Electron impact ionization of the hydroxyl radical

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We employed the fast-neutral-beam technique in a measurement of absolute partial cross sections for the electron-impact ionization and dissociative ionization of the hydroxyl free radical from threshold to 200 eV. The deuterated OD radical rather than the protonated OH radical was used as a target in our studies in order to allow a better separation of the various product ions in our apparatus. The total (single) OD ionization cross section was found to have a value of slightly less than 2.0×10^{-16} cm^2 at 70 eV. The ionization of OD is dominated by the formation of parent ions with a parent ionization cross section of 1.85×10^{-16} cm^2 at this energy. A comparison of the experimentally determined total single OD ionization cross section with a calculated OH cross section using a modified additivity rule showed good agreement in terms of the absolute value and the cross section shape (at least above 50 eV). In the course of this work, we also measured the partial ionization cross sections for the D_2O molecule and found good agreement between our cross sections and the most recent measurements of Straub *et al.* [J. Chem. Phys. **108**, 109 (1998)] as well as with recent calculations. © *1998 American Institute of Physics.* [S0021-9606(98)00627-8]

I. INTRODUCTION

Water, H_2O, is among the most abundant molecules in the universe. It is a prominent constituent of many planetary atmospheres and it plays an important role in radiation chemistry and in biological systems. The interaction of water with energetic photons and charged particles resulting in the dissociation and dissociative ionization of water are particularly important processes which lead to the formation of various neutral and ionic fragments. Among those, the neutral hydroxyl (OH) radicals play a prominent role due to their importance in secondary chemical reaction processes in environments which contain H_2O in gaseous, liquid, or solid form. The collisional interaction of photons and charged particles with H_2O has been studied by many groups. Electron collision processes with water vapor have received considerable attention from both experimentalists and theorists. Absolute cross sections for the electron impact ionization of H_2O (and D_2O) have been determined by eight different groups[1–8] over a period of 30 years. Those authors who reported measurements of ionization cross sections for both H_2O and D_2O found no isotope effects in the absolute partial and total ionization cross sections for the two targets. However, there are significant discrepancies among the ionization cross section data reported by the various groups, e.g., a difference of a factor of 4 in the total H_2O ionization cross section and significant differences in the partial ionization cross sections and in the cross section shapes. In contrast to the broad data base on collisions with H_2O (and D_2O), there are far fewer collisional data in the literature for the abundant hydroxyl radical (OH, OD). Most studies involve the dissociative excitation of H_2O (and other OH-containing species) and focus on the analysis of the subsequent emission of the prominent 306 nm radiation of the OH radical.[9]

This paper reports absolute partial cross sections for the electron-impact ionization and dissociative ionization of the OD radical from threshold to 200 eV. We used the deuterated rather than the protonated target species as was done in our previous studies of CD_x ($x=1-4$) and ND_x and SiD_x ($x=1-3$) (Refs. 10–12) to facilitate a better separation of the various product ions in our apparatus. The experimental work was complemented by extensive ion trajectory modeling calculations[13] in an effort to quantify the loss of light D^+ fragment ions in our apparatus. In the course of this work, we also carried out partial ionization cross section measurements for the D_2O molecule, which are compared with the various previously reported H_2O and D_2O ionization cross sections. For OD and D_2O, the total single ionization cross section was derived from the measured partial ionization cross sections. A comparison with calculated total single ionization cross sections showed good agreement for both targets.

II. EXPERIMENT

A detailed description of the fast-beam apparatus and of the experimental procedure employed in the determination of absolute partial ionization cross sections has been given in previous publications from this laboratory.[10–12,14–17] A dc discharge biased at typically 2–3 kV through D_2O served as

the primary ion source. The primary ions were mass selected in a Wien filter and were subsequently passed through a charge-transfer cell filled with Xe where a fraction of the ions was neutralized by near-resonant charge transfer. Xe with an ionization energy of 12.14 eV (Ref. 18) was found to be an appropriate charge neutralization target for both OD and D_2O which have ionization energies of 13.0 eV (OD) and 12.6 eV (D_2O).[18–20] The residual ions were removed from the target gas beam by electrostatic deflection and most species in Rydberg states were quenched in a region of high electric field. The neutral beam was subsequently crossed at right angles by a well-characterized electron beam (5–200 eV beam energy, 0.5 eV FWHM energy spread, 0.03–0.4 mA beam current). The product ions were focused in the entrance plane of an electrostatic hemispherical analyzer which separates ions of different charge-to-mass ratios (i.e., parent ions from fragment ions). The ions leaving the analyzer were detected by a channel electron multiplier (CEM). The neutral beam density in the interaction region can be determined from a measurement of the energy deposited by the fast neutral beam into a pyroelectric crystal whose response is first calibrated by a well-characterized ion beam.[14] Alternatively, the well-established Kr or Ar absolute ionization cross sections can serve as a convenient normalization standard to put the relative cross section functions on an absolute scale.[16–18] This is done by using the Kr or Ar benchmark cross sections to calibrate the pyroelectric crystal. The calibrated detector, in turn, is then used to determine the flux of the neutral target beam in absolute terms. This procedure avoids the frequent and prolonged exposure of the sensitive pyroelectric crystal to fairly intense ion beams.[16,17]

