

## Vibrationally elastic cross sections for electron scattering from water molecules

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Received 24 July 1992, in final form 17 November 1992

**Abstract.** Differential, integral and momentum transfer cross sections are calculated for the vibrationally elastic scattering of electrons from  $\text{H}_2\text{O}$ . An *ab initio* static potential is used for the interaction. Effects of electron exchange and target polarization are taken into account approximately. In particular, the contribution from the dipole potential is evaluated carefully so that an accurate cross section is obtained for the forward scattering. Calculations are carried out for electron energies of 6–50 eV and a detailed comparison is made with experimental data. The differential and momentum transfer cross sections calculated are in good agreement with experimental results. The theoretical value of the integral cross section deviates greatly from the measured one. It is suggested that this discrepancy comes from an insufficient extrapolation of the measured differential cross section to the forward direction, where the cross section increases very steeply. It is also pointed out that the measurement of the total scattering cross section suffers from a similar problem, i.e., an insufficient correction for the small-angle scattering.

### 1. Introduction

An electron collision with water molecules is a fundamental process in various fields such as radiation physics and chemistry, atmospheric physics and astrophysics. For instance, two recent papers, one on radiation physics (Ishii *et al* 1990) and the other a research on the cometary ionosphere (Korosmezey *et al* 1987), studied the behaviour of electrons in  $\text{H}_2\text{O}$  gas on the basis of knowledge of the cross section for the  $\text{e} + \text{H}_2\text{O}$  collision. A water molecule, furthermore, has often been chosen as a representative target in the theory of electron collisions with polyatomic molecules, which are characterized by a multicentre nature and a long-range force due to a dipole or other multipole moment. In the present paper, an elastic scattering (more strictly, a vibrationally elastic scattering, because it is difficult to experimentally resolve rotational transitions) is studied extensively with a theoretical method. The study is concentrated mainly in the region of collision energies below 50 eV.

Differential cross sections (DCS) for the elastic scattering have been measured several times (Jung *et al* 1982, Danjo and Nishimura 1985, Katase *et al* 1986, Shyn and Cho 1987, Johnstone and Newell 1991). The most recent paper by Johnstone and Newell (1991) gives a detailed comparison of their own data with other measurements. General agreement among the experimental data is qualitatively good, but there are some quantitative disagreements. Owing to the experimental difficulty, the DCS has only been measured for angles neither smaller than  $5^\circ$  nor larger than  $150^\circ$ . To obtain experimental values of the integral cross section, an extrapolation procedure must be resorted to. This introduces a rather large uncertainty. It is desirable, therefore, to have a reliable theoretical DCS, particularly for the forward and the backward scattering.

Several theoretical studies have already been reported on the elastic scattering of electrons from H<sub>2</sub>O (Brescansin *et al* 1986, Gianturco and Scialla 1987, Jain 1988, Sato *et al* 1988, Gianturco 1991, Yuan and Zhang 1992). These theoretical cross sections, except for the most recent one by Yuan and Zhang, are compared by Johnstone and Newell (1991) with experimental ones. The results of the calculations of Brescansin *et al* (1986) and Sato *et al* (1988) are in general agreement with experiment. Neither of the calculations, however, takes into account the effect of the target polarization. Furthermore, in some particular cases, the two calculations disagree very greatly with each other. Gianturco and co-workers (Gianturco and Scialla 1987, Gianturco 1991) included the polarization effect in their calculation. Their result agrees with the experimental values at scattering angles smaller than 60°. For angles larger than that, their DCS deviates greatly from the measured one. (Johnstone and Newell compared their data with the value of the Gianturco group in their older paper (Gianturco and Scialla 1987), but, even if a comparison were to be made with the newer one (Gianturco 1991), the conclusion should not be changed.) Jain (1988) also calculated the elastic cross section. He first calculates the cross section taking only the spherical part of the potential and then simply adds to that the contribution from the anisotropic dipole interaction using the Born approximation. He does not show any DCS except at 100 eV, where no dipole contribution is added. Very recently Yuan and Zhang (1992) reported their calculation, which is based on a procedure similar to Jain's and carried out in a lower energy region (0.5–20 eV). They showed the importance of the polarization potential at the lower energies (<10 eV), particularly in small-angle scattering. Their result, however, does not agree with the experimental data at angles larger than 30°.

In the present work a more detailed theoretical study is made of the process. The target molecule is described by an *ab initio* multicentred wavefunction and account is taken of the effects of the electron exchange and the target polarization. Differential cross sections are calculated for energies from 6 to 50 eV and compared with the corresponding experimental data. The effect of the anisotropy of the potential is made clear by comparing with the spherical-potential model. In particular, the dipole interaction is treated so carefully that an accurate value of the DCS is obtained in the forward direction. In terms of the resulting DCS, the correction for the forward scattering is re-examined for the previous experimental data on the elastic integral cross section and the total scattering cross section.

