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Low-energy electron collisions with water: elastic and rotationally inelastic scattering

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Abstract

Differential, integral and momentum transfer cross sections for the vibrationally elastic and rotationally inelastic scattering of electrons from water at low collision energies ($E < 7$ eV) are reported. The R-matrix method is used to compute the body-fixed T-matrices while the scattering calculations are performed within the fixed-nuclei approximation corrected with the standard Born-closure formula. Our calculations are compared with the very recent experimental results of Cho *et al* (2003 *Radiat. Phys. Chem.* **68** 115). The differential and momentum transfer cross sections are in good agreement with the experimental results. The relative contribution of the rotationally inelastic processes is investigated in some detail. In particular, the importance of the pure elastic process at very low energy is emphasized.

1. Introduction

Water is an extremely important molecule: it is ubiquitous in the universe and fundamental to life. Collisions of electrons with water molecules thus play an important role in a variety of research fields such as astrophysics and atmospheric physics, radiation biology and plasma physics. In the last two decades, these collisions have been studied extensively, both experimentally and theoretically (for a review, see Mason and Itikawa (in preparation)). In particular, differential cross sections (DCS) for the vibrationally elastic scattering have been computed and measured by several authors for collision energies below 50 eV. Elastic DCS of water indeed provide crucial parameters for modelling the radiation effects on biological matter (e.g. Champion (2003)). The recent experimental paper by Cho *et al* (2003) gives absolute DCS at four incident energies between 4 and 50 eV and over scattering angles of 10–180° measured with an original device to extend the measurements to backward angles. A detailed comparison of this data with previous measurements and calculations shows general good agreement among the experimental data up to 100°. At higher angles, however, the available data show very different behaviours. In particular, the results of Cho *et al* (2003) are consistently lower than previous experimental DCS in the backward direction. The elastic integral cross section (ICS) and the momentum transfer cross section (MTCS) were also derived by Cho *et al* (2003) by extrapolating the DCS at the forward scattering angles that are difficult to measure experimentally. As discussed by Okamoto *et al* (1993), such an extrapolation procedure introduces rather large uncertainties because the large dipole moment of water leads to heavily forward peaked cross sections. Reliable theoretical DCS for the forward scattering are therefore highly desirable, as we shall further discuss below.

In this paper, we report differential, integral and momentum transfer cross sections for vibrationally elastic electron scattering from water at collision energies below 7 eV. The water molecule is described by an *ab initio* multicentred wavefunction using the R-matrix method while the scattering calculations are performed within the fixed-nuclei (FN) approximation. A comparison with the most recent experimental results is presented. The theoretical and computational treatment is briefly introduced in the next section. Results are discussed in section 3. Conclusions are summarized in section 4.

2. Theory

All calculations were performed using the electron–H_2O wavefunctions developed by Gorfinkiel *et al* (2002) who calculated cross sections for different molecular geometries (see paper for full details). In this paper, the R-matrix calculations were performed at the equilibrium geometry of H_2O ($r_{\mathrm{OH}} = 1.81\,a_0$ and $\widehat{\mathrm{HOH}} = 104.5°$) using an R-matrix sphere of radius $10\,a_0$. The total wavefunction takes the form

$$\Psi_k = \sum_{ij} a_{ijk}\phi_i(x_1, \ldots, x_N)u_{ij}(x_{N+1}) + \sum_i b_{ik}\chi_i(x_1, \ldots, x_{N+1}), \qquad (1)$$

where ϕ_i are target wavefunctions, $u_{ij}(x)$ are continuum orbitals and χ_i are two-centre quadrically integrable (L^2) functions constructed from the target occupied and virtual molecular orbitals. These last functions are important both for relaxing the enforced orthogonality between the target and continuum orbitals, and for representing short-range polarization effects not included in the truncated partial wave expansion. The present scattering model includes the seven lowest electronic states of water generated using a complete active space configuration interaction (CASCI) procedure and averaged natural orbitals. This model gives a dipole moment of 1.864 D, which can be compared with the experimental value of 1.854 D (Suresh and Naik 2000). The continuum orbitals were represented using the Gaussian-type orbitals basis set developed by Faure *et al* (2002) which includes all angular momentum up to $l = 4$ and is optimized to span energies below 68 eV.

