Electron-impact vibrational excitation of water molecules

Tamio Nishimura and Yukikazu Itikawa
Institute of Space and Astronautical Science, Yoshinodai, Sagamihara 229, Japan

Received 21 October 1994, in final form 6 February 1995

Abstract. Cross sections (differential and integral) for the electron-impact vibrational excitation of H₂O are calculated at the collision energies 6–50 eV. Excitation of the three fundamental modes of vibration, (100), (010) and (001), is considered separately. The calculation is based on the rotationally sudden and a vibrationally close-coupling method taking an ab initio electrostatic potential. The effects of electron exchange and target polarization are taken into account approximately. The resulting cross sections are compared with the experimental data available. A comparison is also made with the Born cross section, which is often cited in experimental papers. Qualitatively, the present differential cross sections well reproduce the experimental data, particularly the angular dependence of the cross section. Quantitatively, on the other hand, there are some disagreements between the present calculation and the experimental data.

1. Introduction

Vibrational excitation is a very important mechanism by which energy is lost in low-energy electrons in a molecular gas. In other words, when an electron slows down in a molecular gas, a considerable amount of the primary energy of the electron goes into the vibrational excitation. The vibrationally excited (i.e. hot) molecule, in turn, plays an active role in collisions with other particles (see, e.g., Mason et al 1994). In some cases, the reactivity of a molecule is enhanced remarkably through vibrational excitation by electron impact. Thus it is of fundamental significance to know how efficient the electron-impact vibrational excitation is.

Polyatomic molecules have a number of different vibrational modes. The electron interaction with these vibrational modes is complicated. Thus it is difficult to study theoretically the vibrational excitation of polyatomic molecules. In 1974 one of the present authors (YI) derived a general formula for the vibrational excitation cross section of polyatomic molecules in the Born approximation (Itikawa 1974a). He applied the formula to the vibrational excitation of the water molecule (Itikawa 1974b). Since then very few calculations have been done for the vibrational excitation of polyatomic molecules. In the present paper, H₂O is again selected and a more elaborate calculation is made in order to obtain the vibrational excitation cross sections for that.

For the vibrational excitation of H₂O by electron impact, several experimental results have been reported so far (Trajmar et al 1973, Seng and Linder 1976, Shyn et al 1988, Furlan et al 1991). All of them measured differential cross sections (DCSS). Seng and Linder and Shyn et al reported DCSS in a relatively lower range of electron energy (less than 20 eV). These two sets of cross sections almost agree with each other. They also reported the corresponding integral cross sections (ICSS). Trajmar et al and Furlan et al reported only ICSS. Trajmar et al gave cross sections in relative values at 15 and 53 eV. Furlan et al obtained DCSS at 30 and 50 eV. Except for the Born calculation by Itikawa
mentioned above, the only theoretical work on the vibrational excitation of H\(_2\)O has been done by Jain and Thompson (1983). By using the adiabatic approximation, they calculated vibrational excitation cross sections in the range 1–10 eV.

The present calculation is based on the rotationally sudden (or, in other words, the fixed nuclear orientation) approximation. The vibrational transition is treated in a vibrationally two-state close-coupling method. The electrostatic potential is calculated from an ab initio multicentred wavefunction. The effects of electron exchange and target polarization are taken into account approximately through a model potential.

The water molecule has three normal modes of vibration. Here the cross sections are calculated for the excitation of the lowest excited state of each mode: symmetric stretching (100), bending (010) and antisymmetric stretching (001) modes. Experimentally the two stretching modes, (100) and (001), cannot be separated with the present technique. All the experimental papers report only combined cross sections for the two stretching modes (being denoted by (100, 001) from now on). Jain and Thompson calculated the cross sections for the (100) and the (010) modes, but not for (001). In the present paper, the cross sections are obtained for all three modes. The resulting cross sections for the (100) and (001) modes are added together, when compared with the experimental data. The DCSSs and ICSSs are calculated at 6–50 eV. A comparison with the Born calculation is also made to test its validity in the present case.

