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On the existence of the hypervalent H_3O, H_2DO, HD_2O, and D_3O radicals

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ABSTRACT

The existence of oxonium radicals on the microsecond time scale has been up for much debate, and strong isotope effects have been reported. Here we show that H_3O, H_2DO, HD_2O, and D_3O all have subnanosecond lifetimes when they are formed in charge-transfer collisions between oxonium cations and cesium. A kinetic isotope effect on hydrogen versus deuterium loss from HD_2O was found to be 2.4, similar to that found in dissociative recombination of HD_2O^+ and for dissociation after electron transfer to HD_2O^+ from potassium.

1. Introduction

The neutral oxonium radical, H_3O, is of fundamental interest in a number of disciplines, and its properties with respect to stability, lifetime, and dissociation channels have been studied both experimentally and theoretically in great detail [1–17]. H_3O is unstable to dissociation into H_2O and H, and no metastable species have yet with certainty been isolated in the gas phase though this issue has been up for some debate. In contrast, $D_3{}^{16}O$ has been reported by Hudgins and Porter [5] to exist on a microsecond time scale based on neutral reionization mass spectrometry experiments. However, the $D_3{}^{18}O$ radical was found to have a subnanosecond lifetime as H_3O. Radicals were formed in keV charge-transfer collisions between oxonium ions and potassium atoms. A similar difference in lifetime between NH_4 and ND_4 as that between $H_3{}^{16}O$ and $D_3{}^{16}O$ has been observed [1,18,19], but the isotope effect by exchange of ^{16}O with ^{18}O is surprising and difficult to explain, which questions the result for $D_3{}^{16}O$. Due to the large significance of these species, we decided to reinvestigate the existence of oxonium radicals. In this communication, we report the results from charge-transfer collisions between H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+ and cesium atoms. Neutrals were ionized either to anions or cations but in no case did we measure a recovery signal of non-dissociated ions. A combination of charge reversal and neutral reionization experiments can be used to extend the time frame to the nanosecond range [20].

2. Experimental

The experimental setup is described in detail elsewhere [21,22]. Briefly, positively charged oxonium ions were formed by atmospheric pressure chemical ionization. The air in the discharge region was partially saturated with D_2O to generate deuterated ions. Ions passed through a heated capillary held at 100 °C and cooled at the exit in a sonic expansion. In the capillary–skimmer region they experienced several collisions (pressure of 1 mbar). The ions were guided and focused by electrostatic lenses to a low-pressure region before they were accelerated to 50-keV energies. An electromagnet was used to select ions of interest according to their mass-to-charge ratio. Two different experiments were then performed. In the first (called "charge reversal"), ions were collided with cesium in collision cell A (Fig. 1) under high enough pressure to allow for double collisions. In the first collision, ions were neutralized, and in the second anions were formed. The average flight time between the two collisions is estimated to be 30 ns. In the second experiment (called "neutral reionization"), ions were neutralized in collisions with cesium in collision cell A under single collision conditions. All ions were then deflected by an electric field of 250 V/cm whereas neutrals moved undisturbed to cell B that was filled with molecular oxygen. Electron stripping collisions in cell B resulted in cations. The flight time between cells A and B was about a microsecond. All