We established for both OD and D_2O that all fragment ions (except for D^+, see discussion below) with an excess kinetic energy of less than 3 eV per fragment ion are collected and detected with 100% efficiency using a combination of *in situ* experimental studies and ion trajectory modeling calculations.[13,21] Furthermore, detailed threshold studies revealed little evidence of the presence of excited target species (vibrationally excited species, metastables, and species in high-lying Rydberg states) in the incident neutral OD and D_2O beams. In addition to these experimental checks, which are necessary for any target studied using the fast-beam technique in order to ensure that the measured cross sections are free from systematic uncertainties to the maximum extent possible,[16,17,21] we also carried out all experimental checks pertaining specifically to hydrogen- and deuterium-containing targets.[10–12]

Ion trajectory modeling calculations using SIMION (Ref. 13) indicated that only D^+ fragment ions from both OD and D_2O with excess kinetic energies of less than about 0.5 eV per fragment ions are collected and detected with 100% efficiency. D^+ and H^+ fragment ions produced by dissociative ionization from most D- and H-containing parent molecules have broad kinetic energy distributions with a significant fraction of ions having excess kinetic energies of up to several electronvolts per ion.[22–24] As a consequence, we were not able to obtain reliable partial ionization cross sections for D^+ from either OD or D_2O.

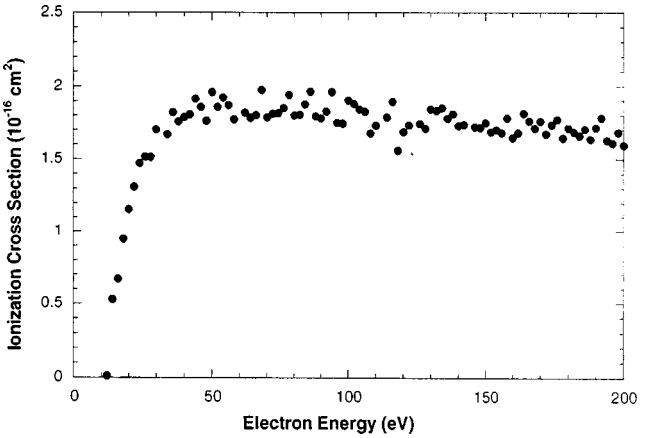

FIG. 1. Absolute cross section for the formation of the OD^+ parent ions (●) from OD as a function of electron energy.

III. RESULTS AND DISCUSSION

For both OD and D_2O, we first measured the relative partial parent ionization cross section from threshold to 200 eV followed by a measurement of the relative partial cross sections for the corresponding fragment ions. All measurements followed the previously described experimental procedure.[14–17] In all cases studied here, the measurements were limited to singly charged ions, since cross sections for the formation of doubly charged ions were found to be at or below the detection sensitivity of our apparatus (peak cross sections below 0.05×10^{-16} cm^2). The parent ionization cross section sections were then put on an absolute scale by employing the procedure described before. All dissociative ionization cross sections were subsequently normalized to the parent ionization cross section for a given target. In all cases, careful threshold studies were carried out to check for the presence of excited species in the incident neutral beam and to determine the appearance energies for the various product ions. This is particularly crucial for dissociative ionization processes, since the appearance energy when compared to thermochemical and spectroscopic data for the formation of a particular fragment ion provides information about the (minimum) excess kinetic energy with which the fragment ion is formed.

The absolute cross sections were determined with uncertainties of $\pm15\%$ for the parent ionization cross sections and $\pm18\%$ for the dissociative ionization cross sections. These error margins, which are similar to what we quoted previously for ionization cross sections measured for other free radicals in the same apparatus,[14–17] include statistical uncertainties and all known sources of systematic uncertainties.

