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LETTER TO THE EDITOR

Electron impact single ionization and dissociative excitation of H_3O^+, HD_2O^+ and D_3O^+

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Abstract

First absolute cross sections for electron impact single ionization of H_3O^+, HD_2O^+ and D_3O^+ and for dissociative excitation (DE) producing H^+ and D^+ are reported. The animated crossed electron–ion beam method has been employed in the energy range from threshold to 2500 eV. The maxima of these cross sections are found to be unusually small ($<1 \times 10^{-17}$ cm^2). The ionization threshold energies are determined to be 24.7 ± 0.5, 24.4 ± 0.5 and 24.0 ± 0.5 eV for H_3O^+, HD_2O^+ and D_3O^+, respectively. The observed DE threshold energies lie in the range 10–12.5 eV and the maximum kinetic energies released are between 3 and 4 eV. Significant differences are observed between the results obtained for the three isotopomers.

The H_3O^+ polyatomic ion (named oxonium) and its hydrates $H_3O^+(H_2O)_n$ are widely present in layers of the terrestrial upper atmosphere, where dissociative recombination plays an important role in producing the neutral fragments (Andersen *et al* 1996). H_3O^+ is considered as the most important tetratomic ion in chemistry (Klein *et al* 1996). It has attracted much attention since 1947 (Bates and Massey 1947), both theoretically and experimentally, due to the search for the understanding of the chemical processes in the terrestrial upper atmosphere.

In this letter we report on first cross section measurements for electron impact single ionization of H_3O^+ and the isotopomers HD_2O^+ and D_3O^+ from threshold to about 2500 eV:

$$e^- + H_3O^+ \rightarrow H_3O^{2+} + 2e^- \quad (1)$$

$$e^- + HD_2O^+ \rightarrow HD_2O^{2+} + 2e^- \quad (2)$$

$$e^- + D_3O^+ \rightarrow D_3O^{2+} + 2e^-. \quad (3)$$

Some of the doubly charged polyatomic ions H_3O^{2+}, HD_2O^{2+} and D_3O^{2+} may spontaneously decay following the various channels of dissociative ionization (DI). The subsequent dissociation products are mixed with those produced by dissociative excitation

(DE) processes. Among these processes, only the detection of H^+ and D^+ was performed in the present experiment:

$$e^- + H_3O^+ \rightarrow H^+ + \cdots \quad (4)$$

$$e^- + HD_2O^+ \rightarrow H^+ + \cdots \quad (5)$$

$$\rightarrow D^+ + \cdots \quad (6)$$

$$e^- + D_3O^+ \rightarrow D^+ + \cdots . \quad (7)$$

Other processes are not considered here.

Measurements are performed by use of the animated crossed beam apparatus described elsewhere (Zambra *et al* 1994). Ions are created in a Penning ion source (PIG), and accelerated to 4000 eV. The ion beam is selected by means of a 90° double focusing magnetic analyser, additionally focused and purified by a 45° electrostatic spherical deflector, and directed into the collision region. Both the magnetic analyser and the electrostatic deflector, which were recently installed, are described in a forthcoming paper (Bahati *et al* 2001). The ribbon-shaped electron beam is focused in the collision region where it crosses the ion beam at right angles. During the measurements, the electron beam is swept across the ion beam in a linear seesaw motion, at a constant velocity. After the collision, product ions are separated from the primary ion beam by means of a 90° magnetic analyser. The primary ion beam is detected by a wide Faraday cup, located inside the magnetic field. Product ions are further deflected by a 90° electrostatic spherical deflector and directed onto a channeltron detector.

