

Theoretical study of the total (elastic+inelastic) cross sections for electron-H₂O (NH₃) scattering at 10-3000 eV

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Received 14 July 1987, in final form 24 November 1987

Abstract. By employing semi-empirical spherical complex optical potentials (SCOP) for the electron-H₂O and NH₃ systems, we report first theoretical results on the total (elastic+inelastic) cross sections over the energy range of 10-3000 eV. The real part of the local SCOP term for each molecule is a sum of three isotropic interactions, namely the static, the polarisation and the exchange; all three potentials are defined in a functional form of the target charge density evaluated from near-Hartree-Fock one-centre molecular wavefunctions. The contribution from the non-spherical interaction terms (such as the permanent dipole, quadrupole, etc) is included incoherently via the first Born approximation under the rotating molecule model in which the integral cross section is finite. The imaginary part of the SCOP (i.e. the absorption potential, $V_{\text{abs}}(r)$) is determined *ab initio* as a function of the charge density of the molecule, static exchange force of the e-molecule system, incident wavenumber and the mean excitation energy of the target. We employ two versions of the $V_{\text{abs}}(r)$: one with undistorted ($\rho_0(r)$) and the other with distorted ($\rho_p(r)$) charge density which is calculated approximately from perturbative techniques. The resulting inelastic cross sections (mainly the total ionisation including dissociation) using the $\rho_p(r)$ version of the $V_{\text{abs}}(r)$ are in agreement both in quality and quantity with experimental data. Finally, our results obtained without any fitting parameter on the total cross sections for both the targets compare very well with the recent measured data. The results on the reduced elastic and momentum transfer cross sections are also presented in the same energy region.

1. Introduction

We recently proposed a simple model potential approach (Jain 1986a, 1987a) in order to predict total (elastic+absorption) cross sections (σ_t) for electron collisions off CH₄ and SiH₄ molecules at low, intermediate and high energies (0-1000 eV). In this paper we are concerned only with intermediate- and high-energy ($E > 10$ eV, where E is the impact energy) electron-polyatomic molecule collisions, where conventional close-coupling theories (see Gianturco and Jain 1986 and references therein) are very difficult to apply due to numerical complexity and convergence problems. In our earlier attempts (Jain 1986a, 1987a), the total interaction of the electron-molecule system is approximated by a local spherical complex optical potential (SCOP) term and the corresponding scattering parameters are obtained exactly in a partial-wave decomposition scheme. The SCOP terms for both molecules (Jain 1986a, 1987a) were computed *ab initio* without any fitting procedure and finally the calculated σ_t were found to be in very good accord with several measurements. A major reason for the success of the SCOP model (even at very low energies) in the case of CH₄ and SiH₄ is the absence of long-range dipole and quadrupole forces.

Here we extend the SCOP approach for polar polyatomic targets with a similar (to that of CH_4 and SiH_4) electronic situation from the molecular structure point of view, i.e. hydrogen atoms around a heavy nucleus, where a one-centre-expansion method (Moccia 1964a, b) is feasible in electron scattering as well as in structure calculations. In the present case of polar molecules we now have significant interaction due to non-spherical long-range dipole and quadrupole terms which make a spherical approximation doubtful and less desirable. Certainly, we cannot employ the spherical methodology at very low energies ($E < 10$ eV) where the higher-order long-range forces in the electron-molecule system play a decisive role in determining the scattering parameters and for which a close-coupling theory is more appropriate. As the impact energy increases (roughly above 20 eV), the short-range interactions become more and more important with the result that the weaker effect of anisotropic potentials (dipole, quadrupole, etc) can be incorporated approximately as a small perturbation in an incoherent manner via the simple prescriptions such as the first Born approximation (FBA). This hybrid approach may be incorrect at the lower end of the present energy region; however, at somewhat higher energies (say, $E > 100$ eV) our final results are quite reliable (see below). Such a hybrid two-potential approach has previously been used for electron-polar (Jain and Tayal 1984) and electron-non-polar (Choi *et al* 1979) molecule scattering at intermediate and high energies.

For this purpose, we have chosen two polyatomic species H_2O and NH_3 having permanent dipole moments with values of 0.728 and 0.574 (in atomic units) respectively. The interest and application of electron- H_2O scattering data are found in radiation chemistry, atmospheric and space sciences (Olivero *et al* 1972). Several experimental studies have been carried out very recently for e- H_2O collisions at intermediate and high energies (Sueoka *et al* 1986, Szmytkowski 1987 and Zecca *et al* 1987). Earlier, Brüche (1929) and Sokolov and Sokolova (1981) measured σ_t for e- H_2O from low to intermediate energies. In spite of this large amount of experimental data on e- H_2O collisions, there is not a single theoretical attempt to predict σ_t values in the present energy regime. (For very low-energy measurements and theoretical work on the e- H_2O system, see the recent review by Gianturco and Jain 1986).

The study of e- NH_3 collisions has applications in space physics. The recent discovery of H_2O and NH_3 molecules by radio astronomers in the interstellar medium has increased interest in these gases (Oka 1973). In the field of plasma chemistry, NH_3 is one of the important molecules as a source of nitrogen atoms for the fabrication of nitride films and other nitrogen compounds (Sato *et al* 1986). Recently, Sueoka and Mori (1985) and Sueoka *et al* (1987) have measured σ_t for the e- NH_3 system at 1-400 eV impact energies. The only earlier measurements on the e- NH_3 σ_t cross sections are due to Brüche (1927). As in the e- H_2O case, no theoretical study exists for the e- NH_3 system either at the energies of concern in this work. (For very low-energy investigations on e- NH_3 collisions, see the review by Gianturco and Jain (1986).)

There are, however, more studies (experimental and theoretical) on the elastic scattering of electrons with water molecules. The differential cross sections (DCS) for water molecules have been measured at intermediate and high energies by several groups (Lassettre and White 1973, Danjo and Nishimura 1985, Katase *et al* 1986, Trajmar *et al* 1973; for very low-energy experimental references, see the article by Trajmar *et al* 1983). At very high energies (in the keV region), the DCS for e- H_2O scattering were measured over a wide range of momentum transfers by Shibata *et al* (1980). Theoretically, the DCS were calculated for e- H_2O elastic scattering by Fujita *et al* (1983) in the Glauber approximation, by Katase *et al* (1986) in the partial-wave

method using a spherical static potential only and by Jain *et al* (1988) via a partial-wave analysis employing spherical optical potentials including polarisation and exchange effects. At very high energies (in the keV region) the DCS have been computed in the first Born theory using different kinds of target wavefunctions (Breitenstein *et al* 1986, 1987, and references therein). For low-energy calculations on the e-H₂O DCS, there are several studies using more elaborate *ab initio* techniques (Jain and Thompson 1982, 1983a, Gianturco and Scilla 1987, Gianturco and Thompson 1980, Brescansin *et al* 1986).

For NH₃, the only experimental study on the DCS is due to Harshbarger *et al* (1971) at small angles (2–10°); the corresponding calculations were made by us (Jain 1983a) with a very good agreement with the data of Harshbarger *et al*. At very high energies (keV region), the elastic DCS were measured by Lahmam-Bennani *et al* (1979) and calculated in the FBA employing molecular wavefunctions of different quality (Sharma and Tripathi 1983, Szabo and Ostlund 1974). It is therefore clear that there is a paucity both of theoretical and experimental information for the e-NH₃ scattering as compared with e-H₂O studies.

