K_1^4+10K_1^2K_2^2+K_2^4}{5K_1} ,$$

$$h_3 = \frac{5K_1^2-K_2^2}{5K_1^3} , \quad h_4 = \frac{35K_1^4+14K_1^2K_2^2-K_2^4}{35K_1^3} , \quad (35)$$

$$h_5 = \frac{105K_1^6+189K_1^4K_2^2+27K_1^2K_2^4-K_2^6}{21K_1^3} ,$$

and

$$K_a = a_0 k_a , \quad K_b = a_0 k_b , \quad (36)$$

while

$$K_1 = \max(K_a, K_b) , \quad K_2 = \min(K_a, K_b) . \quad (37)$$

The quantities c and d are constants. They have the approximate values

$$c = 0.8, \quad d = 0.3; \quad \text{nonexponential cutoff}, \quad (38)$$

and

$$c = 0.3 , \quad d = 0; \quad \text{exponential cutoff}, \quad (39)$$

for the short-range forms for the polarization interaction given by Eqs. (11) and (13), respectively, p is introduced to account for the slight energy dependence of r_0:

$$p = [r_0(\epsilon_a) + r_0(\epsilon_b)]/2a_0 . \quad (40)$$

Also we use the quantities $f_u(b,a), \cdots, g_w(b,a)$, defined similarly, except that K_a and K_b are interchanged and K_1 and K_2 unchanged in Eqs. (29)-(35). Of course, $f_v(a,b)$ and $g_v(a,b)$ are seen to be symmetrical in a and b. Finally, use is made of the radial integrals

$$U(a,b) = 3\int_0^\infty \frac{dr}{r} D(r) u_{a0}(r) j_2(k_b r) , \quad (41)$$

$$V(a,b) = 3\int_0^\infty \frac{dr}{r} D(r) u_{a1}(r) j_1(k_b r) , \quad (42)$$

$$W(a,b) = 3\int_0^\infty \frac{dr}{r} D(r) u_{a1}(r) j_3(k_b r) , \quad (43)$$

$$X(a,b) = 3\int_0^\infty \frac{dr}{r} D(r) u_{a1}(r) u_{b1}(r) , \quad (44)$$

---

[21] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), pp. 60 and 61.

[22] P. M. Morse and H. Feshback, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 622.

[23] R. C. Mjolsness and D. H. Sampson, General Electric Company TIS Report R65SD22, 1965 (unpublished).

and $U(b,a)$, $V(b,a)$, and $W(b,a)$ defined by Eqs. (41)–(43) with a and b interchanged.

With these definitions, partial cross sections can be expressed as follows:

$$\frac{\sigma_c}{\sigma_{GS}}=1-\frac{r_c^2(K_a^2+K_b^2)}{5a_0^2}+\frac{3\pi\alpha_2}{8Q}\times\left[h_1-cp(K_a^2+K_b^2)+\left(dp^2-\frac{r_c^2}{10a_0^2}\right)h_2\right]+\left(\frac{3\pi\alpha_2}{16Q}\right)^2\left[K_a^2+K_b^2-2cph_2+p^2(2d+c^2)\times\left(K_a^4+\frac{10}{3}K_a^2K_b^2+K_b^4\right)\right], \quad (45)$$

$$\frac{\sigma_1}{\sigma_{GS}}=\left\{\left[f_u(a,b)+\frac{3\pi\alpha_2}{8Q}g_u(a,b)\right]\times\mathrm{Re}U(b,a)+|U(b,a)|^2\right\}+[a\leftrightarrow b], \quad (46)$$

$$\frac{\sigma_2}{\sigma_{GS}}=\left[f_w(a,b)+\frac{3\pi\alpha_2}{8Q}g_w(a,b)\right]\mathrm{Re}W(b,a)+[a\leftrightarrow b]+\left[f_v(a,b)+\frac{3\pi\alpha_2}{8Q}g_v(a,b)\right]\times[\mathrm{Re}V(b,a)+\mathrm{Re}V(a,b)+\mathrm{Re}X(a,b)], \quad (47)$$

$$\frac{\sigma_3}{\sigma_{GS}}=\frac{6}{5}|V(a,b)+V(b,a)|^2+\frac{9}{5}\{|W(a,b)|^2+|W(b,a)|^2\}, \quad (48)$$

$$\frac{\sigma_4}{\sigma_{GS}}=\frac{6}{5}\{X(a,b)[V(a,b)+V(b,a)]^*+X^*(a,b)[V(a,b)+V(b,a)]\}, \quad (49)$$

and

$$\frac{\sigma_5}{\sigma_{GS}}=\frac{6}{5}|X(a,b)|^2, \quad (50)$$

where the symbol $[a\leftrightarrow b]$ entering Eqs. (46) and (47) denotes the preceding term with a and b interchanged. Finally, the total rotational cross section is given by the sum

$$\sigma=\sigma_0+\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5. \quad (51)$$

