

# Electron scattering by nitrogen molecules: Theory and application to elastic scattering and rotational excitation at 30–75 eV\*

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An effective potential model applicable to electron scattering by small or large molecules, including rotational and vibrational motions, is developed for electron scattering by  $N_2$ . The INDO/1s method is used to calculate the static potential at a large number of distances and a simple model is used for the polarization potential. The rotational and vibrational matrix elements of these potentials are accurately calculated and the scattering is treated by a truncated close-coupling expansion. With no adjustable parameters, calculated electronically and vibrationally elastic scattering cross sections are in reasonable agreement with experiment for angles  $40^\circ$ – $50^\circ$  and less at energies 30–75 eV. The rotational excitation cross sections have never been measured for  $N_2$  but are predicted to be large (as large as half the pure elastic cross sections when integrated over scattering angles and larger than the pure elastic differential cross sections at a range of large scattering angles at each energy).

## I. INTRODUCTION

This article describes a realistic effective interaction potential for an electron and a nitrogen molecule as a function of molecular orientation and internuclear distance. It also presents several calculations of elastic scattering and rotational excitation differential and integral cross sections for electron scattering by  $N_2$  in the energy range 30–75 eV. The interaction potential and scattering calculations presented here have also been used for calculations of vibrational excitation cross sections which will be published separately.<sup>1</sup> The goal of this work is to treat intermediate-energy scattering where the potentially more accurate treatments<sup>2</sup> recently applied (with neglect of polarization and without yet treating the nuclear motion) to low energy scattering of small molecules are difficult to apply accurately and the Born approximation<sup>3</sup> is not accurate. In addition, we wish to test methods which would not be prohibitively difficult to apply to much larger molecules.

The electronic many-body problem is reduced to scattering from the effective interaction potential as described in Sec. II. Section III reviews the scattering theory (the close-coupling approximation) appropriate for scattering of an electron by a vibrating rotator with the effective interaction potential described in Sec. II. The solutions of the close-coupling equations defined in Sec. III require the evaluation of vibrational matrix elements of the effective interaction potential of Sec. II. Section IV describes the methods used in evaluating these matrix elements. Section V describes the numerical solution of the close-coupling equations. Section VI presents the theoretical elastic scattering cross sections and rotational excitation cross sections for the  $j=0$  to  $j'=2$  rotational transition. Section VII compares the results of these cross section calculations to the available experiments.

## II. EFFECTIVE POTENTIAL

The exact calculation of cross sections for electron scattering by  $N_2$  requires solving the time-independent Schrödinger equation

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

where  $H$  is the many-body Hamiltonian for the  $e^-N_2$  system and  $E$  is the total energy, for the total system wavefunction  $\Psi$  with the appropriate scattering boundary conditions. However, it is well known that the numerical solution to (1) is not yet practicable since  $H$  is a function of the coordinates of 15 electrons and 2 nuclei. The approach used here for approximating the solution to (1) is to replace  $H$  by an effective few-body Hamiltonian  $H$  which depends explicitly only on the position of one electron and two nuclei. Removing the center-of-mass motion, this Hamiltonian may be written in a space-fixed coordinate system as

$$H = (-\hbar^2/2\mu)\nabla_r^2 + H_{\text{int}} + V(\mathbf{r}, \mathbf{R}), \quad (2)$$

where  $\mu$  is the electron mass,  $\mathbf{r}$  denotes the position vector going from the center of mass of the  $N_2$  nuclei to the scattering electron,  $\mathbf{R}$  denotes the position vector pointing in the direction of the internuclear axis of  $N_2$  and equal in magnitude to the internuclear separation distance  $R$ ,  $H_{\text{int}}$  is the vibrational-rotational Hamiltonian for  $N_2$  in the absence of the scattering electron, and  $V(\mathbf{r}, \mathbf{R})$  is the effective interaction potential of the scattering electron with the  $N_2$  molecule in its electronic ground state. In this model the dependence of  $V(\mathbf{r}, \mathbf{R})$  on  $R$  is the cause of vibrational excitation and the dependence on  $\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}$  (where the carets denote unit vectors) is the cause of rotational excitation. Only the ground electronic state of  $N_2$  is explicitly included in this model. The possibility of real electronic excitation of  $N_2$  can be included in this model by making  $V(\mathbf{r}, \mathbf{R})$  have a positive imaginary part. This would lead to a decrease in the probability of the scattering electron leaving the  $N_2$  molecule in its ground electronic state. However, the effects of virtual (temporary) electronic excitation can be mimicked by a real effective interaction potential.

Although Feshbach<sup>4</sup> has presented a theory for exactly including in the effective interaction potential the omitted degrees of freedom, his theory is difficult to apply and has only been used for treating small atoms.<sup>5</sup>

Therefore, a model effective interaction potential which includes the important interactions for vibrational excitation of  $N_2$  is used instead. The model is defined in terms of three quantities as

$$V(\mathbf{r}, \mathbf{R}) = V^s(\mathbf{r}, \mathbf{R}) + V^e(\mathbf{r}, \mathbf{R}) + V^p(\mathbf{r}, \mathbf{R}), \quad (3)$$

where the three terms are described in the remainder of this section.

The static potential  $V^s(\mathbf{r}, \mathbf{R})$  is the electrostatic interaction between the scattering electron and the unperturbed ground electronic state charge distribution of  $N_2$  as a function of geometry. The ground electronic state charge distribution of  $N_2$  and the static potential were calculated at each  $\mathbf{R}$  in the INDO/1s approximation using methods described elsewhere.<sup>6</sup> It has been shown that the static potential calculated using the INDO/1s approximation compares well to the static potential calculated using an accurate *ab initio* Hartree-Fock-Roothaan wavefunction.<sup>6</sup>

The exchange potential  $V^e(\mathbf{r}, \mathbf{R})$  is the exchange interaction between the scattering electron and the bound electrons of  $N_2$  as a function of geometry. Although electron exchange is an important effect in many scattering processes for impact energies below 100 eV, this interaction was set to zero in the calculations presented in this article. Electron exchange becomes less important at high impact energies but it cannot generally be neglected for impact energies below 100 eV.<sup>7</sup> However, Skerbele *et al.*<sup>8</sup> have pointed out that "based on previously reported results<sup>9</sup> for  $N_2$ , it is expected that electron exchange will be relatively unimportant at kinetic energies as high as 53 eV. . . ." Nevertheless, it is not known in any more quantitative way how important electron exchange is for the present studies of electron scattering by  $N_2$  in the impact energy range 30–75 eV. Riley and one of the authors<sup>10</sup> have recently tested some reasonably accurate approximate exchange potentials for the energy range treated here. One of these approximate exchange potentials (e.g., the semiclassical exchange approximation or the asymptotically adjusted free-electron-gas exchange approximation or a similar potential due to Hara<sup>11</sup>) should be included in future calculations.

The polarization potential  $V^p(\mathbf{r}, \mathbf{R})$  includes all the interactions which are not a part of  $V^s(\mathbf{r}, \mathbf{R})$  or  $V^e(\mathbf{r}, \mathbf{R})$ . As discussed already, since the energy region studied here is above the threshold for electronic excitation,  $V^p(\mathbf{r}, \mathbf{R})$  should contain a positive imaginary part to account for the loss of flux due to real electronic transitions in  $N_2$ . However, no such effect is included here. The main effect included here in  $V^p(\mathbf{r}, \mathbf{R})$  is the charge-induced dipole interaction due to the polarization of the molecular charge distribution of  $N_2$  by the scattering electron. Thus, the polarization potential is written as<sup>12,13</sup>

$$V^p(\mathbf{r}, \mathbf{R}) = -e^2 \left[ \frac{\alpha_0(R)}{2r^4} + \frac{\alpha_2(R)}{2r^4} P_2(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}) \right] g(r), \quad (4)$$

where  $P_2(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}})$  is a Legendre polynomial,  $\alpha_0(R)$  and  $\alpha_2(R)$  are given in terms of the static dipole polarizability of the molecule parallel [ $\alpha^{\parallel}(R)$ ] and perpendicular