2. Theory

We consider the vibrationally inelastic scattering of electrons from water molecules. The present calculation is based on the fixed nuclear orientation approximation (e.g. see Gianturco and Jain 1986). The three normal modes of vibration of H\(_2\)O are treated as uncoupled and harmonic.

The interaction potential for an electron with the molecule is expanded in terms of the nuclear coordinates (\(\xi_i\)) around their equilibrium values (\(\xi^e_i\)) as

\[
V(\xi, r) = V(\xi^e, r) + \sum_i \left[ \frac{\partial V(\xi^e_i, r)}{\partial \xi_i} (\xi_i - \xi^e_i) + \text{higher-order terms} \right] + \text{higher-order terms}
\]

where \(i\) denotes each vibrational mode and \(r\) is the position vector of the incident electron with respect to the gravity centre of the target molecule. Since we consider the excitation of lower excited states, we can assume the terms \((\xi_i - \xi^e_i)^p \quad (p \geq 2)\) to have only a small contribution to the vibrational matrix element \(\langle n|V|n'\rangle\) and we retain the first two terms in equation (1). Atomic units are used in the present paper unless otherwise stated. From equation (1), the relevant vibrational matrix element of the potential is derived as follows:

\[
\langle n|V|n'\rangle = V(\xi^e, r)\delta_{nn'} + \sum_i \left[ \frac{\partial V(\xi^e_i, r)}{\partial \xi_i} (n|\xi_i - \xi^e_i|n') \right]
\]

where \(n\) (or \(n'\)) denotes the three vibrational quantum numbers collectively, that is \(n = (n_1, n_2, n_3)\). Assuming a harmonic oscillator, \(\langle n|\xi_i - \xi^e_i|n'\rangle\) can be calculated as

\[
\langle n|\xi_i - \xi^e_i|n'\rangle = \left[ \left( \frac{n_i + 1}{2} \right) \delta_{n_i, n_i+1} + \left( \frac{n_i}{2} \right) \delta_{n_i, n_i-1} \right] \prod_j \delta_{n'_j, n_j}
\]

We adopt three types of interaction potential: electrostatic (\(V^w\)), electron exchange (\(V^{ex}\)) and correlation-polarization (\(V^{pol}\)). The electrostatic potential is obtained with an
**Vibrational excitation of H\textsubscript{2}O by electrons**

*ab initio* target wavefunction. The effects of electron exchange and target polarization are approximately taken into account through the model potentials, \(V^{\text{ex}}\) and \(V^{\text{pol}}\), respectively. For \(V^{\text{ex}}\), use is made of the Hara version of the free-electron gas model (Hara 1967). For \(V^{\text{pol}}\), we take the parameter-free correlation-polarization model of Padial and Norcross (1984). Details of the two-model potentials have been given in a previous paper (Okamoto *et al* 1993), in which a vibrationally elastic scattering is studied.

The potential which is the sum of \(V^{\text{ex}}\), \(V^{\text{ex}}\) and \(V^{\text{pol}}\) is expanded in terms of the symmetry-adapted angular basis functions \(X_{\lambda}^\nu(r)\) as follows:

\[
V(\xi, r) = \sum_{\lambda\nu} V_{\lambda\nu}(\xi, r) X_{\lambda}^\nu(r).
\]

Here \(\nu\) collectively denotes the indices specifying the irreducible representation and those distinguishing the degenerated members (Okamoto *et al* 1993). In a manner similar to equation (4), the wavefunction of the whole system is expanded as

\[
F(r, \xi) = \sum_{l\nu n} r^{-1} f_{l\nu n}(r) X_{l}^\nu(\hat{f}) \chi_n(\xi).
\]

Here \(\chi_n\) is the vibrational wavefunction of the molecule.

The radial part of the scattering wavefunction then satisfies a set of coupled differential equations,

\[
\{d^2/dr^2 - (l(l + 1))/r^2 + k_n^2\} f_{l\nu n}(r) = 2 \sum_{l'\nu' n'} \langle l\nu n| V| l'\nu' n'\rangle f_{l'\nu' n'}(r)
\]

where \(k_n\) is the wavenumber of the electron in the channel \((l\nu n)\), and

\[
\langle l\nu n| V| l'\nu' n'\rangle = \int d\xi \int d\hat{f} (\chi_n X_{l}^\nu)^* V(\chi_n X_{l}^\nu).
\]

The interaction matrix element can be evaluated as

\[
\langle l\nu n| V| l'\nu' n'\rangle = \int d\hat{f} X_{l}^\nu \langle n| V| n'\rangle X_{l'}^\nu
\]

by taking \(\langle n| V| n'\rangle\) in equation (2).