Finally, we would like to mention that the present SCOP model including the hybrid scheme, in order to yield final σ_t values for both the e-NH₃ and e-H₂O cases, involves no fitting parameter. Thus, a good agreement between our results and the experimental data makes this study more useful and interesting. Experimentally, σ_t can be measured with statistical error less than 1%; however, larger uncertainty may be introduced due to forward scattering. So far, experimentalists (Sueoka *et al* 1986, 1987, Zecca *et al* 1987, Szmytkowski 1987) have not been able to find theoretical cross sections with which to compare their measurements on the e-H₂O (NH₃) collisions.

In the next section a brief account of the present theory and numerical procedure is given. The results are discussed and compared with several sets of experimental data in § 3. Concluding remarks are made in § 4. We use atomic units throughout this work.

2. Theory and numerical procedure

The details of the SCOP model can be found in our previous articles (Jain 1986a, 1987a, b, c; see also Jain 1983b, 1984). Here we provide only a summary. The central part of the calculation is to generate the optical potential between the e-molecule system, i.e.

$$V_{\text{opt}}(\mathbf{r}) = V_{\text{st}}(\mathbf{r}) + V_{\text{ex}}(\mathbf{r}) + V_{\text{pol}}(\mathbf{r}) + i V_{\text{abs}}(\mathbf{r}). \quad (1)$$

It is now straightforward to treat the $V_{\text{opt}}(\mathbf{r})$ exactly in a partial-wave analysis to determine the S_l matrix $S(E)$ as a function of complex phaseshifts at each energy E . We employ a variable phase approach (VPA) (Calogero 1973) to evaluate complex phases. In (1) V_{st} , V_{pol} , V_{ex} and V_{abs} are respectively the static, polarisation, exchange and absorption potentials of the electron-molecule system. Various cross sections can be defined in terms of $S_l(E)$. For example, the elastic, absorption and the total (elastic absorption) cross sections are written as

$$\sigma_{\text{el}}(E) = \frac{\pi}{k^2} \sum_{l=0}^{l_{\text{max}}} (2l+1) |1 - S_l(E)|^2 \quad (2)$$

$$\sigma_{\text{abs}}(E) = \frac{\pi}{k^2} \sum_{l=0}^{l_{\text{max}}} (2l+1) (1 - |S_l(E)|^2) \quad (3)$$

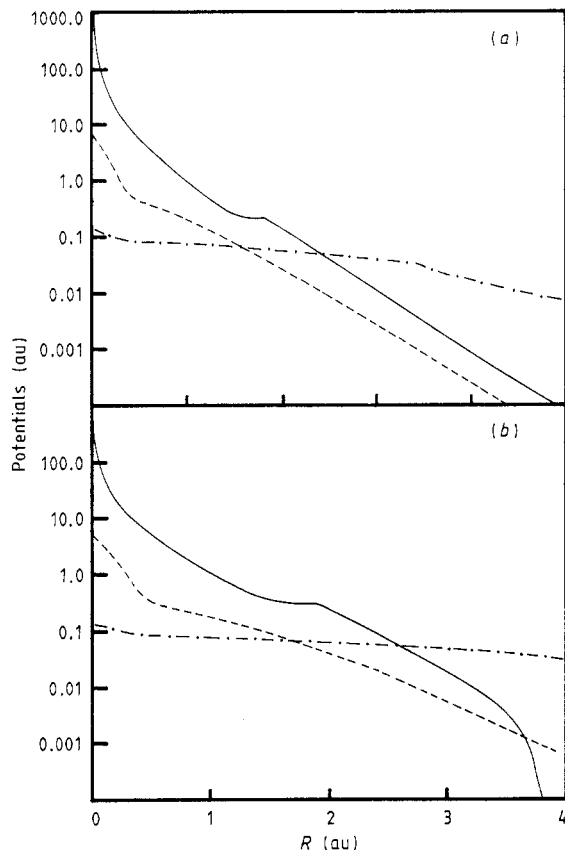


Figure 1. Real part of the optical potential (SCOP) for (a) H_2O and (b) NH_3 molecules. Full curves, static potential; broken curve, exchange (FEGE) potential at 100 eV; chain curve, correlation-polarisation (CP) potential. All the potentials are multiplied by a minus sign.

$$\sigma_t(E) = \frac{2\pi}{k^2} \sum_{l=0}^{l_{\max}} (2l+1)(1 - \text{Re } S_l(E)). \quad (4)$$

The value of l_{\max} in (2)–(4) is chosen in such a way that the corresponding quantities are converged perfectly. In general, l_{\max} varies with incident electron energy. Finally, as mentioned earlier in the case of polar molecules we adopt a two-potential hybrid approach in which the total cross section is defined as an incoherent sum of total cross sections calculated separately from the spherical (SCOP of equation (1)) and non-spherical (mainly the dipole scattering) interactions, i.e.

$$\sigma_t(E) = \sigma_t^S(E) + \sigma_t^{\text{NS}}(E). \quad (5)$$

The σ_t^S is simply equation (4), while σ_t^{NS} is determined via the FBA in a rotating dipole model (Collins and Norcross 1978):

$$\sigma_t^{\text{FBA}}(E) = (8\pi/3k^2) D^2 \frac{J'}{2J+1} \ln \left(\frac{k+k'}{|k-k'|} \right). \quad (6)$$

Here we assume that the contribution from higher-order terms (quadrupole, etc) is small and therefore neglected in this work. In (6), D is the dipole moment of the

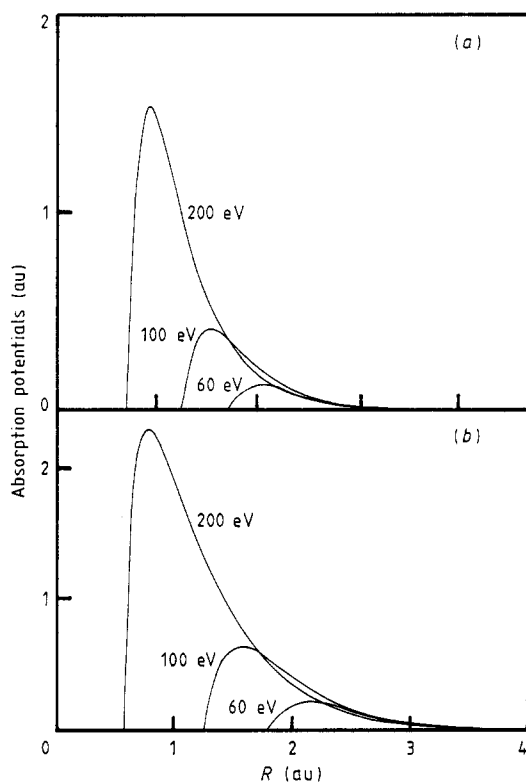


Figure 2. Imaginary part of the optical potential (SCOP) (absorption interaction) for (a) H_2O and (b) NH_3 targets at 60, 100 and 200 eV. All the numbers are multiplied by a minus sign.

molecule and the k'^2 is the final energy of the outgoing electron after exciting the dipole-selected rotational level of the target. For NH_3 , the k' is given by

$$2k'^2 = 2k^2 + E_{JK} - E_{J'K'} \quad (7)$$

where the energy of a particular rotational state (JK) is calculated from

$$E_{JK} = BJ(J+1) + (A-B)K^2 \quad (8)$$

with $A = 2.87 \times 10^{-5}$ and $B = 4.53 \times 10^{-5}$ au (Herzberg 1966). For H_2O , the rotational energy levels E_{JK} and $E_{J'K'}$ are determined from a program (Jain and Thompson 1983b) for the asymmetric top energy levels. Here for both molecules we consider only the lowest rotational states ($J=0$ and $J'=1$) for the $\Delta J=1$ dipole scattering.

