

Studies of elastic e -NH₃ collisions

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We report differential and momentum-transfer cross sections for elastic scattering of electrons by NH₃ for collision energies from 2.5 to 20 eV. These cross sections were obtained in the fixed-nuclei static-exchange approximation using the Schwinger variational principle. Although fixed-nuclei cross sections for electron-polar-molecule collisions are inherently divergent at small angles, such results can provide useful estimates of the differential cross sections at intermediate and larger angles. The agreement at intermediate and larger scattering angles between the calculated and relative experimental cross sections, which are available at 8.5 and 15 eV, is good. The differential cross sections also show evidence of a weak d -wave enhancement around 8 eV. A significant feature seen in these cross sections, particularly at 15 and 20 eV, is their substantial backward peaking beyond 120°.

INTRODUCTION

Cross sections for low-energy electron-molecule collisions are known to play an important role in the modeling of planetary atmospheres,¹ gas-discharge lasers, plasma etching, plasma deposition, and switching devices.² Although theoretical and experimental values of these cross sections can be expected to become increasingly available for diatomic molecules,² progress in the study of nonlinear molecules has been slow.^{3,4} On the theoretical side, this is primarily due to the substantial reduction in numerical complexities which arises from the cylindrical symmetry of linear systems. Methods which are generally applicable to target molecules of arbitrary geometry are needed to provide quantitatively reliable estimates of elastic and inelastic cross sections for the wide range of molecules of interest in various applications.

In this paper we present results of our studies of cross sections for elastic scattering of electrons by ammonia for incident energies ranging from 2.5 to 20 eV. The results of similar studies of H₂O and CH₄ have been previously reported.^{5,6} These cross sections for elastic e -NH₃ collisions are obtained from fixed-nuclei, body-frame, and static-exchange calculations using Schwinger's variational principle. An essential feature of these applications is that the fixed-nuclei treatment of electron scattering by polar molecules leads to divergent elastic cross sections. This divergence arises from the $l^{-1/2}$ behavior of the phase shifts for higher angular momenta for electron scattering from a fixed polar molecule in the body frame. As a result, total scattering cross sections, averaged over all molecular orientations, diverge logarithmically in the fixed-nuclei approximation. This divergence can only be removed by introducing nuclear rotational motion. However, the low-partial-wave contributions in a fixed-nuclei calculation can still be directly useful since they provide quantitatively meaningful estimates of the differential cross sections at intermediate and larger scattering angles.⁷ Furthermore, these contributions to the fixed-nuclei cross sections can be appropriately augmented by laboratory-frame Born estimates for the higher partial

waves.⁷ Moreover, the low partial waves probe the more "molecular" aspects of the potential and, as will be seen later, cause significant backward peaking of the elastic cross sections. Such behavior of the differential cross sections can strongly influence derived values of momentum-transfer cross section.

In the following section we give a brief review of the Schwinger variational formulation used in these studies. We then discuss the application of this approach to elastic e -NH₃ scattering and compare the cross sections with available experimental data and the results of other calculations.

METHOD

The formulation of the Schwinger-like variational method used in these studies has been discussed in some detail previously.^{8,9} Only a few essential results will be given here. It can be shown that the full scattering wave function $\Psi_m^{(+)}$ satisfies the equation⁸

$$\left[\frac{1}{2}(PV + VP) - VG_p^{(+)}V + \frac{1}{N+1} \left[\hat{H} - \frac{(N+1)}{2}(P\hat{H} + \hat{H}P) \right] \right] \Psi_m^{(+)} = A^{(+)}\Psi_m^{(+)} = VS_m, \quad (1)$$

where $\hat{H} = E - H$, H is the full $(N+1)$ -electron Hamiltonian, V is the interaction between the incident electron and the nuclei and electrons of the target, S_m is an eigenfunction of $H_0 = H - V$, i.e., $\Phi_m \exp i\mathbf{k}_m \cdot \mathbf{r}_{N+1}$ with Φ_m a target eigenstate, and P is a projection operator defined on the target states assumed open in the collision, i.e.,

$$P = \sum_l^{\text{open}} |\Phi_l(1, 2, \dots, N)\rangle \langle \Phi_l(1, 2, \dots, N)|. \quad (2)$$

$G_p^{(+)}$ is a projected outgoing-wave Green's function given by

$$G_p^{(+)} = \sum_l^{\text{open}} |\Phi_l\rangle g_l^{(+)}(\mathbf{r}_{N+1}, \mathbf{r}'_{N+1}) \langle \Phi_l|, \quad (3)$$

where $g_l^{(+)}(\mathbf{r}_{N+1}, \mathbf{r}'_{N+1})$ is the free-particle Green's function at energy $E - E_l$.