Solving equation (6) with an appropriate boundary condition, we obtain the scattering matrix. From the scattering matrix, the differential and integral cross sections are calculated in a way similar to the case for elastic scattering (Okamoto *et al* 1993). Since a water molecule has a permanent dipole moment, high partial waves contribute significantly to the cross section. We use the Born approximation to evaluate such a contribution.

In the present paper, we calculate the cross section for the excitation of three fundamental modes of vibration: \((100)\), \((010)\) and \((001)\). For each excitation, we retain only the initial (i.e. the ground) and the final (i.e. the first excited) vibrational states in the coupled equation (6). In this sense, our method is a vibrationally two-state close-coupling approximation. In our calculation, therefore, we take into account neither transitions among different modes of vibration nor excitations of higher harmonics. These transitions occur through the higher-order terms in the interaction or anharmonicity of the vibration. They are small in the present case. In fact Trajmar *et al* (1973) demonstrated very small cross sections measured for the excitation of the higher harmonic vibration.
3. Numerical calculation

To generate the wavefunction of H$_2$O in its electronic ground state, an *ab initio* molecular orbital code GAMESs (the North Dakota State University version, see Schmidt *et al* 1990) is employed in the SCF approximation. At the equilibrium geometry of the target, the H–O distance and the H–O–H angle are taken to be 1.809 au and 104.5°, respectively. The molecule is placed in the yz plane with the origin in the centre of mass. The z axis is taken along the symmetry axis with the O atom on the negative side. We use the same basis set (Dunning 1971) as that employed in Okamoto *et al* (1993).

To evaluate the potential derivative, $\frac{\partial V}{\partial \xi_j}$ in equation (2), we use the method of numerical differentiation with respect to the symmetry coordinates (John *et al* 1979). There is a method to obtain the potential derivative more directly. With the use of the CPHF (coupled perturbed Hartree–Fock) method (Gerratt and Mills 1968), we can calculate the derivative of the electron density, from which the potential derivative can be obtained. In a preliminary calculation, we have tried both methods and found no serious difference in the results. The method of numerical differentiation needs much less computing time than the CPHF, so that the former is employed in the present calculation. Table 1 shows the derivatives of the dipole ($\mu_\alpha$) and the quadrupole ($\theta_{\alpha\beta}$) moments for each mode, determined from the asymptotic part of the present static potential. These values are consistent with those obtained with other SCF calculations (see, for example, Amos (1987), which shows infrared intensities calculated in the SCF approximation with various basis sets). For the long-range part of $\frac{\partial V_{\text{lr}}}{\partial \xi_j}$, the derivatives of polarizabilities determined experimentally are adopted (Murphy 1977, 1978). The frequencies of the normal vibrations are taken from experiment (i.e. 3657, 1595 and 3756 cm$^{-1}$ for the symmetric stretching, bending and antisymmetric stretching modes, respectively).

<table>
<thead>
<tr>
<th>Derivative of multipole</th>
<th>Present</th>
<th>Experiment$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\partial \mu_x / \partial \xi_1$</td>
<td>$-2.344 \times 10^{-2}$</td>
<td>$8.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\partial \mu_x / \partial \xi_2$</td>
<td>$-8.453 \times 10^{-2}$</td>
<td>$-7.058 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\partial \mu_y / \partial \xi_3$</td>
<td>$4.050 \times 10^{-2}$</td>
<td>$3.82 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\partial \theta_{xx} / \partial \xi_1$</td>
<td>$-3.962 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$\partial \theta_{xx} / \partial \xi_2$</td>
<td>$-0.0000$</td>
<td></td>
</tr>
<tr>
<td>$\partial \theta_{xx} / \partial \xi_3$</td>
<td>$0.2242$</td>
<td></td>
</tr>
<tr>
<td>$\partial (\theta_{xz} - \theta_{yz}) / \partial \xi_1$</td>
<td>$-0.0393$</td>
<td></td>
</tr>
<tr>
<td>$\partial (\theta_{xz} - \theta_{yz}) / \partial \xi_2$</td>
<td>$-0.6519$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Dipole derivatives derived from the experimental IR intensities by Flaud and Camy-Peyret (1975) and Camy-Peyret and Flaud (1976).