Let us now look at the approximations used for various terms in the optical potential (equation 1). Note that both molecules have closed-shell electronic structure; therefore the $V_{opt}(r)$ along with the V_{st} , V_{ex} , V_{pol} and V_{abs} components belongs to the totally symmetric irreducible representation 1A_1 of the molecular point group in question. The static potential $V_{st}(r)$ is determined accurately from near-Hartree-Fock one-centre target wavefunctions with a large basis set. For NH_3 , we include 27 functions of a_1 type and 25 of e-type orbitals. For H_2O , we have 26 functions of a_1 type and 16 each of b-type (b_1 and b_2) orbitals. Full details about computing the $V_{st}(r)$ potential surface at each r value are given by Gianturco and Thompson (1976).

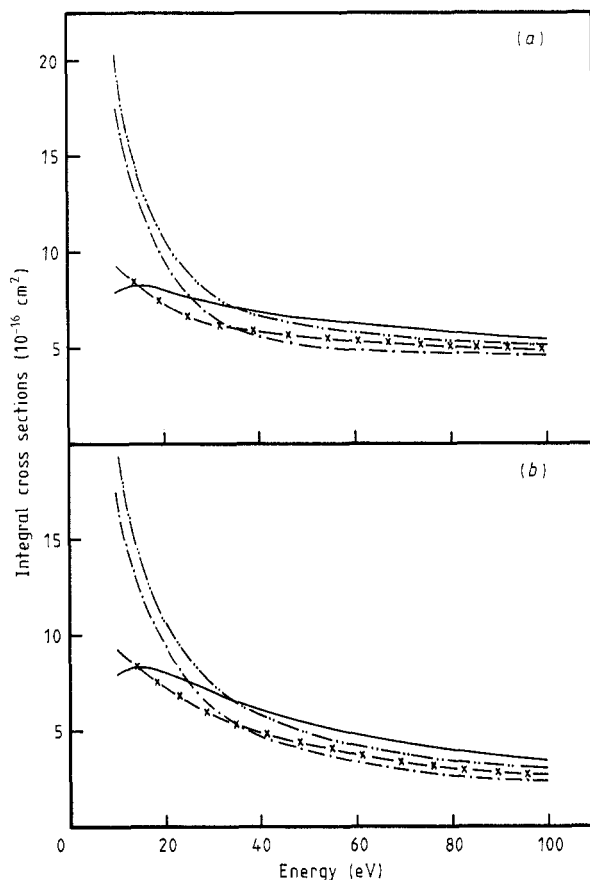


Figure 3. Total (σ_t) and integral (σ_i) cross sections for e-H₂O scattering using various models. (a) σ_i values in Sal(— · —), SPa1(— · · —), SEa1(— × —) and SEPa1(—) models; (b) σ_i values in S(— · —), SP(— · · —), SE(— × —) and SEP(—) models. For notation, see text.

In the present intermediate- and high-energy region the choice of the model-exchange interaction is not too crucial. We have employed the usual energy-dependent free-electron-gas-exchange (FEGE) approximation (see Salvini and Thompson 1981 and references therein) for $V_{ex}(r)$. For the polarisation force, we determine an energy-dependent parameter-free form

$$V_{pol}(r) = -\frac{\alpha_0 r^2}{2(r^2 + r_c^2)^3} \quad (9)$$

where the cut-off radius r_c is calculated from $r_c = \frac{3}{8}k/\Delta$. The value of α_0 for H₂O and NH₃ are taken to be 9.83 (Landolt-Bornstein 1951) and 15.0 (Bridge and Buckingham 1966) (in atomic units) respectively.

The value of the mean excitation energy (Δ) is computed from the relation, $\Delta = 2\langle\Psi_0|z^2|\Psi_0\rangle/\alpha_0$. The values of Δ for H₂O and NH₃ molecules are found to be 18.68 and 14.96 respectively. Below 100 eV, however, we have employed another parameter-free but energy-independent model for $V_{pol}(r)$: this is the so-called correlation-polarisation (CP) potential (see Gianturco *et al* 1987 and references therein; for the first application of the CP term in e-molecule studies see Padial and Norcross (1984a, b)).

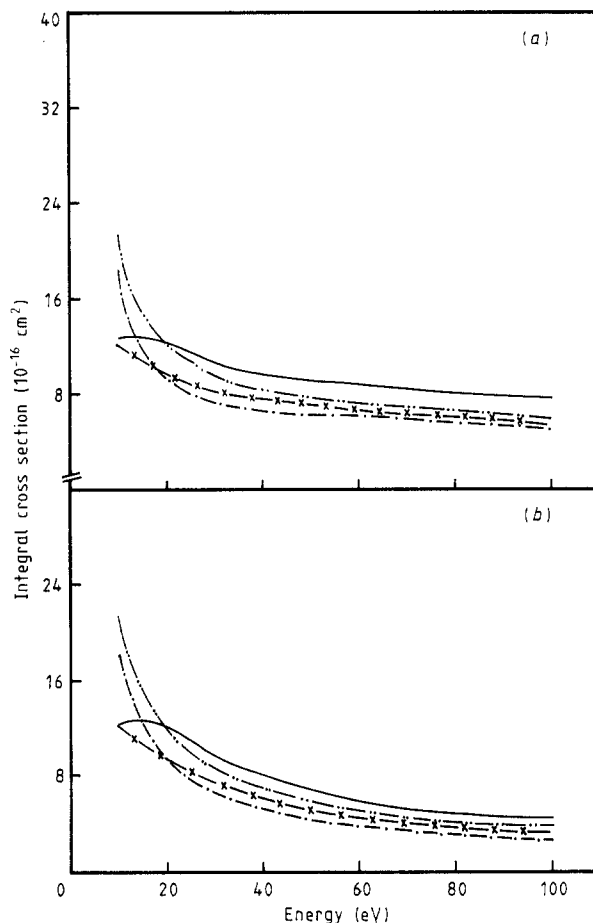


Figure 4. Same legend as in figure 3, but for e^- - NH_3 scattering.

We have compared both the polarisation potentials by calculating σ_i below 100 eV (see below). Above 100 eV, the total cross sections are not very sensitive to the choice of $V_{pol}(r)$; however, below 100 eV, the two choices for $V_{pol}(r)$ give results which differ significantly with each other particularly around 20 eV.