[ $\alpha^{\perp}(R)$ ] to the internuclear axis by

$$\alpha_0(R) = \frac{1}{3} [\alpha^{\parallel}(R) + 2\alpha^{\perp}(R)], \quad (5)$$

$$\alpha_2(R) = \frac{2}{3} [\alpha^{\parallel}(R) - \alpha^{\perp}(R)], \quad (6)$$

and  $g(r)$  is a cutoff function. We use the cutoff function previously applied to  $e^-H_2$  scattering by one of the authors and Rice<sup>13</sup> and to  $e^-N_2$  scattering by Burke and Chandra.<sup>14</sup> It is given by

$$g(r) = 1 - \exp(r/a)^6, \quad (7)$$

where  $a$  is a parameter. The large- $r$  form of this polarization potential accounts exactly for the charge-induced dipole interaction. The cutoff is included at small  $r$  because within the molecular charge distribution the kinetic energy of the scattering electron increases and the polarization effect is reduced.<sup>15</sup> Rice and one of the authors<sup>13</sup> have shown that a cutoff function of this form can be used to fit the *ab initio* nonpenetrating polarization potential determined by Lane and Henry<sup>16</sup> for  $H_2$ . Hara's independent calculation<sup>17</sup> of the polarization potential for  $H_2$  had a similar form. Such attempts to calculate the polarization potential by *ab initio* methods have not been carried out for  $N_2$  but the form would be expected to be similar for  $H_2$  and  $N_2$ . It has been suggested<sup>18</sup> that the cutoff function should cause  $V^p(\mathbf{r}, \mathbf{R})$  to vanish at the nuclei rather than at the center of mass of the nuclei. Such a cutoff function should be tested by future calculations.

Since the charge polarization of the target is reduced when the scattering electron penetrates the target's charge cloud, Breig and Lin<sup>12</sup> used properties of the N and  $N_2$  charge clouds to deduce approximate upper and lower limits to the cutoff parameter  $a$ . They obtained  $1.3a_0 \lesssim a \lesssim 2.1a_0$  where  $a_0$  is the first bohr radius. It would be consistent with the present approach (i.e., to use methods which could be easily applied to larger molecules) to use a model to obtain any value in that range. Burke and Chandra<sup>14</sup> determined the value of  $1.592a_0$  semiempirically in low-energy electron scattering calculations. To avoid unnecessary arbitrariness we use their value although at the energies considered here the model should be insensitive to small variations of  $a$  and considerations such as employed by Breig and Lin could be used for this or other molecules.

For use later we note that the cylindrical and reflection symmetries of the  $N_2$  molecule allow the effective interaction potential to be expanded in even-order Legendre polynomials as

$$V(\mathbf{r}, \mathbf{R}) = \sum_{L=0}^{\infty} V_L(r, R) P_L(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}). \quad (8)$$

While this expansion is known to be slowly convergent near the nuclei, a spherical-harmonic or Legendre expansion is convenient enough to be used even for much larger molecules and one of the purposes of this article is to test such methods.

Although the model used here contains many approximations, previous calculations of nonresonant vibrational excitation of molecules larger than  $H_2$  by electron impact have used only relatively crude approximations to the effective interaction potential. For example,

Itikawa<sup>19</sup> has based his calculations of vibrational excitation of H<sub>2</sub>O on considerations involving only the large- $r$  form of the interaction potential without a realistic treatment of either  $V^s(\mathbf{r}, \mathbf{R})$  or  $V^a(\mathbf{r}, \mathbf{R})$ . Further, he used a treatment of the scattering caused by his effective potential which is less accurate than the one we use and which we describe next.

### III. SCATTERING THEORY: CLOSE-COUPPLING EQUATIONS

The effective Hamiltonian of Eq. (2) treats the N<sub>2</sub> molecule as a vibrating rotator and a brief review of the theory<sup>20-23</sup> of the scattering of a structureless particle by a vibrating rotator is given next.

The vibrational-rotational Hamiltonian  $H_{\text{int}}$  is composed of three parts.

$$H_{\text{int}} = H_{\text{rot}} + H_{\text{vib}} + H_{\text{rot-vib}}. \quad (9)$$

For the case treated here  $H_{\text{rot-vib}}$  was set to zero. A member  $u_{vjm_j}(\mathbf{R})$  of the complete set of orthonormal eigenfunctions of  $H_{\text{int}}$  with eigenvalue  $E_{vj}$ , where  $v$  is the vibrational quantum number and  $j$  and  $m_j$  are the rotational angular momentum and magnetic quantum numbers of N<sub>2</sub>, is written, using the most common phase convention,<sup>21-23</sup> as

$$u_{vjm_j}(\mathbf{R}) = \phi_v(R) Y_{jm_j}(\hat{R}), \quad (10)$$

where  $Y_{jm_j}$  is the spherical harmonic of Condon and Shortley<sup>24</sup> and Messiah<sup>25</sup> satisfying

$$H_{\text{rot}} Y_{jm_j}(\hat{R}) = \frac{\hbar^2}{2I} j(j+1) Y_{jm_j}(\hat{R}), \quad (11)$$

where  $I$  is the moment of inertia of the N<sub>2</sub> nuclei, and  $\phi_v(R)$  satisfies

$$H_{\text{vib}} \phi_v(R) = E_v \phi_v(R), \quad (12)$$

and is phased so that it approaches +0 for large  $R$ . The energy  $E_{vj}$  is

$$E_{vj} = E_v + \frac{\hbar^2}{2I} j(j+1). \quad (13)$$

The total wavefunction  $\Psi_n(E, \mathbf{r}, \mathbf{R})$ , where  $n = (vjm_j)$  denotes one of the  $(2j+1)$ -fold degenerate initial states of N<sub>2</sub> with energy  $E_{vj}$  and  $E$  is the total energy in the barycentric coordinate system, is expanded as

$$\Psi_n(E, \mathbf{r}, \mathbf{R}) = \sum_{n'} \psi_{n'n}(E, \mathbf{r}) u_{n'}(\mathbf{R}), \quad (14)$$

where  $n' = (v'j'm'_j)$  denotes one of the  $(2j'+1)$ -fold degenerate final states of the N<sub>2</sub> molecule and the sum includes all the possible values of  $n'$ . The convention that unprimed quantum numbers denote initial states and primed quantum numbers denote final states will be followed throughout. The  $\psi_{n'n}(E, \mathbf{r})$  are expanded in products of total angular momentum eigenfunctions and radial functions  $\psi_{\lambda'\lambda}^J(E, r)$ , where  $J$  is the magnitude of the total angular momentum,  $\lambda' = (v'j'l')$ , and  $l'$  is the quantum number for orbital angular momentum of relative motion. The radial functions are the solutions of the following set of coupled second order homogeneous differential equations,<sup>20-23</sup> written in matrix notation, for each  $J$

$$\left[ \frac{d^2}{dr^2} \mathbf{I} - \frac{1}{r^2} \mathbf{l}^2 + \mathbf{k}^2 \right] \psi^J(E, r) = \mathbf{U}^J(r) \psi^J(E, r), \quad (15)$$

where  $\mathbf{I}$  is the unit matrix,  $\psi^J(E, r)$  is the matrix of radial functions,

$$(\mathbf{l}^2)_{\lambda'\lambda''} = l'(l'+1) \delta_{\lambda'\lambda''}, \quad (16)$$

$$(\mathbf{k}^2)_{\lambda'\lambda''} = k_{v'j'}^2 \delta_{\lambda'\lambda''} = (2\mu/\hbar^2)(E - E_{v'j'}) \delta_{\lambda'\lambda''}, \quad (17)$$

$$\mathbf{U}_{\lambda'\lambda}^J(r) = \frac{2\mu}{\hbar^2} \sum_L f_L(l'j'; lj; J) V_{Lv'v}(r), \quad (18)$$

where  $f_L(l'j'; lj; J)$  is the real coefficient of Percival and Seaton<sup>26</sup> and

$$V_{Lv'v}(r) = \int_0^\infty R^2 \phi_{v'}^*(R) V_L(r, R) \phi_v(R) dR \quad (19)$$

