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REVIEW OF THE REACTION OF O⁺ WITH H₂O AND ITS BEARING ON COMPOSITION MEASUREMENTS FROM THE SPACE SHUTTLE

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Abstract. The rate of reaction of ground state O⁺ with H₂O has been measured in the energy range, E_{cm}, 0.05²-11 eV. The measurements show that the rate coefficient does not decrease drastically with increasing energy, contrary to previous work. The rate constant measured here is then applied to a simple model, which includes reactions of O⁺ with water dimers, to calculate water concentration in the vicinity of the Space Shuttle. The results suggest that the pressure of water vapor may be lower than previously thought, with an upper limit of 1 x 10⁹ molecules/cm³.

for the formation of water dimer by evaporation would lead to better agreement between the data derived from the neutral mass spectrometer measurements and those derived from ion mass spectra.

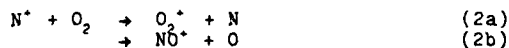
Experimental and Results

The results reported here were obtained in a triple cell Ion Cyclotron Resonance mass spectrometer, whose operation has been described previously [Heninger et al., 1986; Mauclaire et al., 1987]. In the present experiment the three cascaded, differentially-pumped, ICR cells are used sequentially for the following purpose: 1. ion production; 2. O⁺ selection; and 3. O⁺ acceleration, reaction and detection.

Production of ground state O⁺ was made by 30 eV electron impact on CO₂, known to give O⁺ (⁴S) with negligible kinetic energy [Murad, 1973]. These primary ions were selected by removing all unwanted ions using selective ejections at cyclotron frequencies in cells # 1 and # 2. The O⁺ ions were drifted and then stored in cell # 3 for a fixed 50 ms duration. At the beginning of this storage time, the O⁺ ions were given the desired kinetic energy by excitation of their cyclotron motion by a resonant radio-frequency field applied perpendicularly to the magnetic field. This energy is given by KE = q²E²t²/8m, where q and m are respectively the charge and mass of the ion, while E and t the amplitude of the rf field and its duration, respectively. t was kept fixed at 1 millisecond, and the amplitude of the rf field was adjusted to obtain the desired kinetic energies.

The end of the accelerating pulse defines the origin of the reaction time, which, using an H₂O pressure of 1x10⁻⁷ torr, was varied from 4 to 30 ms, and was followed by detection of the ions. Because of the fast secondary reactions of H₂O⁺ with H₂O, for each O⁺ kinetic energy reported, the reaction rates were obtained from the decay of O⁺ as a function of time.

Although the width of the energy distribution is rather difficult to ascertain, the validity of this experimental procedure has been tested using a reaction whose branching ratio is strongly dependent on kinetic energy:



Our measured k_{2a}/k_{2b} varied with kinetic energy in a manner which agreed with the flow-drift tube determination [Howorka et al., 1980].

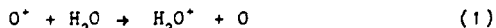
The pressure of H₂O was measured with an ionization gauge calibrated by the determination of the rate of reaction of Kr⁺ with H₂O at thermal energy [Marx et al., 1983]. The validity of this procedure is supported by the agreement between our thermal rate constant and previous determinations.

Figure 1 shows the results obtained here for the cross section of reaction (1) as a function of energy in the range E_{cm} = 0.035-11.5 eV. This cross section curve is different from that

Introduction

The flight of the space shuttle and the availability of composition data [Hunten and Calo, 1985; Wulf and von Zahn, 1986; Grebowsky et al., 1987a; Grebowsky et al., 1987b] has renewed interest in the rates of ion-neutral reactions at high kinetic energies. The high orbital velocity of the space shuttle (7.7 ± 0.2 km s⁻¹) leads to reactions between the ambient atmospheric ions (principally O⁺) and the local gaseous constituents of the space shuttle at collision energies of ≤ 4.5 eV for O⁺ (depending on the neutral target and on the orientation of the space shuttle with respect to the velocity vector).

Understanding the origin of large amounts of H₂O⁺ ions in the bay of the space shuttle [Narcisi et al., 1983] has not been straight-forward; relating the intensity of H₂O⁺ to the local pressure of H₂O is not easy, although an estimate of [H₂O] = 0.6-2.4 x 10⁹ cm⁻³ has been made [Caledonia et al., 1987]. The complicating circumstances are: (1) the uncertainty in the interaction energy for the reaction of O⁺ with H₂O; and (2) whether the measured O⁺ and H₂O⁺ abundances can be derived from the mass spectrometer data since the velocities (and hence collection efficiency of the mass spectrometer) of O⁺ and H₂O⁺ are likely to be quite different [Hunten and Calo, 1985; Grebowsky et al., 1987b]. A previous measurement of the cross section for the reaction



as a function of collision energy in a beam-target experiment [Murad and Lai, 1986] lead to a question as to the origin of H₂O⁺ in view of the large amounts of accompanying H₂O⁺. By comparison with [H₂O] derived from ion abundances, results from the neutral mass spectrometer [Wulf and von Zahn, 1986] suggest that [H₂O] ~ 2 x 10⁸ cm⁻³. This work was undertaken in order to remeasure the cross section for reaction (1) as a function of energy under conditions where the state of O⁺ is much better controlled and the collision energy is better determined. It was hoped that the new measurement and the introduction of a mechanism