## 2. Theory

We consider the scattering of an electron from a molecule in the fixed-nuclei approximation. The general theory of the scattering has been presented many times before (e.g., see a review by Gianturco and Jain 1986). In the following a brief outline of the theory is given according to the paper by Burke *et al* (1972). In the case of a polar molecule, the partial-wave expansion of the cross section diverges in the fixed-nuclei approximation. A procedure to circumvent this problem is also described in this section.

In order to take into account the molecular symmetry, a symmetry-adapted angular basis function is introduced as

$$X_l^{sh}(\hat{r}) = \sum_{\mu} b_{l\mu}^{sh} Y_{l\mu}(\hat{r}). \quad (1)$$

Here  $s$  denotes the particular irreducible representation (i.e., in the case of H<sub>2</sub>O,  $s = A_1, A_2, B_1$  or  $B_2$ ) and  $h$  distinguishes the different bases with the same ( $s, l$ ). The coefficient

$b_{l\mu}^{sh}$  for the  $C_{2v}$  symmetry is given by Burke *et al* (1972). With the use of these basis functions, the wavefunction of the scattered electron is expanded as

$$F(\mathbf{r}) = \sum_{l\nu} r^{-1} f_{l\nu}(r) X_l^\nu(\hat{\mathbf{r}}) \quad (2)$$

where the index  $\nu$  represents ( $sh$ ) collectively. The radial part of the wavefunction satisfies the equation (atomic units being used in the present paper unless otherwise stated)

$$\left( \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2 \right) f_{l\nu}(r) = 2 \sum_{l'\nu'} \langle l\nu | V | l'\nu' \rangle f_{l'\nu'}(r). \quad (3)$$

Here it has been assumed that electron exchange is taken into account by a local potential, which is included in the interaction potential  $V$  (see (12)). The matrix element of  $V$  is given by

$$\langle l\nu | V | l'\nu' \rangle = \int d\hat{\mathbf{r}} X_l^\nu(\hat{\mathbf{r}})^* V X_{l'}^{\nu'}(\hat{\mathbf{r}}). \quad (4)$$

We solve equation (3) with the boundary condition

$$f_{l\nu}^{l\nu}(r) \xrightarrow{r \rightarrow \infty} k^{-1/2} \{ \delta_{l\nu} \delta_{\nu\nu'} \exp[-i(kr - \frac{1}{2}l'\pi)] - S_{l\nu}^{l\nu'} \exp[i(kr - \frac{1}{2}l'\pi)] \}. \quad (5)$$

The differential cross section is obtained in the form

$$q = \sum_L A_L P_L(\cos \theta) \quad (6)$$

where  $P_L$  is the Legendre function and

$$\begin{aligned} A_L = & \frac{1}{4k^2} (2L+1) \sum_{l\nu} \sum_{l'\nu'} \sum_{l_1\nu_1} \sum_{l'_1\nu'_1} \sum_{\mu\mu'} \sum_{\mu_1\mu'_1} i^{l-l'-l_1+l'_1} (-1)^{\mu+\mu'} \\ & \times [(2l+1)(2l'+1)(2l_1+1)(2l'_1+1)]^{1/2} \\ & \times \begin{pmatrix} l & l_1 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l'_1 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l_1 & L \\ \mu & -\mu_1 & m \end{pmatrix} \begin{pmatrix} l' & l'_1 & L \\ \mu' & -\mu'_1 & m \end{pmatrix} \\ & \times (b_{l'\mu'}^{\nu'} b_{l\mu}^{\nu*} T_{l'\nu'}^{l\nu}) (b_{l'_1\mu'_1}^{\nu'_1} b_{l_1\mu_1}^{\nu_1*} T_{l'_1\nu'_1}^{l_1\nu_1})^*. \end{aligned} \quad (7)$$

Here the  $T$  matrix is defined by

$$T_{l'\nu'}^{l\nu} = \delta_{l\nu} \delta_{\nu\nu'} - S_{l'\nu'}^{l\nu}. \quad (8)$$

The integral cross section is given by

$$Q = (\pi/k^2) \sum_{l\nu} \sum_{l'\nu'} |T_{l'\nu'}^{l\nu}|^2. \quad (9)$$

It should be noted that the present cross sections,  $q$  and  $Q$ , correspond to the vibrationally elastic (i.e., summed over the final rotational states) ones. In the fixed-nuclei approximation, those cross sections are independent of the initial rotational state.

In the present calculation, the interaction potential is composed of three terms: static ( $V^{\text{st}}$ ), exchange ( $V^{\text{ex}}$ ), and polarization ( $V^{\text{pol}}$ ) potentials. The static potential is obtained from the charge density  $\rho$  of the target molecule as

$$V^{\text{st}}(\mathbf{r}) = - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (10)$$

The charge density can be expressed in the form

$$\rho(r) = -\rho_e(r) + \rho_N(r) \quad (11)$$

where  $\rho_e$  is the electron density of the molecule and  $\rho_N$  is the contribution from the nuclear charge.

