

Theoretical total cross sections of e -H₂O collisions in water, ice and dimer forms

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Abstract : We have calculated various inelastic (including ionizing) collision parameters for the impact of electrons on H₂O molecules in the liquid (water), ice as well as cluster environments. Corresponding to incident energies E_i above the ionization threshold upto about 2000 eV, an imaginary part of complex optical potential is employed to obtain total inelastic cross sections Q_{inel} , and these are used to derive the total ionization cross sections Q_{ion} . The present calculations are extended to obtain the bulk or the macroscopic cross sections Σ_{tot} and the inelastic electron mean free path Λ as functions of energy E_i . The present results are compared with other available data.

Keywords : Electron scattering, ionization, total cross sections, macroscopic cross sections

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1. Introduction

The H₂O molecule, in its free (vapour) state or in condensed matter forms such as ice, liquid or clusters has been an interesting target of investigations. Experimental and theoretical work on different cross sections for the impact of electrons on isolated H₂O molecules is quite extensive, see e.g., Zecca *et al* [1], Straub *et al* [2], Viktor and Kurepa [3], Joshipura and Minaxi [4], Hwang *et al* [5] and Khare and Meath [6]. The studies on electron collisions with H₂O in liquid or ice phases are only a few. Electron energy loss measurements in ice were done by Safwan *et al* [7]. Theoretical work on e -H₂O (liq) has been done by Dingfelder *et al* [8], whereas Joshipura and Minaxi [9] calculated electron scattering cross sections for H₂O (liq) as well as H₂O (ice). Probably there are no experimental studies in both these cases. Hence it is of interest to calculate the e -H₂O cross sections, especially those above the ionization threshold in the condensed phases. This affords a comparison of electron scattering parameters in the condensed phases, with the corresponding results on H₂O (free), which are well-known.

In the present calculations we show that the relevant cross sections are dependent on the basic molecular properties (see Table 1) that vary from vapour to liquid or ice. The electron interactions in water and in ice have an applied importance. Astrophysical objects like comets, interstellar clouds *etc.*, are found to contain icy matter.

The e -H₂O collision as an isolated scattering event at energies above threshold comprises of elastic as well as inelastic (ionization and electronic excitation *etc.*) processes. At high energies of impact say above $E_i = 1000$ eV the non-elastic scattering is dominated by ionization. We define presently for the ($e + \text{H}_2\text{O}$) scattering system, a complex energy-dependent optical potential $V_{opt} = V_R + iV_I$, that accounts for all allowed inelastic channels cumulatively. The imaginary component of V_{opt} , called the absorption potential V_{abs} , is chosen in the form of a very successful model first given by Staszewska *et al* [10], and employed frequently in atomic and molecular collisions. It includes the effect of exchange and polarization correlations locally and is such that $V_{abs} = 0$, for incident energy $E_i \leq \Delta_{gap}$, the 1st electronic

excitation energy. The quantity obtained directly from V_{abs} is the total inelastic cross section $Q_{\text{inel}}(E_i)$ which we have calculated separately for H_2O (liq.) and H_2O (ice). The cross section Q_{inel} does not include the (small) bulk effect of plasmon vibration *etc.*, but is a good approximation to total ionization cross section $Q_{\text{ion}}(E_i)$, say from 1000 eV onwards.

We have chosen energies in the range 20–2000 eV to calculate Q_{inel} . These are used to infer Q_{ion} and further to obtain the macroscopic (inelastic) cross section Σ_{tot} , also called the inverse mean free path (IMFP). The electron (inelastic) mean free path $\Lambda = 1/\Sigma_{\text{tot}}$, is also studied as a function of electron impact energy E_i . We made adequate comparisons wherever possible. A short discussion on the mean path of electrons in solids has been given in view of the present work on ice, *vis-à-vis* that of Briggs and Seah [11] on various other solids *e.g.*, metals.