Based on Eq. (1), we can write a multichannel variational functional for the scattering amplitude

$$[f_{m,n}] = -\frac{1}{2\pi} (\langle S_m | V | \tilde{\Psi}_n^{(+)} \rangle + \langle \tilde{\Psi}_m^{(-)} | V | S_n \rangle - \langle \tilde{\Psi}_m^{(-)} | A^{(+)} | \Psi_n^{(+)} \rangle), \quad (4)$$

Expansion of the trial scattering wave functions $\tilde{\Psi}_m$ and $\tilde{\Psi}_n$ in Eq. (4) in a basis of $(N+1)$ -electron Slater determinants gives the variational expression

$$\tilde{f}(\mathbf{k}_m, \mathbf{k}_n) = -\frac{1}{2\pi} \sum_{i,j} \langle S_m | V | \chi_i \rangle (A^{-1})_{ij} \langle \chi_j | V | S_n \rangle, \quad (5)$$

where χ_i is a Slater determinant and A_{ij} is a matrix element of $A^{(+)}$ in this basis. If these determinants are restricted to be of the form $A[\Phi_0\mu]$, where Φ_0 is the Hartree-Fock wave function for the target and μ denotes a scattering orbital, Eq. (5) can be shown to reduce to the Schwinger variational principle for elastic scattering by the static-exchange potential associated with Φ_0 . Equation (5) is, however, a general multichannel variational expression which includes both open- and closed-channel effects.^{8,9}

Some important features of this variational principle are as follows. First, the trial scattering wave function can be expanded in a discrete basis. Furthermore, if the orbitals appearing in the $(N+1)$ -electron Slater determinants in the expansion of the trial wave function are chosen to be Cartesian Gaussians, all matrix elements arising in Eq. (5), except those of $VG_p^{(+)}V$, can be evaluated analytically for a molecule of arbitrary geometry. For the matrix elements of $VG_p^{(+)}V$, the on-shell contribution is obtained by numerical quadrature. The principal-wave contribution to the matrix elements of $VG_p^{(+)}V$ cannot be evaluated analytically. In these studies these terms were obtained approximately via an insertionlike quadrature of Cartesian Gaussian functions around $G_p^{(+)}$.

Finally, Eq. (5) provides an analytical approximation to the full scattering amplitude $\tilde{f}(\mathbf{k}_m, \mathbf{k}_n)$ in the body frame. To obtain the laboratory-frame amplitude, the body-frame amplitude is decomposed into partial waves via a Gauss-Legendre quadrature. The resulting expansion is then transformed to the laboratory frame and averaged over molecular orientation.¹⁰

APPLICATIONS

We have used the formulation outlined above to obtain elastic scattering cross sections for e -NH₃ collision for energies ranging from 2.5 to 20 eV. The cross sections were obtained in the fixed-nuclei, static-exchange approximation. In these studies it is convenient to construct the self-consistent field SCF wave function for NH₃ using a

TABLE I. Cartesian Gaussian basis. [Cartesian Gaussian functions, with \mathbf{A} locating the origin and N_{lmn} the normalization constant, are defined as

$$\chi_{lmn}^{(\alpha)} = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha |\mathbf{r} - \mathbf{A}|^2}.$$

Basis set used for SCF target wave function, expansion of the scattering functions, and for the quadrature insertion in the $VG_p^{(+)}V$ terms.]

Center and type	Exponent		
N(15s)	5909.0, 887.5, 204.7, 59.84, 20.00, 7.193, 2.686, 0.700, 0.2133, 0.0533, 0.0133, 0.00333, 0.00083, 0.00021, 0.00007,		
	N(10p)	26.79, 5.956, 1.707, 0.5314, 0.1654, 0.0418, 0.0103, 0.00258, 0.000650, 0.000163,	
		N(3d)	0.921, 0.272, 0.0680,
		H(5s)	13.3615, 2.0130, 0.4538, 0.1233, 0.0200

large uncontracted (15s10p3d) Cartesian Gaussian basis on the nitrogen and 5s basis on each hydrogen. Table I lists the exponents of these basis functions. At the experimental geometry of $R(\text{N-H})=1.92a_0$ and $\theta(\text{H-N-H})=106.7^\circ$ assumed here, this basis gives an SCF energy of -56.2071 a.u. and a dipole moment of 0.6278 a.u. The experimental value of the dipole moment is 0.5831 a.u.¹¹ The basis provides 73 virtual orbitals ($31a_1$, $21e_x$, $21e_y$) which are used to expand the trial scattering wave function and in the insertion quadrature technique for evaluating matrix elements of $VG_p^{(+)}V$. The present basis does not provide any orbitals of a_2 symmetry. For scattering energies and angles of interest here, the lack of orbitals of this symmetry should not affect the scattering amplitudes significantly since the lowest partial wave to which this symmetry contributes is $l=3$, $m=3$.