The potential is expanded in terms of the symmetry-adapted angular basis functions as is shown in equation (4). We then retain the terms up to $\lambda = 8$. The coupled equations (6) are solved with the partial waves up to $l = 8$ in each irreducible representation. For partial waves higher than that, the Born approximation with the asymptotic part of the (dipole and quadrupole) interactions is used to obtain the relevant $T$-matrix elements.
4. Results and discussion

4.1. Differential cross section

We have calculated the vibrationally inelastic differential cross sections (DCSS) for each mode with an incident electron energy in the range 6–50 eV. The resulting DCSS are compared with those measured by Trajmar et al (1973), Shyn et al (1988) and Furlan et al (1991). Trajmar et al reported their DCSS only in a relative scale. Here their results are normalized at 20° to the present DCSS. Since the DCSS measured by Shyn et al are in good agreement with those by Seng and Linder (1976), we have omitted the latter in the present comparison. Furlan et al measured the ratios of the vibrationally inelastic DCSS to the elastic ones and employed the elastic DCSS measured by Danjo and Nishimura (1985) to obtain the vibrationally inelastic DCSS. Here we employ the theoretical elastic DCSS obtained in Okamoto et al (1993) instead. As is shown in Okamoto et al, their theoretical elastic DCSS reproduce very well those of the more recent measurement by Johnstone and Newell (1991). It should be noted here that the present work can also give DCSS for elastic scattering but the result agrees reasonably (within a few percent) with the DCSS obtained by Okamoto et al.

![Figure 1. Differential cross section (in cm² sr⁻¹) for the vibrational excitation of the (010) mode by electron impact at 6 eV. The present calculation (full curve) is compared with the experiment by Shyn et al (1988) (open circles with error bars) and the calculation by Jain and Thompson (1983) (triangles).](image1)

![Figure 2. Differential cross section for the (010) at 10 eV. The present calculation (full curve) is compared with the experiment by Shyn et al (1988) (open circles), the Born calculations with the dipole and quadrupole interactions (curve through closed circles) and with only the dipole interaction (curve through crosses).](image2)

Figures 1–6 show the DCSSs for the (010) excitation. The present DCSS reproduce the experimental data generally well at 6–20 eV. Shyn et al (1988) claim that their DCSS has a 20% uncertainty. This is explicitly indicated in the figures. At 30 and 50 eV, the theoretical values are relatively large compared with the experimental data. The experimental uncertainty of Furlan’s data is 3–9%. Figures 7–13 show the DCSSs for the (100) and the (001) modes. As is mentioned in the introduction, it is impossible at present to measure the cross sections for (100) and the (001) separately. Therefore, we show the sum of these two cross sections, together with individual ones. For the (001) mode, no calculation has been reported so far except one in the Born approximation. A good agreement with experiment is also seen in this case in the energy region above 10 eV. Especially at 15 eV, the agreement between our calculation and the experiment by Trajmar...
et al. is remarkably good (see figure 10). At the energies of 6 and 8 eV, however, our DCSs are too small compared with the experimental ones over all scattering angles (see figures 7 and 8). The cause of these discrepancies is unclear, but this might be attributed to insufficient accuracy in our target wavefunction (see the discussion below).

Figures 1 and 8 show a comparison between the present DCSs and the ones calculated by Jain and Thompson (1983) for the (010) and (100) excitations, respectively. They obtained the DCSs on the basis of the fixed nuclei (or vibrationally sudden) approximation and a single-centre target wavefunction. The method of taking account of the electron exchange and the target polarization is similar to ours. Comparing our DCSs with theirs (the (010) at 6 eV in figure 1 and (100) at 8 eV in figure 8), the two calculations agree with each other in the range of scattering angles less than 70°, while at the larger angles, there appears to
be some disagreement. This can be attributed to the difference in the target wavefunctions used.