Finally, for the $V_{abs}(r)$, we use the quasi-free model with Pauli blocking as first discussed by Truhlar and co-workers (Staszewska *et al* 1983a, b, 1984a, b) for atomic systems and later extended by us for polyatomic molecules (Jain 1986a, b, 1987a, b). The $V_{abs}(r)$ is a function of target charge density, static-exchange potential, incident electron energy and the mean excitation energy (Δ). We found, however, for the CH_4 and SiH_4 cases that the use of a polarised electronic density ($\rho_p(r)$) in the evaluation of $V_{abs}(r)$ gives better agreement with experiment both in quality and quantity. This seems more physical since during absorption the target charge cloud is distorted significantly. In the present work, we have calculated an approximate polarised charge density function at each radial point, given by (Jain and Thompson 1983c)

$$\rho_p(r_1) = 2N \int \Psi_0 \Psi_1 dr_2 dr_3 \dots dr_N + \rho_0(r_1) \quad (10)$$

where N is the number of spin orbitals in the target with coordinates r_1, r_2, \dots, r_N

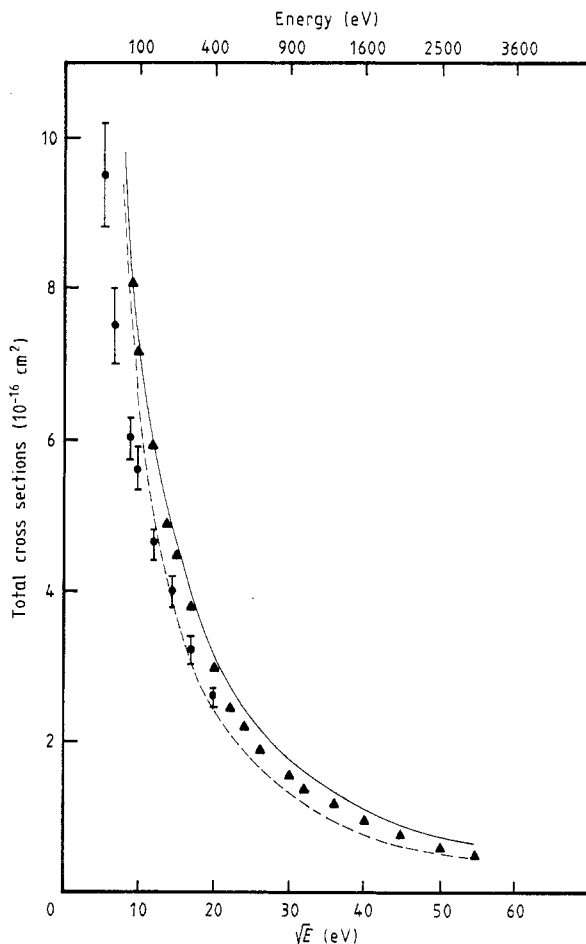


Figure 5. Total (elastic+absorption) cross sections (equation 5) for e-H₂O scattering by employing the polarisation potential of equation (9). Present calculations: full curve, SEP a1; broken curve, SEP a0. The experimental points are from Sueoka *et al* (1986) (circles) and Zecca *et al* (1987) (triangles). For notation, see text.

and Ψ_1 is the first-order wavefunction calculated approximately by the method of Pople and Shofield (1957) (for more details see Jain and Thompson 1983c). The values of $\rho_p(r)$ (not shown) are quite different from the values of $\rho_0(r)$ and, in general, $\rho_p(r) > \rho_0(r)$ at all r values. Thus the calculated V_{abs}^0 (using $\rho_0(r)$) and V_{abs}^1 (using $\rho_p(r)$) are also quite different from each other (see, for example, the CH₄ and SiH₄ cases in Jain (1986a and 1987a)).

For notation purposes, various approximations to the SCOP are abbreviated as follows: SEP(CP), static+exchange+correlation-polarisation; SEP(ED), static+exchange+energy-dependent polarisation of (9); SEP a1, SEP (with CP or ED) plus V_{abs}^1 absorption potential; SEP a0, SEP (with CP or ED) plus the V_{abs}^0 absorption potential.

3. Results and discussion

3.1. The scattering potentials for H₂O and NH₃

First we plot our $V_{opt}(r)$ for both targets in figures 1 and 2. Figure 1 displays $V_{st}(r)$,

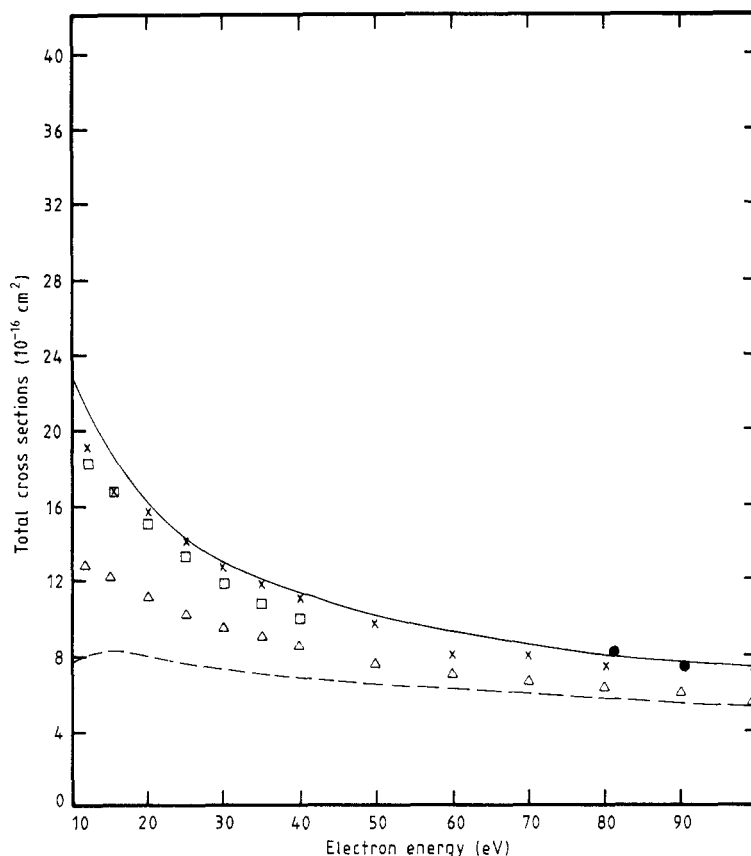


Figure 6. Total (elastic+inelastic) cross sections for e^- -H₂O collisions by using the CP potential (figure 1) at 10–100 eV. Theory: full curve, SEPai with dipole contribution via the FBA; broken curve, SEPai without dipole contribution. Experiment: Δ , Sueoka *et al* (1986); \bullet , Zecca *et al* (1987); \square , Brüche (1929); \times , Szymtkowski (1987). For notation, see text.

$V_{\text{ex}}(r)$ and $V_{\text{pol}}(r)$ (only the CP term shown) and figure 2 the $V_{\text{abs}}(r)$ at several impact energies for both the H₂O and NH₃ targets. As we see from figures 1 and 2, the optical potential is attractive throughout. Figure 2 indicates that the absorption takes place mostly near the surface of the respective molecule. At small radial distances, the short-range force, $V_{\text{st}}(r)$, dominates, while away from the molecular charge cloud the $V_{\text{pol}}(r)$ is responsible for the scattering phaseshifts and requires a large number of partial waves at higher energies. However, for these higher-order phaseshifts the polarised Born approximation (O'Mally *et al* 1961) is good enough, i.e.

$$\delta_l^{\text{Born}} = \frac{\pi \alpha k^2}{(2l+3)(2l+1)(2l-1)} \quad (11)$$

for $l > l_B$. The value of l_B is chosen in such a way that the corresponding VPA phaseshift is very close to δ_l^{Born} and the imaginary part of the phaseshift is almost negligible. Since $V_{\text{abs}}(r)$ is of short-range nature, we need only a moderate number of imaginary part of the partial waves even at the higher end of the present energy regime.