Figures 1–5 show our calculated fixed-nuclei elastic differential cross sections for collision energies of 2.5, 5.0, 8.5, 15, and 20 eV. In these figures we report results only for scattering angles beyond about 30° to 40° since, as discussed above, the fixed-nuclei approximation used here inherently leads to divergent cross sections for polar targets and, furthermore, the higher partial waves responsible for this low-angle behavior are not properly described by our basis set. The differential cross sections at these energies are characterized by a minimum around 120° , which becomes broader at the higher energies, and a backward peak. The backward peaking becomes quite pronounced at higher energy, behavior similar to what has been seen in calculated elastic cross sections for e -H₂O and e -CH₄ collisions^{5,6} and in the more recent experimental data of Shyn and Cho¹² for e -H₂O scattering which extended out to 150° .

There have been no absolute measurements of the elastic differential cross sections for e -NH₃ collisions in the energy range of interest here. However, the recent rela-

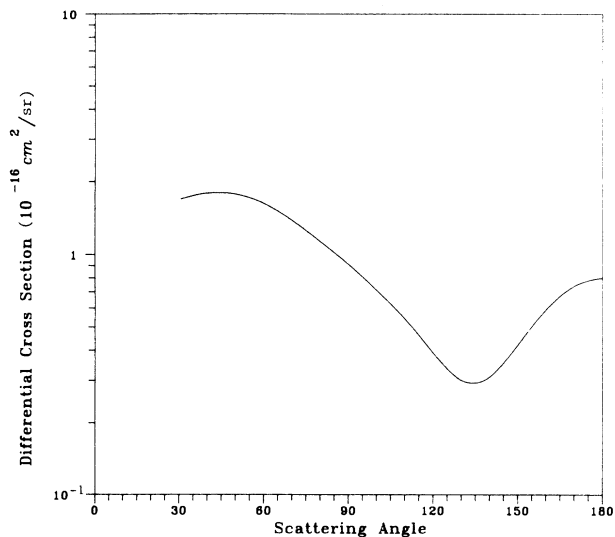


FIG. 1. Differential cross sections (DCS) for elastic $e\text{-NH}_3$ scattering at 2.5 eV: Solid line, present static-exchange results.

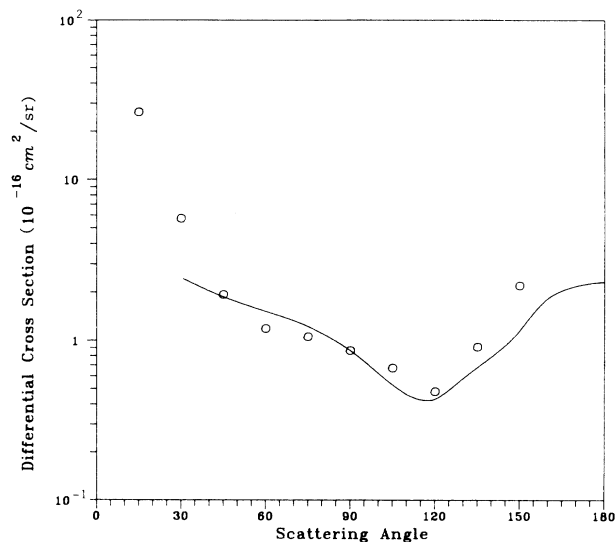


FIG. 3. DCS for elastic $e\text{-NH}_3$ scattering at 8.5 eV: Solid line, present static-exchange results; circles, relative measured values of Shyn (Ref. 13) normalized to the calculated cross sections at 90° .