Various models have been proposed for the local exchange potential (e.g., see Gianturco and Jain 1986), but no definite conclusion has yet been drawn about which of them should be the best. We employ here one of the simplest models: the Hara version of the free electron gas model (Hara 1967). That is

$$V^{\text{ex}}(r) = -\frac{2}{\pi} k_F(r) \left( \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right) \quad (12)$$

where

$$\eta(r) = (k^2 + 2I + k_F^2)^{1/2} / k_F \quad (13)$$

$$k_F(r) = [3\pi^2 \rho_e(r)]^{1/3}. \quad (14)$$

In equation (13),  $I$  is the ionization potential of the molecule.

The effect of the target polarization is considered through the parameter-free correlation-polarization model (Padial and Norcross 1984, Gianturco *et al* 1987). In this model, the long-range asymptotic form of the polarization potential is matched to the short-range correlation interaction. The latter is calculated from the electron density with the local density approximation of electron gas. The detailed form of the short-range correlation interaction is given by Padial and Norcross (1984). This model has been applied to many calculations of electron-molecule collisions (e.g., Morrison and Saha 1986, Malegat and Le Dourneuf 1988, Gianturco 1991, Jain and Norcross 1992, Yuang and Zhang 1992).

To evaluate the interaction matrix element in (4), all the potential terms are expanded as

$$V(r) = \sum_{\lambda\nu} V_{\lambda\nu}(r) X_{\lambda}^{\nu}(\hat{r}). \quad (15)$$

In the case of polar molecules, the partial wave expansion of the cross section does not converge, if the fixed-nuclei approximation is applied as it stands. To remedy this difficulty, we use the following closure formula instead (Gianturco and Scialla 1987)

$$q = q^B + \sum_L (A_L - A_L^B) P_L(\cos \theta). \quad (16)$$

Here the superscript B denotes the quantity calculated in the Born approximation with an electron-point-dipole interaction. The summation over  $L$  in (16) converges rapidly, because the contribution from the higher partial waves to  $A_L$  is dominated by the electron-dipole interaction and can be calculated in the Born approximation. Thus we can evaluate the second term in (16) in the fixed-nuclei approximation as described above and have a result independent of the initial rotational state. The first term in (16) is calculated with the formula

$$q^B = \sum_{j'\tau'} q_{\text{rot}}^B(j\tau \rightarrow j'\tau'). \quad (17)$$

Here  $(j\tau)$  denotes the rotational state of  $\text{H}_2\text{O}$  and  $q_{\text{rot}}^B(j\tau \rightarrow j'\tau')$  is the Born DCS for the rotational transition  $j\tau \rightarrow j'\tau'$  calculated with a point-dipole interaction. This has

the form (Itikawa 1972)

$$q_{\text{rot}}^{\text{B}}(j\tau \rightarrow j'\tau') = \frac{4}{3} \frac{k'}{k} (2j' + 1) \mu^2 |\langle j'\tau' | j\tau \rangle_{100}|^2 (k^2 + k'^2 - 2kk' \cos \theta)^{-1} \quad (18)$$

where  $k$  and  $k'$  are the wavenumbers of the incident and the scattered electrons and  $\mu^2 |\langle j'\tau' | j\tau \rangle_{100}|^2$  is the squared dipole transition moment.

The integral cross section is calculated similarly by

$$Q = Q^{\text{B}} + 4\pi(A_0 - A_0^{\text{B}}) \quad (19)$$

with

$$Q^{\text{B}} = \sum_{j'\tau'} Q_{\text{rot}}^{\text{B}}(j\tau \rightarrow j'\tau') \quad (20)$$

and the Born cross section (Itikawa 1972)

$$Q_{\text{rot}}^{\text{B}}(j\tau \rightarrow j'\tau') = \frac{8\pi}{3} (2j' + 1) \mu^2 |\langle j'\tau' | j\tau \rangle_{100}|^2 \frac{1}{k^2} \ln \left| \frac{k + k'}{k - k'} \right|. \quad (21)$$

It should be noted that  $q^{\text{B}}$  and  $Q^{\text{B}}$  depend on the initial rotational state ( $j\tau$ ) and hence  $q$  and  $Q$  also do. The formulae (16) and (19) can be regarded also as a correction to the Born approximation, which is expected to work well for a polar molecule. Clark (1977) discussed this point in the case of diatomic molecules.

### 3. Numerical calculation

First we need the electron density of the target molecule to evaluate the potential terms,  $V^{\text{st}}$ ,  $V^{\text{ex}}$  and  $V^{\text{pol}}$ . In the present calculation, a quantum chemistry computer code, GAMESS (the North Dakota State University version, see Schmidt *et al* 1990), is employed to generate the multicentred target wavefunction.

We use a Gaussian-type-orbital (GTO) basis set (Dunning 1971) for the ground configuration of the H<sub>2</sub>O molecule. For oxygen, the primitive set (10s6p1d) is contracted to [5s3p1d] and for hydrogen (5s1p) to [3s1p]. The total number of functions included is 32. The calculation is carried out at the experimental nuclear geometry of H<sub>2</sub>O (1.809 au of the O-H distance and 104.5° of the H-O-H angle). The total energy obtained is -76.0533 au, which is compared with the near-Hartree-Fock value -76.0666 au (Davidson and Feller 1984). This wavefunction gives the dipole and the quadrupole moments as:  $\mu = 0.9078$  au (0.728),  $\Theta_{zz} = -0.1078$  au (-0.097),  $\Theta_{xx} - \Theta_{yy} = -3.6602$  au (-3.82), where the numbers in the parentheses are the corresponding experimental values. The molecule is placed in the  $yz$  plane with the coordinate origin at the nuclear centre of mass and the  $z$ -axis along the  $C_2$  symmetry axis.