is a vibrational matrix element of the effective interaction potential and is discussed in greater detail in Sec. IV. Since  $L$  is even and  $f_L(l'j'; lj; J)$  is real,  $\mathbf{U}_{\lambda'\lambda}^J(r)$  is nonzero only if  $j' - j$  is even, i.e.,  $\mathbf{U}^J(r)$  is block diagonal and contains two subblocks, one containing only even values of  $j$  and the other containing only odd values of  $j$ . This means that (15) can be solved separately for the two cases. Also, since the total system parity  $(-1)^{l+j}$  is conserved, each of the subblocks of  $\mathbf{U}^J(r)$  is block diagonal and contains two subblocks, one for even values of  $l+j$  and the other for odd values of  $l+j$ . Therefore, to calculate cross sections for which the initial state has  $j=0$ , it is only necessary to include those values of  $l$  for which  $|J-j| \leq l \leq J+j$  and for which  $l+J$  is even. When  $j_{\text{max}}$  is the maximum value of  $j$  included in the expansion of the wavefunction, then it is useful to know that  $f_L(l'j'; lj; J)$  is zero for  $L > 2j_{\text{max}}$  when  $j' \leq j_{\text{max}}$  and  $j \leq j_{\text{max}}$ . We restrict  $j_{\text{max}}$  to less than or equal to 2 so the potential is only required for  $L \leq 4$ .

Equation (15) is the close-coupling equation to be solved with the appropriate scattering boundary conditions. From the solutions we calculate the reactance and transition matrices from which the cross sections may be calculated. If the cross sections are converged with respect to including more rotational and vibrational states in the expansion, then they are exact for the scattering caused by the model potential  $V(\mathbf{r}, \mathbf{R})$ . However, in applying the close-coupling equations the usual practice is to include in the wavefunction only those internal states of the molecule which make the most important contributions to the scattering cross sections being calculated and we have followed this practice.

### IV. VIBRATIONAL MATRIX ELEMENTS OF THE EFFECTIVE INTERACTION POTENTIAL

A detailed description of the numerical integration procedure and computer program which was used in the evaluation of (19) for the static potential is given elsewhere.<sup>27</sup> The program was used to calculate  $\phi_v^R(R) \equiv R \phi_v(R)$  for the low-energy vibrational states at  $NR$  equally spaced values of  $R$  in the region  $0.85 a_0 \leq R \leq 3.9 a_0$  by solving (12) with the Levine potential curve<sup>28</sup> in the definition of  $H_{\text{vib}}$ . This potential curve provides a very good fit to the experimental Rydberg-Klein-Rees potential curve for N<sub>2</sub>.<sup>28</sup> The contribution to the integrand of (19) for  $0 \leq R < 0.85 a_0$  and  $3.9 a_0 < R \leq \infty$  is

TABLE I. Vibrational matrix elements  $\alpha_{Lv'v}$  of the polarizability functions  $\alpha_L(R)$ ,  $L=0, 2$ .

$v'$	$v$	$\alpha_{0v'v}(a_0^3)$			
		0	1	2	3
0	0	11.925 <sup>a</sup>	3.46(-1) <sup>a,b</sup>	-1.94(-2)	1.79(-3)
1	0		12.008 <sup>a</sup>	4.91(-1)	-3.40(-2)
2	0			12.093	6.03(-1)
3	0				12.178
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$v'$	$v$	$\alpha_{2v'v}(a_0^3)$			
		0	1	2	3
0	0	3.157	2.18(-1)	-1.23(-2)	1.13(-3)
1	0		3.209	3.09(-1)	-2.14(-2)
2	0			3.263	3.80(-1)
3	0				3.317

<sup>a</sup>Truhlar (Ref. 29).<sup>b</sup>Numbers in parentheses are powers of 10 by which the preceding numbers should be multiplied.

negligible and was neglected. A detailed description of how the static potential coefficients  $V_L^s(r, R)$  needed for these calculations are evaluated is given in Sec. IV.B.1 below. The program calculated three estimates of (19) for the values of  $V_L^s(r, R)$ ,  $i=1, 2, \dots, NR$  using three sets of mesh points corresponding to  $NR=500, 725$ , and  $950$ , respectively. The final value, called  $V_{Lv'v}^s(r)$ , was calculated from the three estimates using Richardson's  $h^4$ -extrapolation method as described elsewhere.<sup>27</sup>

As described in Sec. II, two contributions were included in the effective interaction potential. Thus

$$V_L(r, R) = V_L^p(r, R) + V_L^s(r, R), \quad (20)$$

where  $V_L^p(r, R)$  and  $V_L^s(r, R)$  are discussed below. The matrix elements of  $V_L^p(r, R)$  are described in Sec. IV.A below and further details of the calculation of matrix elements of  $V_L^s(r, R)$  are given in Sec. IV.B.2 below.

### A. Polarization potential

Comparing (3), (4), and (8) with (20) yields the following for the vibrational matrix elements of the polarization potential

$$V_{Lv'v}^p(r) = \begin{cases} -\frac{\alpha_{Lv'v} e^2}{2r^4} g(r) & \text{for } L=0, 2, \\ 0 & \text{for } L>2, \end{cases} \quad (21)$$

where

$$\alpha_{Lv'v} = \int_0^\infty \phi_{v'}^{R*}(R) \alpha_L(R) \phi_v^R(R) dR. \quad (22)$$

To compute the integral in (22) one requires the components of the polarizability as functions of  $R$ . Although  $\alpha_0(R)$  and  $\alpha_2(R)$  are strongly dependent on  $R$  and provide an important mechanism for vibrational excitation, no accurate calculations of  $\alpha_0(R)$  or  $\alpha_2(R)$  for  $N_2$  are available yet. However, the most important region of  $R$  for vibrational excitation of  $N_2$  is that near the equilibrium internuclear distance  $R_e = 2.068 a_0$  so  $\alpha_0(R)$  and  $\alpha_2(R)$  are expanded in a Taylor series about  $R_e$  as

$$\alpha_L(R) = \alpha_L(R_e) + \sum_{n=1}^{\infty} \frac{d^n \alpha_L(R)}{dR^n} \bigg|_{R=R_e} \frac{(R-R_e)^n}{n!}, \quad L=0, 2. \quad (23)$$

Then the series is truncated only retaining the first two terms (through  $n$  equals 1) in both cases. Using these truncated series, one of the authors<sup>29</sup> has estimated  $\alpha_0(R_e)$  from the best experimental value<sup>30</sup> of  $\alpha_{000}$  (11.925  $a_0^3$ ) and from the best available estimates<sup>12,31</sup> from experiment of  $[d\alpha_0(R)/dR]_{R=R_e}$  (5.71  $a_0^2$ ). He obtained  $\alpha_0(R_e) = 11.884 a_0^3$ .

The internuclear distance dependence of the asymmetric part of the polarizability is hard to estimate but was estimated as follows. We estimated  $\alpha_2(R_e)$  as being equal to the experimental value<sup>30</sup> of  $\alpha_{200}$  (3.131  $a_0^3$ ) and using (5) and (6) yields

$$\alpha^L(R_e) = \alpha_0(R_e) - \frac{1}{2} \alpha_2(R_e) = 10.32 a_0^3. \quad (24)$$

The theoretical approximation of Kirkwood<sup>32-34</sup> in terms of the second moments of the charge distribution is expected to be more accurate for  $\alpha^L(R)$  than for  $\alpha^u(R)$ . It yields

$$\alpha^L(R) = \alpha_{xx}(R) = 4n \alpha_0^{-1} \langle x_i^2 \rangle^2, \quad (25)$$

where  $n$  is the number of electrons,  $\langle x_i^2 \rangle$  is the  $R$ -dependent expectation value of  $x^2$  for the  $i$ th electron, and we have taken the  $z$  axis to lie on the internuclear axis. Using values of  $\langle x_i^2 \rangle$  calculated as a function of  $R$  by Wahl<sup>35</sup> in the Hartree-Fock approximation, we estimate using (25) that

$$\frac{d\alpha^L(R)}{dR} \bigg|_{R=R_e} \approx 0.38 a_0^{-1} \alpha^L(R_e). \quad (26)$$

Putting (24) into (26) and using (5) and (6) yields

$$\frac{d\alpha_2(R)}{dR} \bigg|_{R=R_e} = 2 \left[ \frac{d\alpha_0(R)}{dR} \bigg|_{R=R_e} - \frac{d\alpha^L(R)}{dR} \bigg|_{R=R_e} \right] \approx 3.6 a_0^2. \quad (27)$$

Using those values of  $\alpha_L(R_e)$  and  $[d\alpha_L(R)/dR]_{R=R_e}$  for  $L=0, 2$  in the truncated Eq. (23), the values of  $\alpha_{Lv'v}$  presented in Table I were calculated using (22) and the program already mentioned<sup>27</sup> with the grid sizes given above. The truncation of (23) after the linear terms means the matrix elements corresponding to  $|v' - v| \geq 2$  are probably less accurate than the others in this table.

