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Dissociative recombination of BH_2^+: The dominance of two-body breakup and an understanding of the fragmentation

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The dissociative recombination of BH_2^+ has been studied at the storage ring CRYRING. The branching fraction analysis shows that dissociative recombination is dominated by the two-body BH+H channel constituting 56% of the total reactivity with the B+H+H and $B+H_2$ channels being 35 and 9%, respectively. Both the measured reaction rate and fragmentation behavior are different than for previously studied XH_2^+ ions, which react both faster and predominantly dissociate through the full fragmentation channel. Explanations for such observations are discussed.

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Dissociative recombination (DR) is a reaction in which a positively charged molecular ion captures a slow electron and subsequently dissociates into neutral fragments. Among the many different molecular ion-electron reactions, DR deserves special attention due to the pivotal role it plays in cold low-density plasmas such as interstellar molecular clouds and planetary atmospheres [1–6]. Despite the fact that DR has been extensively studied over the last sixty years, one of the most significant experimental advances has been achieved through the introduction of the ion storage rings into this field in the early nineties [7–9]. Such techniques, in contrast to previous methods, provide the ability to study the DR process under well-defined and controlled conditions, at a much higher energy resolution, and with better statistics, giving higher quality data both on the reaction rate and the reaction products.

Almost two decades of storage ring experimental investigations have established that for the majority of molecules the DR rate coefficient at room temperature is usually in the range of $10^{-7}-10^{-6}$ cm^3 s^{-1}. However, the detailed fragmentation process of the molecule in DR is not completely understood and in some cases shows extremely unexpected behavior [10,11]. Several models have traditionally been used to predict the chemical branching for the DR reaction [12–15], though none of them has proven suitable in providing a general description of the DR fragmentation. One of the most recent models, developed by Strasser *et al.* [16], correctly predicts the energy-dependent branching fractions in the DR of H_3^+ as that measured by Datz *et al.* for rotationally hot ions [17]. However, subsequent experiments revealed that the fragmentation is also dependent on the rotational temperature of the ions [1], an effect that the model is not able to explain. In an attempt to gain more insight into the branching behavior of such small molecular ions we have initiated a systematic study into the DR of triatomic dihydrides, XH_2^+. In the experiments reported to date, the results show that for all covalently bonded XH_2^+ ions (X=H, D, C, N, O, and P) there is a tendency for the molecule to predominantly fragment into its three constituent atoms [1,17–23]. Due to the overwhelming importance of the three-body breakup for these ions, the dynamics of this channel has been investigated in more detail with a position-sensitive imaging detector and some similarities in the reaction dynamics have been observed [22–25]. In this Brief Report, we present the results observed from an investigation into the DR of the boron dihydride ion (BH_2^+).

The experiment was performed at the storage ring CRYRING located in the Manne Siegbahn Laboratory, Stockholm University, Sweden. A detailed description of the apparatus and the experimental techniques has been given elsewhere [26] and so it will only be described briefly here. The ions were produced in a discharge ion source from a mixture of BF_3 and H_2 resulting in a BH_2^+ ion current of 10 nA after extraction from the source by a potential of 40 kV. The ions were further accelerated in the ring to an energy of 3.25 MeV by an rf cavity. The interaction between the ion beam and a cold homogeneous electron beam occurred over a length of 0.85 m in an electron cooler placed in one of the straight sections of the ring. Since the electrons were much colder than the ions ($kT_e \approx 2$ meV), heat was transferred from the ions to the electrons by means of their Coulomb interaction resulting in a reduction of the phase-space occupied by the ions [27]. The neutral products arising from the DR reactions and background collisions traveled out of the ring where they were detected by an energy-sensitive ion-implanted silicon detector (IISD), while the ions were confined in the ring by a magnet located after the electron cooler.

In the DR of BH_2^+ at ≈0 eV interaction energy all possible product channels are energetically available,

$$BH_2^+ + e \rightarrow \begin{cases} BH + H + 5.03 \text{ eV} & (\alpha), \\ B + H_2 + 6.08 \text{ eV} & (\beta), \\ B + H + H + 1.56 \text{ eV} & (\gamma), \end{cases} \qquad (1)$$

where the quoted kinetic energies released (KER) correspond to the case when the fragments are formed in their ground

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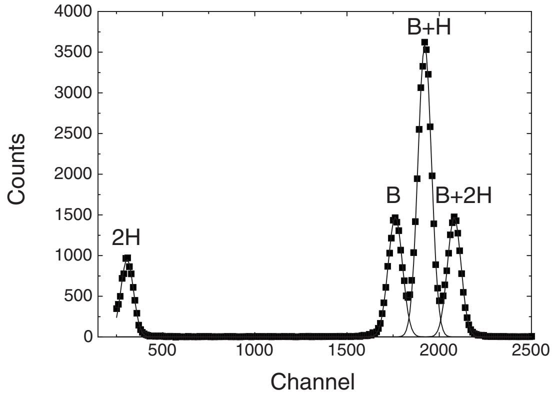

FIG. 1. The solid squares show the measured background subtracted pulse-height spectrum. The solid lines show Gaussian curves best fitted to the data.