From the target wavefunction thus calculated, we evaluate the electron density and from that the interaction potential. For the long-range part of  $V^{\text{pol}}$ , the experimental value of the polarizability (Murphy *et al* 1977) is adopted:

$$\alpha_{xx} = 9.546 \text{ au} \quad \alpha_{yy} = 10.314 \text{ au} \quad \alpha_{zz} = 9.906 \text{ au}.$$

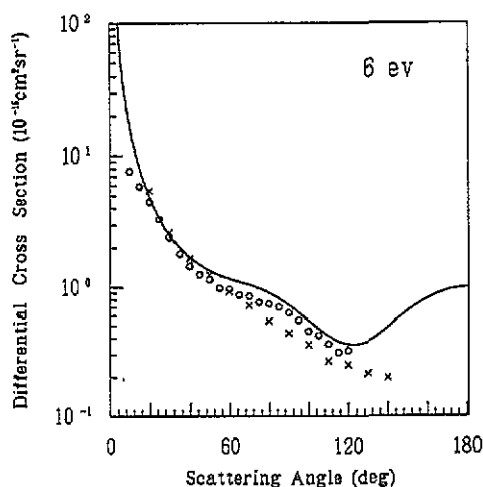
The resulting potential is expanded in terms of the symmetry adapted angular basis as in (15). We retain the terms up to  $\lambda = 6$ . This has been confirmed to be enough in the present calculation. To make a more meaningful comparison to experiment, the dipole term ( $\lambda = 1$ ) is adjusted so as to have the asymptotic form with the experimental value of the dipole moment ( $\mu = 0.728$  au). This dipole moment is used also in the Born calculation.

The coupled equations (3) are solved with inclusion of the partial waves up to  $l=8$  in all the symmetries. For the partial waves higher than this, the Born approximation can be used to obtain the relevant  $T$ -matrix element.

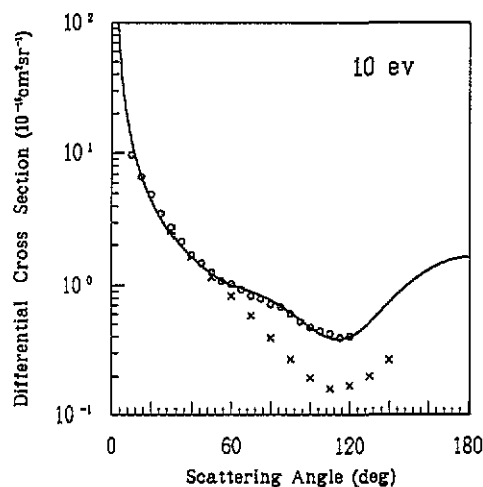
## 4. Results and discussion

### 4.1. Differential cross section

We calculate the differential cross section (DCS) at the electron energies 6, 10, 15, 20, 30, 50 eV and compare them with the most recent experimental results of Johnstone and Newell (1991). Figures 1-6 show the comparison. Our calculation reproduces the



**Figure 1.** Differential cross section (in  $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$ ) for the elastic scattering of electrons from  $\text{H}_2\text{O}$  at 6 eV. The present calculation (full curve) is compared with the experiment by Johnstone and Newell (1991) (open circles) and the calculation by Gianturco (1991) (crosses).



**Figure 2.** Same as figure 1, but at 10 eV.

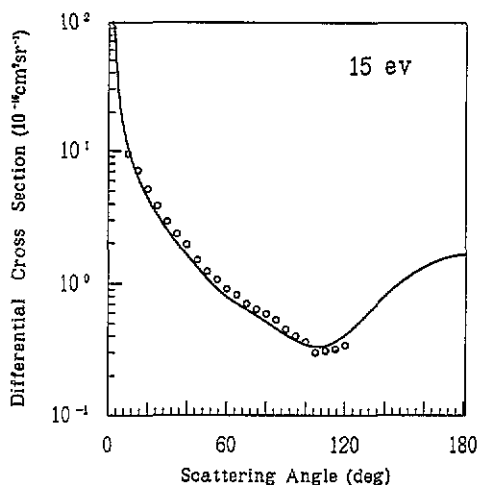


Figure 3. Differential cross section (in  $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$ ) at 15 eV. The present calculation (full curve) is compared with the experiment by Johnstone and Newell (1991) (open circles).