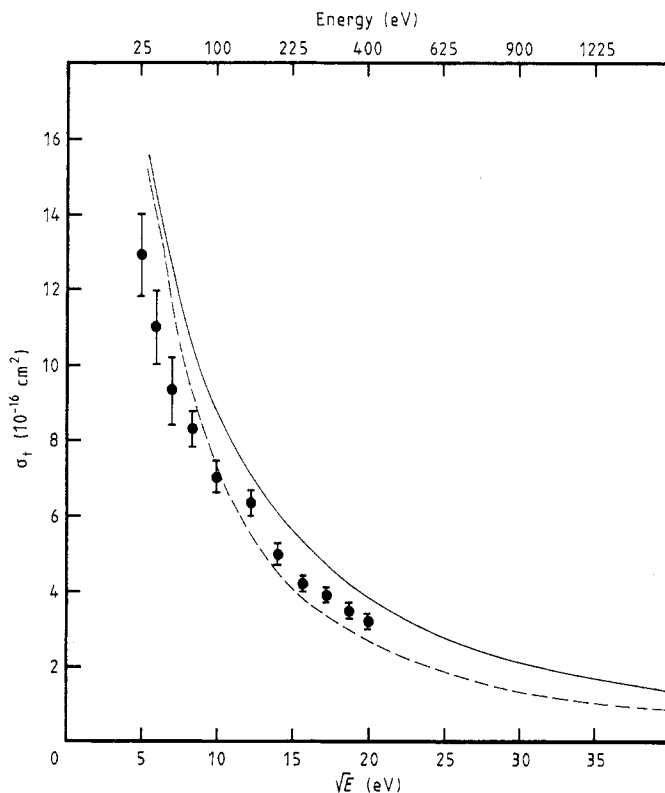


Figure 7. Same legend as for figure 5 but for the e-NH₃ case. The experimental data are from Sueoka *et al* (1987).

3.2. Total cross sections for both targets

Before we discuss our final σ_t values, we would like to point out that in the present intermediate- and high-energy region, the static term dominates over the exchange and polarisation contributions. Only at low-energy cases ($E < 20$ eV), the contributions of exchange and polarisation interactions are significant in reproducing the structures in the cross sections. In order to demonstrate the relative contributions of various optical potential terms (i.e. static, exchange, polarisation and absorption) at intermediate energies ($E \leq 100$ eV), we have shown in figure 3 the e-H₂O σ_t and σ_i cross sections using the s (static only), SE (s plus HFEGE exchange), SP (s plus CP polarisation) and SEP (SE plus CP polarisation) models. Figure 4 displays the corresponding data for the e-NH₃ case. Only at low energies ($E < 20$ eV), the exchange and polarisation interactions play important roles. In this low-energy region, the present results may not be adequate due to neglect of higher-order terms in exchange and static potentials. Above 20 eV, the contribution of both the exchange and polarisation terms seems to be constant, which is due to the fact that the CP potential is energy independent. It may be worthwhile to employ a better energy-dependent polarisation potential below 100 eV energy. Above 100 eV, therefore, we make use of an energy-dependent polarisation potential (equation (9)). Qualitatively, the behaviour and contribution of various potential terms to the total cross section is similar for both molecules, H₂O and NH₃ (see figures 3 and 4). At higher energies ($E \geq 100$ eV) the contribution of exchange

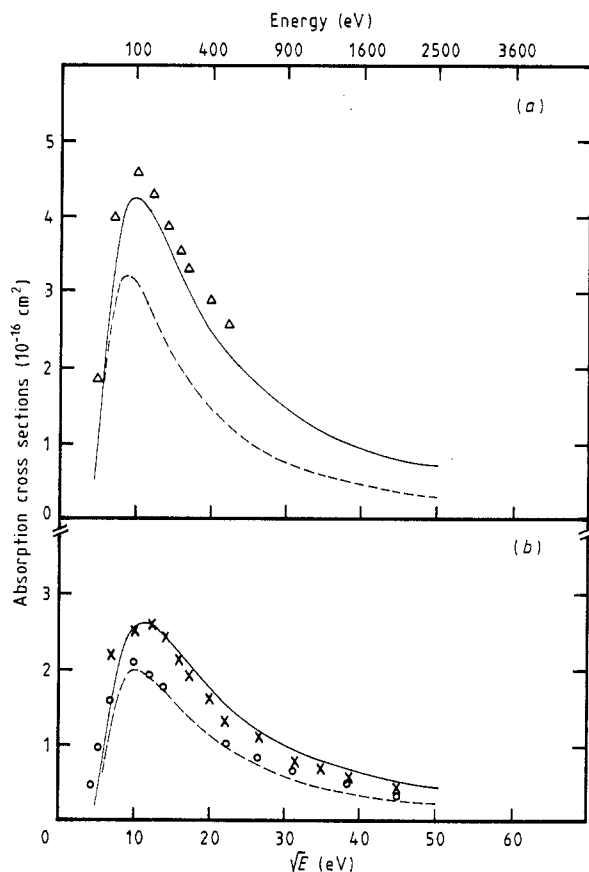


Figure 8. Absorption cross sections for (a) e - NH_3 and (b) e - H_2O scattering. Theory: full curves, SEP(ED)_{a1} model; broken curves, SEP(ED)_{a0} model. Experimental data are for the total ionisation (including dissociative ionisation) taken from: Δ , for NH_3 , Orient and Srivastava (1987a); \times , for H_2O , Bolorizadeh and Rudd (1986); \circ , for H_2O , Schutten *et al* (1966).

and polarisation interactions to the integral cross section is not important. In table 1 we have given σ_i values for both the targets using s , SE , $SP(ED)$ and $SEP(ED)$ approximations. At 1000 eV, for example, the static potential contributes about 96% to the integral cross section, while at 200 eV, the contribution of exchange and polarisation terms is about 20%.

We now discuss our σ_i values and compare them with measured data for both the molecules H_2O and NH_3 in figures 5–7. Figure 5 shows the present σ_i calculations in the SEP(ED)_{a1} and SEP(ED)_{a0} models (i.e. using polarisation potential of (9)) along with experimental points of Sueoka *et al* (1986) and Zecca *et al* (1987) on a linear scale over the 100–3000 eV range. In this energy region our calculated cross sections agree very well with the measurements of Zecca *et al* within the experimental error bars (not shown). Although it is quite difficult to judge from figure 5 which model (SEP_{a1} or SEP_{a0}) is better, we, however, recommend from our previous experience that the SEP_{a1} model is better than the SEP_{a0} model. The experimental data of Sueoka *et al* (1986) are given up to an energy of 400 eV only and lie significantly lower than the measurements of Zecca *et al*. Below 100 eV also, the measurements of Sueoka *et al* (1986) are smaller than all other measured cross sections (figure 6). In figure 6, we have plotted