Cross sections were calculated following the procedure implemented in the program `POLYDCS` (Sanna and Gianturco 1998). The general theory of the scattering of an electron from a polyatomic molecule in the fixed-nuclei (FN) approximation has been presented many times before (see, for example, the review by Gianturco and Jain (1986)). In this approach, the cross section is expressed as a partial-wave expansion within the adiabatic–nuclei–rotation (ANR) approximation which assumes that the initial and final target states are degenerate (Lane 1980). For low partial waves (here $l \leqslant 4$), the cross section is computed from the FN T-matrices obtained via the R-matrix calculations. In the case of a polar molecule, the partial-wave expansion does not converge in the FN approximation, owing to the very long-range nature of the electron–dipole interaction. To circumvent this problem, the standard procedure is to use the dipolar Born approximation to obtain the cross section for the high partial waves not included in the FN T-matrices. The final cross section is then calculated as the sum of two contributions and can be regarded as a short-range correction to the Born approximation. The DCS is thus given by the familiar expression (e.g. Gianturco *et al* (1998)):

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\mathrm{d}\sigma^B}{\mathrm{d}\Omega} + \sum_L \left(A_L - A_L^B\right) P_L(\cos\theta), \tag{2}$$

where $P_L(\cos\theta)$ is the Legendre function and A_L are coefficients which depend explicitly on products of T-matrix elements and on algebraic factors. The superscript B denotes that the relevant quantity is calculated within the dipolar Born approximation. The ICS and MTCS are calculated similarly by

$$\sigma = \sigma^B + 4\pi\left(A_0 - A_0^B\right), \tag{3}$$

and

$$\sigma_m = \sigma_m^B + 4\pi\left(A_0 - A_0^B\right) - \frac{4}{3\pi}\left(A_1 - A_1^B\right), \tag{4}$$

respectively. It should be noted that the present cross sections correspond to the vibrationally elastic ones, which are summed over all final rotational states. As shown by Okamoto *et al* (1993), $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}$ does not depend on the initial rotational state of the target molecule unless the scattering angle is very close to 0°. This means that theoretical DCS can be computed for the target in its ground rotational state, whatever the (rotational) temperature at which the experiment was performed. The averaging over a particular rotational state distribution would appear necessary at energies close to rotational thresholds, where the ANR approximation becomes invalid (Morrison 1988). In the following, cross sections have therefore been calculated for the water molecule in its ground rotational state $(j\tau) = (00)$.

3. Results

A comparison between our calculations and the experimental results of Cho *et al* (2003) is presented in figure 1, where the elastic (rotationally summed) DCS are plotted for a collision energy of 4 eV. The first electronic excitation threshold of H_2O at equilibrium geometry is around 7 eV. Three Feshbach resonances, the lowest lying just below the first threshold, were found for $E < 16$ eV (Gorfinkiel *et al* 2002); their positions are strongly dependent on molecular geometry. Hence, above 7 eV, electronic excitation and geometry effects will start to have some effect. For this reason, we made no attempt to investigate the other energies (15, 40 and 50 eV) reported by Cho *et al* (2003). It can be noted that our calculation reproduces the experimental data very well, especially for backward angles (130–180°), where previous experimental data were consistently higher than the present results. Comparisons for intermediate angles (10–120°) at 6 eV with the experimental results of Johnstone and Newell (1991) and the theoretical results of Gianturco *et al* (1998) also give good agreement (Faure *et al* 2004).

Also shown in figure 1 is the partial state-to-state $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(00 \rightarrow j'\tau')$ summed over the τ' pseudo quantum number. The expected dominant contribution of the dipolar $(0 \rightarrow 1)$ rotational transition at forward angles is clearly shown. However, in contrast to the higher energy calculations by Gianturco *et al* (1998), the pure elastic $(0 \rightarrow 0)$ transition becomes dominant at backward angles. This result indicates the crucial role of the short-range interactions, as described by the low-partial waves, in the backward scattering region. In the minimum