2. Theoretical models and calculations

Considering the H_2O in a particular phase, the e -molecule inelastic cross sections are calculated by treating the complex energy-dependent optical potential V_{opt} exactly in the partial wave decomposition. The absorption potential V_{abs} required towards this is basically of a local form [10], which we have modified for the present purpose. This potential is given by,

$$V_{\text{abs}}(r, E_i) = -\rho(r) \cdot (T_{\text{loc}}/2)^{1/2} \cdot (8\pi/10k_F^3 E_i) \cdot \theta(p^2 - k_F^2 - 2\Delta) \cdot (A_1 + A_2 + A_3). \quad (1)$$

Here, $\rho(r)$ is the spherical charge-density of H_2O , $k_F = (3\pi^2\rho(r))^{1/3}$, $p = \sqrt{2E_i}$ is the incident momentum, in au and $\theta(x)$ is the Heaviside function. The local kinetic energy of the impinging electron is, $T_{\text{loc}} = E_i - V_R(r, E_i)$ where, the real part of the complex potential is

$$V_R = V_{\text{st}}(r) + V_{\text{ex}}(r, E_i) + V_{\text{pol}}(r, E_i). \quad (2)$$

The three terms on the RHS of (2), are the static, exchange and target-charge polarization potentials, which are calculated through the charge-density $\rho(r)$ by employing well-known and successful models as outlined in Joshipura and Minaxi [4]. We omit here the details of the functions A_1 , A_2 and A_3 , which are given in [10]. These functions depend on the target charge-density $\rho(r)$, incident momentum p and an energy parameter Δ , for which different choices exist in literature. We note that out of the above terms A_1 , A_2 and A_3 , the last one is significant mainly in the outer region of the target charge-cloud. Since the inner shells are harder to be ionized, we choose presently $\Delta = I$, the first ionization energy for the term A_3 , and set $\Delta > I$ for the rest. With this the V_{abs} mainly describes the ionization of valence electrons, especially at high energies. In the well-known case of H_2O

(free), this choice yields $Q_{\text{inel}} \approx Q_{\text{ion}}$ for energies $E_i \geq 1000$ eV. Towards the scattering calculations, the V_{abs} employed in the Schrödinger equation yields the imaginary part of the phase shifts $\text{Im } \delta_l(k)$ and hence the total inelastic cross section,

$$Q_{\text{inel}}(E_i) = \pi/k^2 \cdot \sum_{l=0}^{l_{\text{max}}} (2l+1)(1-\eta_l)^2, \quad (3)$$

with $l = \exp(-2\text{Im } \delta_l(k))$. Thus, the present calculation needs the $\rho(r)$ as the basic input. For an isolated H_2O molecule the accurate (average) MO charge density can be expressed parametrically (in au), as

$$\rho(r) = 1/4\pi r^2 \cdot [ar^2 e^{-r/b} + cr^3 e^{-r/d}], \quad (4)$$

where $a = 4478$, $b = 0.0602$;

$$c = 0125, \quad d = 0.3220 \quad (5)$$

In the condensed phases, the molecular charge-density is expected to be different; hence we do the modeling, as follows.

H_2O charge-density in ice and in liquid :

In crystalline ice the O–O bond distance between two molecules is $R_{\text{O-O}} = 5.22 a_0$. Hence, we assume the H_2O in ice to be “caged” in a sphere of radius $\frac{1}{2} \cdot R_{\text{O-O}}$. The model charge-density $\rho_{\text{ice}}(r)$ in this case is calculated by expanding [12] the H-atom charge-densities at the O-atom, corresponding to the actual bond-length $R_{\text{O-H}}$ (Table 1)

Table 1. Properties of H_2O molecule in various phases.

Property	Vapour (free)	Liquid	Ice	Dimer
O–H bond-length (a_0)	1.81	1.81	1.912	1.912
O–O bond-distance (a_0)	∞^b	∞^b	5.22	5.63 ^{a1}
Ionization energy (eV)	12.6	10.5	11.0 ^d	10.5

^{a1}Yoon *et al* [13]; ^bIsolated molecule; ^cChristophorou [14]; ^d[14]

The single-center molecular charge-density thus determined must correspond to all 10 electrons with the “cage”, hence it is truncated to $R_0 = \frac{1}{2} \cdot R_{\text{O-O}}$, and re-normalized to electrons per molecules *viz.*,

$$4\pi \int_0^{R_0} \rho_{\text{ice}}(r) r^2 dr = 10. \quad (6)$$

The charge-density ρ_{ice} thus constructed is realistic in that it incorporates the relevant condensed-phase properties. The quantities Q_{inel} calculated from this charge-density, represent the electronic excitation and ionization of H_2O (ice) by electron impact. For H_2O (liq.) the only change made with

respect to free case, is that of the ionization energy, as given in Table 1.

