Vibrationally elastic $e^- - \text{H}_2\text{O}$ scattering at intermediate energies

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Abstract. Vibrationally elastic total cross-sections of $e^- - \text{H}_2\text{O}$ scattering are calculated at intermediate energies $E_i = 10 - 300$ eV. The interaction potentials are treated in spherical models. The dipole rotational excitation, which is significant but not dominant above 10 eV, is treated incoherently. Effects of electronic excitation-ionization, significant above 30 eV or so, are considered through a complex optical potential. A dynamically distorted charge-density is employed to calculate the imaginary part of the complex potential. Comparisons are made with recent theoretical and experimental data. The mutual agreement is better in total cross-sections than in differential cross-sections.

Keywords. Elastic and inelastic electron-scattering; optical potential, total cross-sections.

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1. Introduction

This paper deals with some of the theoretical aspects of the scattering of electrons by water molecules. This has been recently investigated by Itikawa and co-workers and by others [1–3]. We confine ourselves mainly to total cross-sections of $e^- - \text{H}_2\text{O}$ scattering, for which experimental data have been given by Johnstone and Newell [4], Sueoka et al [5] and others. All these workers have also emphasized the importance of the study of $e^- - \text{H}_2\text{O}$ scattering.

The interaction of an electron with a molecule like H$_2$O is in general nonspherical. Rotational excitation of the molecule due to the long range dipole potential dominates the $e^- - \text{H}_2\text{O}$ total cross-sections at low energies. At intermediate and high energies, short range interactions become more significant. At such energies the total $e^- - \text{H}_2\text{O}$ cross-section can be calculated by assuming the molecule to be spherical and the only important nonspherical effect, that of the dipole rotation, may be incorporated incoherently [3]. We have presently adopted this approach to calculate the total $e^- - \text{H}_2\text{O}$ cross-sections at intermediate energies. $E_i = 10 - 300$ eV. Jain [3] calculated these cross-sections by starting with a polarized target charge-density to generate the spherical complex optical potential. Now, the target charge-polarization is a dynamic (energy-dependent) phenomenon, hence we have presently obtained the polarized part of the charge-density through a dynamic polarization potential as well as through its asymptotic form. On the other hand Okamoto et al [1] have considered the static (unperturbed) charge-density in their calculations at $E_i = 6 - 50$ eV. They made no allowance for the electronic excitation–ionization channels in their calculations. They
K N Joshipura et al have given a theoretical forward-scattering correction to the experimental total $e^-\cdot H_2O$ cross-sections.

We have employed complex optical potential to calculate the total (elastic + inelastic) cross-sections $Q_T^S$, within a spherical charge-density, distorted by a dynamic as well as static polarization potential. The nonspherical contribution $Q_T^{NS}$ to the total cross-section, corresponding to rotational excitation is treated separately in the point dipole first Born approximation (PDFBA), following Itikawa [6]. We also examine the overall effect of electronic excitation and ionization channels on elastic $e^-\cdot H_2O$ scattering. Our total as well as differential cross-sections are compared with the recent theoretical and experimental data. The differences in the present results, arising out of (a) unperturbed and perturbed target charge density, and, (b) real and complex potential, are discussed.

2. Theory

Considering the incident electron energies to be intermediate and high, we write the total $e^-\cdot H_2O$ scattering cross-section $Q_{tot}$ as an incoherent sum of the spherical and nonspherical contributions in the following manner

$$Q_{tot} = Q_T^S + Q_T^{NS}$$

Okamoto et al [1] calculated the total cross-sections in two ways viz. (i) by starting with the complete nonspherical real potential and (ii) by starting with real spherical potential and adding the dipole correction, as in (1). The difference between their two calculations is significant at low energies, roughly below 30 eV. Thus in the present energy range the incoherent approach of (1) is quite suitable.

Now the spherical contribution $Q_T^S$ to the total cross-section (1) is obtained here by starting with an accurate charge-density $\rho_0(r)$ of H$_2$O, given by Katase et al [7]. We represent the $e^-\cdot H_2O$ system by a complex, spherical, energy-dependent optical potential,

$$V_{opt}(r, E_i) = V_{st}(r) + V_{ex}(r, E_i) + V_{pol} + iV_{abs}(r, E_i)$$

where $V_{opt}$ is the static potential obtained directly from the static charge-density $\rho_0(r)$. The exchange potential $V_{ex}$ is obtained following the free-electron-gas-exchange model of Hara [8]. For the absorption potential $V_{abs}$ we have adopted the quasi-free Pauli-blocking model given by Truhlar and coworkers [9]. The polarization effects (represented by $V_{pol}$ in (2)) are adequately described, at intermediate energies, by the correlation-polarization potential (see [10, 11]). Towards high energies ($E_i \geq 80$ eV here) we have adopted for $V_{pol}$, a dynamic polarization potential,