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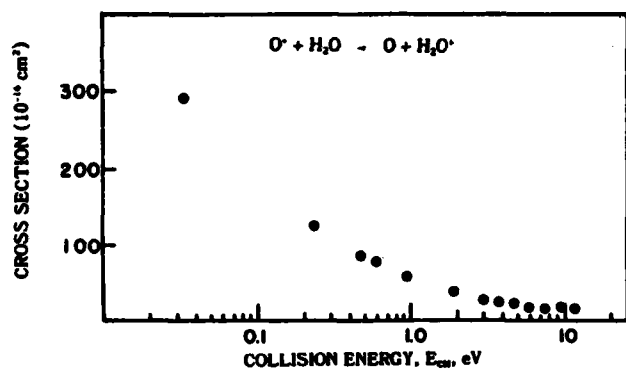


Figure 1—Rate constant for reaction (1) as a function of kinetic energy of O⁺.

reported earlier [Murad and Lai, 1985]: At the lowest energy ($E_{cm}=0.2$ eV) reported by Murad and Lai, the ICR cross sections are nearly a factor of 3 higher than the beam experiment, while at $E_{cm} = 10$ eV, the ICR data is about a factor of 2 higher. The reason for this discrepancy is not clear at this time, although it is possible that both the energy calibration (measuring the point of maximum slope in the retarding potential curve for the primary ions) and the cross section calibration (which was done by comparing the measured cross section with that of $N_2+D_2 \rightarrow N_2D^++D$) may be

incorrect. In any case, we believe the present results are more reliable, especially since now the rate constant does not vary much in going from thermal energies to 11 eV, as given in Table 1.

TABLE 1

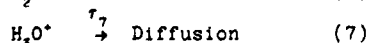
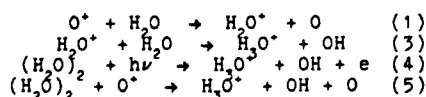
Energy, E_{cm} (eV)	k_1^*	σ_1^{**}
0.0327	2.5	230
0.23	2.9	125
0.46	2.8	85.5
0.58	2.8	77.7
0.92	2.6	57.6
1.46	2.5	42.8
1.84	2.4	37
2.92	2.0	24.9
3.68	2.0	21.9
4.63	2.1	20.2
5.83	1.8	15.4
7.3	1.9	14.8
9.2	2.6	17.7
11.6	2.2	13.5

* Rate Constants in units of 10^{-9} cm³ molec⁻¹ s⁻¹, and are accurate to $\pm 0.5 \times 10^{-9}$ cm³ molec⁻¹ s⁻¹.

** Cross sections are in units of 10^{-16} cm².

Discussion

These results can now be incorporated into a simple model:



Reactions (1), (3), (6), and (7) have been proposed and discussed in previous studies

[Caledonia et al., 1987; Hastings et al., 1988]. Reactions (4) and (5) have not been suggested as a source of H₂O⁺ in the shuttle environment previously, although Reaction (4) has been postulated a source of H₂O⁺ in cometary atmospheres [Murad and Bochsler, 1988]. Reaction (3) is assumed to occur at thermal energy at a temperature of ~ 275 K; k_3 was taken to be 2×10^{-9} cm³ molec⁻¹ s⁻¹ [Anicich and Huntress, 1986].

As discussed in another study, the vaporization of dimers generates a significant quantity of dimers [Murad and Bochsler, 1987]. Observations made on the shuttle indicate large amounts of particles coincident with water dumps [Green et al., 1987], leading to the supposition that the particles are ice crystals. Moreover, measurements of the surface temperature of the shuttle when it is in darkness indicate it to vary between 278°K and 258°K [Humphries and Coyle, 1983]. From these facts we can assume that the gaseous water environment of the shuttle contains some dimers, since these are generated in the equilibrium vaporization of water; in this analysis we take the dimer mole fraction to be 0.12, the fraction at 250°K [Murad and Bochsler, 1987]. The photoionization of the water dimer, reaction (4), will be unimportant compared with either (3) or (5), since its estimated rate, J_4 , is 6×10^{-7} s⁻¹ [Murad and Bochsler, 1987]. The dominant loss term for H₂O⁺ is diffusion, as indicated earlier [Caledonia et al., 1987].

