Rotational state effect and fragmentation of small polyatomic molecular ions

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Abstract. In the paper we report the first experimental observation of rotational state effects in dissociative recombination of H2+. We also report the branching fractions from the DR of BH2+, N3+ and O3+ and the dynamics occurring in the full fragmentation channel are discussed.

1. Introduction
Dissociative recombination (DR) is a process in which a molecular ion recombines with an electron and subsequently dissociates into neutral fragments. The DR reaction first time attracted attention in 1931 when it was put forward to be a depletion mechanism for ionized oxygen molecules in the terrestrial ionosphere in attempt to explain aurora and night airglow [1]. Beyond such atmospheric applications, DR is also of great interest for cold astrophysical environments such as diffuse and dense interstellar clouds where H3+ is by far the dominant molecular ion species [2,3]. Due to the overwhelming importance of the DR process in all low-temperature and low-density plasmas great deal of attention has been addressed to its study.

The earlier theoretical treatments of the DR reaction were devoted to the simplest molecular ion, H2+ [4,5]. The total cross section was calculated from the interference between the direct and indirect mechanisms [6,7]. The calculations showed that the contribution from the direct mechanism is more significant for vibrationally excited states due to the poor overlap between the ground state and dissociative $^{1}\Sigma_g^+(2p\sigma_g)$ curve. The results also showed that contribution from the indirect mechanism involving pre-dissociative Rydberg states appeared as narrow dips in the cross section. The first experimental DR investigation of H2+ became possible due to the development of a single-pass merge-beam machine enabling high energy resolution measurements to be performed [8]. The experimental results supported the theoretical calculations regarding positions of resonances and the behavior of the indirect mechanism, i.e., narrow dips in the cross section were observed [9]. It is noted that the
rotational population of the ions was experimentally uncontrolled and therefore must have reflected the thermal distribution. Moreover, the theoretical calculations did not take into account the molecular rotation since it was believed to be unimportant. The question of the influence of the rotational motion was first put forward by Takagi, who theoretically predicted a significant rotational effect [10]. Existing contradictions between the latest calculations reported by Takagi and earlier theoretical and experimental results has led us to investigate rotational effects in the DR of H$_2^+$ at the storage ring CRYRING.

It is well established that the DR rate coefficient at room temperature is usually on the order of $10^7$ cm$^3$s$^{-1}$, while the fragmentation behaviour is not completely understood. An early model developed by Bates argued that fragmentation favours the least rearrangement of valence bonds [11]. However, three-body break-up has been observed to be a main route for many polyatomic ions. Moreover, observation of four-body break-up was reported, though it was not a dominant channel [12]. A systematic investigation into the fragmentation of XH$_2^+$ ions (X=H, C, N, O and P) has revealed a propensity for the three-body break-up [13-17]. To shed more light on the DR fragmentation of XH$_2^+$ ions we chose to investigate the next ion from this series; BH$_2^+$. The investigation of the homonuclear triatomic molecular ions N$_3^+$ and O$_3^+$ has also been undertaken.

2. Experiment

The experiment was performed at the heavy-ion storage ring CRYRING located at the Manne Siegbahn Laboratory, Stockholm. For investigation of the rotational state effects, para- and normal-H$_2^+$ were separately introduced into a supersonic-expansion ion source at a pressure of 2 atm [18]. The rotational temperature of the produced ions is 30 K which means that para-H$_2^+$ occupies only the rotational ground state (J=0) while the population of normal-H$_2^+$ corresponds to 25% of J=0 and 75% of J=1. In order to suppress contribution from vibrationally excited states ion-molecular reaction involving Ne + H$_2^+$(v>1) → NeH$^+$+H was employed by introducing Ne into the ion source; Ne:H$_2$ 90%:10%. For production of BH$_2^+$, O$_3^+$ and N$_3^+$ a cold plasma ion source was used. Before injection into the ring H$_2^+$ ions were pre-accelerated to 600 keV by RFQ, while BH$_2^+$, O$_3^+$ and N$_3^+$ ions were injected into the ring at the energy of 40 keV. All ions were further accelerated by a RF cavity to final energies of 8, 3.25, 1.96 and 2.25 MeV, respectively. The interaction between the ion and electron beams occurred over a length of 0.85 m in the electron cooler. The neutral products of the DR reaction were separated from the ion beam by a bending magnet and left the ring tangentially where they were detected with a silicon detector. For measurement of the branching fractions from the DR of the BH$_2^+$, O$_3^+$ and N$_3^+$ ions a well-known grid technique was utilized [19].

