Energetic Rydberg neutrals from water dissociation

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Abstract. Dissociation of isolated water molecules has been addressed using the technique of time-of-flight spectrometry employing multi-hit detection in an ion-molecule collision experiment. Ar⁹⁺ ions having energy of 450 keV were used as projectiles for inducing dissociation. We have detected neutral fragments (fast, energetic Rydberg hydrogen atoms) originating from the dissociation process in coincidence with charged fragments. The kinetic energies of the neutral atoms have been determined by time-of-flight measurements. The formation of transient Rydberg molecular ions is also inferred from the experimental data. The implications of the results are discussed in context of the observation of energetic neutral atoms in extra-solar planets and radiation damage in living systems where water plays a major role.

1. Introduction
Radiation in the form of either photons or energetic particles interact with matter causing ionization and excitation of its constituent atoms and molecules. The result is the formation of a host of ions and electrons spanning a wide energy range. We address the role of water in influencing the processes occurring in living systems and upper planetary atmospheres under the impact of ionizing radiation. The ionization and dissociation of water molecules is known to play an important role in a wide variety of situations where water is a major component. On earth, water is the major constituent of the biological composition of living organisms. It is also predicted to be among the most abundant molecular species after hydrogen in the atmospheres of close-in extrasolar giant planets [1]. The ionization and dissociation of water is therefore of intrinsic interest to a wide variety of fields.

To get a fundamental insight into dynamics of the breakup of this unique molecule, ion induced fragmentation of single isolated water molecules was investigated using the technique of time-of-flight mass spectroscopy employing multi-hit detection. The kinetic energies for the neutral and charged fragments are measured and the mechanism of their production is discussed. We show that ion impact dissociation of isolated water molecules leads to the production of highly excited, fast, neutral hydrogen atoms.

2. Experiment
The ion-molecule collision setup at the Low energy ion beam facility [2] of Inter-University Accelerator Centre, New Delhi, India was used for the measurement. Ar⁹⁺ ions at an energy of 450 keV were made to interact with isolated water molecules under single collision conditions. The dissociation products generated from the interaction were extracted into a time-of-flight
spectrometer (TOFMS) using a weak homogeneous electric field of 120 V/cm. The start signal for the DAQ is generated when a particle hits the channeltron detector. The recoil ions are detected using a micro-channel plate detector. The direction of the extraction field is such that electrons are directed towards the channeltron but in addition any neutral particle from the interaction can also be detected by it. The MCP detector is connected to a multi-hit time to digital converter which enables detection of all ions simultaneously from a single dissociation event. Further details on the setup can be found in reference [3]. The collected multihit data was analysed to obtain the kinetic energy spectra of neutral as well as charged fragments [4].

3. Results

Figure 1 shows the time-of-flight (TOF) spectrum for ion-induced dissociation of water molecules. Fragment peaks corresponding to \( \text{OH}^+ \), \( \text{O}^q^+ \) (\( q = 1 \) to 5) and \( \text{H}^+ \) are clearly observed in the spectrum. In addition some broad features are also visible in the TOF spectrum. These broad features do not correspond to any particular mass number. Similar broad features were observed when the experiment was repeated with \( \text{D}_2\text{O} \) as target. To identify the origin of these, a two dimensional (2D) coincidence map was constructed using the time-of-flight data of the first and the second stop corresponding to the same start signal (figure 2). A 2D coincidence map thus depicts the various double fragment correlations originating from the dissociation process. The coincidence map shows some dark spots and also some streak like patterns. The inset of figure 2 is a blow up of the spots which correspond to \( \text{(D}^+, \text{OD}^+) \), \( \text{(D}^+, \text{O}^q^+) \) with \( q = 1 \) to 5 and \( \text{(D}^+, \text{D}^+) \) fragment correlations. The start signal for these spots is generated by an electron emitted during the dissociation process. The 2D map for \( \text{D}_2\text{O} \) shows some contamination from \( \text{H}_2\text{O} \) but with an event by event analysis of the data we were able to isolate the two while determining the kinetic energies of hydrogen and deuterium fragments.