Since k_5 has not been measured, we assume that k_5/k_1 is equal to the ratio of the calculated rate constants using the parametric formula of Su and Chesnavich (1980):

$$k = k_L(0.3371P+0.62) \quad (7)$$

with

$$k_L = 2we(\alpha/m_r)^{1/2} \quad \text{and} \quad P = \mu/(\alpha kT)^{1/2} \quad (8)$$

where k_L is the Langevin rate coefficient, α and μ are the polarizability and the dipole moment of the neutral and m_r the reactant reduced mass. Taking $\mu(H_2O) = 1.84D$, $\mu((H_2O)_2) = 2.6D$ and $\alpha((H_2O)_2) \approx \alpha(H_2O) = 1.54 \times 10^{-16}$ cm³, we calculate $k_1 = 3.06 \times 10^{-9}$, $k_3 = 2.9 \times 10^{-9}$, and $k_5 = 3.5 \times 10^{-9}$ cm³ molec⁻¹ s⁻¹, leading to $k_5/k_1 \approx 1.14$. At a collision energy of 4.5 eV, the center-of-mass kinetic energy is 2.1 and 1.4 eV for reactions (1) and (5), respectively. From our data we obtain $k_1 = 2.35 \times 10^{-9}$ at $E_{cm} = 2.1$ eV and 2.5×10^{-9} at $E_{cm} = 1.4$ eV. Then at $E_{cm} = 1.4$ eV, $k_5 = 2.85 \times 10^{-9}$ cm³ molec⁻¹ s⁻¹, suggesting that with 12% dimer 14% of the H₂O⁺ may be due to reaction (5).

Following the above analysis we can now deduce the steady state equations for [H₂O⁺] and [H₃O⁺]:

$$k_1[O^+][H_2O] = k_3[H_2O][H_2O^+] + (1/\tau_6)[H_2O^+] \quad (10)$$

and

$$k_3[H_2O][H_2O^+] + J_4[(H_2O)_2] + k_5[O^+][(H_2O)_2] = (1/\tau_7)[H_3O^+] \quad (11)$$

As discussed above, the second term in equation (11), the photoionization of (H₂O)₂, can be ignored, and we take [(H₂O)₂] = 0.12[H₂O]. Equations (10) and (11) can be rewritten:

$$[O^+]/[H_2O^+] = k_3/k_1 + (1/\tau_6)/k_1[H_2O] = \delta \quad (10')$$

and

$$k_3[H_2O] + 0.12 k_5[O^+][H_2O]/[H_2O^+] = (1/\tau_7)[H_3O^+]/[H_2O^+] \quad (11')$$

Since $k_5 \approx k_1$, we derive:

$$[H_2O] = (1/\tau_6)/k_1(\delta - 1)$$

and

$$(1/\tau_6)(k_1 + 0.12\delta k_5)/k_1(\delta - 1) = (1/\tau_7)[H_3O^+]/[H_2O^+]$$

If we now make two reasonable assumptions, namely $k_5 \approx k_1$ and $\tau_6 \approx \tau_7$, we obtain

$$[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}^+] = (1 + 0.12\delta)/(\delta - 1)$$

Comparing this expression with the ion current ratio of 0.1-0.4 reported by Narcisi et al. [1984], we find the limiting condition $\delta \leq 5$ corresponding to $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}^+] \leq 0.4$. There is no upper limit for δ since $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}^+] > 0.12$.

The limit $\delta \leq 5$ gives an upper limit for $[\text{H}_2\text{O}]$, depending on k_1 and τ_6 . With $\tau_6 = 0.1$ s and $k_1 = 2.5 \times 10^{-9}$ mol cm⁻³ s⁻¹ we obtain $[\text{H}_2\text{O}] \leq 1 \times 10^9$ mol cm⁻³ ($\sim 3 \times 10^{-8}$ torr) which is somewhat lower than the values calculated by Caledonia et al. [1987]: $[\text{H}_2\text{O}] = 0.6 - 2.4 \times 10^9$ mol cm⁻³. It is, however, consistent with the values calculated by Wulf and von Zahn [1986] from neutral mass spectrometer measurements ($[\text{H}_2\text{O}] = 2 \times 10^9$ cm⁻³ under quiescent conditions and 10^{12} cm⁻³ during RCS firings). The lower value of $[\text{H}_2\text{O}]$ calculated in this work is due both to the new value of k_1 and due to the inclusion of reaction (5), the reaction between O⁺ and water dimers. Of course, since water concentration is inversely proportional to the ion drift times, τ_6 and τ_7 , shorter drift times would lead to higher water pressures.

We conclude from this study that the partial pressure of water is likely lower than previously thought, suggesting that the Space Shuttle environment is more benign for optical measurements than previously thought.

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