Because of the paucity of elaborate calculations, the Born calculation, particularly the one with a point dipole interaction is compared with experimental data in most cases. In the present paper, the Born calculation taking into account the interaction with the dipole and quadrupole moments is also carried out. The derivatives of the dipole and the quadrupole moments obtained by the present target wavefunction (see table 1) are used in the Born calculation. Since the dipole interaction dominates in the forward scattering, the Born calculation with the dipole interaction gives almost the same values for the DCS as the
Figure 11. Same as figure 7, but at 20 eV.

Figure 12. Differential cross sections for the (100) (long-dashes), the (001) (short-dashes) and the (100, 001) (full curve) at 30 eV. A comparison is made with the values for the (100, 001) obtained by the experiment (Furlan et al 1991, squares) and the Born calculations with the dipole and quadrupole interactions (curve through closed circles) and with only the dipole interaction (curve through crosses).

Figure 13. Same as figure 12, but at 50 eV. A comparison is made also with the experimental data obtained by Trajmar et al (1973) at 53 eV (closed circles, normalized at 20° to the present calculation).

close-coupling calculation in the region, say, \( \theta < 20^\circ \) for the (010) (see figures 2, 5 and 6) and \( \theta < 5^\circ \) for the (100, 001) (see figures 9 and 12). As the scattering angle increases, the Born DCS with the dipole interaction falls rapidly. When we include the quadrupole interaction also, the rapid fall of the DCS at large angle stops and we have an almost constant value for the DCS in this region. In the case of the (010) excitation, the derivative of the quadrupole moment is large in absolute magnitude compared with those for other modes (see table 1) and the Born calculation with the dipole and quadrupole interactions gives a DCS not so very different from those obtained in the close-coupling calculation. Strictly speaking, however, the detail of the angular distribution is different. For the (100, 001) excitation, on the other hand, the Born calculation even with the dipole and quadrupole interactions is completely unable to reproduce the experimental DCS in the lower energy region (see figure 9). At 30 and 50 eV, the Born cross section with the dipole and quadrupole interactions has a magnitude similar to the experimental value. But the comparison can be
for the vibrational excitation of the (010) mode as a function of the electron energy (in eV). The present calculation (full curve through closed circles) is compared with the experimental values of Seng and Linder (1976) (squares) and Shyn et al (1988) (open circles), and the Born calculations with the dipole and quadrupole interactions (short-dashes through triangles) and with only the dipole interaction (short-dashes through crosses).

made only in the range of scattering angles: $\theta < 60^\circ$.

The present assessment of the Born calculation is supported by the comparison of ICS in figures 14 and 15.

4.2. Integral cross section

Figures 14 and 15 show the integral cross sections (ICSs) obtained in the present calculation for the (010) and the (100, 001) excitations, respectively. The present ICSs are compared with the two sets of measurements (Seng and Linder 1976, Shyn et al 1988) and the Born calculations. Table 2 displays the numerical values of the present ICSs for each mode.

Table 2. Vibrationally inelastic integral cross sections for electron collisions with water molecules. All cross sections are in $10^{-16}$ cm$^2$.

<table>
<thead>
<tr>
<th>$E$(eV)</th>
<th>(010)</th>
<th>(100)</th>
<th>(001)</th>
<th>(100, 001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.1974</td>
<td>0.1042</td>
<td>0.1098</td>
<td>0.2140</td>
</tr>
<tr>
<td>8</td>
<td>0.2046</td>
<td>0.1567</td>
<td>0.1609</td>
<td>0.3175</td>
</tr>
<tr>
<td>10</td>
<td>0.2170</td>
<td>0.1882</td>
<td>0.1894</td>
<td>0.3777</td>
</tr>
<tr>
<td>15</td>
<td>0.1891</td>
<td>0.1331</td>
<td>0.1387</td>
<td>0.2719</td>
</tr>
<tr>
<td>20</td>
<td>0.1539</td>
<td>0.0643</td>
<td>0.0699</td>
<td>0.1342</td>
</tr>
<tr>
<td>30</td>
<td>0.0995</td>
<td>0.0175</td>
<td>0.0193</td>
<td>0.0369</td>
</tr>
<tr>
<td>50</td>
<td>0.0536</td>
<td>0.0076</td>
<td>0.0082</td>
<td>0.0158</td>
</tr>
</tbody>
</table>