### B. Static potential

#### 1. INDO/1s approximation

As discussed in Sec. II,  $V^s(r, R)$  is calculated here using semiempirical molecular orbital theory in the INDO/1s approximation. The coefficients  $V_L^s(r, R)$  [see (3), (8), and (20) for notation] were calculated at each  $(r, R)$  by using (8) truncated at  $L=L_{\max}$  together with  $V^s(r, R)$  calculated at nine equally spaced values of  $\chi$ , defined by  $\chi = \cos^{-1}(\hat{r} \cdot \hat{R})$ , in the range  $0^\circ \leq \chi \leq 90^\circ$ . For  $L_{\max}=16$ , this procedure determines nine simultaneous linear equations which may be solved for  $V_L^s(r, R)$  at each  $(r, R)$ . Correction for higher- $L$  contributions due to the nuclear attraction was made as elsewhere.<sup>6</sup> Then we found that the  $V_L^s(r, R)$  for  $0 \leq L \leq 6$  were con-

verged at each  $(r, R)$  with respect to including more values of  $\chi$  and simultaneously increasing  $L_{\max}$ . The INDO/1s calculation is in reasonable agreement with accurate *ab initio* results for small  $r$  but not for large  $r$ . For example, the quadrupole moment, which is given by

$$Q(R_e) = -2 \lim_{r \rightarrow \infty} r^3 V_2^s(r, R_e), \quad (28)$$

is predicted to be much too large by the INDO/1s approximation. However, since the accurate quadrupole vibrational matrix elements were already available,<sup>36,37</sup> the INDO/1s approximation was used to obtain the static potential at small  $r$  and the static potential was adjusted to have the correct form at large  $r$ . Since the INDO/1s values of  $V_0^s(r, R_e)$  and  $V_4^s(r, R_e)$  are more accurate than  $V_2^s(r, R_e)$  at large  $r$ , only  $V_2^s(r, R)$  was adjusted at large  $r$ . The small- $r$  region is very important for vibrational excitation processes and the present treatment using the INDO/1s approximation to predict the small- $r$  dependence of  $V_{Lv',v}(r)$  represents a significant improvement over previous calculations.<sup>12,19</sup>

Clearly the static potential is infinite when the scattering electron is at the position of one of the nuclei, i. e., when  $\mathbf{r} = \pm \frac{1}{2}\mathbf{R}$ . This causes the coefficients  $V_L^s(r, R)$  to have cusps when  $R = 2r$ . These cusps will be dealt with in the next subsection.

As mentioned above up to 950 values of  $R$  were required in the calculation of

$$V_{Lv',v}^s(r) = \int_0^\infty \phi_{v'}^{R*}(R) V_L^s(r, R) \phi_v^R(R) dR \quad (29)$$

for each  $r$  value. To obtain the static potential at so many  $R$  values we calculated  $V_L^s(r, R)$  for each  $r$  at 39 values of  $R$  and evaluated it at the other  $R$  values by an interpolation procedure which is described next. Thus,

in summary,  $V^s(\mathbf{r}, \mathbf{R})$  was calculated at  $29 \times 39 \times 9 = 10\,179$  values of  $(r, R, \chi)$ .

## 2. Chebyshev interpolation procedure

The interpolation was carried out using second order Chebyshev polynomials.<sup>38-41</sup> There were three reasons for this choice of interpolation scheme. The first two reasons are ease of application and accuracy. The third reason is that Chebyshev interpolation on an interval  $(R_i, R_{i+1})$  does not use the interpolant at either endpoint of the interval. This property of Chebyshev interpolation was used to eliminate the difficulties associated with integrating over the cusps of  $V_L^s(r, R)$  at  $R = 2r$ . The procedure by which these cusps were treated in carrying out the integral in (29) is as follows. Eventually,  $V_{Lv',v}^s(r)$  is fit to an analytic function of  $r$ . The fit is based on least-squares adjustment to values of  $V_{Lv',v}^s(r)$  calculated at 29 values of  $r$  denoted  $r_k$ ,  $k = 1, 2, \dots, 29$ . Thus, it is only necessary to calculate  $V_{Lv',v}^s(r)$  for these 29 values of  $r$ . For these calculations,  $V_L^s(r, R)$  was calculated for 39 values of  $R$ , denoted  $R_i$ ,  $i = 1, 2, \dots, 39$ , for each of the 29 values of  $r$ . The region used in evaluating (29) is divided into 13 intervals, each containing three values of  $R_i$  to be used to define a Chebyshev interpolating polynomial for that interval. The 14 endpoints of these intervals were chosen to be  $2r_k$ ,  $k = 4, 5, \dots, 17$ , which cover the integration region used in evaluating (29). But in Chebyshev interpolation one does not use the values of the interpolant at the endpoints of the interval. Thus, it was possible to choose the  $R_i$  values so that none of them equal  $2r_k$  for any  $k$ . This means it was not necessary to evaluate  $V_L^s(r, R)$  at  $R = 2r$ .

Having calculated  $V_{Lv',v}^s(r)$  at 29 values of  $r$  for all  $v \leq v' \leq 3$  and  $L = 0, 2, 4$ , they were fit to the following analytic forms:

$$V_{L,v+n,v}^s(r) \simeq F(r) = \frac{b_1 r^L (r - b_2^2)^4 e^{-b_3^2 (r - b_2^2)^2}}{1 + b_4^2 (r - b_2^2)^2} + b_5 r^L e^{-b_6^2 r^2} + b_7 r^L (r - b_2^2)^k e^{-b_8^2 (r - b_2^2)^2} + \frac{r I_{v+n,v} (1 - \delta_{L0})}{b_9 + r^{L+2}} + b_{10} r^L e^{-b_{11}^2 r^m}, \quad (30)$$

where the dependence of the fitting parameters,  $i, j, k, m$ , and  $b_\alpha$ ,  $\alpha = 1, 2, \dots, 11$ , on  $L, n$ , and  $v$  has been suppressed in the notation. The fit was accomplished using the method of Marquardt.<sup>42</sup> All the parameters were allowed to vary independently except for  $b_9$  in some cases and  $I_{v+n,v}$ . For  $L = 2$ ,  $I_{v+n,v}$  was kept at  $-\frac{1}{2}Q_{v+n,v}$  where  $Q_{v+n,v}$  is the vibrational matrix element of the quadrupole moment function appropriate for the Levine potential curve and is listed in Table V of Ref. 36. For  $L = 4$ ,  $I_{v+n,v}$  was determined by assuming that

$$V_{L,v+n,v}^s(r) = (I_{v+n,v}/r^{L+1}) \quad (31)$$

for  $r = 5.0 a_0$  and was kept at that value during the fitting. Due to instability problems in the fitting program encountered when  $n = 2, 3$  in Eq. (30),  $b_9$  was fixed at its initial value during those fittings. The fitted curves to  $V_{L0}^s(r)$ ,  $V_{L10}^s(r)$ ,  $V_{L20}^s(r)$ , and  $V_{L30}^s(r)$  are presented in Figs. 1-4. The matrix elements  $V_{L11}^s(r)$ ,  $V_{L22}^s(r)$ , and  $V_{L33}^s(r)$  differ only slightly from  $V_{L00}^s(r)$  and are not

shown. Similarly, the matrix elements  $V_{L21}^s(r)$  and  $V_{L32}^s(r)$  differ little from  $V_{L10}^s(r)$  and  $V_{L31}^s(r)$  from  $V_{L20}^s(r)$  and are not shown.