A. Measured partial ionization cross sections for the OD free radical

The electron-impact ionization of OD is dominated by formation of OD^+ parent ions. Figure 1 shows the absolute cross section for the formation of OD^+ ions from OD from threshold to 200 eV. This curve represents the result of a single data run. We find a cross section value at 70 eV of $1.85\pm0.25\times10^{-16}$ cm^2. The OD^+ cross section values are also listed in Table I for easier reference. Note that the cross

TABLE I. Absolute cross section for the formation of OD^+ from OD by electron impact. The cross sections are given in units of 10^{-16} cm^2. Also given is the total single OD ionization cross section (see text for details).

Electron energy (eV)	Ionization cross section (in 10^{-16} cm^2) OD^+ partial ionization cross section	Total single OD ionization cross section
13.0	<0.01	<0.01
14.0	0.22	0.22
15.0	0.42	0.42
16.0	0.64	0.65
17.0	0.77	0.78
18.0	0.90	0.92
19.0	1.01	1.04
20.0	1.10	1.14
22.0	1.20	1.25
24.0	1.29	1.35
26.0	1.36	1.43
28.0	1.47	1.53
30.0	1.58	1.66
35.0	1.67	1.75
40.0	1.78	1.86
45.0	1.81	1.91
50.0	1.83	1.93
60.0	1.85	1.95
70.0	1.85	1.95
80.0	1.84	1.94
90.0	1.82	1.92
100.0	1.79	1.88
120.0	1.74	1.82
140.0	1.71	1.78
160.0	1.69	1.76
180.0	1.63	1.70
200.0	1.58	1.65

section values in Table I represent the average of several individual data runs. The cross section table (with particular emphasis on the low energy regime) is presented primarily for the convenience of practitioners who use these cross section data for modeling purposes or other applications. Also listed in Table I is a total single OD ionization cross section which has been obtained by adding an estimate for the unobserved O^+ and D^+ partial cross sections to the measured OD cross section (see discussion below). The measured appearance energy of the OD^+ parent ion of 13.3 ± 0.5 eV is in very good agreement with the known 13.0 eV ionization energy of OD in its vibrational ground state.[18–20] The near-threshold region of the OD^+ cross section with the 13.0 eV ionization threshold marked by a vertical bar is shown in Fig. 2. We found no evidence of an extended curvature in the near-threshold region or of a significant shift of the measured appearance energy to lower values. This indicates that the vibrational excitation of the OD radicals in the target beam is negligible and that there is little, if any contamination of the target beam due to the presence of metastable OD radicals or OD radicals in long-lived Rydberg states.

We found only a very small ion signal corresponding to the formation of D^+ fragment ions. Since ion trajectory modeling calculations indicate that our apparatus is not able to collect energetic D^+ fragment ions with 100% efficiency (see discussion earlier), we are not able to determine a reliable absolute value for the D^+ ionization cross section from OD. However, for the purpose of estimating the total single OD ionization cross section, we estimate based on trajectory

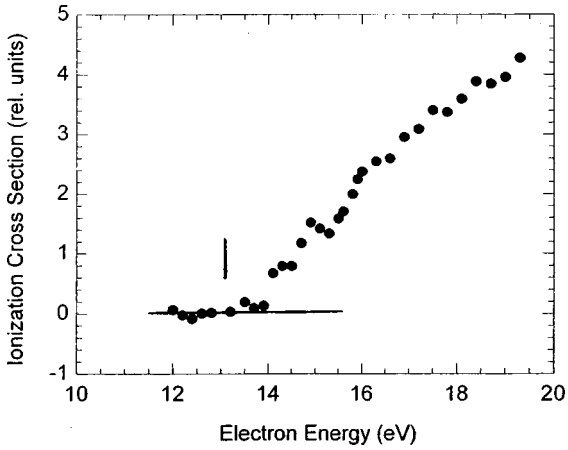

FIG. 2. Near-threshold region of the OD^+ partial ionization cross section. The ionization energy of OD in its vibrational ground state is indicated by a vertical bar.

modeling calculations and the measured ion signals that the combined (O^++D^+) ionization cross section contributes at most 0.1×10^{-16} cm^2 to the total single OD ionization cross section at 70 eV. The total single OD ionization cross section in Table I has been obtained by adding a ''generic'' cross section shape with a peak value of 0.1×10^{-16} cm^2 at 70 eV representing the unobserved (O^++D^+) cross section to the OD^+ partial cross section.

