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Ionizing collisions of electrons with H_2O molecules in ice and in water

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Abstract

Total inelastic cross sections for electron impact on H_2O molecules in condensed matter phases have been calculated for incident energies from ionisation thresholds up to about 3000 eV. They approach total ionisation cross sections in the high energy limit. The cross sections are calculated through an absorption potential for which a model charge density is developed for H_2O in ice. For H_2O in liquid phase we use the charge density of the free molecule. Differences in the properties of H_2O in condensed phases give rise to differences in the respective cross sections. H_2O (ice) exhibits the highest inelastic cross sections, with H_2O (liq) showing the lowest values from among the three phases, in the peak region. Our cross sections for H_2O (liq) are higher than the previous calculations, based on the Born approximation along with model generalised oscillator strength. (Int J Mass Spectrom 177 (1998) 137–141) © 1998 Elsevier Science B.V.

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1. Introduction

This article presents theoretical total inelastic cross sections Q_{inel} (E_i) for collisions of electrons having energies $E_i \geq 20$ eV, with H_2O molecules. The target molecule is assumed to be in the condensed matter, i.e., in liquid or in ice, and the earlier calculations [1] of the cross sections for H_2O in vapour (free) state serve as a useful reference. The cross sections Q_{inel} (E_i) consist of contributions from electronic excitations and ionisation, and they approach total ionisation cross sections Q_{Ion} at high energies. The quantities Q_{Ion} for H_2O (free) are well known, both theoretically [2,3] as well as experimentally [4,5]. There has been a fundamental and an applied interest in the processes of electron scattering by H_2O in various phases [6]. Interactions of electrons in water are important in view of molecular radiation biology [7]. Icy materials are known to constitute astrophysical objects from comets on one hand to molecular clouds on the other. Electron impact dissociative ionisation with H_2O (ice) has been earlier studied experimentally in terms of ionic mass spectrum and significant differences compared to H_2O (free) have been observed [8]. However, there is practically no study on total inelastic cross sections for this target. For H_2O (liquid) these cross sections have been recently calculated by Dingfelder et al. [9] who used the Born approximation along with the Kramers–

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Table 1
Properties of H_2O molecule in different phases

Phase	O–H bond length (a_0)	O–O bond distance (a_0)	Ionisation energy (eV)
Vapour (free)	1.81	∞	12.6 [a]
Liquid	1.81	∞	10.5 [b]
Ice	1.912 [c]	5.63	11.0 [d]

[a] [6].
[b] [9].
[c] [10].
[d] [11].

Kronig relations for a complex dielectric response function. The present work offers a comparable theoretical data for Q_{inel} of H_2O (liquid).

Thus, the present work focuses attention on the e^-–H_2O cross sections Q_{inel} in these three phases, with a view to link the knowledge on vapour phase with that on condensed phases. Our calculations are based on a complex, energy-dependent spherical potential approach [1] such that the imaginary part of the potential yields the Q_{inel} for the target molecule. The basic input in these calculations, like the ionisation energy I and the electron charge density $\rho(r)$, etc., are modified suitably in going from vapour to liquid or solid state. The structure properties of H_2O molecule [6,9–11] employed in our work are exhibited in the form of Table 1. The results of the present work offer a reasonable theoretical picture of total inelastic cross sections as functions of E_i in the three phases, vis-a-vis the structural properties (Table 1). We have also made graphical comparisons of our results with several other recent data.

2. Theoretical aspects

In this section we outline our scattering calculation method and the physical models developed for this purpose.

2.1. Scattering calculations

The interaction of an incident electron with a target H_2O molecule is represented by a complex, energy-dependent spherical optical potential. As discussed in [1], this approach is quite successful and reliable at the energies of our present interest. The imaginary part V_{abs} of the optical potential accounts for all the allowed electronic excitation and ionisation processes collectively. We employ the well known model given in [12] to express V_{abs} that has been successfully used for a number of atoms and molecules. Thus, according to [12]

$$V_{\mathrm{abs}}(r, E_i) = -\rho(r)\ (T_{\mathrm{loc}}/2)^{0.5}\ (8\pi/5k^2k_f^3) \times H\ (k^2 - k_f^2 - 2\Delta_g)\ (A_1 + A_2 + A_3) \tag{1}$$