states. Due to the relatively low exothermicity of the three-body breakup channel the formed atomic products cannot be electronically excited, though internal excitation of the molecular products in the first two channels as well as electronic excitation of the boron atom arising from the second channel are possible. The IISD is too slow to establish from which channel the fragments have been produced. In order to make branching fractions measurement possible a grid with a known transmission, $t=0.297\pm0.015$, was inserted in front of the IISD [3,17]. As a result of this, the pulse-height spectrum recorded by a multichannel analyzer splits into a series of peaks corresponding to the total mass of the fragments which passed through the grid. Signals arising from background processes, such as charge transfer from the residual gas molecules present in the ring, were also taken into consideration by recording a spectrum taken at an interaction energy of 1 eV where the DR cross section is vanishingly small and the count rate is entirely dominated by background events [25]. These contributions were then normalized to the ion current and subtracted from the spectrum obtained at ≈0 eV interaction energy (Fig. 1). In order to determine the contributions from each channel, N_α, N_β, and N_γ, the following system of linear equations was solved:

$$\begin{bmatrix} P_{2H} \\ P_B \\ P_{B+H} \\ P_{B+2H} \end{bmatrix} = \begin{bmatrix} 0 & t(1-t) & t^2(1-t) \\ 0 & t(1-t) & t(1-t)^2 \\ t(1-t) & 0 & 2t^2(1-t) \\ t^2 & t^2 & t^3 \end{bmatrix} \begin{bmatrix} N_\alpha \\ N_\beta \\ N_\gamma \end{bmatrix}, \qquad (2)$$

where P_{2H}, P_B, P_{B+H}, and P_{B+2H} are the intensities of the four peaks plotted in Fig. 1. The branching fractions were determined after normalization of the result to be

$$n_\alpha = 0.56 \pm 0.03,$$

$$n_\beta = 0.09 \pm 0.02,$$

$$n_\gamma = 0.35 \pm 0.05. \qquad (3)$$

The quoted errors are dominated by the uncertainty in the grid transmission.

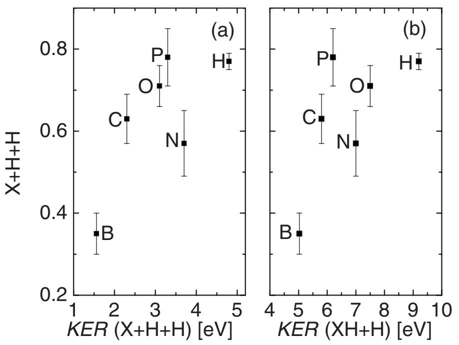

FIG. 2. The fraction of the three-body breakup for the DR of XH_2^+ ions versus KER in the three-body breakup (a) and KER in the two-body breakup of XH+H (b). All the KER values are quoted for the case in which the fragments occupy their ground states.

The accuracy of the branching fraction values reported here is related to the purity of the ion beam, since contamination of the $^{11}BH_2^+$ beam by $^{10}BH_3^+$ ions could have a dramatic effect on the obtained result. Indeed, if the contamination was significant and the DR of $^{10}BH_3^+$ was dominated by the BH_2+H fragmentation then the measured branching fractions would show the predominance of the BH+H channel in the DR of $^{11}BH_2^+$. However, some information on the likelihood of such contamination can be drawn. First, ^{11}B is naturally more abundant with the ratio to the ^{10}B isotope of 4:1. Second, since the ions were produced from BF_3 and H_2 containing plasma, the formation of the less hydrogenated BH_2^+ ions are expected to be more favorable. Third and most importantly, the background collisions are known to lead to a high degree of fragmentation in the parent ions [3] which would manifest itself in peaks corresponding to 3H and ^{10}B in the pulse-height spectrum. However, such peaks are absent in both spectra recorded at ≈0 and 1 eV interaction energies and, therefore, it is concluded that if the $^{10}BH_3^+$ isotope contamination indeed existed then it was vanishingly small.

In the light of previous results from studies on the DR of XH_2^+ ions, it is surprising that the dominant channel in the DR of the boron dihydride ion is that which involves the cleavage of only a single B–H bond, BH+H. It is noted that this is the first observation, to the best of our knowledge, for which full fragmentation does not dominate in the DR of a covalently bonded triatomic dihydride. The corresponding channel for other XH_2^+ ions is reported to constitute about 60–80 % of the total reactivity [1,17–23], while for BH_2^+ it is only 35%. In Ref. [28] the predominance of the three-body breakup was suggested to be related to the exothermicity of this channel, i.e., the importance of the three-body breakup increases with the available KER. Indeed, of all covalently bonded XH_2^+ ions studied, BH_2^+ has the smallest KER and the smallest fraction in the full fragmentation channel [Fig. 2(a)]. Such a dependence is related to the fact that the reaction exothermicity is dependent on the various bond energies in the parent molecule, i.e., if a stronger bond is ruptured then there is less kinetic energy available to the fragments. This implies that in the DR reaction the cleavage of weaker bonds is more likely. Indeed, in the D_2O-D^+-D_2O and Na^+-D_2O clusters the cleavage of the weak cluster bonds is observed to occur in ≈90% of the DR events, producing