tive measurements of Shyn and collaborators¹³ at 8.5 and 15 eV, normalized to our calculated cross sections at a scattering angle of 90° , are shown in Figs. 3 and 4. The agreement between these measured and calculated results at intermediate and larger angles is encouraging. The differences between these sets of cross sections in this angular range are probably due to polarization effects which are not included in the present static-exchange results. The shoulderlike structure between 60° and 90° in both

the calculated and measured differential cross sections at 8.5 eV may be indicative of a weak d -wave enhancement in this energy region. The energy dependence of the ${}^2E_{x,y}$ eigenphase sums also suggests broad shape-resonance ($l=2$) behavior centered around 8 to 9 eV. The mild enhancement of the differential cross sections at 90° around this energy seen in Fig. 6 could also arise from such a weak d -wave shape resonance in this region. Similar shape-resonant behavior has been observed experi-

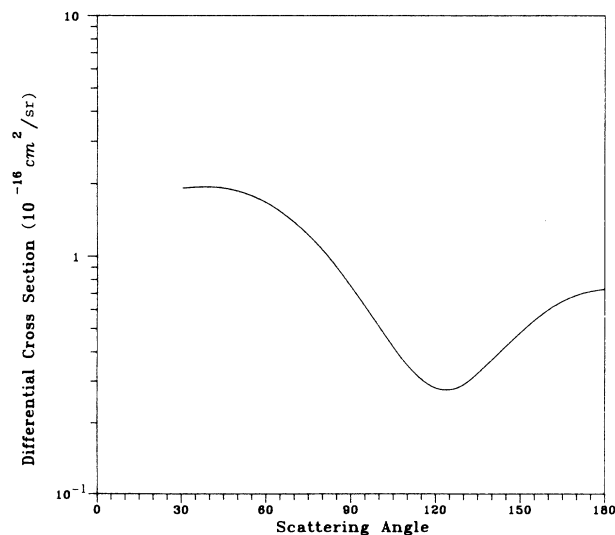


FIG. 2. DCS for elastic $e\text{-NH}_3$ scattering at 5 eV: Solid line, present static-exchange results.

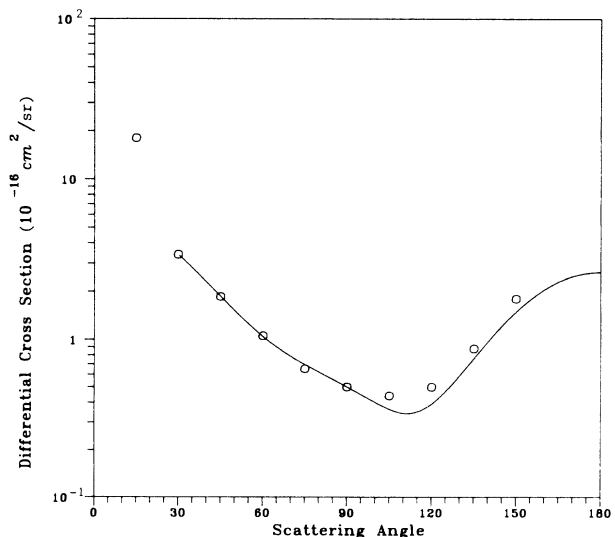


FIG. 4. DCS for elastic $e\text{-NH}_3$ scattering at 15.0 eV: Solid line, present static-exchange results; circles, relative measured values of Shyn (Ref. 13) normalized to the calculated cross sections at 90° .

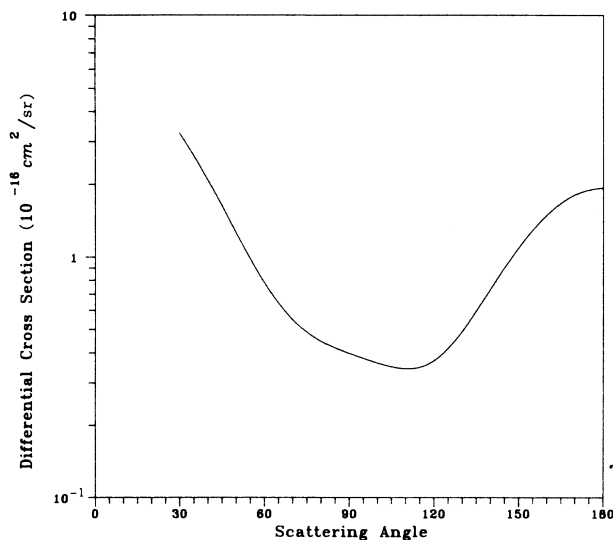


FIG. 5. DCS for elastic e -NH₃ scattering at 20 eV: Solid line, present static-exchange results.

mentally in the differential cross sections for vibrational excitation of NH₃ around 7.3 eV.¹⁴