σ_0 is the Born approximation to the total cross section. It reduces to the Dalgarno-Moffett result when $r_c=0$ and $c=d=0$ (corresponding to $r_0=0$). The other partial cross sections give the corrections due to distortion. σ_1 gives the correction due to distortion of the initial and final s waves and σ_2, σ_3, σ_4, and σ_5 the corrections due to distortion of the initial and final p waves. In most cases, the dominant effect is the positive contribution arising from the last term in σ_2. However, the σ_1 contribution, which is negative, dominates for near-threshold energies where $l=2$ to $l'=0$ scattering becomes of importance. Also, for high energies, the contribution $(6/5)\sigma_{\mathrm{GS}}|V(a,b)+V(b,a)+X(a,b)|^2$ arising from σ_5, σ_4 and the first term in σ_3 becomes significant. The terms involving the W's are never of much importance. The $X(a,b)$ contribution becomes relatively unimportant at small energies, but is comparable with the contribution of the V's at high energies.

V. NUMERICAL PROCEDURES

A wave-function code and a cross-section code are used to obtain numerical results for particular initial electron energies and rotator transitions. The former code gives numerical values for $k_a r u_{al}'(r)\exp(-i\delta_{al})$ using a series solution for the first nonzero point and a Runge-Kutta integration using two mesh sizes for succeeding points. It was hand checked, was able to generate correct free wave functions, and at low energies gave $l=1$ and $l=2$ phase shifts in agreement with the O'Malley asymptotic formula.[24] The assignment of the correct multiple of π to the computed phase shift was made by fitting our potential to the soluble exponential potential and using Levenson's theorem. This was verified by choosing a typical r_0 value and a small energy and computing phase shift as a function of α_0.

The wave functions and phase shifts were put on tapes and used as inputs for the cross-section code. Integrals were done via Simpson's rule using two mesh sizes. The partial contributions due to the static and the polarization interactions were output, allowing one to compute results for a variety of α_2 and Q values using only one set of integrations. In addition, all the coefficients Eqs. (29)–(34), the total cross section, the Born approximation, and the partial cross sections due to the polarization and to the static interactions were output. The program was hand checked. Detailed outputs are given in Ref. 23.

About 1.5 min on an IBM 7094 were required per cross section at high energies and about 4 min at low energies. The purely numerical errors in the results are expected to be somewhat under 1%, in all cases, partly because our method separates off the essentially exactly known Born value from distortion effects. At low energies, the distortion effects are hard to calculate accurately, but they are also small.

The parameter r_0 was determined by assuming the momentum transfer cross section σ_m is entirely due to elastic scattering and varying r_0 until use of the computed phase shifts in the equation

$$\sigma_m=\sin^2(\delta_0-\delta_1)+2\sin^2(\delta_1-\delta_2)+3\sin^2\delta_2 \quad (52)$$

gave agreement with the values for σ_m measured by

---

[24] T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).

TABLE I. r_0/a_0 as a function of electron energy.

ϵ (eV)	10^{-3}	10^{-2}	0.03	0.05	0.1	0.2	0.4	0.6	1.0
r_0/a_0 (N_2, nonexponential cutoff)	1.256	1.251	1.250		1.245	1.236	1.217	1.190	
r_0/a_0 (H_2, nonexponential cutoff)	0.9436	0.9396	0.9368	0.9364	0.9389	0.9421	0.9455	0.9485	0.9565
r_0/a_0 (H_2, exponential cutoff)	1.1763	1.1700	1.1649	1.1638	1.1667	1.1697	1.1692	1.1676	1.1655

Phelps and co-workers.[4,14,25,26] The parameters input into the calculation are

$$\alpha_0 = 2.75 \text{ for } H_2 \quad \text{and} \quad \alpha_0 = 5.93 \text{ for } N_2. \tag{53}$$