where

$$k_f = (3\pi^2\rho^2)^{1/3} \tag{2}$$

In Eq. (1), $\rho(r)$ is the target charge density, T_{loc} is the local kinetic energy of the projectile in the target region, k is the incident momentum (in a.u.), and H(x) is the Heaviside function. Further, Δ_g is the first electronic excitation energy, and A_1, A_2, and A_3 are different functions of k, k_f, and Δ_g. In the case of a free H_2O molecule, we have taken $\Delta_g = 10.2$ eV, corresponding to its transition $X^1\ A_1 \rightarrow {}^3A_1$ [13]. Often in practice the parameter Δ_g is replaced by the ionisation energy I, because I is very well known quantity and the replacement does not affect the results at high energies. Now, the scattering phase shifts $\delta_l(k)$ are determined by the numerical solution of the Schrödinger equation with the potential V_{abs}. The total inelastic cross section is obtained through the standard expression [14]

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

where

$$\eta_l = \exp(-2\ \mathrm{Im}\ \delta_l) \tag{4}$$

Here $l_{\max} \simeq 30$ depending on energy, and Im δ_l is the imaginary part of the phaseshift.

The absorption potential, Eq. (1), depends on the charge density $\rho(r)$ which is known accurately in a single-centre form [1] for H_2O (free). For H_2O in ice or water, a modeling is required, because the charge distribution is expected to change in view of changes in its properties.

2.2. Model charge density for H_2O

We obtain a model $\rho(r)$ for H_2O (ice) by considering the molecules to be separated in the ice structure by a finite distance $R_{O\text{–}O} = 5.63\ a_0$ (Table 1). The charge density is truncated at a distance one-half ($R_{O\text{–}O}$), and renormalised to 10 electrons (of H_2O) within that limit. The expression of $\rho(r)$ itself is also different here. We have expanded the charge density of the (light) hydrogen atoms at the nucleus of the oxygen atom in H_2O, following [15]. The expansion involving the Bessel functions depends parametrically on the bond length $R_{O\text{–}H}$, which is larger in H_2O (ice). The single-centre charge density $\rho_I(r)$ is truncated and renormalised as shown below:

$$4\pi \int_0^{R_0} \rho_I(r) r^2\, dr = 10, \tag{5}$$

where

$$R_0 = 1/2 \cdot (R_{O\text{–}O}) = 2.81\ a_0$$

This charge density is approximate but realistic and has a dependence on the properties of ice structure. This is now employed in V_{abs}, where again an appropriate value of I is used. The total inelastic cross section Q_{inel} for the collisions of electrons with the H_2O molecule in ice is then calculated in the standard formalism. We omit here the expression of the $\rho_I(r)$ for H_2O (ice) based on these physical arguments. Let us note, however, that it has two somewhat different forms depending on whether $r \leq R_{O\text{–}H}$ or $r > R_{O\text{–}H}$ (see [15]).

In the case of H_2O in liquid, we have used the $\rho(r)$ of H_2O (free) as in [1], but a correction has been made for its asymptotic behaviour $\rho(r) \simeq \exp\,[-2\sqrt{2I_0}\ r]$, by introducing the ionisation energy of H_2O (liq) given in Table 1.

3. Results and discussion

The inelastic cross sections for e^-–H_2O collisions in the three phases calculated as above have been exhibited, along with the other data, in Figs. 1 and 2. The curves plotted as functions of E_i from threshold to 3000 eV in these figures have a broad peak around 100 eV or so. Our cross sections Q_{inel} for H_2O (free) are larger than the ionisation cross sections Q_{Ion} (Fig. 1). The difference between the two cross sections accounts for the sum of all the relevant excitation cross sections. There is some difference between the theoretical Q_{Ion} of Hwang et al. [2] and the measured ionisation cross sections of Vikor and Kurepa [4], especially near the peak. The Q_{inel} tends to merge with both the data on Q_{Ion} at high energies ($\geq$ 1000 eV), where ionisation is a dominant process. Fig. 1 also compares our present Q_{inel} values of H_2O (ice) and H_2O (liq) along with that of H_2O (free). The cross sections for H_2O (ice) are larger than those of the other two phases. This is attributed to the larger bond length and hence a larger geometrical cross section of H_2O in the ice structure. The experiments on electron impact ionisation in ice at 700 eV [8] also point to a higher cross section in that phase. The Q_{inel} values for H_2O (liq) are the lowest from among the three phases. The ionisation energy (Table 1) of H_2O (liq) corresponding to its $1b_1$ shell is only slightly smaller than that for H_2O (free). Further, no structure (i.e. finite O–O distance) has been considered here for the liquid phase. Hence, the cross sections for the liquid and the vapour do not differ largely. All these differences in our results are significant in the peak region. Beyond 500 eV, the inelastic cross sections of the three targets gradually converge and they lie marginally above Q_{Ion} of the free molecule. Regarding the relative contribution of different collision processes in H_2O (free), let us note that at 100 eV the theoretical ionisation cross section given by Hwang et al. [2] is about 75% of the present total inelastic cross section. This may approximately hold true for the condensed phases too.