## V. SOLUTION OF THE CLOSE-COUPPING EQUATIONS

The numerical method used for integrating the close-coupling equations was the variable-step-size Numerov method.<sup>43-46</sup> The method of Blatt<sup>45</sup> was used to determine the step size which was generally in the range  $2 \times 10^{-5} - 10^{-2} a_0$ . Periodic reorthogonalization<sup>47</sup> was applied to the solution vectors in classically forbidden regions (at small distances) to maintain linear independence of the solutions. At large distances the solutions were matched to Burke-McVicar-Smith functions<sup>48,49</sup> or, in a few cases, to spherical Bessel functions.

The sub-blocks  $\mathbf{T}^J$  of the transition matrices, differential cross sections  $I(\theta)$ , where  $\theta$  is the scattering

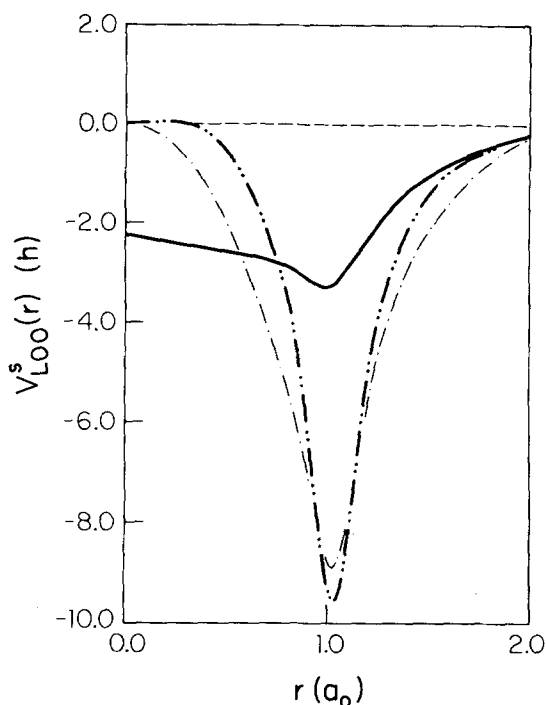


FIG. 1. Vibrational matrix elements of the static potential for  $v'=0$ ,  $v=0$ ,  $L=0, 2, 4$ , plotted as a function of  $r$ . The solid line (—) is the plot for  $L=0$ , the dash-dot-dashed (— · —) line is the plot for  $L=2$ , and the dash-dot-dot-dashed (— · · —) line is the plot for  $L=4$ . The dashed (---) line is the abscissa.

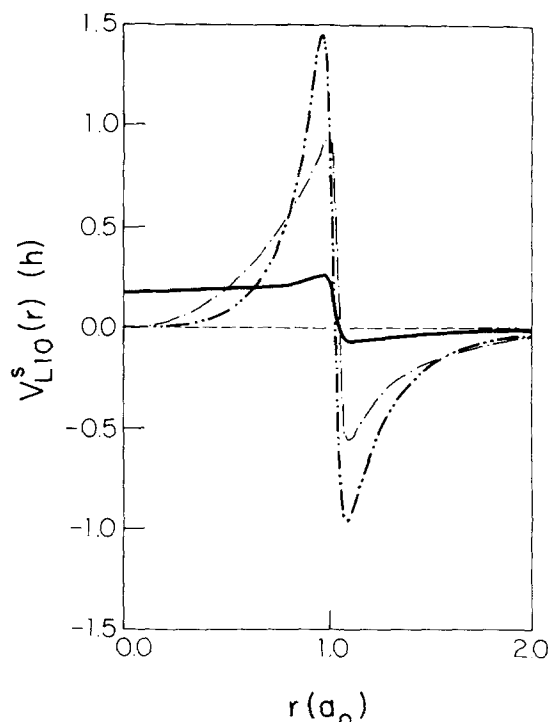


FIG. 2. Vibrational matrix elements of the static potential for  $v'=1$ ,  $v=0$ ,  $L=0, 2, 4$  plotted as a function of  $r$ . The lines have the same meaning as in Fig. 1.

angle, integral cross sections, and momentum transfer cross sections were calculated from the reactance matrices using equations given elsewhere.<sup>50-52</sup>

A few single-channel calculations were performed for high  $J$  (see below). The program used for these calculations is described elsewhere.<sup>53</sup>

## VI. RESULTS

We used  $\hbar^2/2I$  equal to<sup>54</sup>  $9.1055 \times 10^{-6}$  hartrees in (11). We truncated the close-coupling equations with four states corresponding to  $(v, j)$  of (0, 0), (0, 2), (1, 0), and (1, 2). The minimum and maximum number of channels corresponding to this truncation of the basis are 4 and 8, respectively. (Note that we use "states" and "channels" in the same way as recommended by Smith.<sup>55</sup>) The minimum is achieved for  $J=0$  and the maximum for  $J \geq 2$ . Some calculations using six-state and eight-state bases including these four states plus  $(vj)$  of (20) and (22) and in some cases (30) and (32) will be published elsewhere.<sup>1</sup>

Cross sections were calculated for pure elastic scattering ( $v=0, j=0 \rightarrow v'=0, j'=0$ ) and pure rotational excitation ( $v=0, j=0 \rightarrow v'=0, j'=2$ ). We also added the elastic and rotational excitation cross sections to obtain the "vibrationally elastic" cross section. The vibrationally inelastic cross sections were also calculated but will be presented elsewhere.<sup>1</sup>

For the cross section calculations we used results from the four-state close-coupling calculations for  $0 \leq J \leq J_1$ , where  $J_1$  is given in Table II. These values of  $J_1$  were large enough that the differential cross sections

for pure vibrational excitation were changed by less than 5% and the differential cross sections for vibrational-rotational excitation were changed by less than 1% at all angles at all energies when  $J_1$  was decreased by 2. The values of  $J_1$  listed in Table II are not large enough for the elastic scattering and rotational excitation differential cross sections to be converged. Thus, two-state basis close-coupling calculations including

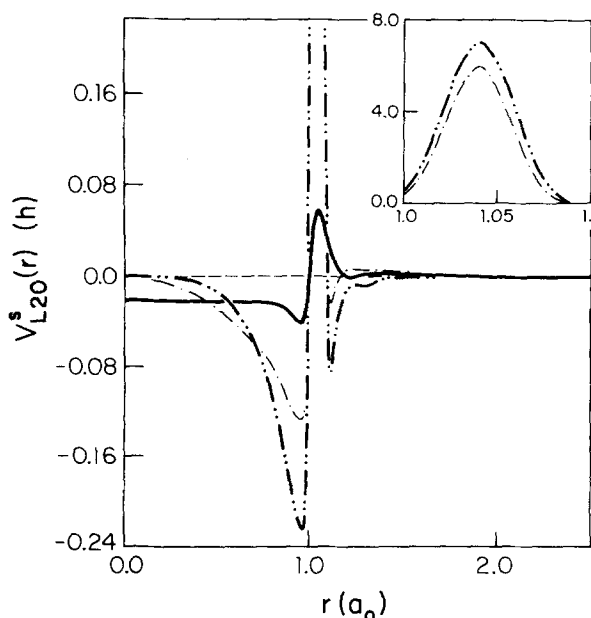


FIG. 3. Vibrational matrix elements of the static potential for  $v'=2$ ,  $v=0$ ,  $L=0, 2, 4$ . The lines have the same meaning as in Fig. 1. For  $L=2, 4$  the region  $1.0 a_0 \leq r \leq 1.1 a_0$  is shown with a different scale in the insert.