3. Experimental results and discussion

If the rotational population of H$_2^+$ was not changed during extraction, acceleration and storage of the ion beam, the conditions in the ion source would mean that para-H$_2^+$ and normal-H$_2^+$ occupied the lowest rotational levels. Moreover, due to the super-elastic collisions in the electron cooler, further de-excitation of vibrationally excited states could be expected [20]. Measurements were made after 3 s and 17 s of storage. It is noted that due to the failure of the ion current measurement, only relative rate coefficient was obtained. To avoid logarithmical scaling and to make DR resonances more pronounced the measured rate coefficient was multiplied with $1/E$. In order to reduce statistical scattering in the raw data, averaging procedure was utilized (figure 1). The rate coefficients measured after storing the ion beam for 17 s for both para- and normal-H$_2^+$ contain sharp peaks, while the rate coefficients measured after 3 s are smooth. This fact confirms that ion beam for different storage times involved different vibrational populations and due to the efficient super-elastic collisions the rate coefficient obtained after 17 s is expected to contain predominantly contribution from the vibrational ground state. The peak at ≈6 meV is a para-feature, while the peak at ≈20 meV is an ortho-feature. Higher energy peaks are present in both para- and normal-spectra. The results show that contribution from
Figure 1. The rate coefficients multiplied by square root from interaction energy for both para- and normal-H$_2^+$ are shown by gray and black curves for storage time of 3 s (a) and 17 s (b).

indirect mechanism appears as windows where the rate coefficient is enhanced. Even if the absolute rate coefficient contains narrow dips, they are smeared out due to the experimental energy resolution and not observed. Our results disagree with the earlier single-pass merged-beam experiment by Van der Donk et al., in which the energy resolution was worse than in CRYRING, but narrow dips in the cross section were obtained [9].

Investigation into fragmentation of BH$_2^+$ revealed the following fractions: $n$(BH+H)=0.56±0.03, $n$(B+H$_2$)=0.09±0.02 and $n$(B+H+H)=0.35±0.05. It is noted that this is the first observation for the fragmentation of XH$_3^+$ ions which is not dominated by the three-body break-up. In order to explain such phenomenon the suggestion of Vikor et al. was utilized: the importance of the three-body break-up increases with available energy [21]. The validity of the suggestion is seen from figure 2. It seems to be inappropriate to compare ions from series of XH$_3^+$ with other ions, for instance, fragmentation of H$_3$O$^+$ is dominated by OH+H+H break-up, where the kinetic energy available in this channel is only $\approx$1.3 eV [19].

In the DR of N$_3^+$ and O$_3^+$ two-body and three-body channels are exothermic. It is surprising that fragmentation of O$_3^+$ almost exclusively proceeds through the three-body break-up (0.94±0.03), while for N$_3^+$ this channel constitutes only 0.08±0.03. So far, such a high fraction of three-body break-up has been observed for D$_2$O$_3^+$ [22]. The result for D$_2$O$_3^+$ might be expected since fragmentation involves ruptures of cluster bonds, while in O$_3^+$ the cleavage is of valence bonds. The suggestion of Vikor et al. is valid for X$_3^+$ ions studied so far as well: N$_3^+$ – 0.08 (0.7 eV), H$_3^+$ – 0.77 (4.8 eV) and O$_3^+$ – 0.94.

Figure 2. Fraction of three-body break-up in DR of XH$_3^+$ ions versus exothermicity [13-17].
(6.27 eV). Another explanation for different fragmentation pattern observed in the DR of $O_3^+$ and $N_3^+$ is based on consideration of bond strength in the molecules. $N_3^+$ is quite strongly bound and the lowest dissociation limit, $N' + N_2$, lies 3.53 eV above the ionic ground states [23], while for $O_3^+$ the dissociation energy into the lowest limit, $O + O_2^+$, is 0.6 eV [24]. It is likely that the likelihood of the bond rupture increases with the weakness of the bond.

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