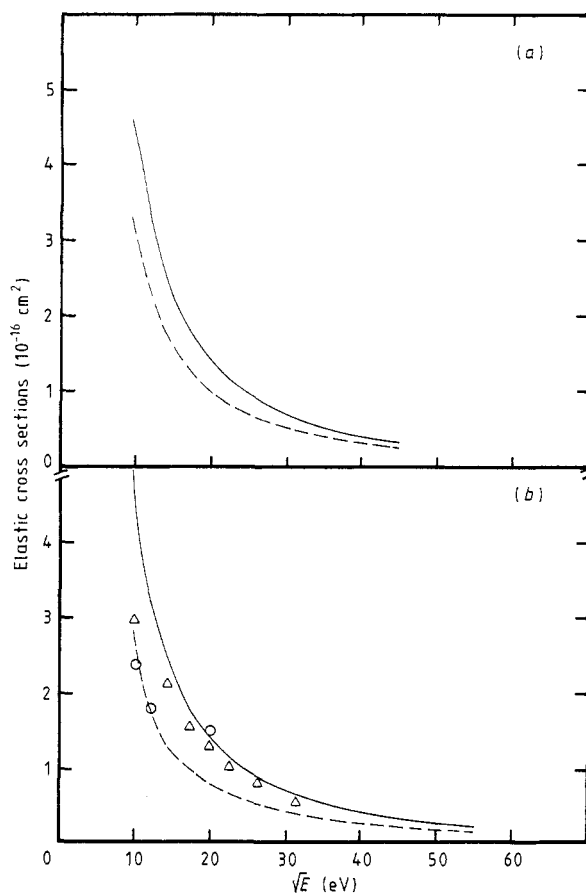


Figure 9. Elastic integral cross sections with absorption effects in the SEP(ED)a1 model for (a) e-NH₃ and (b) e-H₂O cases. Theoretical results are shown by full (with dipole contribution via FBA) and broken (without dipole contribution) curves. For H₂O, the experimental points are taken from Danjo and Nishimura (1985) (open circles) and Katase *et al* (1986) (open triangles). For notation, see text.

SEP(CP)a1 (using CP polarisation) σ_i results at 10–100 eV along with the experimental cross sections due to Sueoka *et al* (1986), Zecca *et al* (1987), Brüche (1929) and Szmytkowski (1987). Also shown in figure 6 are our SEP(CP)a1 total cross sections without the dipole FBA term (broken curve). We see that the dipole interaction is important in this energy region. Our best agreement is seen with the measurements of Szmytkowski (1987), Brüche (1929) and Zecca *et al* (1987). Here too, the measured values of Sueoka *et al* (1986) are much smaller than the other experimental studies. This good agreement between our parameter-free calculations and several sets of experimental investigations is remarkable. Although we cannot expect too much success with this simple model in the present energy region (figure 6), nevertheless it seems to work surprisingly well even around 20 eV.

Figure 7 illustrates our total cross sections for the e-NH₃ system along with the measurements of Sueoka *et al* (1987). Here the measurements seem to agree with our SEP(ED)a0 model: however, from the previous experience of H₂O results (figures 5 and 6) it may be assumed that the measurements of Sueoka *et al* give somewhat smaller values of the σ_i ; therefore, we still believe that our SEP a1 curve (figure 7) is more

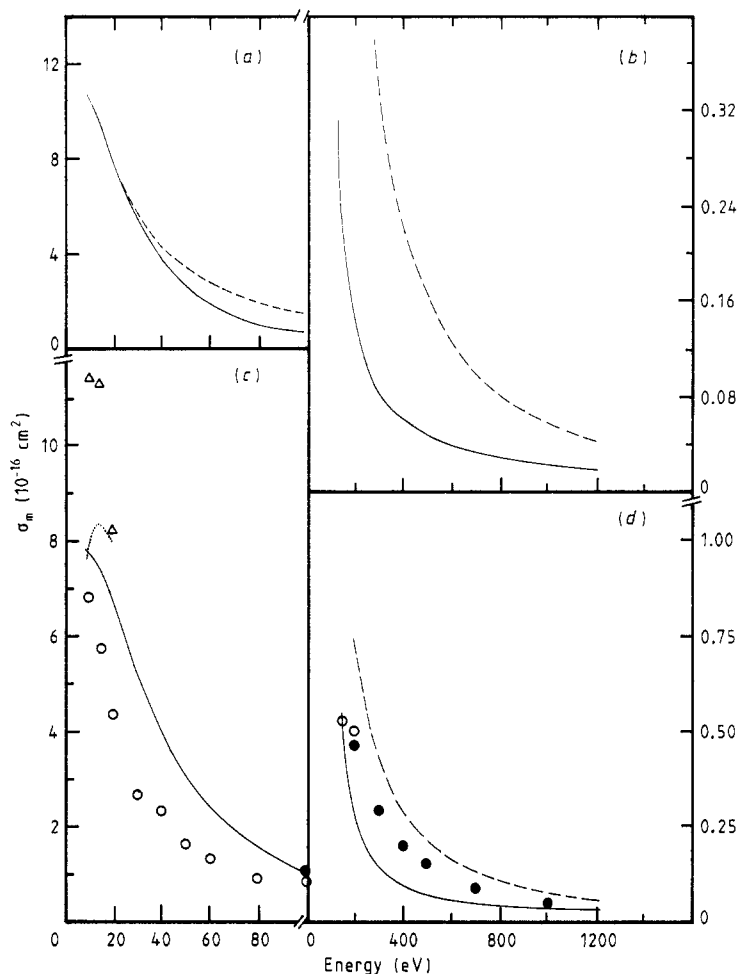


Figure 10. Momentum transfer cross sections for (a)–(b) e^- - NH_3 and (c)–(d) e^- - H_2O collisions from 10 to 1200 eV. Theory: full curves, SEP(ED)a1 approximation; broken curves, SEP(ED) model. For (c) H_2O only, the measured data are due to Danjo and Nishimura (1985) (open circles), Katase *et al* (1986) (full circles) and Shyn and Cho (1987) (open triangles). The dotted curves (up to 20 eV only) are the static-exchange calculations of Brescansin *et al* (1986). For notation, see text.

reliable and accurate than the corresponding SEP_{a0} numbers. Unfortunately there are no other data (experimental or theoretical) available at this time for ammonia to further assess the accuracy of our SEP_{a1} results of figure 7.

3.3. Absorption cross sections for both the NH_3 and H_2O molecules

In this SCOP approach we also obtain information on the absorption (all inelastic channels energetically possible in this energy region) cross sections. At intermediate energies (from threshold to up to about 200 eV) the dominant inelastic channels for electron–molecule collisions are the ionisation (direct and dissociative) and dissociation of the molecule. There are many laboratory studies on the total ionisation of ammonia (see Djuric-Preger *et al* 1976, Mark *et al* 1977, Crowe and McConkey 1977, Bedersi

Table 1. Integral (σ_i) cross sections for e-H₂O and e-NH₃ collisions using pure static (S), static+exchange (SE), static+polarisation (SP) and static+exchange+polarisation (SEP) models at 200–1000 eV. Note that the contribution from the dipole term is not included. All quantities are in units of 10⁻¹⁶ cm².