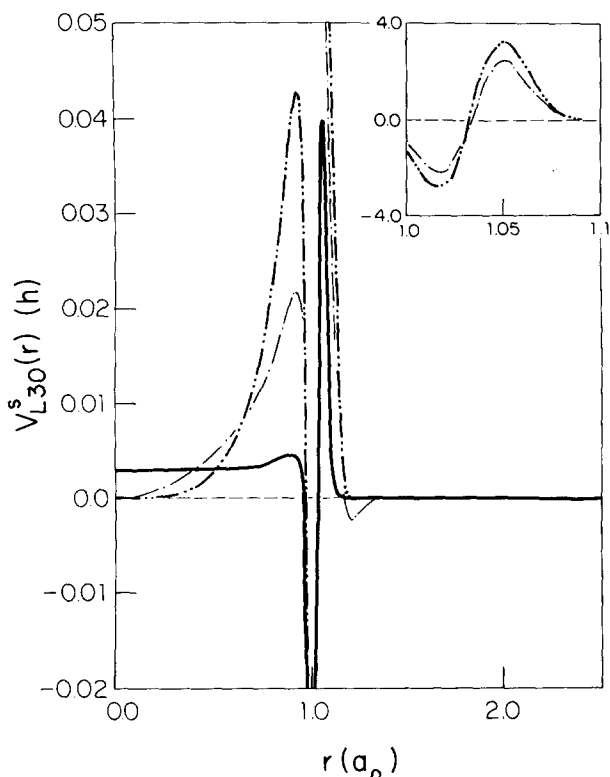


FIG. 4. Vibrational matrix elements of the static potential for  $v'=3$ ,  $v=0$ ,  $L=0, 2, 4$ . The lines have the same meaning as in Fig. 1. For  $L=2, 4$  the region  $1.0 a_0 \leq r \leq 1.1 a_0$  is shown with a different scale in the insert.

$(v, j)$  of  $(0, 0)$  and  $(0, 2)$  were performed for  $(J_1 + 1) \leq J \leq 20$ . This is a large enough maximum value of  $J$  that the rotational excitation cross sections are changed by less than 1% at all angles at all energies when the calculations are repeated with a maximum  $J$  value of 18. However, this is still not a large enough  $J$  for the pure elastic scattering differential cross sections to be converged at small angles. Thus, we used single-channel calculations including only the target ground state for  $21 \leq J \leq J_2$  where  $J_2$  was estimated to be large enough that the elastic scattering differential cross section would be converged to within 1%. These values of  $J_2$  are given in Table II. Then checks were performed which showed that the sum of the pure elastic and pure rotational excitation cross sections were changed by less than 0.1% at all angles at all energies when  $J_2$  was decreased by 2.

The differential cross sections resulting from all these calculations are given as a function of the scattering angle  $\theta$  in Tables III–V and Figs. 5–7.

TABLE II. Total angular momentum limits for scattering calculations.

$E$ (eV)	$J_1$	$J_2$
30	8	67
35	8	72
45	10	81
50	10	86
75	11	105

TABLE III. Differential cross sections (in  $a_0^2/\text{sr}$ ) for pure elastic scattering.<sup>a</sup>

$E$ (eV)	30	35	45	50	75
$\theta$ (deg)					
0	45.7	52.6	61.4	64.6	81.0
5	36.0	41.4	48.1	50.3	60.6
10	26.6	30.6	35.4	36.8	42.2
15	19.1	21.9	25.2	26.0	28.2
20	13.3	15.1	17.2	17.6	17.9
25	9.06	10.1	11.3	11.5	10.9
30	6.07	6.56	7.15	7.20	6.45
35	4.14	4.29	4.49	4.49	3.86
40	2.99	2.99	2.96	2.92	2.43
50	2.05	2.05	1.82	1.69	1.14
60	1.65	1.74	1.44	1.23	0.51
70	1.14	1.20	0.90	0.71	0.21
80	0.58	0.53	0.32	0.23	0.17
90	0.25	0.15	0.06	0.07	0.26
100	0.30	0.13	0.18	0.23	0.33
110	0.25	0.25	0.42	0.47	0.34
120	0.15	0.22	0.46	0.51	0.28
130	0.01	0.08	0.28	0.32	0.16
140	0.13	0.15	0.18	0.17	0.06
150	0.76	0.77	0.50	0.36	0.08
160	1.81	1.86	1.26	0.95	0.23
170	2.82	2.94	2.09	1.61	0.43
180	3.25	3.38	2.45	1.90	0.52

<sup>a</sup>Including contributions from  $0 \leq J \leq J_2$ .

In Tables VI and VII are given the integral cross sections and momentum transfer cross sections for vibrationally elastic scattering. The values are all converged with respect to increasing the maximum  $J$  included.

TABLE IV. Differential cross sections (in  $a_0^2/\text{sr}$ ) for pure rotational excitation.<sup>a</sup>

$E$ (eV)	30	35	45	50	75
$\theta$ (deg)					
0	0.75	0.53	0.29	0.27	0.31
5	0.75	0.54	0.29	0.27	0.30
10	0.76	0.56	0.32	0.29	0.31
15	0.74	0.55	0.33	0.31	0.32
20	0.69	0.52	0.32	0.31	0.35
25	0.64	0.49	0.35	0.35	0.44
30	0.61	0.49	0.41	0.43	0.60
35	0.56	0.48	0.47	0.52	0.77
40	0.53	0.48	0.54	0.61	0.95
50	0.53	0.54	0.74	0.85	1.26
60	0.60	0.65	0.90	1.03	1.35
70	0.75	0.81	1.05	1.14	1.24
80	0.93	0.99	1.14	1.17	1.00
90	1.09	1.14	1.17	1.12	0.71
100	1.22	1.24	1.14	1.03	0.45
110	1.27	1.25	1.05	0.89	0.27
120	1.28	1.19	0.91	0.73	0.17
130	1.28	1.10	0.73	0.56	0.14
140	1.31	1.01	0.55	0.39	0.11
150	1.42	0.99	0.41	0.26	0.08
160	1.57	1.03	0.34	0.19	0.04
170	1.72	1.11	0.34	0.17	0.02
180	1.78	1.15	0.35	0.17	0.01

<sup>a</sup>Including contributions from  $0 \leq J \leq 20$ .

TABLE V. Comparison between theoretical values and experimental values of differential cross sections (in  $\text{\AA}^2/\text{sr}$ ) for vibrationally elastic scattering.

$\theta$ (deg)	$E = 30$ eV		$E = 35$ eV		$E = 50$ eV		$E = 75$ eV	
	Theory	Exptl	Theory	Exptl <sup>b</sup>	Theory	Exptl	Theory	Exptl <sup>a</sup>
5	36.8		42.0		50.5	45.3 <sup>c</sup>	60.9	
6	34.8		39.7		47.6	78.0 <sup>d</sup>	56.8	
8	31.0		35.3		42.0	35.3, <sup>c</sup> 57.0 <sup>d</sup>	49.4	
10	27.4		31.2		37.0	30.1, <sup>c</sup> 47.0 <sup>d</sup>	42.5	
14	21.2		24.0		28.2	22.4 <sup>c</sup>	31.0	
15	19.9		22.5		26.3	27.0 <sup>d</sup>	28.5	
20	14.0	12.9 <sup>a</sup>	15.6		17.9	12.1, <sup>a</sup> 14.3, <sup>c</sup> 16.0 <sup>d</sup>	18.3	9.82
23	11.3		12.4		14.0	12.3 <sup>d</sup>	13.7	
25	9.70	9.49 <sup>b</sup>	10.6	25.4	11.8	9.84, <sup>c</sup> 9.10 <sup>d</sup>	11.3	
27	8.35		8.99		9.92	7.10 <sup>d</sup>	9.33	
30	6.68	7.14 <sup>a</sup>	7.05		7.63	5.71, <sup>a,d</sup> 6.91 <sup>c</sup>	7.04	3.75
35	4.70		4.78		5.01	3.20 <sup>d</sup>	4.63	
40	3.52	3.71 <sup>a</sup>	3.47		3.54	2.57, <sup>a</sup> 2.10 <sup>d</sup>	3.38	1.54
45	2.89		2.85		2.84	1.39 <sup>d</sup>	2.76	
50	2.58	2.14, <sup>a</sup> 2.68 <sup>b</sup>	2.59	6.07	2.54	1.29, <sup>a</sup> 1.01 <sup>d</sup>	2.40	0.71
55	2.40		2.48		2.39	0.74 <sup>d</sup>	2.11	
60	2.25	1.29 <sup>a</sup>	2.39		2.25	0.75, <sup>a</sup> 0.57 <sup>d</sup>	1.86	0.46
65	2.09		2.23		2.08	0.47 <sup>d</sup>	1.64	
70	1.88	0.75 <sup>a</sup>	2.01		1.84	0.46 <sup>a</sup> , 0.40 <sup>d</sup>	1.45	0.29
75	1.67		1.75		1.60	0.32 <sup>d</sup>	1.29	
80	1.50	0.54 <sup>a</sup>	1.52		1.39	0.36, <sup>a</sup> 0.29 <sup>d</sup>	1.17	0.29
90	1.35	0.46, <sup>a</sup> 0.71 <sup>b</sup>	1.28	3.21	1.19	0.25, <sup>a</sup> 0.26 <sup>d</sup>	0.97	0.32
100	1.43	0.50 <sup>a</sup>	1.37		1.26	0.32, <sup>a</sup> 0.23 <sup>d</sup>	0.78	0.29
110	1.52		1.50		1.36	0.30 <sup>d</sup>	0.61	
115	1.50	0.92 <sup>a</sup>	1.49		1.34	0.82 <sup>a</sup>	0.53	0.57
120	1.43		1.41		1.24	0.45 <sup>d</sup>	0.45	
130	1.29		1.17		0.88	0.63 <sup>d</sup>	0.30	
135	1.30	2.43 <sup>a</sup>	1.11		0.69	2.32 <sup>a</sup>	0.23	1.54