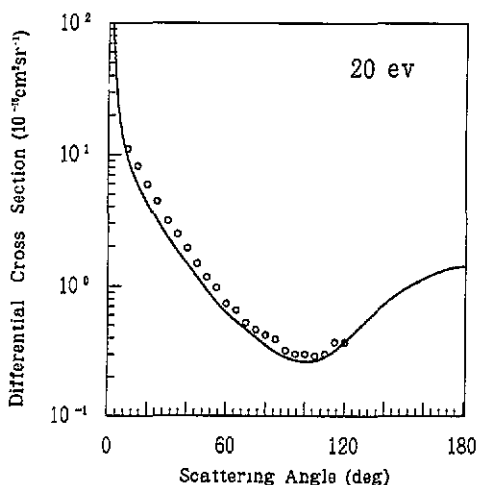


Figure 4. Same as figure 3, but at 20 eV.

experimental data well. As is mentioned in the introduction, several other measurements of DCS have been reported. Johnstone and Newell (1991) compared their data with others. They found an overall agreement among the different experimental data, though a quantitative disagreement is seen in some cases. It should be mentioned here that our DCS shown in figures 1–6 have actually been calculated for the water molecule in its rotational state  $(j, r) = (0, 0)$ . As is shown below, however, the DCS in the angular range shown there (i.e.,  $\theta > 1^\circ$ ) does not depend on the initial rotational state. The present DCS in the figures, therefore, can be compared to the experiment, which was done at room temperature.

Among the recent theoretical calculations of the DCS, Brescansin *et al* (1986) and Sato *et al* (1988) included no polarization. Jain (1988) and Yuan and Zhang (1992) calculated the DCS using a spherical potential and corrected that with the Born cross section for the dipole potential. This procedure is not adequate to obtain an accurate

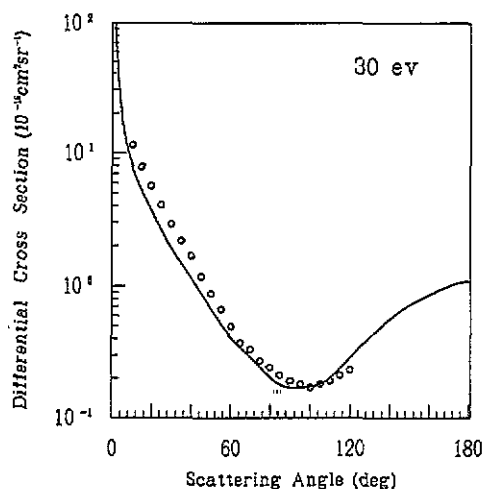


Figure 5. Same as figure 3, but at 30 eV.

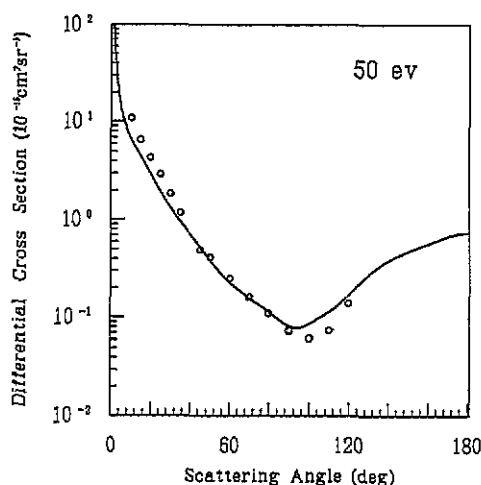


Figure 6. Same as figure 3, but at 50 eV.

DCS as discussed below. The calculation by Gianturco and co-workers (Gianturco and Scialla 1987, Gianturco 1991) is elaborate enough to be compared with the present calculation. We and the Gianturco group follow the same procedure to calculate the cross section, except for minor technical details. Gianturco employed, however, a single-centred wavefunction for  $\text{H}_2\text{O}$ . That may give a rather different electron density near the target nuclei from our multi-centred wavefunction. We show their DCS at 6 and 10 eV in figures 1 and 2, respectively. The agreement of the two calculations is good for angles less than  $60^\circ$ , but very poor at angles larger than that. A similar discrepancy is found at 15 and 20 eV. (They made no calculations at energies above 20 eV.) This disagreement can be attributed to the difference in the target wavefunctions.

Now we test the spherical-potential model. In this model, only the term with  $\lambda = 0$  is retained in equation (15). In figure 7 we compare, at 10 eV, the result of the spherical-potential model with the calculation including all the potential terms. The



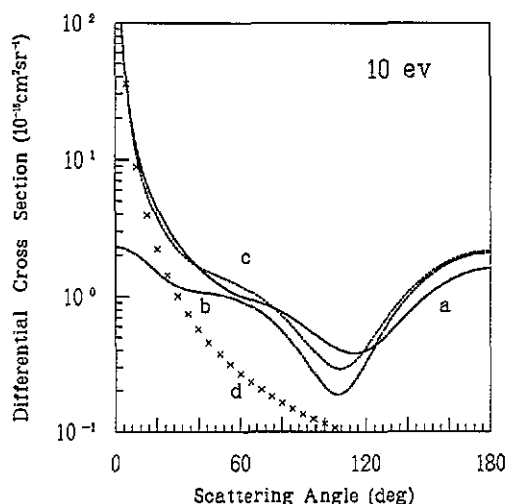


Figure 7. Differential cross section (in  $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$ ) calculated at 10 eV. The calculation with all the potential terms (a, full curve) is compared with the calculation with only the spherical term retained (b, broken curve), the Born cross section with a point dipole interaction (d, crosses), and the sum of the latter two (i.e., b + d) calculations (c, dotted curve).