$$V_{dp}(r, E_i) = \frac{1}{2} \frac{\alpha_0 \cdot r^2}{(r^2 + r_c^2)^3}$$

with

$$r_c = 0.375 \Delta$$

where $\alpha_0$ and $\Delta$ are respectively, the average spherical polarizability and the average excitation energy of the target molecule. Further, $k$ is the incident momentum (in a.u.). In (3) a shorter-range term varying asymptotically as $r^{-6}$ may be added, but
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that requires a reliable value of the quadrupole polarizability of the molecule. Moreover, the extra term would be ineffective in view of (7) to follow. Now, the incident electron perturbs the target charge distribution, hence the exchange and the absorption potentials (effective near the target) must be derived from a polarized (rather static) charge-density. We have presently calculated the polarized part of the charge-density, denoted by $\rho_{pol}(r, E_i)$, from the dynamic polarization potential $V_{dp}(r, E_i)$, through the Poisson equation,

$$\nabla^2 V_{pol}(r, E_i) = -4\pi \rho_{pol}(r, E_i). \tag{4}$$

Using (3) and (4), the dynamic correction to the charge-density is,

$$\rho_{pol}(r, E_i) = \frac{1}{4\pi} \left[ \frac{3\alpha_0}{(r^2 + r_c^2)^3} - \frac{21\alpha_0 r^2}{(r^2 + r_c^2)^4} + \frac{24\alpha_0 r^4}{(r^2 + r_c^2)^5} \right]. \tag{5}$$

If we start with the static asymptotic form $-\alpha_0/2r^4$ of the polarization potential and use the Poisson equation, we obtain the static-correction to the charge-density as

$$\Delta \rho = 3\alpha_0/2\pi r^6.$$

Thus, we introduce the dynamically distorted charge-density,

$$\rho'(r, E_i) = \rho_0(r) + \rho_{pol}(r, E_i). \tag{6a}$$

The statically distorted charge-density would be,

$$\rho(r) = \rho_0(r) + \Delta \rho \tag{6b}$$

Note that unlike $\Delta \rho$, the correction $\rho_{pol} \to 0$ at high energies, making it theoretically more satisfying.

The polarization potential of (3) fails to account for the polarization effect at low energies [11]. Actually at small $r$, the picture of dipole charge-polarization of the target by an external electron breaks down. For $e^- - H_2O$ scattering this may be the case, typically at $r \lesssim r_{O-H}$, where $r_{O-H}$ is the O–H bond length in $H_2O$. At such separations the static-exchange potentials dominate, hence we take

$$\rho_{pol}(r, E_i) = 0, \quad \text{if} \quad r \lesssim r_{O-H} \tag{7}$$

Thus, we have considered (6a, 6b) along with (7) to derive the short range potentials.

It is the absorption potential that is modified appreciably by the use of corrections over $\rho_0(r)$. Towards scattering calculations we solved the Schrödinger equation numerically for the real and the imaginary parts of $V_{opt}$ (for details see [12]). The partial wave phase-shifts thus obtained were employed to calculate the total (elastic + inelastic) cross-sections $Q_{T}^S$, viz,

$$Q_{T}^S = Q_{el} + Q_{inel} \tag{8}$$

where, $Q_{el}$ is the total elastic cross-section and $Q_{inel}$ is the total inelastic cross-section, in the complex potential. We have also calculated the purely elastic cross-sections, $\sigma_{el}$ obtained by setting $V_{abs} = 0$ in (2).

The dipole contribution $Q_{T}^{NS}$ in (1) was obtained in the PDFBA [6]. This differs somewhat from the expression of Collins and Norcross [13] in that the former treats $H_2O$ as an asymmetric top.