<sup>a</sup>Srivastava *et al.* (Ref. 65).<sup>b</sup>Pavlovic *et al.* (Ref. 61).<sup>c</sup>Dubois and Rudd (Ref. 64). Based on a private communication from Rudd a 7% enhancement of the data given in their abstract has been included in the table.<sup>d</sup>Kambara and Kuchitsu (Ref. 60) normalized to Ref. 65 at  $\theta = 30^\circ$ .

## VII. DISCUSSION

Elastic differential cross sections for electron-nitrogen-molecule scattering in the 30–75 eV impact energy range have been measured by Kollath<sup>56</sup> (1928), Arnot<sup>57</sup> (1931), Bullard and Massey<sup>58</sup> (1931), Mohr and Nicholl<sup>59</sup> (1932), Kambara and Kuchitsu<sup>60</sup> (1972), Pavlovic *et al.*<sup>61</sup> (1972), Shyn *et al.*<sup>62</sup> (1972), Finn and Doering<sup>63</sup> (1975), DuBois and Rudd<sup>64</sup> (1975), and Srivastava *et al.*<sup>65</sup> (1976). We make no comparison to the 1932 and earlier experiments. Srivastava *et al.* made a thorough comparison to the experiments of Shyn *et al.* and of Finn and Doering, so we do not compare our results directly to the

latter two groups, but rather we compare them to the absolute measurements of Srivastava *et al.* We also compare to the experimental results of DuBois and Rudd and Kambara and Kuchitsu since they cover angular regions and to the experimental results of Pavlovic *et al.* since they cover energies not covered by Srivastava *et al.*

Due to a lack of good enough energy resolution, the rotational excitation cross sections and pure elastic

TABLE VI. Integral cross sections ( $Q$ ) and momentum transfer cross sections ( $Q_m$ ) in  $\text{\AA}^2$ .

$E$ (eV)	Pure elastic		Pure rotational excitation	
	$Q$	$Q_m$	$Q$	$Q_m$
30	24.1	8.55	12.7	14.9
35	25.9	8.78	11.7	13.3
45	27.1	8.07	10.5	10.5
50	26.8	7.41	9.92	9.24
75	24.8	4.57	7.84	5.37

TABLE VII. Comparison between theoretical values and experimental values of integral and momentum transfer cross sections (in  $\text{\AA}^2$ ) for vibrationally elastic scattering.

$E$ (eV)	Integral cross section		Momentum transfer cross section	
	Theory	Exptl	Theory	Exptl
30	36.7	31.4 <sup>a</sup>	23.5	22.8 <sup>a</sup>
35	37.6	b	22.0	b
45	37.5	b	18.5	b
50	36.7	28.6 <sup>a</sup>	16.7	21.1 <sup>a</sup>
75	32.7	20.7 <sup>a</sup>	9.94	13.2 <sup>a</sup>

<sup>a</sup>Srivastava *et al.* (Ref. 65).<sup>b</sup>Not available.



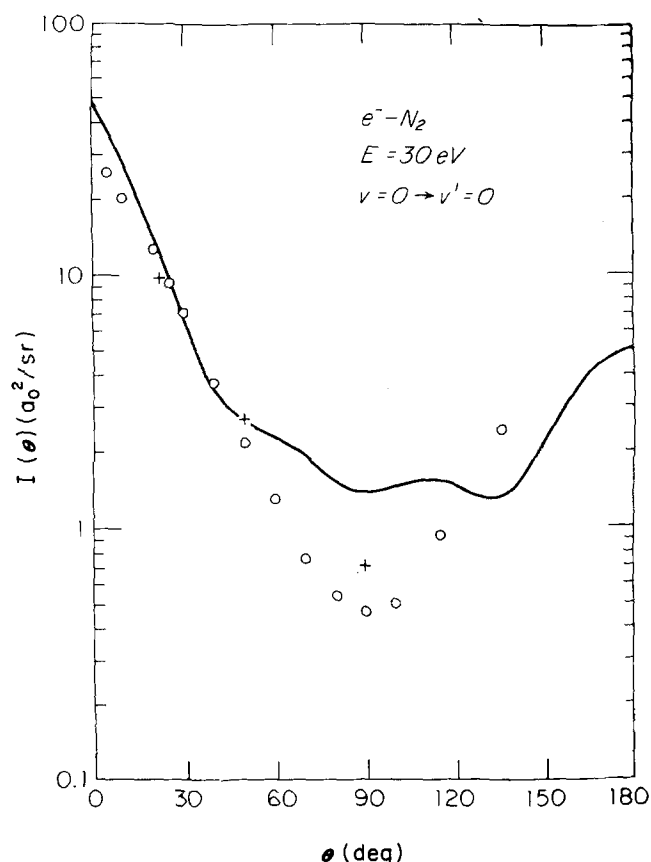


FIG. 5. Differential cross section for vibrationally elastic scattering at  $E=30$  eV as a function of scattering angle. The solid curve is the theoretical result. Crosses are the experimental results of Pavlovic *et al.* (Ref. 61). Circles are the experimental results of Srivastava and Trajmar (private communication) for  $\theta < 20^\circ$  and Srivastava *et al.* (Ref. 65) for  $\theta \geq 20^\circ$ .

scattering cross sections have not yet been measured separately, so we compare our vibrationally elastic cross sections to the measured vibrationally elastic cross sections. Note also that the theoretical calculations are all for scattering by the ground state of  $N_2$ , whereas the experiments are averaged over a Boltzmann distribution. The only measurements of rotational excitation differential cross sections for electron-molecule scattering are those of Ehrhardt and Linder, Linder and Schmidt, Joyez *et al.*, and Srivastava *et al.*,<sup>66</sup> who measured the  $(v=0, j=1 \rightarrow v'=0, j'=3)$  rotational excitation cross sections for electron scattering by  $H_2$  in the 0.3–40 eV energy range. It is interesting to note that the experiments of Srivastava *et al.* show that the rotational excitation cross sections exceed the pure elastic scattering cross sections for scattering angles  $115^\circ \leq \theta \leq 135^\circ$  at 40 eV. This trend is also evident in our calculations which show that the rotational excitation cross sections exceed the pure elastic scattering cross sections for  $76^\circ \leq \theta \leq 157^\circ$  at 30 eV,  $75^\circ \leq \theta \leq 151^\circ$  at 35 eV,  $69^\circ \leq \theta \leq 148^\circ$  at 45 eV,  $64^\circ \leq \theta \leq 147^\circ$  at 50 eV, and  $49^\circ \leq \theta \leq 105^\circ$  at 75 eV.