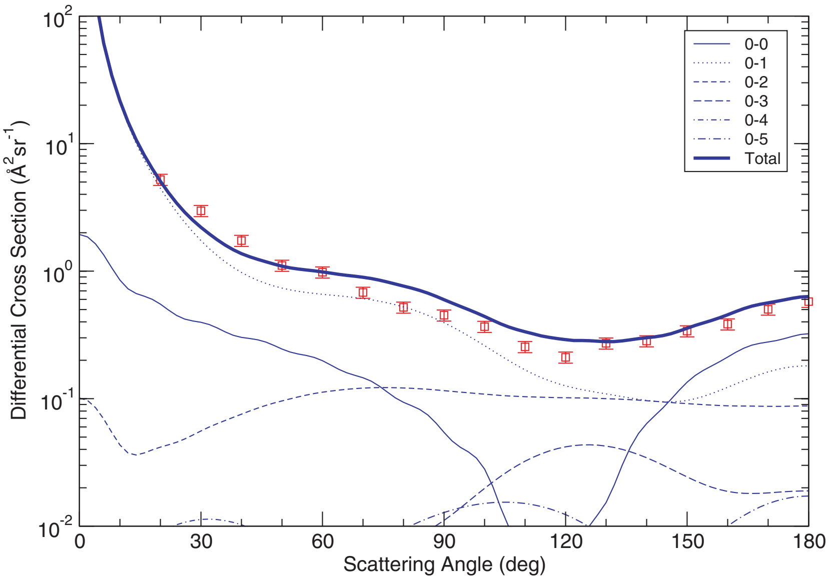

Figure 1. Elastic (rotationally summed) DCS of water at 4 eV. The squares are the experimental points from Cho *et al* (2003). The present calculation is given by the thick solid line. Other lines denote partial state-to-state DCS.

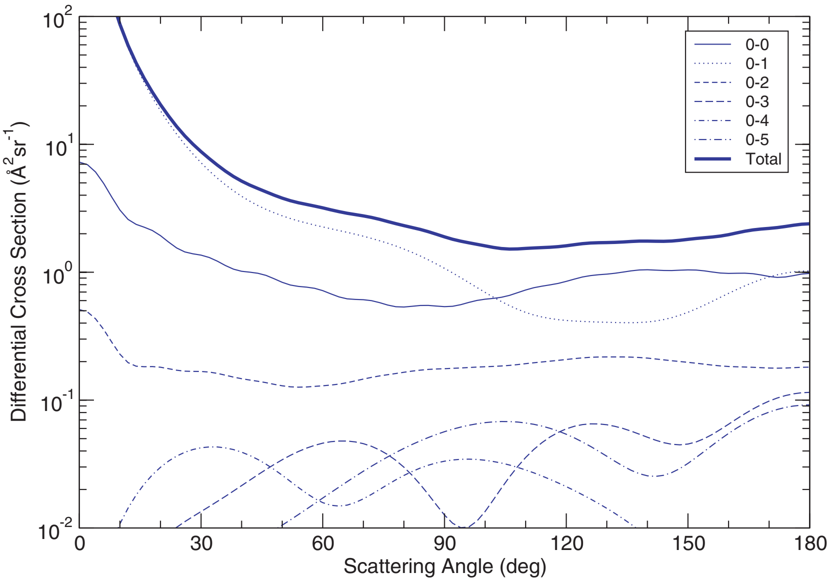

Figure 2. Elastic (rotationally summed) DCS of water at 1 eV. The present calculation is given by the thick solid line. Other lines denote partial state-to-state DCS.

region (120–140°), we note that the $(0 \rightarrow 2)$ transition is also important. Similar features are observed at lower energy, as illustrated in figures 2 and 3. It can be noted, in particular, that the contribution of the pure elastic transition at 250 meV becomes dominant for scattering angles larger than 60°.