The value for H_2 is a compromise between the recent computations of Kolos and Wolniewicz[13] and the slightly different new experimental value obtained by Bridge and Buckingham.[12] The value for N_2 was used before the value $\alpha_0 = 5.96$, based on the recent experimental results of Ref. 12, was available, and the difference was considered too small to be significant. This procedure is tested by requiring the variation of r_0 with electron energy to be small. As seen from Table I, this condition is well satisfied. For N_2, no reasonable fit to σ_m was possible above $\epsilon = 0.3$ eV using the exponential cutoff. Hence, only the nonexponential cutoff potential was used in calculations. Both potentials are used in calculations for H_2, since both potentials lead to a good fit; however, the exponential cutoff gives smaller deviations in r_0. Values of the rotational cross section are insensitive to the energy variation of r_0 and, in test cases, change by less than 2% if a constant r_0 is used.

In Table II, phase shifts for $l=0$, 1 waves in the H_2 case are given for the two potentials. The δ_0 values are quite similar, but the differences in δ_1 values are of importance for the rotational excitation cross section, which is primarily determined by $l=l'=1$ scattering. A few values for the N_2 phase shifts are $\delta_0 = 2.9238$, $\delta_1 = 0.1131$ at $\epsilon = 0.6$ eV, and $\delta_0 = 3.0495$, $\delta_1 = 0.01824$ at $\epsilon = 0.1$ eV. For all cases treated here, δ_2 is very small and is given by the O'Malley asymptotic formula.[24]

VI. RESULTS AND DISCUSSION

In plotting results for the cross section versus initial electron energy ϵ_a, we find it convenient to plot $\sigma(j \to j+2)/\sigma_{GS}(j \to j+2)$ rather than $\sigma(j \to j+2)$, where σ_{GS} is given by Eq. (28). This ratio also gives the value for de-excitation $\sigma(j+2 \to j)/\sigma_{GS}(j+2 \to j)$, except that ϵ_a must then correspond to the final electron energy.

TABLE II. Phase shifts for electron scattering by H_2.

ϵ (eV)	Nonexponential cutoff δ_0	Nonexponential cutoff δ_1	Exponential cutoff δ_0	Exponential cutoff δ_1
1.0	2.6004	0.07592	2.6434	0.1098
0.2	2.9298	0.01632	2.9323	0.01922
0.05	3.0478	0.00419	3.0481	0.00456

The results for N_2 for the transition $j=4 \to 6$ are given in Figs. 1 and 2. This transition was chosen for the purpose of making comparison with the analysis of swarm experiments given in Ref. 25. However, it also gives the value for σ/σ_{GS} for other transitions for the range tested $(0 \leq j \leq 30)$ to within somewhat better than 1%, except for a slightly larger deviation very near the transition thresholds. This approximate independence of j is due, in part, to the small value $B_0 = 0.249 \times 10^{-3}$ eV for the rotational constant for N_2 and, in part, to the fact that the variation with j of the Born cross section is mostly canceled by the variation with j of distortion effects. Figure 1 is similar to Fig. 1 of Ref. 7, except that here we use the new experimental value $\alpha_2 = 1.57$ based on the measurements of Bridge and Buckingham[12] in place of the old value[27] $\alpha_2 = 2.09$. The choice $Q = -1.1$ has been well established recently experimentally[28–31] and verified as to sign and approximate magnitude theoretically, as well.[32,33] The difference between the two solid curves gives an indication of the uncertainty resulting from an imprecise knowledge of the interaction at short range. It is seen that this difference is small below the vibrational threshold at 0.29 eV. As mentioned in Ref. 7, one finds for almost any choice of charge distribution which leads to a negative value for Q that the static part of $V_2(r)$ changes sign after appreciable penetration into the charge distribution. For this reason, we expect that for negative Q the contribution from the static interaction part of $V_2(r)$ for $r<R$ mainly cancels out and the choice $r_c = 2.1a_0 \simeq R$ gives the best results for the rotational excitation cross section for N_2. The dashed and dotted curves in Fig. 1 are the Born approximation results when Eqs. (4), (5), and (6) are used for all r and when our modified interaction, Eqs. (8)–(12), is used,

---

[25] A. G. Engelhardt, A. V. Phelps, and C. G. Risk, Phys. Rev. **135**, A1566 (1964).

[26] A. V. Phelps (private communication).

[27] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

[28] J. A. A. Ketelaar and R. P. H. Rettschnick, Mol. Phys. **7**, 191 (1963).