Energy (eV)	S	SE	SP	SEP
e-NH ₃				
200	1.75	1.94	1.92	2.112
300	1.36	1.46	1.42	1.522
400	1.12	1.19	1.15	1.217
500	0.954	1.00	0.97	1.02
600	0.834	0.872	0.845	0.884
800	0.668	0.693	0.673	0.698
1000	0.557	0.575	0.56	0.578
e-H ₂ O				
200	1.53	1.69	1.69	1.88
300	1.21	1.29	1.27	1.37
400	1.01	1.05	1.04	1.11
500	0.87	0.90	0.89	0.94
600	0.77	0.79	0.78	0.82
800	0.63	0.64	0.63	0.66
1000	0.53	0.54	0.53	0.55

et al 1980, DeMaria *et al* 1963, Melten 1966, Lampe *et al* 1957, Brion *et al* 1977, Gomet 1975) and water (Schutten *et al* 1966, Mark and Egger 1976, Bolorizadeh and Rudd 1986, Orient and Srivastava 1985, 1987a) molecules by electron impact from threshold to a few thousand eV. Semi-empirical calculations in the Born approximation have been carried out for the total ionisation cross sections of NH₃ and H₂O molecules from ionisation threshold to 10 keV by Khare and Meath (1987) (and references therein for earlier calculations). Figure 8 displays our σ_{abs} cross sections for both the molecules at 20–2500 eV. We have shown only the recent experimental data on the total ionisation cross sections from Orient and Srivastava (1987b) (for NH₃), Bolorizadeh and Rudd (1986) and Schutten *et al* (1966) (for H₂O) in figure 8. It is clear from figure 8 that the present σ_{abs} results are in very good accord both in quality and quantity with all these recent measurements. Note that the other channels, like the electronic and vibrational excitation, are very small in this energy range to make any sizeable contribution to the σ_i . Only the $\Delta J = 1$ rotational transition process is significant which we consider only approximately. The σ_{abs} are not sensitive to the choice of polarisation or exchange potentials in the real part of $V_{\text{abs}}(r)$. In particular, the peaking structure around 100 eV is reproduced remarkably well in our σ_{abs} values for both the NH₃ and H₂O targets. It is, however, possible to vary the mean excitation energy (Δ) in the evaluation of $V_{\text{abs}}(r)$ to improve present values of σ_{abs} (and therefore σ_i also). This is not done for obvious reasons.

We note that the ammonia cross sections are larger throughout than the corresponding water molecule cross sections (figure 8). This is true also for elastic and total cross sections i.e.

$$\sigma_{\text{el}}(\text{NH}_3) > \sigma_{\text{el}}(\text{H}_2\text{O}) \quad \sigma_{\text{abs}}(\text{NH}_3) > \sigma_{\text{abs}}(\text{H}_2\text{O})$$

and

$$\sigma_i(\text{NH}_3) > \sigma_i(\text{H}_2\text{O}).$$

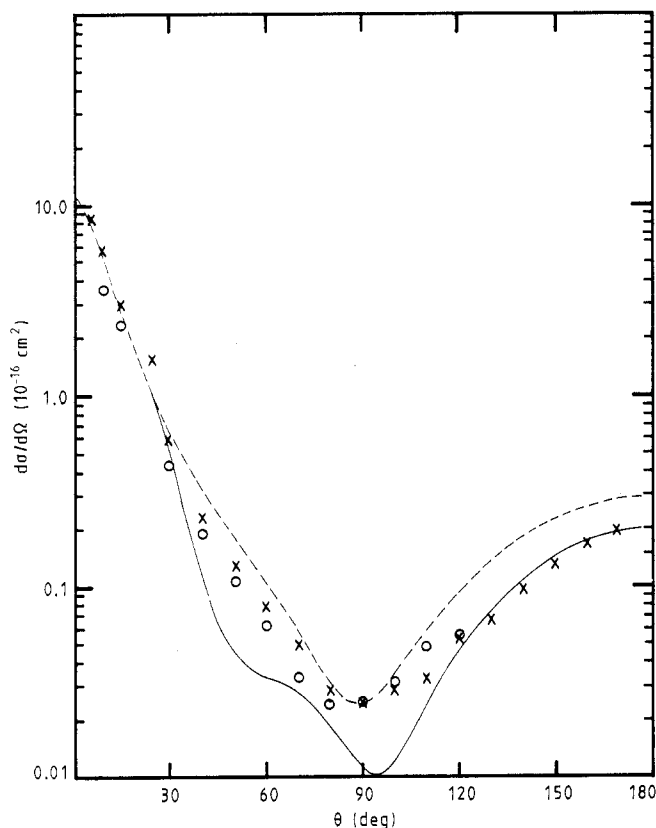


Figure 11. The differential cross sections for e^- -H₂O scattering at 100 eV. Present theory: full curve, SEP(CP)a1 (with absorption); broken curve, SEP(CP) (without absorption). Experiments: ○, Danjo and Nishimura (1985); ×, Katase *et al* (1986).

The direct ionisation cross sections in ammonia are expected to be closer to (or a little larger than) the corresponding H₂O cross sections (the ionisation potentials (IP) of NH₃ and H₂O are 10.15 and 12.61 eV respectively). However, the dissociative ionisation (which is the next dominant process after direct ionisation) producing NH₂⁺ ions in e^- -NH₃ collisions is much larger (by a factor of 2–3) than the corresponding dissociative ionisation channel in H₂O producing OH⁺ ions (for example, dissociation energy for H–NH₂ and H–OH fragments are respectively 4.3 and 5.113 eV; also the IP of NH₂ (11.4 eV) is smaller than the IP of the OH radical). For the σ_{el} , we can roughly expect that the NH₃ may have higher values due to its larger bond length and polarisability than the water molecule. However, at certain lower energies, H₂O cross sections may be larger than the corresponding NH₃ ones due to its (H₂O) higher dipole moment value. It is interesting to note that the other isoelectronic molecule CH₄ has higher cross sections (σ_t , σ_{el} , σ_{abs}) relative to the H₂O and NH₃ values. The CH₄ molecule has larger values for bond length and the polarisability than the corresponding values for either H₂O or NH₃.

3.4. Elastic (reduced) and momentum transfer cross sections

With the inclusion of absorption effects, the usual elastic (DCS and consequently the σ_{el} and momentum transfer (σ_m)) cross sections are reduced by a significant amount.

This reduction produces pronounced structure in the DCS (see Jain 1986a, 1987a). Very recently Joachain and Potvliege (1987) have computed reduced DCS for positron-argon scattering and compared them with the elastic DCS measurements: since the measured data were not absolute, it is not clear whether one should compare the usual DCS (without absorption effects) or the reduced DCS with experimental elastic differential cross sections. In the past, however, for electron scattering where absolute experimental DCS are available for comparison, the usual DCS are compared with the measurements rather than the reduced DCS. Here, first we discuss both the σ_{el} results (i.e. with and without absorption effects) and compare them with several experimental data on the elastic scattering of the e-H₂O system (for e-NH₃, there are no data known to us on the DCS, σ_{el} or σ_m quantities).

Figure 9 shows our reduced σ_{el} values in SEP(ED)a1 (full curves) and SEP(ED)a0 (broken curves) for both molecules considered here. For the H₂O case, we have experimental values from Danjo and Nishimura (1985) and Katase *et al* (1986) for comparison. Note that the experimental points are obtained by the integration of measured DCS after extrapolating towards zero and 180°; this procedure always involves a certain amount of error. However, there is good agreement between theory and experiment (figure 9). Note that the inclusion of dipole effects improves the SCOP calculations at all impact energies considered in this work. Our σ_{el} cross sections without absorption effects are also shown in this figure; this gives us an idea of the reduction in σ_{el} values due to absorption effects.