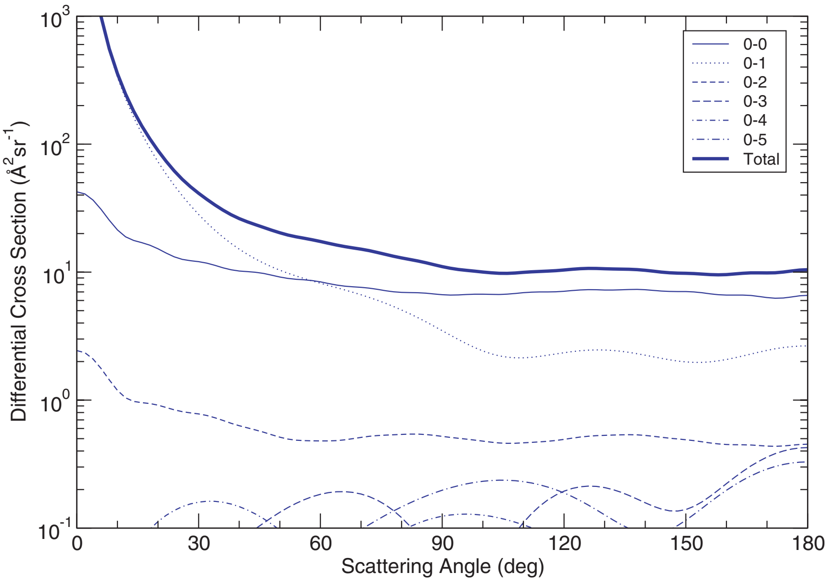

Figure 3. Elastic (rotationally summed) DCS of water at 0.25 eV. The present calculation is given by the thick solid line. Other lines denote partial state-to-state DCS.

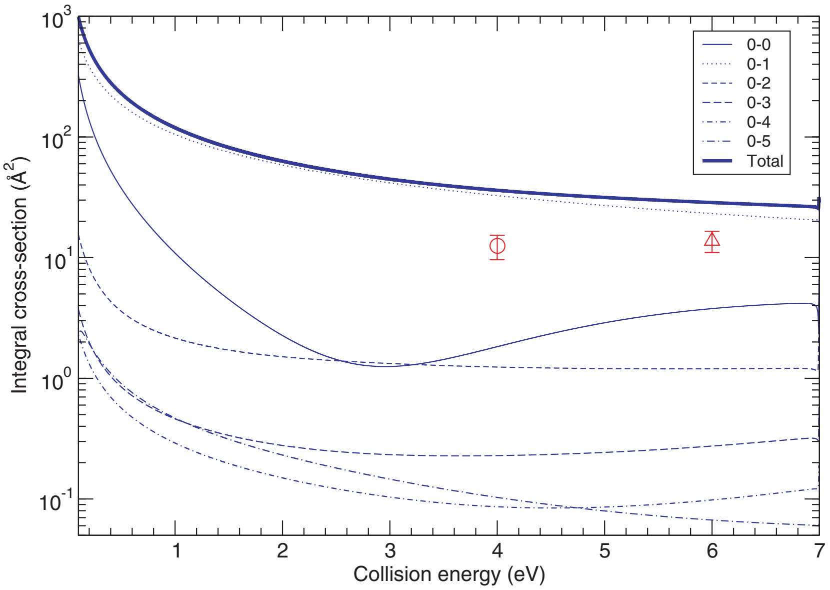

Figure 4. Elastic (rotationally summed) ICS of water as a function of the collision energy. The experimental determinations of Cho *et al* (2003) (open circle) and Johnstone and Newell (1991) (open triangle) are plotted for comparison. Partial state-to-state ICS are also shown.

Figure 4 presents the vibrationally elastic ICS, as well as partial state-to-state ICS with $\Delta j = 0$–5 for collision energies in the range 0.1–7 eV. We note, again, that the $\Delta j = 1$ rotational excitation is the most efficient process in the whole range of collision energies. However, it is interesting to note that below about 3 eV, the relative contribution of the pure