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3. Results and discussion

3.1 Total cross-sections

We calculated vibrationally elastic $e^{-} - \text{H}_2\text{O}$ total cross-sections $Q_{\text{tot}}$ at energies $E_i = 10 - 300$ eV. The polarized charge density, (6) and (7), affects the absorption potential and hence $Q_S^T$. The total inelastic cross-section $Q_{\text{inel}}$ is enhanced by the corrections via (6a) and (6b) in the charge-density, as observed by Jain [3]. However, our correction $\rho_{\text{pol}}$ is energy-dependent. This is not so with the calculations of Jain [3], which therefore, overestimate the cross-sections at higher energies. Towards lower energies ($\leq 10$ eV) the polarized part of the charge-density has no significant effect on the cross-sections. Table 1 shows our calculated cross-sections $Q_{\text{inel}}$ at $E_i = 30 - 300$ eV. These are compared here mutually in three models for $V_{\text{abs}}$, with (i) no correction over $\rho_0$, (ii) dynamic correction via (6a), and (iii) static correction via (6b). The quantity of column 3 (table 1) calculated via (6a) is closer to the theoretical ionization cross-sections $Q_{\text{ion}}^T$ (column 5) given by Khare and Meath [14], especially towards high energies. The $Q_{\text{inel}}$ including the static correction (column 4, table 1) are higher at high energies, similar to the results of Jain [3]. We have not included the experimental $Q_{\text{ion}}^T$ data of Orient and Srivastava [15] which are still higher at the peak. Recent measurements of Rao [16], not shown, lie somewhat above the

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>No correction ($\rho_0$ only)</th>
<th>Dynamical correction eq. (6a)</th>
<th>Static correction eq. (6b)</th>
<th>$Q_{\text{ion}}^T$ (theoretical)</th>
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<tbody>
<tr>
<td>30</td>
<td>0.33</td>
<td>0.71</td>
<td>0.76</td>
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<td>1.62</td>
<td>1.88</td>
<td>2.93</td>
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<td>100</td>
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<td>1.91</td>
<td>3.00</td>
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<tr>
<td>300</td>
<td>1.31</td>
<td>1.30</td>
<td>1.89</td>
<td>1.4</td>
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</table>

*Values obtained from the graphical ionization cross-sections of Khare and Meath [14]

Table 2. The present total cross-sections $\sigma_{\text{el}}$, $Q_T^S$ and $Q_{\text{el}}$ (all in $10^{-16}$ cm$^2$) for $e^{-} - \text{H}_2\text{O}$ scattering, in spherical interactions.

<table>
<thead>
<tr>
<th>$E_i$ (eV)</th>
<th>$\sigma_{\text{el}}$</th>
<th>$Q_T^S$</th>
<th>$Q_{\text{el}} = Q_T^S - Q_{\text{inel}}$</th>
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</thead>
<tbody>
<tr>
<td>10</td>
<td>10.2</td>
<td>10.2</td>
<td>10.2</td>
</tr>
<tr>
<td>30</td>
<td>7.7</td>
<td>8.3</td>
<td>7.6</td>
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<tr>
<td>50</td>
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<td>80</td>
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<td>2.9</td>
<td>4.3</td>
<td>2.4</td>
</tr>
</tbody>
</table>
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values of columns 3 and 5 of table 1 and exhibit a similar energy-dependence. At high energies the entries of columns 2 and 3 tend to agree. This justifies the use of the dynamically perturbed charge-density in our results shown next.

Also investigated presently is the effect of inelastic scattering on elastic scattering at intermediate energies. We calculated the purely elastic cross-sections $\sigma_{el}$ in a real spherical $e^-\text{-}H_2O$ potential. Table 2 exhibits the total cross-sections $\sigma_{el}$ and the total (elastic + inelastic) cross-sections $Q^S_T$, together with the total elastic cross-sections, $Q_{el}$ (see (8)). The quantity $Q_{inel}$ represents the overall effect of the electronic (excitation and ionization) channels, at a given energy. It becomes significant above 30 eV and shows a broad peak near 100 eV. Therefore, our values of $\sigma_{el}$ and $Q^S_T$ (table 2) are close to each other up to about 30 eV only. As $E_i$ increases they differ significantly, with $Q^S_T > \sigma_{el}$, and $\sigma_{el} > Q_{el}$. Thus for $E_i > 30$ eV or so, the effects of electronic channels must be taken into account. This has not been done by Okamoto et al [1] in their calculations at $E_i = 6$–50 eV.

Now a quantity that offers a meaningful comparison with experimental data is $Q_{tot}$ of (1). To compare the theoretical results with the experimental ones, we have considered the forward-scattering correction to the measured total cross-sections $Q_{tot}$, as given theoretically by Okamoto et al [1]. The correction $\Delta Q_{tot}$, corresponds to the strong forward scattering by polar molecules like $H_2O$ and is found to fit well with the formula,

$$\Delta Q_{tot}(E_i) = a \cdot (E_i)^{-b}$$

where $a = 30$, and $b = 0.75$.

This formula holds good in the present energy range. The (undetected) correction $\Delta Q_{tot}$ must be added to the measured total cross-section $Q_{tot}$ for a comparison with the theoretical value at a given energy. Table 3 shows the present values of $Q_{tot}$ along with that of Jain [3]. Also shown are the total cross-sections averaged over the rotational-state distribution at the gas ($H_2O$) temperature 300 K, i.e. $Q$ (300 K) given by Okamoto et al [1]. The last column of table 3 shows the measured cross-sections, with the correction of (9) given in the brackets.