[29] J. D. Poll, Phys. Letters **7**, 32 (1963).

[30] D. R. Bosomworth (private communication) and thesis, Physics Department, University of Toronto (unpublished).

[31] A. D. Buckingham (private communication). (This is the only experimental work that gives the sign of Q.) The method used is given by A. D. Buckingham and R. L. Disch, Proc. Roy. Soc. (London) **A273**, 275 (1963).

[32] P. Cade, K. D. Sales, and A. C. Wahl, Bull. Am. Phys. Soc. **9**, 102 (1964); and (private communication). They obtain $Q = -1.091$ for internuclear separation $R = 2.068a_0$. More extended calculations giving $Q = Q(R)$ are to be published.

[33] R. K. Nesbet, J. Chem. Phys. **40**, 3619 (1964). Here the same sign but lower magnitude $Q = -0.9$ is obtained.

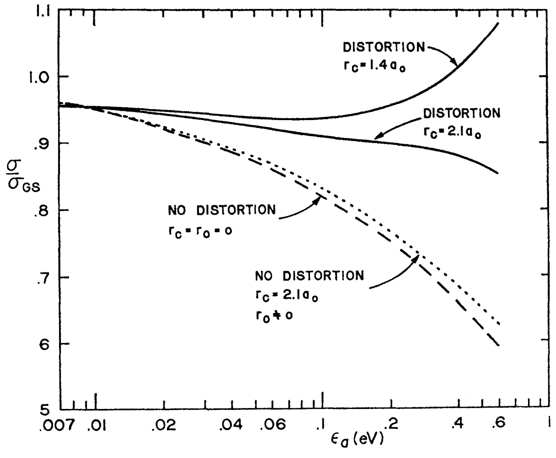

FIG. 1. Ratio of the rotational excitation cross section to the value given by the Gerjuoy-Stein theory versus initial electron energy for the $j=4 \rightarrow 6$ transition for N_2 with $Q=-1.1, \alpha_2=1.57$, and $\alpha_0=5.93$.

respectively. It is seen that the negative effect due to inclusion of polarization is almost canceled by the positive effect resulting from distortion. This is apparently the explanation why use of the Gerjuoy-Stein theory with a magnitude for Q a little less than 1.1 has lead to very good agreement with experiment.[4,25,34] From inspection of the $r_c=2.1a_0$ curve in Fig. 1 and in Fig. 3 of Ref. 25, it appears that use of the new value $\alpha_2=1.57$ does not alter the conclusion reached in Ref. 7 that use of the value $Q=-1.1$, inclusion of distortion and polarization, and use of a reasonable approximate form for the short-range interaction leads to essentially perfect agreement between theory and experiment for rotational excitation of N_2. Although $Q=-1.1$ is thought likely to be very nearly the correct value, for completeness we have included in Fig. 2 results obtained for various other negative values of Q when $r_c=2.1a_0$.

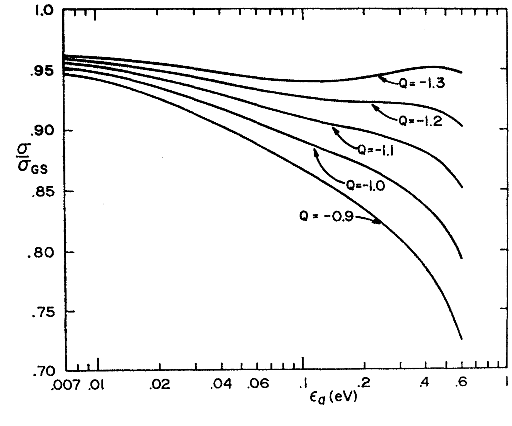

FIG. 2. Rotational excitation versus initial electron energy for the $j=4 \rightarrow 6$ transition for N_2 for various values of the electric quadrupole moment and $\alpha_2=1.57, \alpha_0=5.93$, and $r_c=2.1a_0$.