Figure 3 shows the calculated total single OH ionization cross sections using a modified additivity rule[25] in comparison with our experimentally determined OD cross section. Also included in Fig. 3 are the predictions of several other additivity rules at some selected energies (for details, see Deutsch *et al.*[25]). Our experimental cross section shows very good agreement with the calculated cross sections (which, in turn, agree very well among each other) in terms of the absolute cross section value and also the cross section shape, at least above about 50 eV. In the low energy regime below about 50 eV, the experimentally determined cross section appears to rise somewhat faster than the calculated cross section.

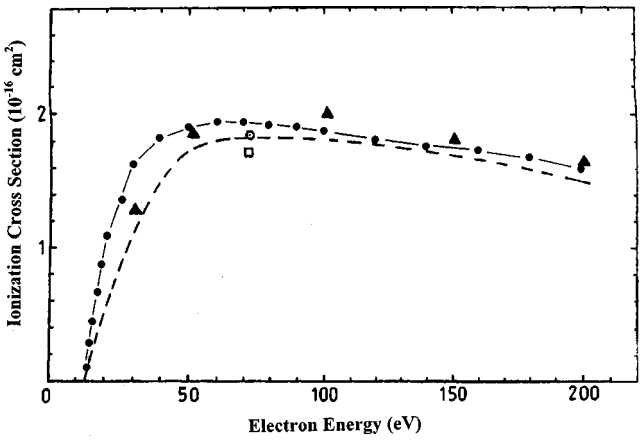

FIG. 3. A comparison of the experimentally determined total single OD ionization cross section (–●–) with a calculated cross section based on a modified additivity rule (Ref. 25) (dashed line). Also shown at selected energies are the predictions of several other additivity rules (▲, ⊙, □) [see Deutsch *et al.* (Ref. 25) for further details].

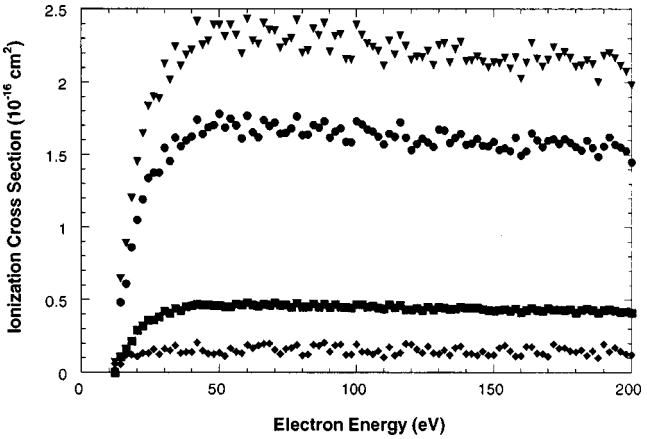

FIG. 4. Absolute cross sections for the formation of D_2O^+ parent ions (●) and OD^+ (■) as well as D^+ (♦) fragment ions from D_2O as a function of electron energy. Also shown is the sum of the partial cross sections (▼).

B. Measured partial ionization cross sections for the D_2O molecule and comparison with calculations

In the course of this work, we also carried out partial ionization cross section measurements for the D_2O molecule. We found the following absolute partial cross section values at 70 eV impact energy: $1.65\pm0.30\times10^{-16}$ cm^2 (D_2O^+), $0.45\pm0.08\times10^{-16}$ cm^2 (OD^+), and less than 0.05×10^{-16} cm^2 (O^+). These cross sections are shown in Fig. 4. We also find a D^+ partial cross section of 0.2×10^{-16} cm^2 which we consider a lower limit of this cross section due to the loss of energetic D^+ fragment ions in our apparatus (see discussion before). This notion is supported by the fact that all partial D_2O ionization cross sections measured here are in very good agreement with the recent D_2O partial ionization cross sections reported by Straub *et al.*[8] with the exception of the D^+ cross section where our value is roughly 40% below their cross section. If we combine our measured partial ionization cross sections, we arrive at a total single D_2O ionization cross section of $2.35\pm0.5\times10^{-16}$ cm^2 at 70 eV. This total D_2O ionization cross section agrees very well with the H_2O data of Djuric *et al.*[6] and with the very recent D_2O measurements of Straub *et al.*[8]

Total (single) ionization cross section calculations for H_2O (D_2O) have been carried out by Deutsch *et al.*[25] using the modified additivity rule as well as by Kim and co-workers using their binary-encounter Bethe (BEB) approach.[26] Partial cross sections for the ionization and dissociative ionization of H_2O were also calculated by Khare and co-workers.[27,28] In general, we find good agreement between our measured D_2O ionization cross sections and the calculated cross sections. This is particularly true for the total ionization cross section.