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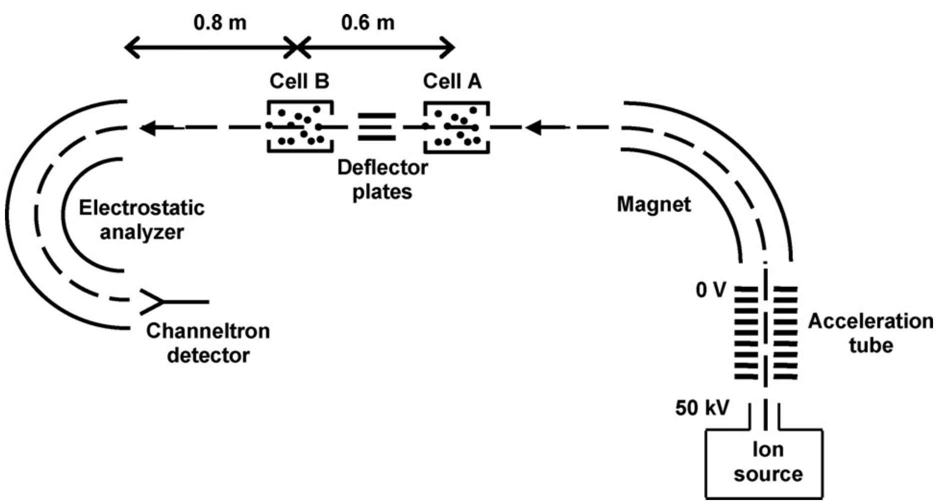

Fig. 1. Instrumental setup.

product ions were analyzed by an 180° electrostatic analyzer, and the number of ions was finally counted by a channeltron detector. The flight time from collision cell B to the analyzer is about a microsecond.

Cesium was used due to its low ionization energy, which is important for most experiments done in our laboratory.

3. Results and discussion

First we consider the charge reversal spectra, $^{+}CR^{-}$, of H_3O^+ and D_3O^+ shown in Fig. 2. The spectra reveal two peaks that are assigned to O^- and OH^-/OD^-. There is a significant background signal which is present even in the absence of cesium in the collision chamber. Hence this signal is ascribed to the intense beam of cations hitting the walls of the analyzer to give scattered anions with a broad range of kinetic energies. The electron transfer processes are nearly vertical since the collisional interaction time is a femtosecond at these high ion velocities (7×10^5 m/s), being less than the vibrational periods. H_3O and D_3O have positive electron affinities (1.5 eV [23]), and the absence of peaks corresponding to H_3O^- and D_3O^- indicates that the neutrals have subnanosecond lifetimes. Dissociation prior to mass analysis of hypothetically formed $D^-(D_2O)$ or $H^-(H_2O)$ cannot be excluded if the internal energy of the anion is larger than the energy required for dissociation (0.75 eV for $H^-(H_2O) \rightarrow H^- + H_2O$ based on data from [23]).

Next we present the results from the neutral reionization, $^{+}NR^{+}$, experiments (Fig. 3). In the case of H_3O^+, there are peaks due to O^+, OH^+, and H_2O^+ but no signal from H_3O^+, in accordance with the previous findings. These ions are a result of ionization of neutrals formed after electron capture since collision-induced dissociation (CID) results in O^+, OH^+, and H_2O^+ ions that are deflected in the electric field. Also the electron transfer process can occur at far distance and therefore with a higher cross section than CID. The $^{+}NR^{+}$ spectrum for D_3O^+ is very similar to that for H_3O^+, and we note in particular that there is no signal due to recovery of D_3O^+.

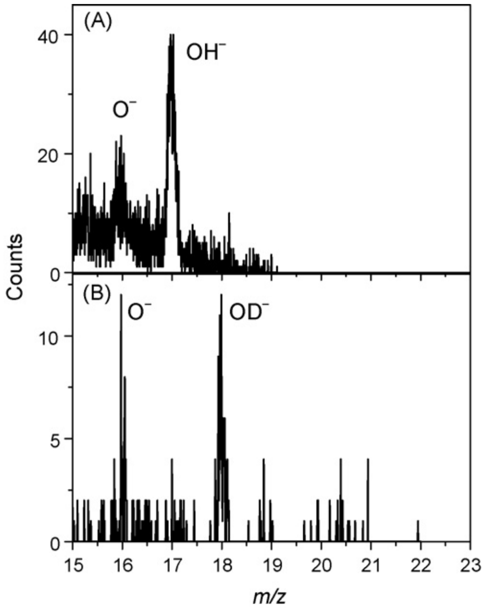

Fig. 2. Charge reversal, $^{+}CR^{-}$, mass spectra of H_3O^+ (*m/z* 19) (A) and D_3O^+ (*m/z* 22) (B). Cesium was used as collision gas.