For the (010) excitation, the present ICSs are larger than the experimental ones by 20–50%. In the low-energy range 6–10 eV, the agreement between the present DCSSs and the experimental ones by Shyn et al is good as far as the experimental DCSSs are available (see figures 1 and 2). The difference in ICSs, therefore, comes mainly from the contribution
of the forward and backward scattering angles for which no DCSSs could be measured. In particular, the dipole interaction in this case leads to a large forward cross section, which is difficult to take into account in the experiment. In the range above 10 eV an over estimate of the present DCSSs in the large angle region also contributes to the difference in the ICS.

For the (100, 001) excitation, both the present and the experimental ICSs have a peak when plotted as a function of the collision energy. The position of the peak of the former ICS, however, is located at a higher energy by a few eV than that of the latter. The height of the peak in the present calculation is considerably smaller than that of the experimental one. This peak is usually interpreted as a shape resonance, which is caused by a temporary capture of the incident electron in the potential of the target molecule (e.g. Seng and Linder 1976). In order to confirm this, we have calculated eigenphase sums by diagonalizing the $R$-matrix obtained from the solutions of the coupled equations (6). However, in the energy range 6–20 eV, there is no sign of a rapid increase in the eigenphase sums so that no definite evidence is available of the shape resonance. The following two reasons may be responsible for this result. First, the direct excitation, particularly due to the long-range (dipole) interaction, is so large that it might obscure the appearance of the resonance effect. Second, the accuracy of the target wavefunction is not sufficient to describe the electrostatic interaction. It is very difficult to assess the reliability of the target wavefunction for the production of the interaction potential. Table 1 shows that the dipole derivatives obtained from the present wavefunction are fairly satisfactory for the (010) and the (001), but too large for the (100), compared with the values derived from the experimental IR intensities.

It is usually said that with an SCF-type wavefunction, it is difficult to produce good results for the nuclear-coordinate dependence of molecular properties. For example, Amos (1987) shows that the IR intensities calculated with an SCF wavefunction scatter widely depending on the basis set used. Calculation of the vibrational cross section by using a wavefunction including electron correlation is a problem for the future.

5. Conclusion

Electron-impact excitation of the vibrational motion of H$_2$O has been studied theoretically. Cross sections have been calculated for the excitation of the lowest excited state of each mode of vibration: (100), (010) and (001). The calculation is based on the rotationally sudden and vibrationally (two-state) close-coupling method. An \textit{ab initio} electrostatic potential is used, while the effects of electron exchange and target polarization are taken into account approximately through a local model potential. The nuclear-coordinate dependence of the interaction potential is considered only through the linear term with respect to the displacement from the equilibrium configuration.

The resulting differential cross sections (DCSS) are compared with experimental data at the collision energies 6–50 eV. Qualitatively, the angular distribution of the experimental DC is well reproduced by the present calculation. As for the absolute magnitude of the DC, we have reasonably good agreement with experiment, except for a few cases. It should be noted that the behaviour of the excitation of the antisymmetric stretching mode has been revealed for the first time in the present calculation. The present cross sections for the (100, 001) excitation at 6 and 8 eV are too small, compared with the corresponding experimental data. These discrepancies may be ascribed to insufficient accuracy in the target wavefunction used. Although being satisfactory for producing the potential at the equilibrium configuration, the present wavefunction (generated with an SCF level) may not be so good at producing the nuclear-coordinate dependence of the potential. It would be
necessary to calculate the cross section with the use of wavefunctions including electron correlation.

Acknowledgments

The present authors would like to thank K Onda and M Takekawa for reading and commenting on the manuscript.

References

Murphy W F 1977 Mol. Phys. 33 1701–14