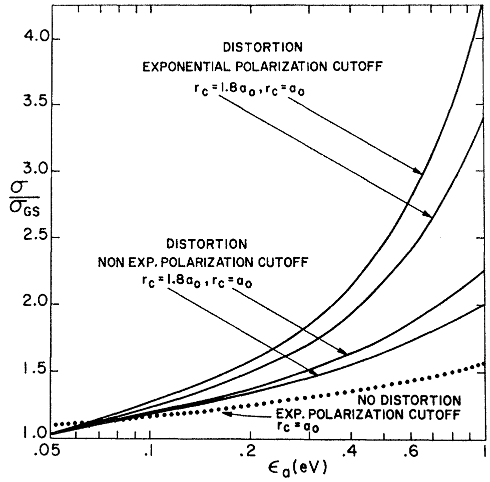

FIG. 3. Ratio of the rotational excitation cross section to the value given by the Gerjuoy-Stein theory versus initial electron energy for the $j=0 \rightarrow 2$ transition for H_2 with $Q=0.49, \alpha_2=0.69$, and $\alpha_0=2.75$.

The results for H_2 have a very different form than those for N_2, principally because Q for H_2 is positive, which causes the contributions from the static and polarization contributions to $V_2(r)$ to have the same sign. In obtaining all results for H_2, we used the new value $\alpha_2=0.69$, based on the recent careful theoretical and experimental results presented in Refs. 13 and 12. The results given in Figs. 3 and 4 were obtained using the value $Q=0.49$, which is again based on the theoretical work of Wolniewicz and Kolos.[13] Results for σ/σ_{GS} for various additional Q's and the $j=1 \rightarrow 3$ transition are given in Fig. 5. These results were obtained using the exponential polarization cutoff, Eq. (13); however, results obtained with the nonexponential cutoff, but the same conditions otherwise, have a similar small (even smaller for high energies) percentage

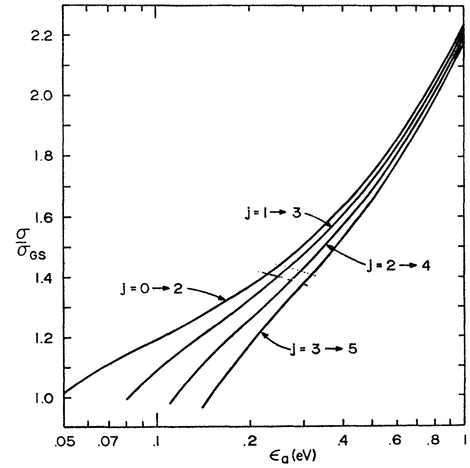

FIG. 4. Rotational excitation versus initial electron energy for various transitions for H_2 with static cutoff at $r_c=a_0$, nonexponential polarization cutoff, $Q=0.49, \alpha_2=0.69$, and $\alpha_0=2.75$.

---

[34] M. H. Mentzoni and R. V. Row, Phys. Rev. **130**, 2312 (1963).

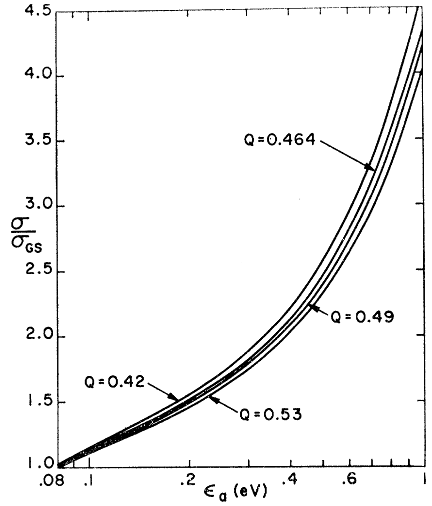

FIG. 5. Rotational excitation versus initial electron energy for the $j=1\to 3$ transition for H_2 for various values of Q using the exponential polarization cutoff, a static cutoff at $r_c=a_0$, $\alpha_2=0.69$, and $\alpha_0=2.75$.

deviation from the corresponding results for $Q=0.49$. The results in Fig. 5 correspond to $r_c=a_0$, which we estimate to be approximately the best choice for the cutoff in the static interaction part of $V_2(r)$. Charge distributions which lead to positive Q can be chosen such that this static interaction either does or does not change sign within the charge cloud. However, the calculations presented by Dalgarno and Henry[9] in their Fig. 1 indicate that the sign does not change. In fact, it would appear perhaps that even a smaller value of r_c should have been chosen for H_2. However, it can be argued that this might be compensated for by an overestimation of the polarization contribution to $V_2(r)$ resulting from choosing r_0 too small when we neglect the static contribution to $V_0(r)$ for $r\lesssim R$. In Fig. 3, the effect of distortion and polarization on the rotational excitation cross section is shown for various choices for the short-range form of the interaction. In Fig. 4, the variation of σ/σ_{GS} with ϵ_a is shown for various transitions when $r_c=a_0$ and the nonexponential cutoff is used. For the same conditions, except that the exponential cutoff is used, the results have a very similar behavior for small initial electron energies and a slightly greater spread with j for high energies. For example, at $\epsilon_a=1$ eV, results for σ/σ_{GS} for the exponential cutoff are 4.259, 4.188, 4.113, and 4.038 for the $j=0\to 2$, $1\to 3$, $2\to 4$, and $3\to 5$ transitions. When $\epsilon_a=0.35$ eV, the exponential cutoff results for σ/σ_{GS} for the same transitions are 1.991, 1.927, 1.855, and 1.769.