figure shows also the Born cross section,  $q^B$ , for  $(j\tau) = (00)$  and the spherical-potential model cross section added to that  $q^B$ . The latter corresponds to the cross section obtained by Jain (1988) and Yuan and Zhang (1992), both of whom take into account the non-spherical part of the potential in such a manner. In the region of small angles ( $<40^\circ$ ), the spherical-potential model completely fails, but the Born cross section with a point dipole potential can recover the failure to give a good cross section. For the scattering at larger angles ( $>40^\circ$ ), both the spherical term of the potential and the anisotropic dipole potential contribute to the DCS. However, a simple addition of the two contributions cannot reproduce the result with the real potential well. In fact, Yuan and Zhang (1992) found that their DCS is not in accord with the experimental data at the angles larger than about  $30^\circ$ . This implies that the details of the angular dependence of the scattering in the region of larger angles is very sensitive to the form of the potential.

As is shown above, the scattering in the forward direction is dominated by the long-range dipole interaction, which is successfully treated in the Born approximation. To be more quantitative, we compare our DCS with the  $q^B$  (for instance, the curves a and d in figure 7). The difference between the two cross sections becomes small with decreasing scattering angle. Here we define a critical angle  $\theta_1$  to be such that for  $\theta < \theta_1$  the DCS can be approximated by  $q^B$  within 1%. At the collision energy of 10 eV, we have  $\theta_1 = 1.5^\circ$ . This angle decreases as the energy goes up and at 50 eV we have  $\theta_1 = 0.5^\circ$ . This estimate of  $\theta_1$  has been made for the target molecule in the rotational state  $(j\tau) = (00)$ , but slightly depends on the state as shown below.

The dependence of the DCS on the initial rotational state arises only from the first part of the formula (16). To study the dependence in more detail, another critical angle  $\theta_2$  is introduced by

$$\theta_2 = \frac{1}{2} |\Delta E / E| \quad (22)$$

for each rotational transition  $j\tau \rightarrow j'\tau'$  with the transition energy  $\Delta E$ . It is easily shown

from formulae (17) and (18) that, for  $\theta \gg \theta_2$ , we have

$$q^B = \frac{4}{3} \mu^2 \frac{1}{2k^2} \frac{1}{1 - \cos \theta}. \quad (23)$$

Here use has been made of the relation

$$\sum_{j'\tau'} (2j' + 1) |\langle j'\tau' | j\tau \rangle_{100}|^2 = 1. \quad (24)$$

The form (23) is independent of the rotational state of the molecule. In the case of  $(j\tau) = (00)$ , only the transition  $(00) \rightarrow (10)$  is dipole allowed. For this transition,  $\Delta E = 4.60$  meV and we have  $\theta_2 = 0.013^\circ$  at  $E = 10$  eV. For other rotational states,  $\Delta E$  may be larger than this, but not much changed unless the state becomes very high. In conclusion, the DCS does not depend on the rotational state unless the scattering angle is very close to  $0^\circ$  (say  $\theta < 0.1^\circ$ ). This ensures that the value of  $\theta_1$  estimated above is independent of the initial rotational state of  $\text{H}_2\text{O}$ .

In the forward direction, the DCS becomes very large. As a typical example, we have

$$q(0^\circ) = 5.08 \times 10^{-10} \text{ cm}^2 \text{ sr}^{-1} \quad (25)$$

for the initial state  $(j\tau) = (00)$  and the collision energy of 10 eV. As is stated above, this value changes depending on the initial state.

#### 4.2. Integral and momentum transfer cross sections

Our integral cross section  $Q$  is shown in table 1. The cross section depends on the initial rotational state of the molecule. The second column of the table shows the cross section averaged over the rotational-state distribution at the gas temperature of 300 K. The Boltzmann distribution with a statistical weight (3 for ortho and 1 for para  $\text{H}_2\text{O}$ ) has been assumed for the rotational-state population. In the calculation of  $Q_{\text{rot}}^B(j\tau \rightarrow j'\tau')$ , use is made of the transition energy  $\Delta E$  and the dipole transition moment

**Table 1.** Comparison of the present integral cross section for the electron scattering from  $\text{H}_2\text{O}$  with experimental values of integral and total scattering cross sections. All the cross sections are in  $10^{-16} \text{ cm}^2$ .