The streaks observed on the 2D coincidence map have a wide span and they point asymptotically to one of the dark spots. The streaks thus collect the same ion fragment pair to which it points but it appears that the start of the DAQ system was delayed. In addition a definite time gap is observed between dark spots and the start of the streak pattern. The start signal for the streak patterns is generated by the detection of a neutral hydrogen atom. To confirm this, the polarity of the time of flight extraction field was reversed such that neither ions nor electrons could reach the channeltron detector. Under these conditions a finite count rate was observed at the channeltron detector which can result only from neutral particle detection. Thus the streak like patterns represent three fragment coincidences, one neutral and two charged.
Water being a tri-atomic species, the streaks thus provide insight into complete fragmentation channels of the type \((H^+, H^+, O^+)\) or \((D^+, D^+, O^+)\).

The time delay between each point on the streak and the corresponding dark spot depends on the kinetic energy of the neutral particle. The neutral particle being much heavier than the electron takes a finite time to reach the detector and hence the time of flight of recoil ions is correspondingly reduced. In addition, if the neutral particle has a range of kinetic energies, it will result in the appearance of a streak in the 2D coincidence plot instead of a localized spot. The neutral particle energy spectra can thus be generated using the time gap between the events which appear in the spot and in the streaks. Running the same experiment using deuterated water \(D_2O\) confirmed the identity of the neutral particle. With similar electronic states being populated in \(H_2O\) and \(D_2O\) we expect similar kinetic energy spectra for the neutral fragment in the two cases. Figure 3 shows a comparison between the neutral particle energy spectra for \((H^+, H^+, O^+)\) and \((D^+, D^+, O^+)\) coincidences. Similarities in the spectra confirms the identity of the neutral fragment.

Both the spectra in figure 3 show a low energy peak at \(\approx 15\) eV and a high energy component extending up to 100 eV. The absolute detection efficiency of a microchannel plate detector for
ground state hydrogen and deuterium atoms having kinetic energies up to 100 eV is reported to be less than 10% [5]. Assuming similar efficiencies for a channeltron detector, we conclude that the neutrals generated in our experiment do not have enough kinetic energy to result in their detection. The detection can only happen if the neutral hydrogen atom releases its electron during impact with the channeltron surface. For this to occur the neutral H atom has to be of Rydberg nature. Rydberg H atoms with principal quantum number (n) up to 40 are expected to survive field ionization in the applied extraction field of 120 V/cm.

A comparison of the kinetic energy spectra of the neutral Rydberg hydrogen atom ($H^*$) and the proton is presented in figure 4. The comparison shows a common low energy peak for both but the high energy tail appears only for neutral fragment. The absence for the high energy charged fragments may be attributed to limitation in the collection efficiency of the time-of-flight spectrometer. The occurrence of the common peak hints towards similarities in the origin of these two fragments. According to the core ion model of dissociation of molecular Rydberg ions [6], the outer Rydberg electron of a molecular Rydberg ion acts as a spectator while the molecular core dissociates. This spectator electron may subsequently be carried away by one of the fragments. Such a dissociation will lead to similarities in the energy spectra for fragments which differ from each other by a single charge. Dissociation of the Rydberg system $[\text{H}_2\text{O}^{3+}]^*$ ($= [\text{H}_2\text{O}^{2+} + e^-]^*$) $\rightarrow H^+ + H^+ + O^+$ can lead to similarities in the energy spectra of $H^*$ and $H^+$ as observed in figure 4. We thus conclude that the transient molecular ion is Rydberg in nature.

4. Conclusions and Discussion
To conclude, ion-impact dissociation of isolated water molecules has been studied using the technique of time of flight mass spectrometry. The neutral and charged fragments produced in the dissociation process are detected in coincidence. The kinetic energies of both the neutral and the charged fragments have been measured. The detected neutral fragments are found to be of Rydberg nature. A comparison of the KER spectra for the $H^*$ and $H^+$ fragments provide signature for the formation of a transient Rydberg molecular ion.

These excited neutral atoms are a hitherto unexplored and unaccounted source for slow electrons and fast neutral atoms across a wide variety of physical systems. On collision with other atoms and molecules, they can result in the ejection of slow electrons. In rarified atmospheres these excited atoms can radiatively decay to form energetic neutral atoms. Low energy electrons have been shown to be effective in causing major damage to DNA and other cell constituents [7]. Fast neutral hydrogen atoms with velocities in the range of 30 to 130 km s$^{-1}$ have been reported in the spectral observations of extrasolar planets [1, 8].
This channel of water dissociation, which leads to the production of Rydberg Hydrogen atoms is suggested as a possible additional source of the energetic neutrals detected in upper atmospheres of extra solar planets, and of slow electrons which are known to play a major role in radiation induced damage to living cells.

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