The important transitions for H_2 for the conditions studied by Engelhardt and Phelps[14] are $j=0\to 2$ and $j=1\to 3$. They found that σ_{GS} should be multiplied by a factor 1.73 in order to give agreement with swarm experiments. Since $Q=0.473$ was used, this means that the average value for σ/σ_{GS} for these transitions in Figs. 3 and 4 and for $Q=0.49$ in Fig. 5 should be $(0.473/0.49)^2 \times 1.73=1.61$. For $r_c=a_0$, this value is obtained for $\epsilon_a\simeq 0.23$ eV for the exponential cutoff and $\epsilon_a\simeq 0.4$ eV for the nonexponential cutoff. A second test is provided by plotting the ratio of our distorted-wave value for σ for these transitions with $r_c=a_0$, $Q=0.49$, and $\alpha_2=0.69$ to σ_{DM}, the value given by the Dalgarno-Moffett Born approximation with no short-range cutoff and with $Q=0.473$ and $\alpha_2=0.486$ (approximately the value used in Refs. 5 and 14). This is done in Fig. 5 of Ref. 23. The average value of this ratio should be 1.54 in order to obtain consistency with swarm experiments according to Ref. 14. This value is obtained at $\epsilon_a\simeq 0.28$ eV for the exponential cutoff and $\epsilon_a\simeq 0.8$ eV for the nonexponential cutoff. Of course, the energy dependence of σ is quite different than it is in the case of the Born approximation. However, it is noted in the footnote on p. 2122 of Ref. 14 that a steeper rise in σ with energy than the Born approximation would give better agreement with experiment. The negative effect of distortion near threshold is probably not too significant because it occurs principally only when k_b/k_a is small, and hence the excitation cross section is small. Thus, it would appear that the positive effect of distortion plus the increases in σ due to the new larger values 0.49 and 0.69 for Q and α_2 are probably sufficient, or very nearly so, to bring theory and experiment into complete agreement when the exponential cutoff, Eq. (13), is used for H_2. However, when the nonexponential cutoff, Eq. (11), is used, the results for σ are still too small to remove completely the discrepancies between theory and the analysis of swarm experiments.

In addition to the fact that the results for the rotational excitation cross section for H_2 are better when Eq. (13) rather than Eq. (11) is used, there are other reasons to prefer Eq. (13). The variation of r_0 with ϵ is smaller (see Table I). Also, although the larger hump in the interaction for $r\simeq r_0\simeq a_0$ obtained with Eq. (13) probably overestimates the polarization and exchange effects in this region, it probably better compensates for the static contribution to $V_0(r)$ (which we have neglected) and the large static contribution to $V_2(r)$ for $r\sim a_0$ indicated by Fig. 1 of Ref. 9. For these reasons, we think Eq. (13) leads to the better representation of the total potential for H_2.

We consider now some of the discrepancies between our results and those of Takayanagi and Geltman[10] who use a single cutoff for both static and polarization interactions, as given by their Eq. (5a). We think our cutoff procedure is better and should lead to more accurate results because it softens the potential to larger distances than theirs and allows for the loss of polarization for an electron closely approaching the charge cloud. It also permits a closer fit to the experimental elastic-scattering cross section at the low energies relevant for the rotational excitation process. Moreover, we can separately choose the static cutoff, which is essentially (completely in our approximation) independent of the elastic scattering, on the basis of independent knowledge of the molecule. However, we certainly do not claim that our procedure is completely satisfactory.