Although these fixed-nuclei elastic cross sections are divergent for this polar target, our calculated cross sections can be used to obtain the momentum-transfer cross sections

$$\sigma^m = 2\pi \int_0^\pi \frac{d\sigma}{d\theta} (1 - \cos\theta) \sin\theta d\theta. \quad (6)$$

Figure 7 shows our calculated cross sections σ^m along with those of Jain and Thompson¹⁵ and the "recommended" values of Itikawa¹⁶ derived from a combination of data from swarm¹⁷ and total cross-section measure-

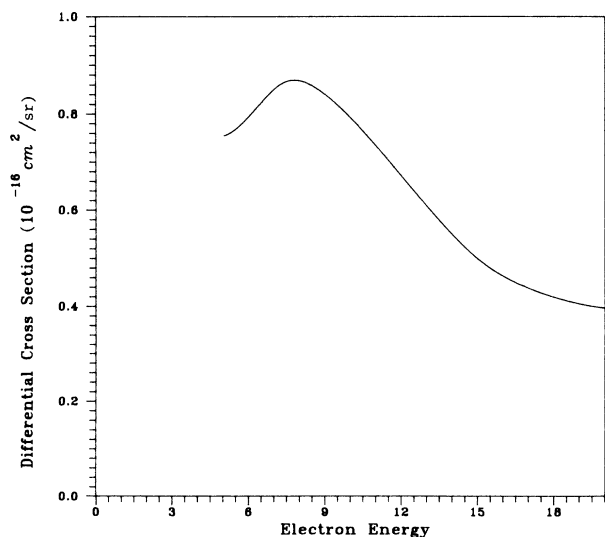


FIG. 6. Calculated DCS for elastic e -NH₃ scattering at 90°.

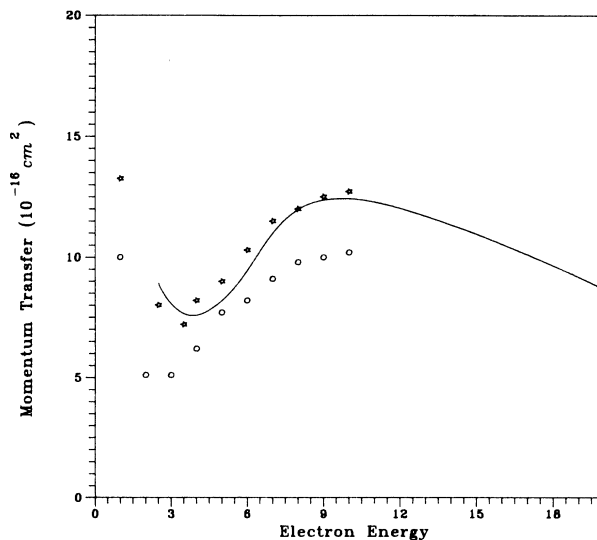


FIG. 7. Momentum transfer cross sections for e -NH₃ scattering: Solid line, present results; stars, results of model potential studies of Ref. 15; circles, "recommended" values of Itikawa (Ref. 16).

ments¹⁸ and Born cross sections.¹⁹ The results of Jain and Thompson¹⁵ were obtained using a truncated static-model exchange-model polarization potential. The agreement between our present results and those obtained with this model potential is very good. Without a further comparison of the differential cross sections associated with these two calculations, particularly the role of polarization effects in the model potentials of Ref. 15, this agreement may not be very significant. The calculated momentum transfer cross sections are seen to be consistently larger than the "recommended" values of Itikawa.¹⁶ The recommended values above 2 eV were obtained by a scaling of the early total scattering cross section measurements of Brüche and hence cannot be considered very reliable. For this reason, the discrepancy between the calculated and recommended values of the momentum-transfer cross sections in Fig. 7 may also not be significant.

CONCLUDING REMARKS

We have used the Schwinger variational method to study the differential cross sections for elastic scattering of low-energy electrons by NH₃. Although the fixed-nuclei approximation assumed here leads to divergent cross sections in the forward direction for this polar system, the results can be expected to provide meaningful estimates of the cross sections at intermediate and higher scattering angles, as seen here in the agreement between the calculated cross sections and the relative measurements of Shyn¹³ at 8.5 and 15 eV. Significant features of these cross sections include their backward peaking, even at 20 eV, and the presence of a weak resonance behavior around 8.5 eV. This backward peaking, which has also been seen in the e -CH₄ and e -H₂O cross section,^{5,6} is obviously important in deriving

momentum-transfer cross sections from differential cross sections which are difficult to measure in the high-angle region.

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