Of more interest are the total ionization cross sections $Q_{ion}(E_i)$, that can be inferred from $Q_{inel}(E_i)$. In order to get more information regarding the former, consider a ratio,

$$R(E_i) = \frac{Q_{ion}(E_i)}{Q_{inel}(E_i)} \quad (7)$$

this is generally less than (but close to) 1 in the energy range from threshold to about 100 eV, and converges to 1 at higher energies. The contributions of electronic excitations, which have thresholds below the ionization energy, quickly fall off above 100 eV or so. We have noted a trend in this ratio for the molecules CH₄, NH₃ and H₂O, for which a lot of experimental data exists. Using our calculated Q_{inel} and the measured values of Q_{ion} , we find that for H₂O,

$$\begin{aligned} R(E_i) &\cong 0.8, & \text{at } E_i &\cong 100 \text{ eV} \\ &\cong 1.0, & \text{at } E_i &\geq 1000 \text{ eV.} \end{aligned} \quad (8)$$

At the present purpose the above ratio may be used along with the present values of Q_{inel} to infer the Q_{ion} for the H₂O molecule in the respective phases. In order to determine the Q_{ion} for H₂O (liq), H₂O (ice) and for the water dimer we employ the above ratio corresponding to H₂O (free).

Results, discussions and conclusions

This paper highlights a new approach to estimate the total ionization cross sections for some of the exotic targets, by considering the ionization contribution to the total inelastic cross section at a given impact energy. Using the charge-density models described above in the absorption potential and feeding the needed inputs we could successfully calculate the total inelastic and total ionization cross sections for H₂O in liquid, in ice and in dimer forms. Our results for the free molecule are found to be in agreement with the available ionization data of Straub *et al* [2] and Vickor and Prepa [3]. The Q_{inel} of H₂O (liq) as given in the semi-empirical approach of Dingfelder *et al* [8] are lower than our values at lower energies, and this is explained below.

In our Figure 1, the E_i versus Q_{inel} curves depict the behavior of this cross section for H₂O in various condensed forms. A comparison has been made with the total inelastic cross sections of H₂O (free), as well as the values of Dingfelder *et al* [8] corresponding to liquid. In our theory Q_{inel} increases along the sequence vapour (free)-liquid-. This is a direct consequence of the molecular properties given in Table 1. In ice structure the molecule has the longest O-H bondlength and hence the largest Q_{inel} . All the solid curves attain a distinct peak value around 80-90 eV and then tend to converge towards the higher regions of the

energy. Slight difference in the ionization energies of the different states also accounts for the variation in the peak positions.

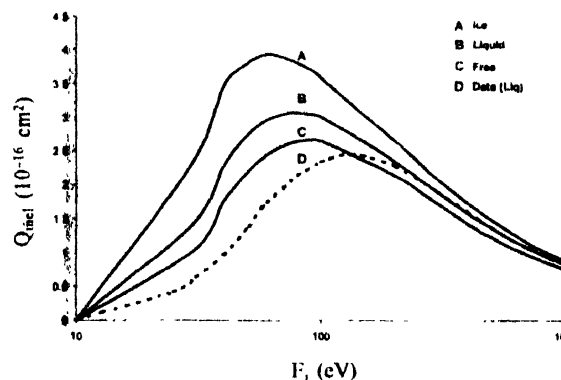


Figure 1. Total inelastic cross sections in 10^{-16} cm^2 at various energies, Curve A - ice, Curve B - liquid, Curve C - free and Curve D - data of Dingfelder *et al* [8].

The calculations of ref. [8], are based on the high energy Born approximation, employing the imaginary part of the complex dielectric response function of the water medium. These authors extended their method to low energies by considering non-Born effects. Hence, their results at low energies may not be reliable. Indeed below 300 eV their cross sections fall below our values for H₂O (liq). Our evaluation of the Q_{inel} is based on the imaginary part of a complex potential that hold good equally at low as well as high energies.

