LETTER TO THE EDITOR

Excitation of the symmetric and antisymmetric stretch vibrations of H_2O by electron impact

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Abstract
Electron energy loss spectra recorded at $135°$ at constant scattered electron energies of 0.05, 0.6 and 3.0 eV, and with 10 meV resolution, reveal that the antisymmetric stretch vibration (001) is excited much less than the symmetric stretch vibration (100). Spectra subtraction indicates that the (001) level is excited about $5\times$ less than (100) at 1 eV. Band profiles recorded 0.6 eV above threshold show that the $\Delta J = 0$ branch dominates the excitation of (010) and (100) vibrations but is absent for the (001) vibration. This indicates that resonant excitation is decisive for the (010) and (100) states but direct dipole mechanism for (001). The R-matrix adiabatic nuclei theory with closure approximation reproduces well the cross section for the (010) state, but dramatically underestimates the cross section for the symmetric stretch vibration and overestimates the cross section for the asymmetric stretch vibration.

1. Introduction

Water represents an attractive target for the study of electron–molecule collisions. It is a suitable prototype for polyatomic molecules and its substantial dipole moment makes it interesting for the study of dipole-related threshold peaks. Understanding electron scattering in water is also of considerable practical interest (Ishii *et al* 1990), for example in discharges and for the description of radiation damage to living tissue.

Vibrationally inelastic cross sections were measured from threshold to 10 eV and between $20°$ and $110°$ by Seng and Linder (1976). This remarkable study remains, together with the subsequent work of Rohr (1977), the only one to report data below 2 eV and to include the threshold peaks. Vibrationally inelastic differential cross sections (DCSs) at higher energies were subsequently measured by Shyn *et al* (1988), Johnstone and Newell (1991) and El-Zein *et al* (2000a, 2000b). The later two publications also review the earlier studies in some detail. Jung *et al* (1982) measured the vibrationally elastic but rotationally inelastic DCSs at 2.14 and 6 eV in a high resolution experiment.

Theoretical studies below 5 eV are rare. Born theory has been developed by Itikawa (1972, 1974). The excitation of the 010 and 100 modes has been calculated in the fixed nuclei, impulse approximation by Jain and Thompson (1983). The latter work has been improved and extended to include the (001) vibration by Moreira *et al* (2001), who also provide a more complete list of citations of earlier work. The theoretical studies have been reviewed and compared to experiments by Itikawa (1997).

An important limitation of the existing experimental studies is that the symmetric and the antisymmetric stretch vibrations (100) and (001), separated by 12 meV in H_2O and 14.5 meV in D_2O, have not been resolved. This letter reports an attempt to use an improved resolution of the electrostatic spectrometer, around 10 meV, to measure the cross sections for the two stretch vibrations separately.

2. Methods

The measurements were performed using a spectrometer with hemispherical analysers described by Allan (1992, 1995). The response function of the spectrometer at very low energies has recently been improved by adding more degrees of freedom in compensating residual electric fields in the collision region, a by-product of the recently installed (Allan 2000) 'magnetic angle changer'. The resolution of the instrument in the energy-loss mode has recently been improved by using rectangular apertures to define the pupil, providing a ribbon-shaped beam in the analysers (Allan 2001). The energy of the incident beam was calibrated on the 19.366 eV ^2S resonance in helium and is accurate to within ± 20 meV. The analyser response function was determined on the elastic scattering in helium. The sample inlet nozzle had a diameter of 0.25 mm and was kept at $\sim 30\,°C$ during the measurements. The pressure was kept low ($\sim 5 \times 10^{-7}$ mbar in the main chamber) while recording energy-loss spectra to reduce cluster formation and double scattering near threshold.

Absolute values of the cross sections were determined by comparison with the elastic cross section of helium of Nesbet (1979) using the relative flow method. Water vapour was found to adsorb strongly to stainless steel surfaces and its flow could consequently not be derived from the rate of pressure increase in the inlet manifold. Instead, the flow was determined from the vapour pressure behind the nozzle using a proportionality constant calibrated on various less adsorbing gases. (The flow was found to depend linearly on the pressure behind the nozzle for the values used for absolute measurements in this study, 0.05–0.2 mbar.)

Details of the theoretical method were given by Moreira *et al* (2001). The calculations for the DCSs were performed with the UK *R*-matrix code (cf Morgan *et al* (1998)) and codes developed in Fribourg. The theory assumes that the main interaction between the water molecule and the incoming electron is due to the dipole moment; thus the corrections to the scattering amplitude are done via a closure approximation. The DCS were calculated with the centre of mass of the water molecule at the origin of coordinates, unlike previous work, where the mass of the oxygen was taken to be infinity (Moreira *et al* 2001, Moreira 2000).