$E$ (eV)	$Q$ (300 K) <sup>a</sup>	$Q$ (00) <sup>b</sup>	$Q$ (sph) <sup>c</sup>	$Q$ (expt) <sup>d</sup>	$Q_T$ <sup>e</sup>	$\Delta Q_T$ <sup>f</sup>
6	28.35 (52%) <sup>g</sup>	31.17	35.08	13.76 (22%) <sup>h</sup>	17.68	7.83
10	23.10 (43%)	24.80	25.06	13.89 (16%)	17.79	5.55
15	19.27 (38%)	20.42	19.26	13.31 (16%)	16.31	4.15
20	16.26 (37%)	17.12	15.93	13.66 (20%)	15.39	3.35
30	12.27 (35%)	12.85	12.09	11.29 (20%)	12.36	2.46
50	8.35 (36%)	8.70	8.44	7.76 (20%)	10.37	1.65

<sup>a</sup> Theoretical cross section averaged over the rotational-state population with the gas temperature of 300 K.

<sup>b</sup> Theoretical cross section for the rotational state  $(j\tau) = (00)$ .

<sup>c</sup> Theoretical cross section calculated with the spherical-potential model with a dipole correction.

<sup>d</sup> Experimental data obtained by Johnstone and Newell (1991).

<sup>e</sup> Total-scattering cross sections measured by Saglam and Aktekin (1990, 1991).

<sup>f</sup> Correction for  $Q_T$  for the undetected forward scattering, estimated theoretically.

<sup>g</sup> Contribution from the angles less than  $10^\circ$ .

<sup>h</sup> Contribution from the extrapolated regions.

$\mu^2 | \langle j' \tau' | j \tau \rangle_{100} |^2$  tabulated in the paper by Chandra *et al* (1984). For comparison, the third column of table 1 gives the cross section for the state  $(j\tau) = (00)$ . It should be noted that the  $(j\tau)$  dependence of  $Q$  comes only from that of the DCS in the very vicinity of the forward direction.

The fourth column of table 1 shows the  $Q$  obtained with the spherical-potential model with the dipole correction (evaluated for  $(j\tau) = (00)$ ). When we compare the fourth to the third columns, the former is too large at the lowest energy, but the difference becomes small at the highest energy.

Now we compare our  $Q$  with experimental values. The integral cross section reported by Johnstone and Newell (1991) is shown in the fifth column of table 1. The difference between theirs and ours (column 2) is very large in the lower energy region. Johnstone and Newell measured the DCS only in the angle region 10°–120°. To obtain  $Q$ , they extrapolated the measured DCS to the forward and the backward directions. The contribution to the  $Q$  from the extrapolated range, estimated by Johnstone and Newell, is indicated in the parentheses following the experimental  $Q$  in the table. Similarly, in the parentheses in the second column, we show the contribution to our  $Q$  from the region of angles less than 10°. From the comparison of columns 2 and 5, it can be concluded that the extrapolation (at least for the small angle region) by Johnstone and Newell was inadequate to obtain  $Q$ . It is very difficult to extrapolate DCS correctly in the forward direction, because of a very steep increase of the DCS in the region due to the dipole interaction. All the experimental cross sections reported so far suffer from this difficulty.

There are several measurements of the total scattering cross section  $Q_T$  (Sueoka *et al* 1986, Zecca *et al* 1987, Szymtkowski 1987, Nishimura and Yano 1988, Saglam and Aktekin 1990, 1991). This cross section includes the contributions of vibrational excitation and other inelastic processes so that we have the relation

$$Q < Q_T. \quad (26)$$

In the sixth column of table 1, we show, as an example, the result of the most recent measurement of  $Q_T$  by Saglam and Aktekin (1990, 1991). In the region of low energy (<30 eV), our  $Q$  (300 K) exceeds the  $Q_T$ , thus violating the above relation.

In the experiment,  $Q_T$  is derived from the attenuation of an incident electron beam through the target gas. The measured cross section,  $Q_T(\text{measured})$ , usually differs from the true  $Q_T$  because the detector of the transmitted beam cannot totally discriminate against electrons elastically scattered at angles which are smaller than the acceptance angle of the detector,  $\Delta\theta$ . Namely the measured cross section should be corrected as

$$Q_T = Q_T(\text{measured}) + \Delta Q_T \quad (27)$$

where

$$\Delta Q_T = 2\pi \int_0^{\Delta\theta} q \sin \theta \, d\theta. \quad (28)$$

Saglam and Aktekin (1990) estimated  $\Delta\theta$  to be 0.89° and ignored the correction  $\Delta Q_T$ . When we evaluate  $\Delta Q_T$  with this  $\Delta\theta$  and using our DCS (at 300 K), we have  $\Delta Q_T$  in the seventh column of table 1. If this  $\Delta Q_T$  is added to the measured  $Q_T$ , the resulting value becomes larger than our  $Q$  (300 K). At 6 eV, the summed cross section is still smaller than  $Q$  (300 K), but, on consideration of the experimental uncertainty and the accuracy of the present calculation, this discrepancy should not be taken seriously. Thus the measured value of  $Q_T$  for H<sub>2</sub>O (and any other polar molecules) may be too

small because of an insufficient correction for the contribution of the missing small-angle scattering. This has been already pointed out by Yuan and Zhang in their recent paper (Yuan and Zhang 1992). As is mentioned before, their calculation is quantitatively less reliable than ours, because their calculation is based on the spherical-potential model with a dipole correction.