The cross section is determined from the measured quantities (number of detected product ions, electron and ion current and speed and sweeping velocity) by means of the standard expression (Defrance *et al* 1981). All the slits and apertures between the collision region and the ion detector are dimensioned as to provide total ion transmission in ionization experiments. In this case, some of the doubly charged ions may dissociate before being detected. As their time of flight from the collision region to the detector lies in the range 8–9 μs, only the ions having a lifetime longer than these values are observed. In the case of dissociation, the product transmission is not total and is evaluated separately for each reaction. (For the details of the procedure, see Bahati *et al* (2001).) In addition, the detection efficiency of low kinetic energy H^+ and D^+ ions is known to be poor. This efficiency was determined in a separate experiment (Defrance 1986) to be 30% and 38%, for H^+ and D^+, respectively.

The total absolute uncertainties for these measurements are obtained as the quadrature sum of uncertainties of all measured quantities: counting statistics (±2%, except for reaction (5), ±13%), sweeping velocity, electron and ion current and detector efficiency. The total uncertainties are ±6% for reactions (1)–(3), ±12% for reactions (4), (6) and (7) and ±14% for reaction (5). The electron energy was calibrated against the well known spectroscopic value for singly charged argon ion ionization, in a separate experiment, and the actual value is corrected for contact potentials and for ion velocity. The error on the true collision energy is ±0.5 eV. The present results were found to be almost independent of the source working conditions.

Results are presented in figures 1–3, for H_3O^+, HD_2O^+ and D_3O^+, respectively. The ionization cross sections are found to be maximum in the same energy range (120–130 eV) for the three ions. The maximum of the cross sections are almost identical for H_3O^+ and HD_2O^+ (4.9×10^{-18} and 5.2×10^{-18} cm^2, respectively) but slightly higher (6.7×10^{-18} cm^2) for D_3O^+. That difference cannot be attributed to the electronic structure of the ions. The observation of the threshold energy should show the presence of electronically excited states.

The experimental ionization threshold energies are found to be identical within the associated uncertainty: 24.7 ± 0.5, 24.4 ± 0.5 and 24.0 ± 0.5 eV, for H_3O^+, HD_2O^+ and D_3O^+, respectively. Indeed, no significant difference between these three values is expected and the

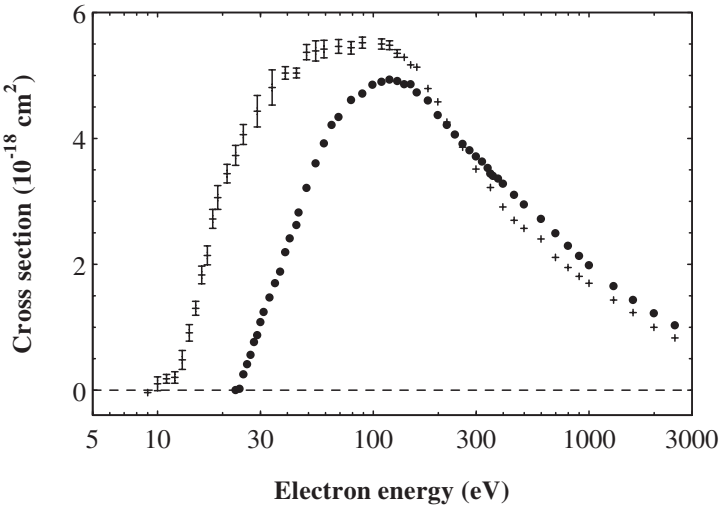

Figure 1. Absolute cross sections for electron impact ionization (●) and dissociation (formation of H^+, (+)) of H_3O^+.