3. Results

The energy-loss spectrum shown in figure 1 was recorded by collecting scattered electrons with a fixed residual energy of $E_r = 0.6$ eV and varying the incident electron energy. All the bands were thus recorded 0.6 eV above their respective excitation thresholds. Both the elastic and the inelastic bands consist of a relatively narrow peaks due to the $\Delta J = 0$ transitions and a relatively broad 'footing' caused by accompanying rotational transitions, presumably mainly
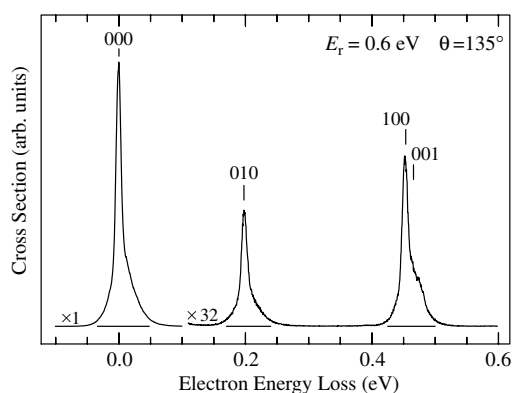
Figure 1. Energy-loss spectrum of H_2O recorded at a fixed energy of the scattered electrons, $E_r = 0.6$ eV.
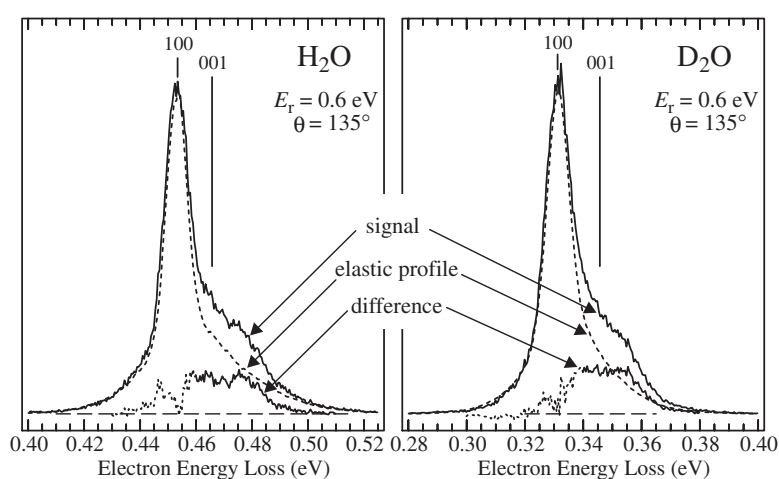

Figure 2. The (100, 001) band (solid curve) is compared to the elastic band profile (dashed curve). The difference of the two profiles indicates an entirely different band shape for the antisymmetric stretch, the $\Delta J = 0$ branch is missing. (The dotted section of curve is a small difference between two large numbers and is not significant.)

$\Delta J = \pm 1$. The excitation of overtone and combination vibrations is weak. The shape of the elastic peak resembles that reported by Jung *et al* (1982) except that the $\Delta J = 0$ peak is more prominent at the present energy and scattering angle. The rotational 'footing' is narrower due to the lower temperature of the present experiment ($\sim$300 K as opposed to 500 K).

The shapes of the vibrationally elastic and the 010 bands are nearly identical in figure 1, but the third band has a clear shoulder on the high-energy side which can be attributed to the transition to the (001) state. The rotational broadening prevents a complete separation of the (100) and (001) vibrations, but the shoulder shows clearly that the excitation of the symmetric stretch dominates, asymmetric stretch is excited only weakly.

Figure 2 shows an attempt to separate the (100) and (001) contributions to the observed band by spectra subtraction. The elastic profile has been horizontally shifted and vertically scaled to match the low energy side of the (100, 001) band. The very good agreement of the $\Delta J = 0$ peak and the low-energy side of the (100, 001) band with the elastic profile indicates

Table 1. DCS (in 10^{-16} cm^2 sr^{-1}) at a residual electron energy $E_r = 0.6$ eV and $\theta = 135°$. E_i is the incident electron energy (rounded) in eV. The experimental error is $\pm 30\%$ for the elastic, $\pm 40\%$ for the inelastic DCSs, a factor of two for the (001) final state. The row labelled (100, 001) lists the sums of the cross sections for these two states.

State	H$_2$O				D$_2$O		
	E_i	Experiment	Theory[a]	J–T[b]	E_i	Experiment	Theory[a]
(000)	0.6	1.6	—	—	0.6	1.6	—
(010)	0.8	0.018	0.016	—	0.75	0.014	0.013
(100, 001)	1.05	0.027	0.018	—	0.95	0.020	0.019
(100)	1.05	0.022	0.003	0.013	0.95	0.016	0.002
(001)	1.05	0.005	0.015	—	0.95	0.004	0.017

[a] Present work.
[b] Jain and Thompson (1983), at 1 eV.

that the (100) band has the same shape, that is the same degree of rotational excitation, as the (000) and the (010) bands. Note that the identical shapes of the low-energy sides of the elastic profile and the (010) and (100) bands also imply identical shapes of the high-energy sides, because the cross sections of the two branches are related by detailed balance (Jung *et al* 1982). The difference band, attributed to the transition to the (001) state, has a very different shape, the $\Delta J = 0$ peak is missing. The area under difference band indicates that the cross section for the excitation of the (001) state is about $5\times$ smaller than that for the (100) state at 135°. The same conclusions are reached for D$_2$O, as shown on the right side of figure 2.