The Inverse Mean Free Path (IMFP) or the macroscopic cross section is defined as,

$$\Sigma_{tot} = N Q_{inel},$$

where N is the number of molecules per unit volume of liquid(water). This quantity is plotted against E_i in the Figure 2, and is compared with the results of [8]. The

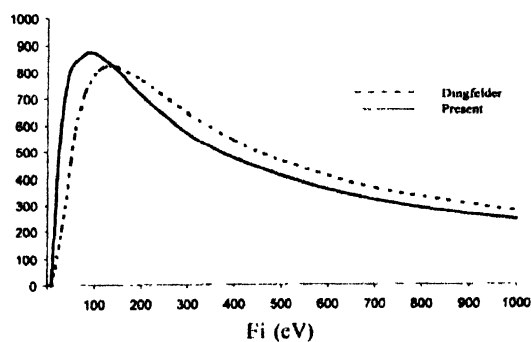


Figure 2. Inverse Mean Free Path ($1/\mu\text{m}$) for electrons in water medium; - Present, - - - - - Dingfelder *et al* [8].

difference in the present and the compared results in this figure are interpreted in terms of the two basic approaches as discussed above. Further the inverse of Σ_{tot} gives the mean free path λ , and this latter quantity is minimum at the

peak of the former. The minimum (inelastic) mean free path of electrons in ice medium is found to be about 9 Å. This is comparable to but more than the electron mean free path in other solids (metals), as obtained by Briggs and Seah [11]. The latter work includes, apart from ionization, the bulk effects of plasmon vibrations *etc.*, hence their minimum MFP is about 5 Å.

Finally consider the total ionization cross section Q_{ion} , which has been obtained in each phase here through the ratio R defined in section 2. The Q_{ion} is found to be 80% of Q_{inel} at the peak of it and matches with the same above 600 eV. The Q_{ion} are exhibited in Figure 3. Here the lowest curve

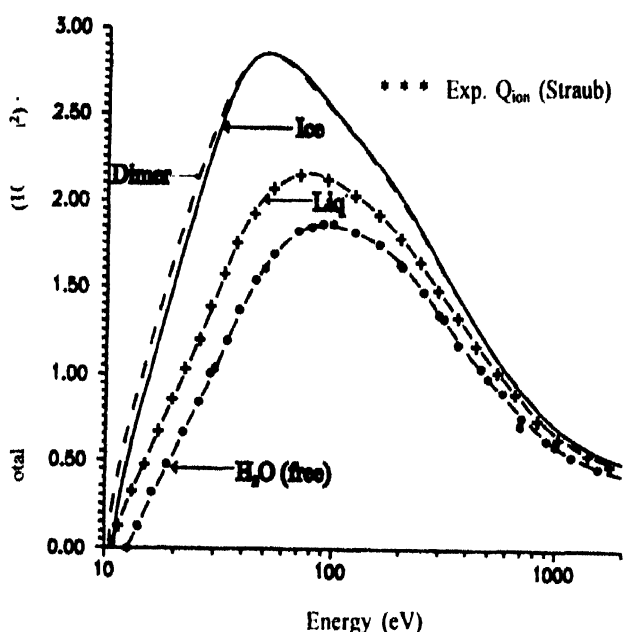


Figure 3. Total ionization cross section of H_2O in various phases; - o - o - o - free, - * - * - * - Experimental Q_{ion} for H_2O (free) given by Straub *et al* [2], - + - + - + - liquid (water), — ice, and - - - - - Dimer.

corresponding to H_2O (free) reproduces the experimental ionization data of [2]. The relative behavior of the three phases in Figure 3 is similar to the Figure 1. In the case of water dimer we calculated Q_{inel} per molecule and estimated Q_{ion} from the knowledge of $R(E_i)$. We must note that the ionization energy of the dimer $[H_2O]_2$ is assumed to be the same as that of the H_2O (ice). It could be somewhat higher in dimer. Among the three phases the Q_{ion} of ice and dimer are the largest, as expected.

In conclusion this article has investigated the total inelastic and ionization cross sections of H_2O in various environments and comparisons have been made with the experimental and other theoretical results, as available. The relative magnitudes of these cross sections are understood in terms of the properties of H_2O molecule in different phases. This work can be extended to amorphous ice and thin water films.

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