Let us now consider Fig. 2 in which our calculated Q_{inel} are compared with the theoretical Q_{inel} given by Dingfelder et al. [9] for the liquid. One notices significant differences with the compared data, especially up to about 300 eV. The compared Q_{inel} [9] are lower than our results for H_2O (liq). The reason for this is twofold. First, Dingfelder et al. [9] have used the Born approximation, which is expected to be reliable at high energies. For $E_i < 500$ eV, however,

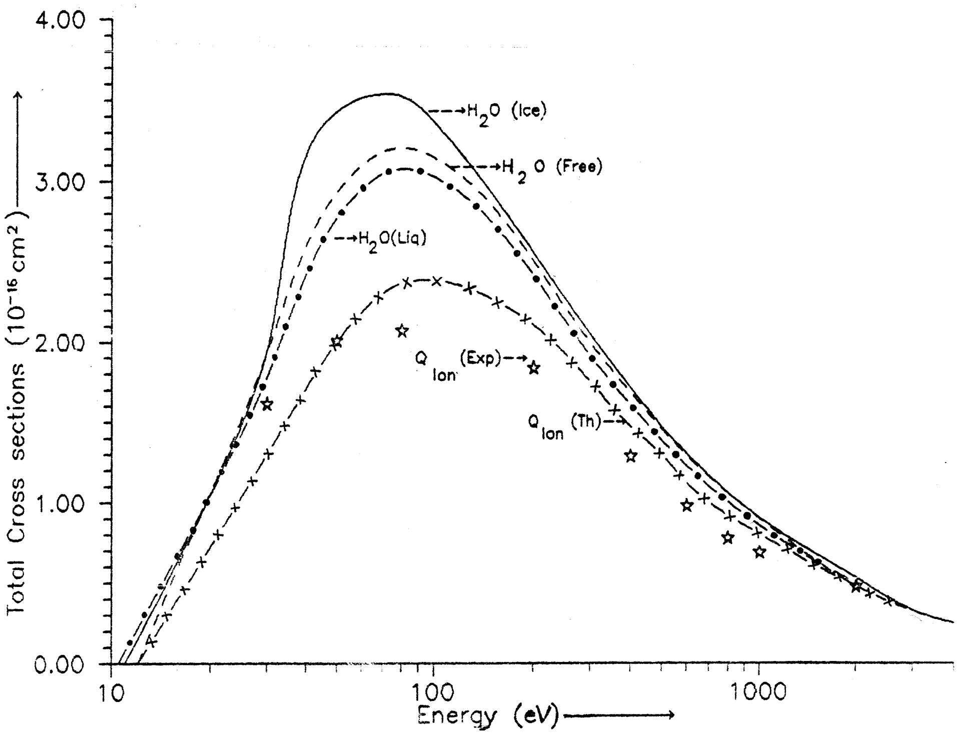

Fig. 1. Total inelastic cross sections for e^-–H_2O collisions. Present results: solid line: H_2O (ice); dashed line: H_2O (free); dash-dot line: H_2O (liq). Other data: dash-X line: theoretical Q_{Ion} of H_2O (free), [2]; stars: experimental Q_{Ion} of H_2O (free), [4].