Our σ_m cross sections for both the molecules are exhibited in figure 10 with and without absorption interaction. For the water molecule, we have several experimental data for comparison. Here again the experimental DCS have to be extrapolated to obtain σ_m cross sections. Note a large difference (almost by a factor of two) at 20 eV between the experimental values of Shyn and Cho (1987) and Danjo and Nishimura (1985). The absorption channel has a large effect on the calculated σ_m results. It is very difficult to draw any conclusion from figure 10 about which theoretical curve (full curve with absorption and broken curve without absorption) is close to the measured momentum transfer cross sections. This, however, can be inferred from a comparison of measured DCS values with that of our angular distributions with and without absorption effects. This is displayed in figure 11 at only one energy of 100 eV. The reason for choosing this energy is obvious since there is some structure (at middle angles) in the DCS at this energy (at $E > 100$ eV the DCS are almost structureless) and below 100 eV the present model is relatively less accurate. Except at small angles ($\theta < 30^\circ$, where absorption has apparently no effect on the DCS) the DCS are decreased significantly with the inclusion of absorption. It seems that in backward scattering, the absorption effects improve the DCS; however, the agreement of the reduced DCS with the experimental absolute DCS is only satisfactory (figure 11). Note that we have not included the FBA DCS in figure 11. If one includes the contribution of non-spherical interaction terms into the DCS curves of figure 11 in an accurate manner, it is possible that the agreement between the full curve and the experimental data points (figure 11) will improve. We may therefore argue that the absorption effects are important in the calculation of elastic DCS as also noted by Joachain and Potvliege (1987) regarding their positron-Ar calculations.

Finally, we summarise our σ_t results for H₂O and NH₃ molecules in tables 2 and 3 respectively. In these tables we have shown our σ_t in all the four (SEP(CP)a1, SEP(CP)a0, SEP(ED)a1 and SEP(ED)a0) models including several sets of experimental data between 10–3000 eV. We recommend the SEP(CP)a1 model below 100 eV and SEP(ED)a1 model above this energy. The FBA term is included in all these values (tables 2 and 3).

Table 2. Total (elastic + inelastic) cross sections for e-H₂O scattering in units of 10^{-16} cm². Note that all SEP_{a1} and SEP_{a0} results include the FBA term. For notation, see text.

Present calculations									
Energy (eV)	CP potential (see figure 1)		Polarisation of equation (9)		FBA ^a	Experimental data			
	SEP _{a1}	SEP _{a0}	SEP _{a1}	SEP _{a0}		b	c	d	e
10	23.18	23.18	25.43	25.43	15.3	12.7	—	20.9	18.1
15	18.93	18.93	30.16	30.16	10.7	12.3	—	—	15.0
20	16.24	16.24	24.42	24.42	8.3	11.3	—	15.7	15.0
30	13.08	13.00	15.55	15.48	5.7	9.5	—	12.7	11.9
40	11.30	11.10	12.98	12.79	4.4	8.5	—	11.0	10.0
50	10.13	9.81	11.40	11.07	3.6	7.5	—	9.7	—
60	9.30	8.86	10.20	9.73	3.1	7.1	—	8.2	—
80	8.14	7.53	8.51	7.89	2.4	6.3	8.17	7.5	—
100	7.71	6.63	7.43	6.71	1.9	5.6	7.19	—	—
150	6.01	5.17	5.89	5.04	1.3	4.6	5.80	—	—
200	5.13	4.24	4.98	4.07	1.0	4.0	4.86	—	—
300	4.00	3.20	3.86	3.03	0.7	3.20	3.62	—	—
400	3.30	2.60	3.17	2.45	0.54	2.6	2.97	—	—
500	2.83	2.21	2.71	2.07	0.44	—	2.48	—	—
600	2.48	1.92	2.38	1.80	0.37	—	2.12	—	—
800	2.01	1.54	1.92	1.44	0.28	—	1.72	—	—
1000	1.69	1.29	1.61	1.20	0.23	—	1.42	—	—
1200	1.46	1.11	1.40	1.03	0.19	—	1.20	—	—
1500	1.22	0.92	1.17	0.86	0.16	—	1.00	—	—
2000	0.96	0.72	0.92	0.67	0.12	—	0.75	—	—
2500	0.79	0.59	0.76	0.55	0.10	0.60	—	—	—
3000	0.68	0.58	0.65	0.47	0.08	0.49	—	—	—

^a Dipole contribution to the σ_t in the first Born approximation.

^b Sueoka *et al* (1986).

^c Zecca *et al* (1987).

^d Szmytkowski (1987).

^e Brüche (1929).

4. Conclusion

We reported first calculations on the total (elastic + absorption) cross sections for e-NH₃ and e-H₂O scattering over a wide energy range 10–3000 eV. These cross sections are obtained in a partial-wave-decomposition scheme by using the semi-empirical (but parameter-free) local spherical complex optical potential for the electron-molecule system. There is no adjustable parameter in the present reported results. The effect of anisotropic interaction terms is included crudely only via the dipole potential in the FBA theory. Above 100 eV, the contribution of the higher-order optical potential terms (non-spherical) to the σ_t is very small. Also the exchange and polarisation effects are not important above 200 eV energy. We also found that the first Born limit is not reached at the highest energy point (3 keV) of this work. Our final σ_t , σ_{abs} and σ_{el} cross sections compare very well with the available experimental results at all energies considered here. In general, the e-NH₃ cross sections are larger than the corresponding e-H₂O values. It is also observed that the absorption effects are important in the

Table 3. Same legend as table 2, but for e-NH₃ scattering. Note that the SEPa1 and SEPao results include the FBA term. For notation, see text.

Present calculations						
Energy (eV)	CP potential (see figure 1)		Polarisation of equation (9)			Experimental data Sueoka <i>et al</i> (1987)
	SEPa1	SEPa0	SEPa1	SEPa0	FBA	
10	22.80	22.80	23.69	23.69	10.21	17.5+1.5
15	19.77	19.76	24.45	24.45	7.09	16.0+1.5
20	17.42	17.38	22.12	22.04	5.47	14.2+1.3
30	14.45	14.20	17.01	16.82	3.79	12.1+1.0
40	12.73	12.24	14.70	14.23	2.92	10.5+1.0
50	11.63	10.91	12.94	12.19	2.38	9.3+0.9
60	10.86	9.94	11.62	10.66	2.02	8.8+0.6
80	9.76	8.53	9.91	8.66	1.55	7.9+0.5
100	8.93	7.50	8.83	7.40	1.26	7.0+0.4
150	7.40	5.78	7.18	5.52	0.87	5.6+0.3
200	6.33	4.78	6.11	4.50	0.67	5.0+0.3
300	4.94	3.60	4.74	3.35	0.46	3.9+0.2
400	4.09	2.92	3.91	2.70	0.35	3.2+0.2
500	3.51	2.47	3.35	2.27	0.287	
600	3.08	2.14	2.94	1.97	0.24	
800	2.48	1.70	2.37	1.56	0.185	
1000	2.09	1.41	1.99	1.30	0.15	
1500	1.50	1.00	1.43	0.92	0.103	
2000	1.17	0.78	1.11	0.71	0.079	
2500	0.96	0.64	0.91	0.58	0.064	
3000	0.82	0.44	0.78	0.49	0.054	

distribution of angular functions for elastic scattering. The present approach has been proved to be quite successful for positron scattering with H₂O and NH₃ targets above 100 eV impact energy (Jain 1987c).

Acknowledgments

These calculations were performed on the VAX/750 machine at the Physics Department, Kansas State University. I am thankful to Drs O Sueoka and S K Srivastava for sending their e-NH₃ experimental data prior to publication. Finally, I thank one of the referees for making some important suggestions.

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