IV. SUMMARY

The fast-beam technique has been employed in a measurement of the partial ionization cross sections of the OD free radical from threshold to 200 eV. The ionization of OD is dominated by the formation of parent ions with a cross section of 1.85×10^{-16} cm^2 at 70 eV. The formation of O^+ and D^+ fragment ions and the formation of multiply charged ions contribute at most 0.1×10^{-16} cm^2 to the total OD ionization cross section at this energy. The experimentally determined OD ionization cross section agrees well with a calculated cross section using a modified additivity rule. We also measured partial ionization cross sections for the D_2O molecule and found good agreement between our data and the most recent measurements of Straub *et al.*[8] as well as with recent calculations.

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[1] J. Schutten, F. J. de Heer, H. R. Moustafa, A. J. H. Boerbroom, and J. Kistemaker, J. Chem. Phys. **44**, 3924 (1966).
[2] J. C. M. Gomet and C. R. Hebd, Seances Acad. Sci. Ser. B **281**, 627 (1975).
[3] T. D. Märk and F. Egger, Int. J. Mass Spectrom. Ion Processes **20**, 89 (1976).
[4] M. A. Bolorizadeh and M. E. Rudd, Phys. Rev. A **33**, 882 (1986).
[5] O. J. Orient and S. K. Srivastava, J. Phys. B **20**, 3923 (1987).
[6] N. Djuric, I. M. Cadez, and M. V. Kurepa, Int. J. Mass Spectrom. Ion Processes **83**, R7 (1988).
[7] M. V. V. S. Rao, I. Iga, and S. K. Srivastava, J. Geophys. Res. **100**, 26421 (1995).
[8] H. C. Straub, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, J. Chem. Phys. **108**, 109 (1998).
[9] See, e.g., K. Becker, B. Stumpf, and G. Schulz, Chem. Phys. **53**, 31 (1980); K. Becker and G. Schulz, Can. J. Phys. **60**, 1168 (1982), and references therein.
[10] V. Tarnovsky, A. Levin, H. Deutsch, and K. Becker, J. Phys. B **29**, 139 (1996).
[11] V. Tarnovsky, H. Deutsch, and K. Becker, Int. J. Mass Spectrom. Ion Proc. **167/168**, 69 (1997).
[12] V. Tarnovsky, H. Deutsch, and K. Becker, J. Chem. Phys. **105**, 6315 (1996).
[13] SIMION-3D (version 6.0), Energy Science and Technology Software Center.
[14] R. C. Wetzel, F. A. Biaocchi, T. R. Hayes, and R. S. Freund, Phys. Rev. A **35**, 559 (1987).
[15] R. S. Freund, R. C. Wetzel, R. J. Shul, and T. R. Hayes, Phys. Rev. A **41**, 3575 (1990).
[16] V. Tarnovsky and K. Becker, Z. Phys. D **22**, 603 (1992).
[17] V. Tarnovsky and K. Becker, J. Chem. Phys. **98**, 7868 (1993).
[18] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levine, and W. G. Mallard, J. Phys. Chem. Ref. Data **17**, 1 (1988).
[19] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Chuney, and R. L. Nutall, J. Phys. Chem. Ref. Data **11**, 1 (1982).
[20] M. W. Chase, Jr., K. A. Davis, J. R. Downey, D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data **14**, 1 (1985).
[21] V. Tarnovsky, P. Kurunczi, D. Rogozhnikov, and K. Becker, Int. J. Mass Spectrom. Ion Processes **128**, 181 (1993).
[22] J. Appell and C. Kubach, Chem. Phys. Lett. **11**, 486 (1971).
[23] K. Furuya, K. Kimura, Y. Sakai, T. Takanayagi, and H. Yonekure, J. Chem. Phys. **101**, 2720 (1994), and references therein to earlier work.

[24] V. Grill, S. Matt, H. U. Poll, N. Abramzon, K. Becker, P. Scheier, and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. (in press).
[25] H. Deutsch, K. Becker, and T. D. Märk, Int. J. Mass Spectrom. Ion Processes **167/168**, 503 (1997).
[26] W. Hwang, Y.-K. Kim, and M. E. Rudd, J. Chem. Phys. **104**, 2956 (1996).
[27] S. P. Khare and W. J. Meath, J. Phys. B **20**, 2102 (1987).
[28] S. P. Khare, S. Prakash, and W. J. Meath, Int. J. Mass Spectrom. Ion Processes **88**, 299 (1989).