Their cutoff procedure, which gives a fairly large static contribution to $V_2(r)$ for $r<R$ is undoubtedly primarily responsible for the large hump at fairly high energies shown in their Fig. 10 for N_2. As mentioned in the discussion of N_2 results, we think that the net static contribution to $V_2(r)$ for $r<R$ should be approximately zero instead. Hence, we expect that the hump in Fig. 10 of Ref. 10 is nonphysical, although the uncertainty in the interaction at small distances is too great to be certain that no hump occurs. On the other hand, it is difficult to see how their cutoff procedure can be completely responsible for the fairly large negative distortion effect they obtain for intermediate and low energies ($\epsilon_a \lesssim 0.1$ eV), where the rotational cross section is relatively insensitive to the short-range form of the potential. This effect is in contrast to the positive distortion effect shown for most of this energy range in Fig. 1 of the present paper, or in Fig. 1 of Ref. 7. Another qualitative difference in results for N_2 is that $\sigma/\sigma_{\mathrm{GS}}$ computed from Table II of Ref. 10 is not so nearly independent of j for the conditions $0\leq j\leq 30$ and $\epsilon_a \leq 0.6$ eV as we have found.

In the case of H_2, it is difficult to make a detailed comparison of results on the basis of comparison with Fig. 9 of Ref. 10. Hence, we have computed $\sigma/\sigma_{\mathrm{GS}}$ from Table I of Ref. 10. The results for the $j=0\rightarrow 2$ transition together with our results for the same transition are given in Fig. 6. Their results pertain to $Q=0.464$, $\alpha_2=0.625$, and $\alpha_0=2.664$, while ours pertain to $Q=0.49$, $\alpha_2=0.69$, and $\alpha_0=2.75$. The principal Q dependence is factored out in dividing by σ_{GS}, as indicated by our Fig. 5. However, with the larger α_2 relative to Q and the larger α_0 used by us, our results should be a little higher than theirs, especially at high energies where the effect of polarization and distortion are greatest. The relatively rapid increase in their values with energy at high energies probably results from the fact that their $V_0(r)$ is significantly stronger than ours for $r\sim 1$ or $2a_0$. For this reason, their potential (especially for the cutoff at $r=1.2a_0$) is probably closer to having a negative ion $l=1$ bound state than ours. This would lead to somewhat larger $l=1$, $l'=1$ distortion effects at high energies.

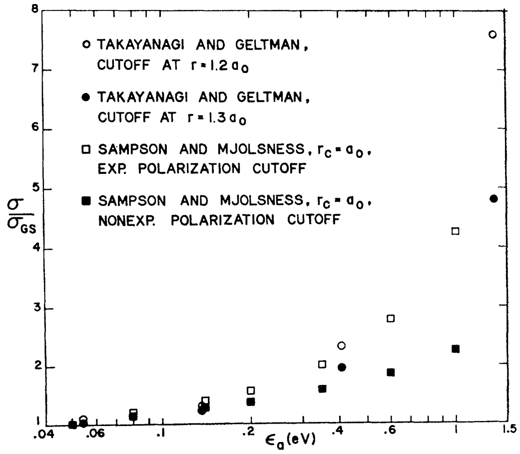

FIG. 6. A comparison between results for the ratio of the rotational excitation cross section to the value given by the Gerjuoy-Stein theory versus initial electron energy for the $j=0\rightarrow 2$ transition for H_2.

TABLE III. Contributions of various partial-wave transitions to the Born-approximation value for the rotational cross section.

Type of interaction	Transition			
	$l=l'=0$	$l=0, l'=2$ and $l=2, l'=0$	$l=l'=1$	$l=l'=2$
Pure quadrupole	0	12.5%	67.5%	8.93%
Pure polarization	0	28.44%	68.27%	1.66%

Near threshold it appears that we obtain a slightly larger negative distortion effect. Since our negative distortion comes through the $l=2$, $l'=0$ partial wave transition, it could also be argued that our neglect of $l=2$ distortion affects our near-threshold results. However, it is very unlikely that this is true, as seen by considering the near-threshold case for which $\sigma/\sigma_{\mathrm{GS}}$ in Fig. 6 was computed. Here $\epsilon_a=0.05$ eV and $\epsilon_b\simeq 0.00476$ eV. In this case, the $l=2$ phase shift is $\delta_2(0.05)\simeq 6\times 10^{-4}$, while the effective $l=0$ phase shift still has the much larger value $\pi-\delta_0(0.00476)\simeq 2.72\times 10^{-2}$.