The comparisons to experimental results for vibrationally elastic scattering at four energies are given in

Table V and Figs. 5–7. (No experiment at 45 eV is available yet.) The experiments are not in complete agreement with one another, especially for the magnitude of the cross section. For example, at 50 eV and small angles some experimental results are larger than the theoretical ones and some are smaller. Thus, discrepancies in magnitude of a factor of 2 or less are not necessarily meaningful. Our calculated cross sections have about the correct shape and magnitude for angles less than  $50^\circ$  at 30 eV and  $30^\circ$  at 50 eV and the correct shape for angles less than  $50^\circ$  at 35 eV and  $30^\circ$  at 75 eV. It is interesting to note the discrepancies in magnitude and angular dependence shown by the experiments at 50 eV. The small angle dependence of the calculated differential cross sections mainly depends<sup>13,15</sup> on the long range form of the effective interaction potential which we have included as accurately as possible. At larger angles the calculated cross sections show a different angular dependence than the experiments do. The large angle scattering depends strongly on the short-range part of the effective interaction potential. This is very anisotropic and inclusion of more rotational states in the state expansion (which would require including more terms in the Legendre expansion of the potential) would probably effect the large-angle

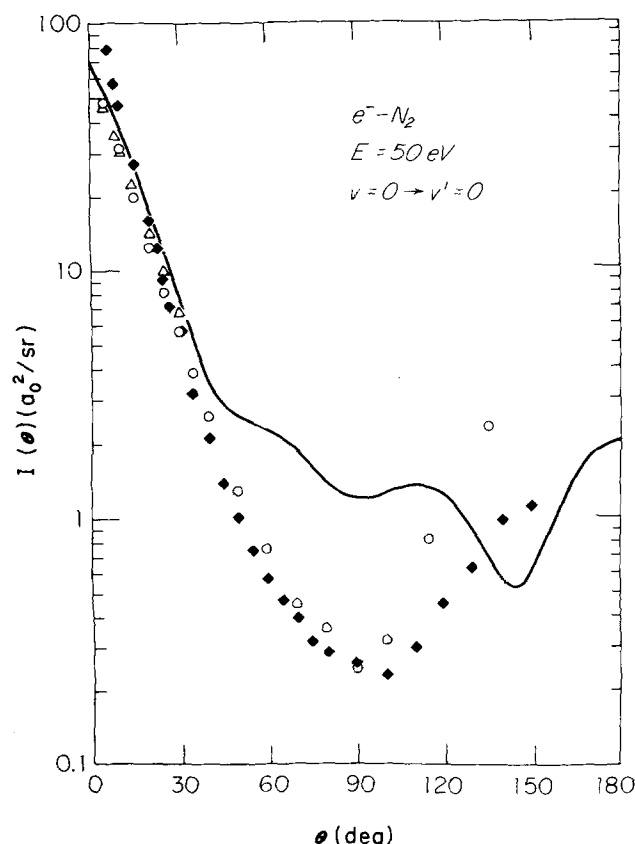


FIG. 6. Differential cross section for vibrationally elastic scattering at  $E=50$  eV as a function of scattering angle. Diamonds are the experimental results of Kambara and Kuchitsu (Ref. 60) normalized to Srivastava *et al.* (Ref. 65) at  $\theta=30^\circ$ . Triangles are the corrected experimental results of DuBois and Rudd (Ref. 64). The solid curve and circles have the same meaning as in Fig. 5.

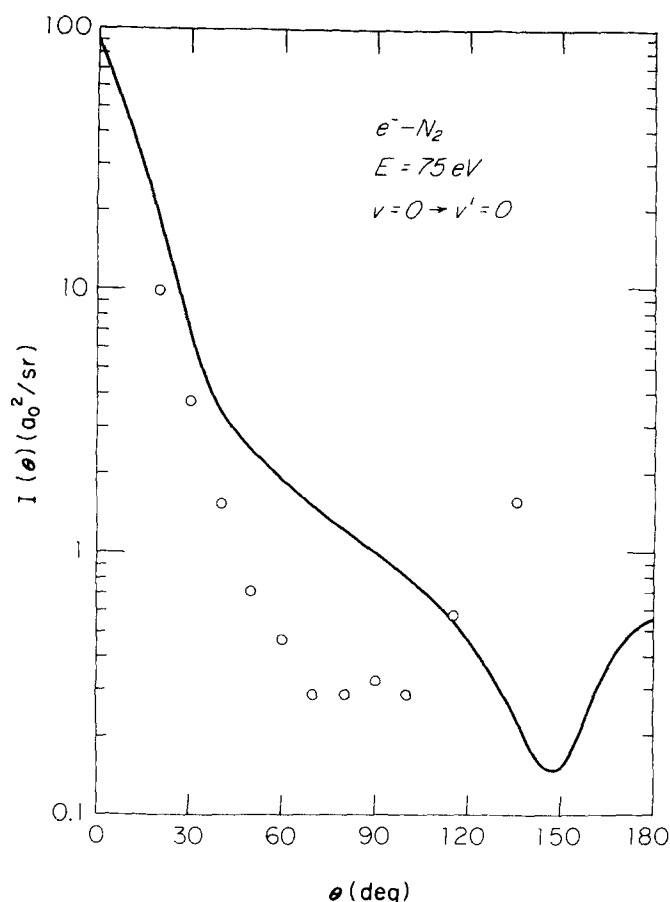


FIG. 7. Differential cross section for vibrationally elastic scattering at  $E = 75$  eV as a function of scattering angle. Circles are the experimental results of Srivastava *et al.* (Ref. 65). The solid curve is the theoretical result.

scattering much more than the small angle scattering. Also, as mentioned above in Sec. II, the short range form of  $V(\mathbf{r}, \mathbf{R})$  can easily be improved by including an approximate exchange potential; however, improving on the short range form of  $g(r)$  in the polarization potential (4) is more difficult. We expect that such improvements would bring the angle dependence of the calculated cross sections at large angles into better agreement with that shown by experiment. Since our calculations did not involve any adjustable parameters, the agreement with experiment is quite good and indicates that the above improvements should be made in future calculations.

The integral and momentum transfer cross sections are compared to experiment in Table VII. Again the calculated values of the integral cross sections exceed the experimental values, as is expected from the above discussion. The momentum transfer cross sections depend strongly on the values of the differential cross sections for large angles. The experimental values of the differential cross sections at the largest angles exceed the calculated values and the experimental values of the momentum transfer cross sections exceed the calculated values. However, it should be recalled that the "experimental" differential cross sections for scattering angles greater than  $135^\circ$  are obtained by extrapolation and so the experimental momentum transfer cross sections obtained by integrating these results

may be less accurate than the experimental integral cross sections.

Since agreement with experiment of the present theoretical calculations with no adjustable parameters is already fairly good, it is almost certain that agreement could be improved by treating the short-range part of the polarization potential semiempirically. This type of adjustment would be in the spirit of optical model studies of nuclear scattering.<sup>67</sup> However, such adjustments should probably be deferred at least until after the exchange effect and more rotational states are included.

In conclusion, for elastic scattering at energies of 30 and 50 eV, we find good agreement between theory and experiment for the magnitude and angle dependence of the differential cross sections in the angular range (scattering angles about  $50^\circ$  and smaller) where the differential cross section is largest. For elastic scattering at 75 eV and scattering angles about  $40^\circ$  and smaller the angle dependence is in good agreement with experiment but the magnitude is about a factor of 2 too large. At all energies the larger angle differential cross sections agree with experiment only within a factor of 2 to 5. The disagreement is presumably due to an inadequate treatment of the short-range part of the effective interaction potential or of the rotational state expansion or of both. Finally, for rotational excitation (which has not been observed experimentally except for  $H_2$ ) we predict that the differential cross section at large scattering angles exceeds the differential cross section for pure elastic scattering and that the integral cross section is about one-third to one-half as large as the pure elastic one.

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