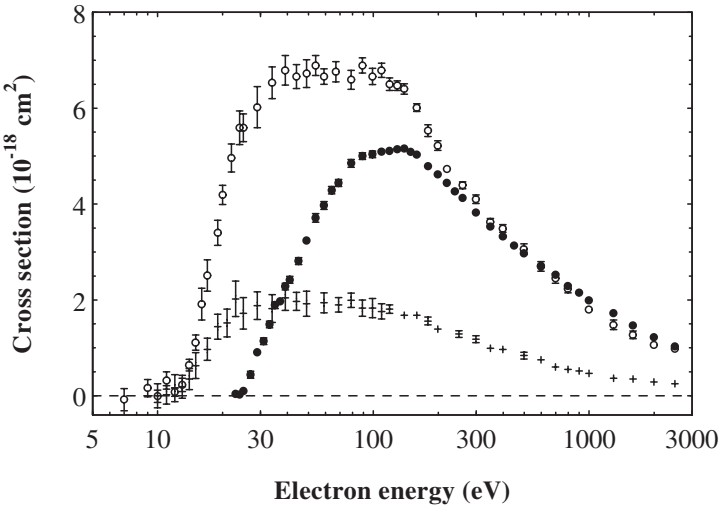

Figure 2. Absolute cross sections for electron impact ionization (●) and dissociation (formation of H^+, (+) and of D^+, (○)) of HD_2O^+.

absence of any signal below the threshold indicates a negligible contribution of electronically excited states in the primary ion beam. To the authors' knowledge, the ionization potential was only deduced from the self-consistent field (SCF) calculation by Raffenetti *et al* (1977) for the total energies for H_3O^+ and for H_3O^{2+}. The result (23.3 eV) is 1.4 eV lower than the experimental result. No definite conclusion can be given about that difference, as the calculated value may vary within a few eV, according to the method adopted for the calculation.

Differences between the respective populations of the vibrationally excited states for the three concerned ions could also influence the cross section magnitude. Some tests were performed in order to observe possible effects resulting from these differences, but none of

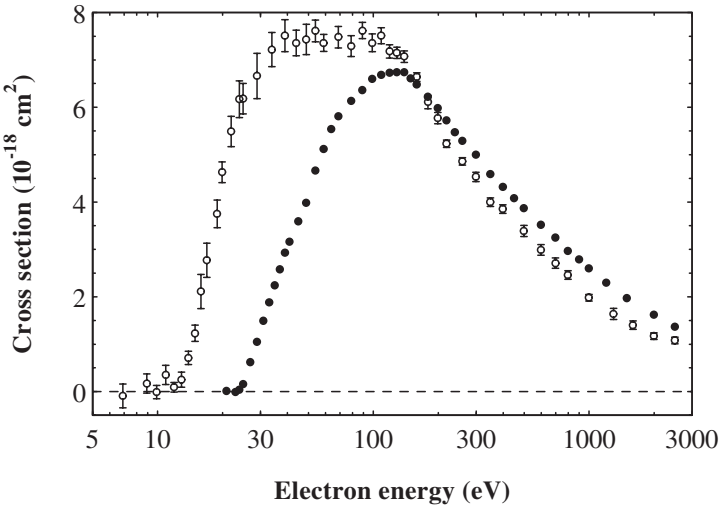

Figure 3. Absolute cross sections for electron impact ionization (●) and dissociation (formation of D^+, (○)) of D_3O^+.

them were successful. In particular, possible vibrationally excited levels would be difficult to observe in the threshold energy region, due to the poor energy resolution of the present electron beam.

The present ionization cross sections are found to be unusually small (a factor of two) with respect to previously investigated cases (see, for instance, Kim *et al* 2000). This should indicate that other processes dominate the electron–ion interaction. These are probably DE or DI.

First, we measured the cross sections for the production of H^+ or D^+ ions from the three concerned ions. The precise determination of the various dissociative thresholds was not possible due to the high-level noise produced by collisional dissociation of ions on the residual gas, resulting in poor counting statistics. Threshold energies lie in the range 10–12.5 eV and the maximum kinetic energies released are between 3 and 4 eV.

The cross sections are found to be of the same order of magnitude as the ionization cross sections. The maximum cross sections are 5.5×10^{-18}, 2.0×10^{-18}, 6.9×10^{-18} and 7.6×10^{-18} cm^2 for reactions (4)–(7), respectively. These low values indicate that other DE processes should dominate the interaction of these ions with electrons. Further investigations of the DE and DI processes will be performed, in particular to explain the differences observed between the cross sections for reactions (4)–(7). Unfortunately, there are no other measurements or theoretical predictions for these processes, to the authors' knowledge, which could be compared with present data.

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