At high energies, $l=2$ distortion is thought to be unimportant, as well, because the relevant phase shifts are still small and the $l=2$ waves do not contribute very heavily to the cross section. This is indicated by the results in Table III where the percentage contributions of various transitions to the total cross section are computed analytically in the Born approximation with pure quadrupole and pure polarization interactions, Eqs. (4) and (6) for all r, using the Arthurs-Dalgarno[19] formalism and assuming $\epsilon_a=\epsilon_b$ (a good approximation at the higher energies for H_2 or almost all energies for N_2).

Finally, we use the validity criteria Eqs. (19) and (20) to test the validity of the approximation made to the diagonal matrix element of the potential and to test the validity of the method of distorted waves. For this purpose, it is again convenient to use the Arthurs-Dalgarno formalism.[19] Their formalism could, of course, have been used for the entire problem, but it would have been necessary to compute additional angular f_2 integrals [Eqs. (54) and (55) below]. In addition, the present formalism facilitates accurate numerical calculation by explicitly separating the Born terms.

Condition (20) may be tested using $l=1$, since $l=l'=1$ distortion dominates the inelastic scattering. For this case, the left-hand side of Eq. (20) has a single term whose value is less than 0.01 for the conditions treated in this paper. Thus, the distorted wave approximation should be good.

As seen from Eqs. (30) and (44) of Ref. 19, the condition for the validity of Eq. (18), our approximation to the distorted-wave method is actually

$$\left|\frac{V_2(r)f_2(jl;jl;J)}{V_0(r)}\right| \ll 1\,, \tag{54}$$

where f_2 is the matrix element of $P_2(\hat{r}\cdot\hat{s})$ for angular momentum states of the total system and has been tabulated for some values by Percival and Seaton.[35] Since $f(j0;j0;J)=0$, Eq. (18) is exact for $l=0$. For $l=1$,

$$f(j1;j1;J)=\frac{1}{5}\left[\frac{j}{2j+3}\delta_{j,J+1}+\frac{j+1}{2j-1}\delta_{J,j+1}\right]. \tag{55}$$

Its magnitude is less than unity and approaches the value 1/10 for large j. Since $\alpha_0 \simeq 4\alpha_2$ for both N_2 and H_2, neglect of the angular-dependent part of the polarization interaction contribution to $V_{aa}(r)$ is a good approximation. However, it is possible that the quadrupole contribution, which always dominates at large r, might be significant. Using $f_2=0.1$ in Eq. (54), we find that the left-hand side <0.2 for $r \lesssim 10a_0$ for H_2 and $r \lesssim 12a_0$ for N_2. This is expected to cover the important range of r except at very low energies, where distortion is not very significant. For H_2, small j is needed and Eq. (54) is not as well satisfied; however, Eq. (18) is probably still quite a good approximation. This is indicated by the results of Dalgarno and Henry[9] who find using only the pure quadrupole interaction for large r and the static contributions to $V_0(r)$ and $V_2(r)$ for small r that the maximum effect of distortion in H_2 for $\epsilon_a \leq 1$ eV is only 12%. Although $f_2(j2;j2;J)$ is a little larger than $f_2(j1;j1;J)$, the conclusion that $l=2$ distortion is small and can be neglected need not be altered.

Our conclusions are that the various approximations made in the present paper lead to little error in results, with the possible exception of the models used for the short-range form for the potential. This has little effect on results for low-electron energies ($\epsilon_a \lesssim 0.1$ eV), but is increasingly significant as ϵ_a is increased. Nevertheless, by fitting the central part of the potential to the elastic-scattering data and making use of the knowledge that the static interaction contribution to $V_2(r)$ must change sign for small r for N_2 (which has a negative value of Q) and by making some use of the computations of Dalgarno and Henry[9] for the static interaction for H_2, we have obtained approximate forms for the interaction at small r which probably mock up the total potential sufficiently well, in both cases, to lead to fairly accurate results for the energies considered. Some indication of this is given by the fact that, with the use of the latest values for polarizabilities and quadrupole moments, we have obtained results which appear to lead to good agreement with the analysis of swarm experiments. However, computations of rotational excitation based on more precisely calculated values for the potential at small r in which polarization and exchange effects have been accurately included would be desirable. This is particularly true for H_2 where the calculation is most feasible and where rotational excitation might be large enough to be significant relative to vibrational excitation above 1 eV.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Jacob Enoch and Dr. Leon Heller for helpful discussions, and Miss Carolyn Adamski, Charles Cook, James Massey, and John Barone for assistance with the numerical work.

---

[35] I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. **53**, 654 (1957).