Towards low energies the theoretical values in table 3 are quite similar, indicating (i) a subdued role of the polarized charge-density, and (ii) the dominance of $Q^{NS}$ over

<table>
<thead>
<tr>
<th>$E_i$ (eV)</th>
<th>Theory</th>
<th>Experimental results</th>
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<tr>
<td></td>
<td>Present $Q_{tot}$</td>
<td>Jain [3]</td>
</tr>
<tr>
<td>10</td>
<td>23.1</td>
<td>23.18</td>
</tr>
<tr>
<td>30</td>
<td>13.8</td>
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<td>7.71</td>
</tr>
<tr>
<td>300</td>
<td>2.8</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*See eqn. (1); **See eqn. (9); $^{a}$ Johnstone and Newell [4]; $^{b}$ Sueoka et al [5, 17]

Table 3. Total (elastic plus inelastic) cross-sections* $Q_{tot}$ (in $10^{-16}$ cm$^2$) for $e^-\text{-}H_2O$ scattering.
As $E_i$ increases, we find $Q_i^{NS} < Q_i^S$. Above 30 eV (nearly) $Q_{tot}$ of Jain [3] are higher than ours because of his energy independent $\rho_{pol}$. At such energies, the cross-sections of Okamoto et al [1] are somewhat lower, mainly because of their neglect of the inelastic electronic channels.

Various experiments done so far on total $e^- - H_2O$ cross-sections differ from each other as well as from the corresponding theories also. Johnstone and Newell [4] integrated their measured elastic differential cross-sections at $E_i = 6-50$ eV. The measurements were done for scattering angles 10–120 degrees and were extrapolated to derive the integrated cross-sections. A comparison in table 3 reveals that the integrated cross-sections of Johnstone and Newell [4] are lower than the present and the other theories, but if the correction $\Delta Q_{tot}$ is added (along with inelastic contribution) to the reported measurements, then the theory and the experiment tend to agree. The directly measured $Q_{tot}$ above 50 eV in table 3 are those of Sueoka et al [5, 17]. The present results are closer to these measurements also. At 300 eV the agreement is not so good.

3.2 Differential cross-sections (DCS)

Vibrationally elastic $e^- - H_2O$ DCS including the dipole-rotation, obtained from our theory are shown in figures 1, 2 and 3 at sample energies 50, 100 and 300 eV respectively. Shown at 50 eV (figure 1) are our theoretical DCS under (i) the complex potential along with the dynamically polarized charge-density and (ii) the real potential, with $V_{abs} = 0$. These two calculations differ marginally and agree qualitatively with

![Figure 1](image-url)
Figure 2. Same as in figure 1 but at 100 eV. Present results with statically polarized charge-density (complex potential); Experimental DCS of Katase et al (1986).

Figure 3. Same as in figure 1 but at 300 eV; Same as in figure 2, but at 300 eV; Present results with real potential Experimental DCS of Katase et al (1986).
the experimental DCS of Johnstone and Newell [4]. Our models of (6a) and (6b) do not differ much here. The minimum in the DCS around 100° is deeper in our theory. At 100 eV (figure 2) the present theory, including the dynamical correction (6a) favours the measurements of Katase et al [7], better than that with the static correction (6b). Towards high energies the DCS in complex potential, tend to be rather lower at intermediate and large angles. As has been noted earlier [12, 18] this is due to an excessive loss of flux to the inelastic channels, at small r, predicted by the present $V_{bs}$. We can see from figure 3 (at 300 eV) that the present DCS in the complex potential are lower than the measured DCS of Katase et al [7] at intermediate and large angles, while those in the real potential are correspondingly higher. The dynamically polarized charge-density, on which we have focussed attention in this paper, does not appreciably correct this behaviour of the theoretical DCS.

Thus from the present study on $e^{-}$–H$_2$O scattering we conclude the following. The rotational excitation cross-sections, represented through PDFBA are dominant up to about 10 eV and significant even at 100 eV or so, but the present method of calculation, via (1) is satisfactory at intermediate and high energies. The electronically inelastic channels are significant from about 30 eV onwards. The distortion of the target charge-density also assumes significance at these energies, but it should be treated dynamically. An energy-independent polarized charge-density results into overestimation in total cross-sections at high energies. The present $Q_{inel}$ with dynamical distortion, are consistent with the ionization cross-sections. Beyond 300 eV the static charge-density would be sufficient to obtain reliable total cross-sections. Our theoretical DCS are not as good as our total cross-sections. The present absorption potential appears to be rather strong at large $E_i$ and small r.

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References