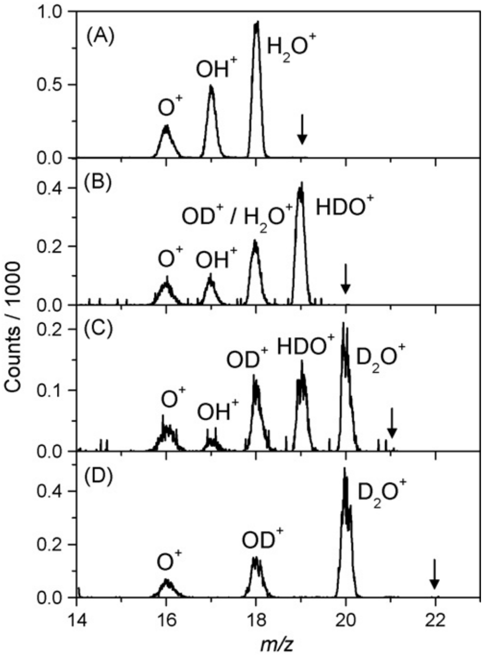

Fig. 3. Neutral reionization, $^{+}NR^{+}$, mass spectra of H_3O^+ (*m/z* 19) (A), H_2DO^+ (*m/z* 20) (B), HD_2O^+ (*m/z* 21) (C), and D_3O^+ (*m/z* 22) (D). Cesium and molecular oxygen were used for first and second collision, respectively. The arrows denote the *m/z* of the parent ions.

Likewise, for H_2DO^+ and HD_2O^+, the hypervalent radical did not make it to the second collision cell. It is evident from the $^+NR^+$ spectrum of HD_2O^+ that there is a kinetic isotope effect (*KIE*) favoring H over D loss. The statistical ratio is 0.5 whereas the measured is 1.2, which implies a *KIE* of 2.4. Based on relative peak intensities for reionized D_2O^+ and HDO^+, published by Gellene and Porter [4], the *KIE* is 2.2 when potassium atoms are the source of electrons. Interestingly, in dissociative recombination of HD_2O^+ where the full recombination energy is absorbed by the neutral, the probability of hydrogen release is also about a factor of 2 higher than that for deuterium release [13]. In the case of H_2DO^+, we cannot quantify the *KIE* since the peaks due to D loss and H_2 loss are at the same nominal m/z.

Taken together, our results indicate that both H_3O and D_3O radicals have subnanosecond lifetimes in contrast to the results of Hudgins and Porter in the case of D_3O. The ionization energy of Cs (3.89 eV) is lower than that of K (4.34 eV) by 0.45 eV [23] but in both cases the internal energy of the hypervalent radical is well above the activation energy for dissociation (0.015 eV for hydrogen loss from H_3O [16]) since the recombination energy of oxonium is more than 6 eV. Also it is noticed that the *KIE* for H versus D loss from HD_2O is about 2, independent of whether the radical is formed after capture of a free electron or after electron capture from cesium or potassium. This suggests that the kinematics does not depend much on internal energy owing to the small barrier to dissociation. Indeed, molecular dynamics simulations by Tachikawa [17] indicate that dissociation of H_3O on the electronic ground state potential energy surface is complete within 60 fs. We suspect that in the earlier experiment where ions were produced by chemical ionization the beam may have been contaminated by isobaric ions, e.g., ND_4^+, that were also studied in the experiments [5]. The ND_4 radical formed in the electron transfer collision between ND_4^+ and K or between ND_4^+ and Na has a lifetime of 1 μs [1]. In our experiment, we assured that the contribution of ND_4^+ was less than 1% based on a comparison of the intensities of H_3O^+ and NH_4^+ before letting in D_2O in the discharge region. The findings in this work are useful for understanding the outcome of charge-transfer collisions between protonated water clusters and cesium, work currently being undertaken.

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