D_2O+D+D_2O and $Na+D_2O$, respectively [29,30]. The dependency of the $XH+H+H$ channel probability versus KER in the DR of XH_3^+ ions (X=C, O, and S) is similar to that observed for XH_2^+ ions: CH_3^+-0.16 ± 0.15 (0.7 eV) [31], H_3O^+-0.67 ± 0.06 (1.3 eV) [3], and SD_3^+-0.58 ± 0.11 (2.3 eV) [32]. Such a tendency is also observed in the full fragmentation channel of X_3^+ type of ions studied so far: N_3^+-0.08 ± 0.03 (0.7 eV) [33], H_3^+-0.77 ± 0.02 (4.8 eV) [17], and O_3^+-0.94 ± 0.03 (6.27 eV) [11].

Herbst and Lee explained the dominance of the three-body channel by secondary fragmentation of electronically and vibrationally excited products produced from an initial two-body breakup [34], i.e., fragmentation to the $XH+H$ channel subsequently gives rise to $X+H+H$. The vibronic excitation of the XH molecule is more probable when more energy is available for this. Indeed, the BH+H channel has the smallest surplus energy which might favor the conservation of the B–H bond [Fig. 2(b)]. However, the results from investigation of the three-body breakup dynamics in the DR reaction of these molecular ions by means of a position-sensitive imaging detector do not support such a general explanation, since no evidence for sequential breakup was observed [22–24,35]. It is noted that Hellberg *et al.* reported that a sequential mechanism might be involved in the DR fragmentation of SD_2^+ [25]. However, due to experimental constraints the absolute branching fractions in the DR of this ion were not measured and cannot be compared with other ions. Conversely, the DR reaction of CH_5^+ is dominated by the CH_3+H+H channel [36], and the sequential pathway is likely to be involved in the fragmentation dynamics [37]. Moreover, in the DR of O_3^+, where the three-body channel constitutes almost 100%, an observation of a sequential breakup was reported, though it was not a dominant pathway [38]. The suggestion of Herbst and Lee is also supported by the model employed by Strasser *et al.* to describe the branching in the DR of H_3^+ [16] and the theoretical calculations undertaken to interpret the branching of NH_4^+ [39]. The latter calculations predicted that the molecular fragment arising from the NH_3+H channel could store as much as 4.0 ± 0.2 eV from the available 4.7 eV as vibrational energy. This leads to 20% of NH_3 molecules that could have sufficient energy to fragment further to NH_2+H, which agrees with experimental observations [39]. It is interesting to note that the fragments produced in the three-body channel in the DR of BH_2^+ are always formed in their ground state, while for NH_2^+, CH_2^+, H_2O^+, and PD_2^+ at least two three-body channels are energetically open and the reaction is dominated by three-body breakup [20–24], i.e., three-body breakup is more efficient when more pathways are open. Indeed, the statistical model developed by Herbst implies that probability of fragmentation into a particular channel is proportional to the number of available states in that channel [12].

The thermal rate coefficient reported here is best fitted by the following expression $(3.3\pm0.4)\times10^{-7}$ $(T/300)^{-0.6}$ $cm^3\,s^{-1}$ for an electron temperature range of 100–1000 K. This rate coefficient at room temperature is smaller than those obtained for other XH_2^+ ions [20,21,23]. H_3^+ is not included in the comparison, since another DR mechanism known as tunneling is involved in the DR reaction, which is usually characterized by a relatively low value of the rate coefficient. We conclude that the dominance of the two-body breakup has an impact on the total rate coefficient making it smaller. This conclusion is supported by the observations that the DR rate coefficient for diatomic molecular ions usually does not exceed 3×10^{-7} $cm^3\,s^{-1}$ [40–44].

Despite the fact that the parent ion has linear H-B-H geometry in the ground state, the $B+H_2$ channel is also populated, though to a much lesser extent than the other channels. This indicates that there is sufficient time after the electron capture to significantly rearrange the molecular geometry. It was believed that for NH_2^+ this channel would be negligible since the geometry of the parent ion is nearly linear and, indeed, results reported from CRYRING revealed the $N+H_2$ channel to constitute only 4% of the total DR events [22]. However, the present result gives a similar fraction for the $X+H_2$ channel to those reported from the DR of the CH_2^+, H_2O^+, and PD_2^+ ions which are known to be bent in their ground states [20,21,23]. It is also worth noting that in the DR of another linear molecular ion, CO_2^+, the channel $C+O_2$ was not observed [5]. This could be due to the greater mobility of hydrogen atoms compared to oxygen atoms and stronger intramolecular bonds in CO_2.

The DR of the boron dihydride ion has been investigated at the storage ring CRYRING. Analysis of the fragmentation of the molecule in the DR process shows a dominating tendency for the two-body BH+H channel, which is significantly different from the behavior observed for other covalent XH_2^+ ions where the full fragmentation channel dominates. Due to the relative simplicity of BH_2^+ in having only six electrons, this molecular ion could be a perfect candidate for theoretical treatment, which would enable us to gain more insight into the DR fragmentation.

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