In figure 8, our result of the momentum transfer cross section  $Q_m$  is compared with the data recommended by Hayashi (1989). He determined his values on the basis of various (theoretical and experimental) DCS and so as to be consistent with the swarm parameters measured. In the case of  $Q_m$ , a contribution from small-angle scattering can be ignored so that the extrapolation of the DCS to the forward direction gives rise to no ambiguity. Furthermore the theoretical  $Q_m$  does not depend on the initial rotational state of the molecule. Figure 8 shows that our  $Q_m$  is in remarkably good agreement with Hayashi's value.

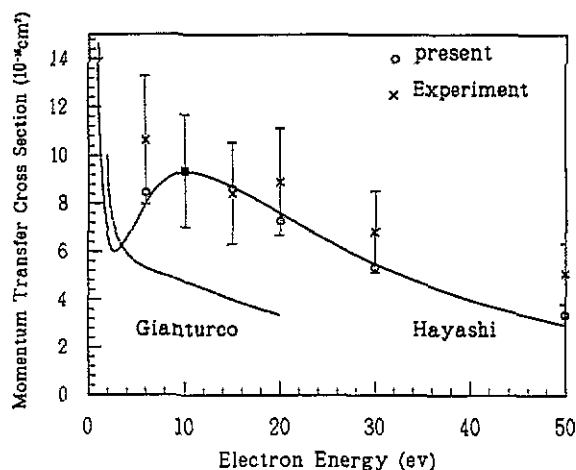


Figure 8. Momentum transfer cross section (in  $10^{-16} \text{ cm}^2$ ) as a function of electron energy (in eV). The present calculation (open circles) is compared with the value recommended by Hayashi (1989) (full curve), the experimental value of Johnstone and Newell (1991) (crosses), and the calculation by Gianturco and Scialla (1987) (broken curve).

We show in figure 8 also the experimental value of  $Q_m$  of Johnstone and Newell (1991) and the theoretical one of Gianturco and Scialla (1987). The  $Q_m$  of the present calculation agrees with that of Johnstone and Newell within the experimental error, except for the value at the highest energy (50 eV). As is discussed in the previous subsection, an extrapolation of the measured DCS to the forward and backward directions is needed to obtain the experimental  $Q_m$ . The contribution of the extrapolated region (in this case, mainly the backward region) is very large, particularly at 50 eV. The experimental value of  $Q_m$  might have more uncertainty than claimed. The difference in the  $Q_m$  of the two calculations (i.e., ours and that of Gianturco and Scialla) may be ascribed to the difference in the target wavefunctions employed, as is described in section 4.1.

Finally we mention the effect of the (electronically) inelastic channels, which is ignored in the present calculation. Jain (1988) studied the effect using an effective absorption potential. He shows no details of the effect on the elastic integral cross

section of  $H_2O$ . This effect is probably small in the energy region (6–50 eV) of the present calculation. In fact, the absorption cross section obtained by Jain decreases rapidly, from the maximum at about 100 eV, with decreasing electron energy.

## 5. Conclusion

We have calculated differential, integral, and momentum transfer cross sections for the vibrationally elastic scattering of electrons from  $H_2O$ . Besides the static potential, the electron exchange and the target polarization are taken into account. The calculation is based on the fixed-nuclei approximation. The closure formula using the Born calculation with a point-dipole potential is adopted to avoid the divergence of the partial wave expansion. This procedure enables an accurate evaluation of the DCS in the forward direction, which turns out to be very large and dependent on the initial rotational state of the molecule.

The resulting DCS is in good agreement with the most recent experimental data by Johnstone and Newell (1991). The momentum transfer cross section agrees well with the recommended value by Hayashi (1989) and with the experimental values of Johnstone and Newell (1991) within the experimental uncertainty. The integral cross section calculated is not compatible with the experimental data of the integral or the total scattering cross section. It is pointed out that this difference arises from the inadequate correction for the small-angle scattering which cannot be detected experimentally. It is very difficult to estimate the correction with a simple extrapolation of the measured values, because the DCS increases very steeply toward the forward direction.

Finally it is worth mentioning the validity of the Born approximation. In the case of electron collisions with the water molecule, the electron-molecular dipole interaction is very strong. The Born approximation, therefore, is expected to be applied to the cross section calculation. In the region of collision energy considered, however, the dipole interaction dominates only in small-angle scattering. In scattering at large angles, shorter-range interaction is also important. Consequently the Born cross section is good only in forward scattering (see figure 7). The contribution of the large-angle scattering to the integral cross section  $Q$  is fairly large in the present energy region (see table 1). As for the momentum transfer cross section, the forward scattering has a much smaller contribution than in the case of  $Q$ . In conclusion, the Born approximation cannot be relied on in the calculation of  $Q$  and  $Q_m$  for the present process at the collision energies considered here (6–50 eV).

## Acknowledgments

The authors would like to thank Professor S Iwata for his valuable advice on the usage of quantum chemistry computer codes.

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