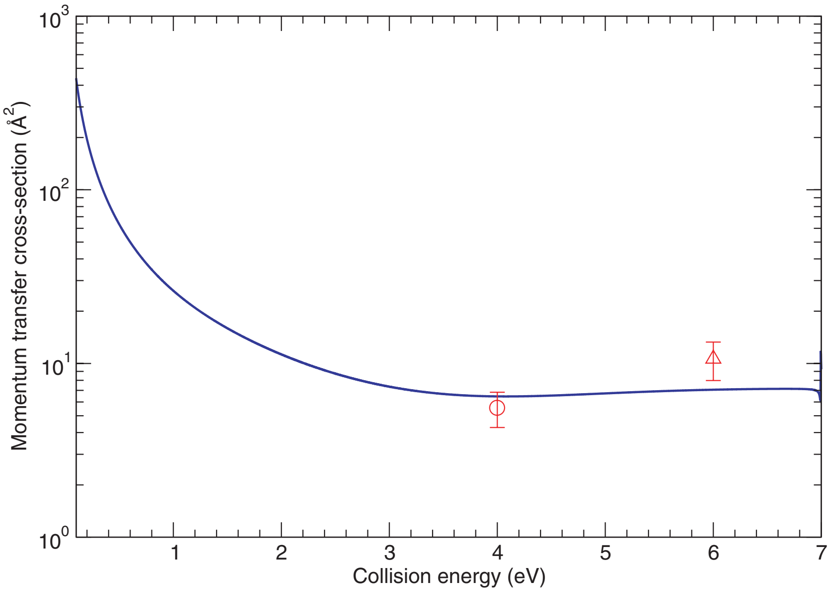

Figure 5. Elastic (rotationally summed) MTCS of water as a function of the collision energy. The experimental determinations of Cho *et al* (2003) (open circle) and Johnstone and Newell (1991) (open triangle) are plotted for comparison.

elastic $\Delta j = 0$ process to the total ICS increases sharply with decreasing energy. Thümmel *et al* (1992) showed in their calculations for vibrationally elastic scattering of HF including non-adiabatic rotational effects that the pure elastic ICS will become larger than the $\Delta j = 1$ ICS at energies close to rotational thresholds. As noted above, the ANR approximation fails near rotational thresholds where a full rotational close-coupling calculation would indeed be necessary. We have consequently restricted the present calculations to energies larger than 100 meV. In any case, it is worth noting that our results are in disagreement with the usual assumption that the pure elastic scattering process is negligible at very low energy (e.g. Field *et al* (2000)).

At energies above 3 eV, the $\sigma(0 \rightarrow 0)$ cross section is found to display a pronounced rise which is probably caused by the Feshbach resonance of $^2B_1$ symmetry that lies just below the first excited electronic state (Gorfinkiel *et al* 2002). As mentioned earlier, the position of this resonance depends strongly on the molecular geometry. Therefore, inclusion of vibrational motion is likely to have a strong effect on the cross section in the resonance region. ICS for higher rotational transitions ($\Delta j = 2, 3, 4$) are also affected, but to a lesser extent, by this resonance (see figure 4).

The ICS determined experimentally by Cho *et al* (2003) at 4 eV is lower than ours by a factor of 3. Since the experimental and calculated DCS are in good agreement over the range of experimental measurements, this difference seems to come from the extrapolation procedure used by Cho *et al* (2003) at forward angles, where the DCS increase very steeply owing to the dipole interaction. This problem, previously highlighted by Okamoto *et al* (1993) and Gianturco *et al* (1998), indicates that ICS deduced from experiment in this fashion is not reliable. Figure 5 presents the vibrationally elastic MTCS as a function of the collision energy. In contrast to the ICS, our results are in good agreement with the value determined by Cho *et al* (2003). This probably reflects the fact that the forward angle contribution of the DCS to the MTCS is small. Conversely, the difference with the results of Johnstone and Newell (1991) emphasizes the importance of the backward direction. Our calculated MTCS is also found to possess a minimum value of 6.46 $\mathring{A}^2$ at about 4 eV, again probably caused by the $^2B_1$ resonance. It is interesting to note that such a feature in the MTCS (minimum value of 6 $\mathring{A}^2$ at about 3 eV) was reported by Hayashi (1989) on the basis of various theoretical and experimental data in the energy range 1–50 eV.

4. Conclusions

Our calculated cross sections are in excellent agreement with the latest differential measurements. The results show that extrapolation of experimental cross sections to small angles still causes problems. The low energy importance of the rotationally elastic process, which is often neglected because it is equal to zero in the pure dipolar approximation, is also shown. Neither this process, nor the $(0 \rightarrow 2)$ transition can be neglected at low energies.

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