The cross sections are compared with theoretical predictions in table 1. Good agreement is found for the bending vibration (010), but dramatic differences are found for the stretch vibrations, conclusions similar to those made by Moreira *et al* (2001) and at higher energies by Jain and Thompson (1983) and Nishimura and Itikawa (1995). The cross section for the excitation of the symmetric stretch 100 is underestimated, that for the asymmetric stretch overestimated. Interestingly, the prediction of Jain and Thompson (1983) for the symmetric stretch vibration (100) is closer to the experimental observation than the present more elaborate result. The cross sections for D$_2$O are found, at the same energy interval above threshold, slightly smaller than the cross sections for H$_2$O, in line with the observation made at 8 eV by Ben Arfa *et al* (1990).

Figure 3 shows spectra recorded 0.05 and 3.0 eV above threshold. No distinct shoulder due to the (001) state can be discerned in the $E_r = 0.05$ eV spectrum, indicating a cross section even smaller in comparison to that of the (100) state in the $E_r = 0.6$ eV spectrum. The vibrationally elastic peak in the $E_r = 3.0$ eV spectrum indicates a substantially higher degree of rotational excitation than in the $E_r = 0.05$ and the $E_r = 0.6$ eV spectra. This observation could be limited to large scattering angles because the calculations of Gianturco (1991) and Varella *et al* (2001) indicate that the $\Delta J = 0$ branch has a deep minimum around 120° at 6 eV.

The tail due to rotational excitation masks the contribution of the (001) state, but the qualitative statement that the (001) cross section is much less than the (100) cross section can be made. The low-energy tails of the (010) and (100) bands are slightly more pronounced than the low-energy tail of the vibrationally elastic band in the $E_r = 0.05$ eV spectrum, in contrast to the $E_r = 0.6$ eV spectrum of figure 1. We do not have a definite explanation but it could be of instrumental origin, caused by rapid decrease of the incident electron beam intensity below 0.05 eV.

A direct comparison of the present experimental cross sections with those of Seng and Linder (1976) is not possible because their measurements extend only to 110°. A generally
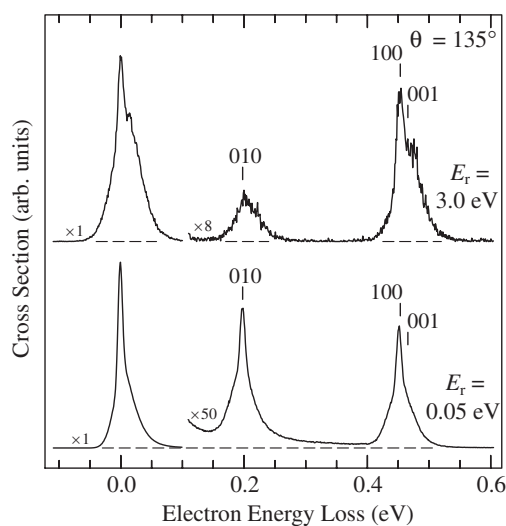
Figure 3. Energy loss spectra recorded at 0.05 eV (bottom) and 3.0 eV (top) above threshold.

satisfactory agreement is found, however, when their angular data is visually extrapolated to 135°. Our results (Allan and Moreira 2001) confirm the observations by Seng and Linder of intense threshold peaks in the bending and the symmetric stretch vibrations.

4. Discussion and conclusions

The symmetric stretch vibration (100) was found to be excited much more than the antisymmetric stretch (001) at all energies covered by the present study. Comparison of this observation with the calculated results reveals a remarkable deficiency of the present theory of vibrational excitation of water: the cross section for the excitation of the symmetric stretch vibration (100) is dramatically underestimated, that for the antisymmetric stretch vibration (001) is overestimated. In contrast, the cross section for the excitation of the bending vibration is reproduced correctly by the calculation.

The vibrationally elastic and the (010) and (100) peaks are dominated by the $\Delta J = 0$ branch at low energies, but this branch appears to be absent in the transition to the (001) state. We note that only the $\Delta J = \pm 1$ branches are allowed in direct dipole excitation, and the observation is thus consistent with a prevailing direct dipole excitation mechanism for the (001) state even at the present large scattering angle. The prevalence of the $\Delta J = 0$ branch for the symmetric stretch and the bending vibrations points to a predominantly resonant excitation. These findings are consistent with the symmetry selection rules of Wong and Schulz (1975) and Gallup (1986), which allow resonant excitation of the totally symmetric vibrations (100) and (010) for the A_1 resonance dominating the low energy scattering (Jain and Thompson 1983), but not of the antisymmetric stretch vibration (001). Resonant excitation of the b_2 antisymmetric stretch becomes possible only in second order, by vibronic coupling between A_1 and B_2 resonances (Estrada *et al* 1986). Alternatively, the selection rules may be relaxed for a B_2 resonance by allowing a change of angular momentum of the electron during scattering, with an outgoing s-wave (Wong and Schulz 1975, Gallup 1986).

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