they used a semiempirical approach. Second, these authors [9] have employed the mean excitation energy corresponding to Bethe stopping power, i.e. $I_{\mathrm{ex}} = 79.75$ eV. Our calculations are based on the model-absorption potential [Eq. (1)], which is very sensitive to the choice of the energy parameter Δ_g, particularly at lower energies. (<300 eV). We have presently fixed Δ_g to be the ionisation energy for H_2O (liq). This value (10.5 eV) is much lower than I_{ex} mentioned above and hence the difference in the Q_{inel}. For energies larger than about 300 eV, our values are in agreement with those of [9], as one would expect from the above discussion. Our calculations are consistent in the sense that the same theoretical approach vide Eqs. (1)–(4) has been followed at all energies, high or low. The physical effects of exchange and polarization are included through T_{loc} in Eq. (1). The present approach essentially considers a single scattering event in e^-–H_2O interaction and therefore does not include any collective excitations that may occur in condensed phases.

4. Conclusion

In conclusion, the present calculations offer reliable total inelastic cross sections for H_2O in ice and in water, over a wide range of energy. These results along with the previous data show a similar high energy behaviour. At intermediate energies, H_2O (ice) gives the largest cross sections followed by the vapour and the liquid, respectively. This trend is understood in terms of the respective properties, although there is a scope here for bringing in condensed matter characteristics further. In the case of H_2O (liq), our intermediate energy results are higher than those of [9], where a mean excitation energy that is quite

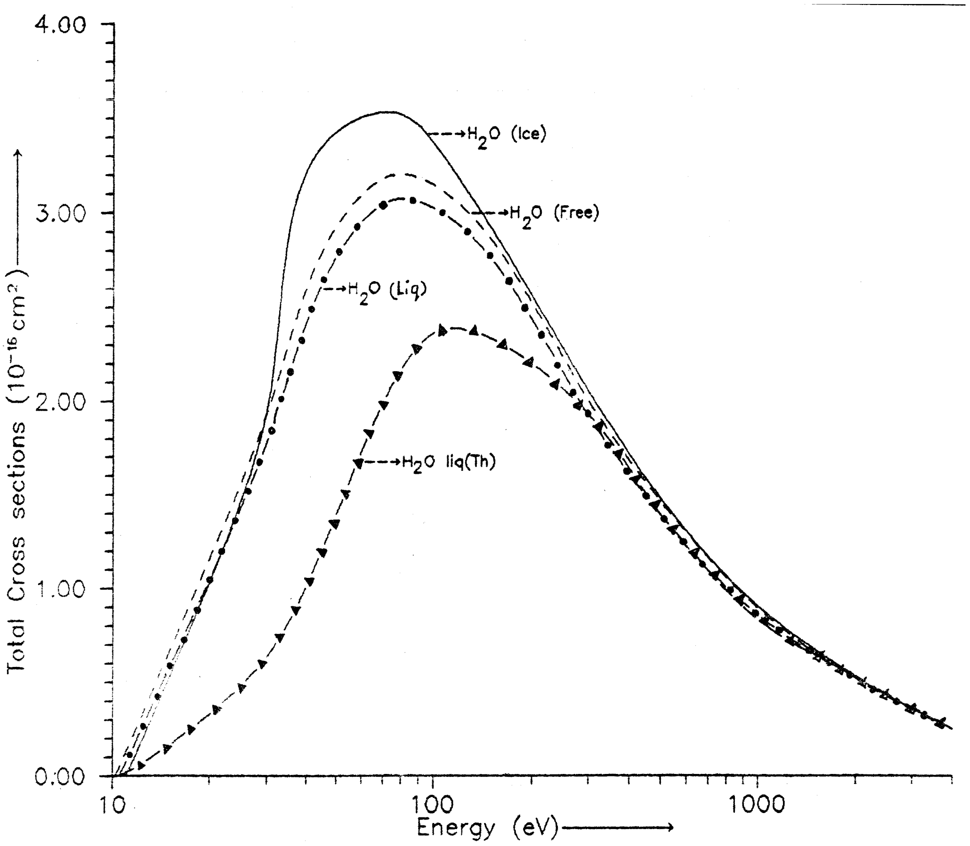

Fig. 2. Total inelastic cross sections in vapour, liquid, and ice. Present results are the same as in Fig. 1. Other data: dash-triangles: Q_{inel} for H_2O (liq) by Dingfelder et al. [9].

larger than the ionisation energy of H_2O (liq) has been employed.

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