

## TRANSLATIONAL ENERGY LOSS OF H<sup>+</sup> FRAGMENTS FROM CAPTURE-DISSOCIATION OF H<sub>2</sub><sup>+</sup> IN COLLISION WITH RARE GAS ATOMS

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Received 9 January 1987; revised manuscript received 20 March 1987; accepted for publication 16 April 1987

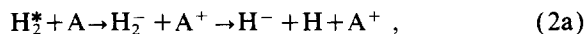
Communicated by B. Fricke

Translational energy spectra have been obtained for capture-dissociation of 6 keV H<sub>2</sub><sup>+</sup> in collision with inert gas targets. Energy loss measurements provide further evidence in support of a double-collision mechanism for the production of H<sup>+</sup> and H<sup>-</sup> fragments via an intermediate H<sub>2</sub><sup>\*</sup> molecule.

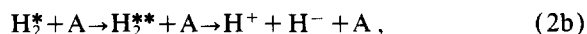
The dissociative capture of H<sub>2</sub><sup>+</sup> ions into H<sup>-</sup> fragments is a subject which has been much neglected in the literature. In a recent study [1], we have reported evidence that the majority of H<sup>-</sup> ions produced from collision-induced dissociation of H<sub>2</sub><sup>+</sup> in H<sub>2</sub> gas target arises from a double-collision mechanism,



followed by a second collisional excitation event



or



where A represents a target atom or molecule in general, and H<sub>2</sub><sup>\*\*</sup> denotes the possibility of a different state of excitation prior to dissociation. The main evidence for such a double collision process ((1) and either or both of (2a), (2b)) is the almost quadratic dependence [1] of product H<sup>-</sup> intensity on the pressure of collision gas A. Process (2a) for capture of a second electron, prior to spontaneous dissociation, is the probable channel [1] for production of H<sup>-</sup> ions. However, the unusual mechanism (2b) involving H<sup>+</sup>-H<sup>-</sup> ion-pair formation has also been proposed by Fournier [2].

In our study [1] of capture-dissociation of 6 keV H<sub>2</sub><sup>+</sup> using a reversed geometry mass spectrometer, translational energy spectra for product H<sup>+</sup> and H<sup>-</sup> ions were measured using the collision gas cell, located at the focal point between the magnetic and electrostatic sectors, "floating" at a positive potential of ≈ 700 V, relative to its earthed entrance and exit apertures. Positive ions were retarded on entry to the cell and accelerated on exit, with the reverse effect for the negative ions. This enabled us to identify the sequences of reactions in this field-free region of the mass spectrometer, and to ascertain the importance of the intermediate neutral H<sub>2</sub><sup>\*</sup> produced from reaction (1).

The H<sup>-</sup> spectrum for H<sub>2</sub><sup>+</sup> in Kr is shown in fig. 1a. Peak I can be identified as the main processes (1), (2a)/(2b) of dissociation occurring inside the collision cell. Peak II is due to H<sup>-</sup> ions produced from H<sub>2</sub><sup>\*</sup> precursors in the collision cell, implying that these neutral H<sub>2</sub><sup>\*</sup> were produced in the field-free region prior to the collision cell via process (1). Peaks III and IV are of minor importance, arising from processes (1) and (2a)/(2b) occurring outside the collision cell [1]. These assertions can be readily verified by applying a deflection field prior to the collision cell to prevent ions in the main beam from entering the cell. Peaks I and III are completely removed from the H<sup>-</sup>-spectrum, leaving peak II virtually unchanged and peak IV with reduced intensity.

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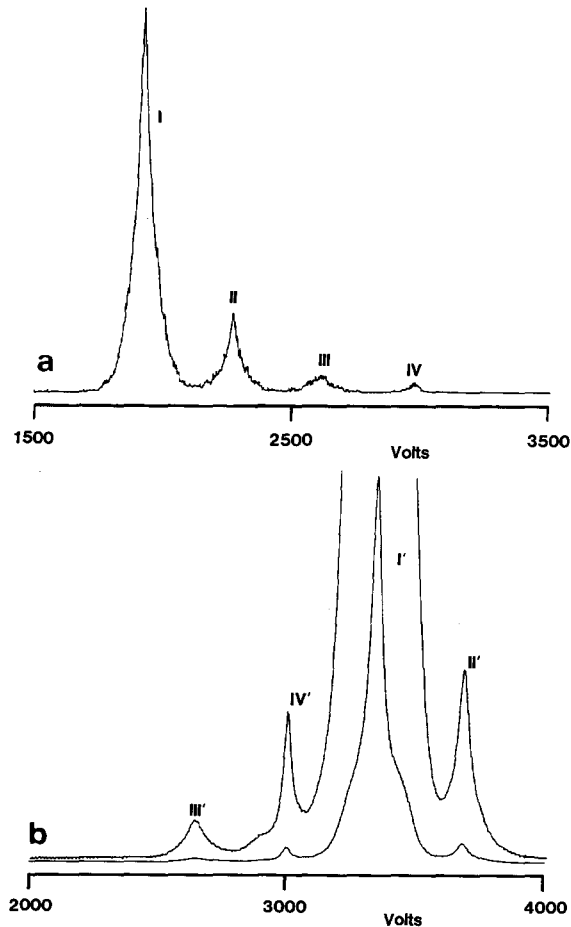
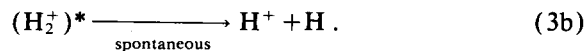


Fig. 1. Translational energy spectra for (a) H<sup>-</sup> ions and (b) H<sup>+</sup> ions produced from capture-dissociation of H<sub>2</sub><sup>+</sup> in collision with Kr target. Cell voltage V<sub>c</sub> ≈ +700 V.

The most probable process for the production of H<sup>+</sup> ions via the intermediate H<sub>2</sub><sup>+</sup> is that of reionization followed by dissociation,



Process (2b) probably only makes a minor contribution to the H<sup>+</sup>-spectra [1]. Contributions arising from reionization of H atoms produced from direct dissociation of H<sub>2</sub><sup>+</sup> also appears to be small [1] as can be deduced from the absence of the characteristic wings [3] signifying the vibrational population of the H<sub>2</sub><sup>+</sup> precursor in the direct dissociation process



H<sup>+</sup> ions resulting from ionization of H atoms produced from process (4) would be expected to exhibit the characteristic spectral profile of the parent H atom.

The translational energy loss incurred in the dissociation process is a further viable test of the validity of the double-collision mechanism previously identified [1], and it is the aim of this present communication to present evidence in support of this mechanism by extending our investigation to collisions of H<sub>2</sub><sup>+</sup> with inert gas targets He, Ne, Ar, Kr and Xe. There is no convenient and reliable means of measuring the energy loss for the combined processes from the H<sup>-</sup>-spectra, but the translational energy loss can be conveniently obtained from the H<sup>+</sup>-spectra. Since the dissociation limit for reionization (3a) is only ≈0.754 eV [4,5] above that for H<sup>+</sup> + H<sup>-</sup> (1s<sup>2</sup>) ion-pair production (2a), a study of H<sup>+</sup>-spectra, at the present energy resolution of ≈0.5 eV cannot distinguish these processes. However, an estimate of the lower limit for the translational energy loss incurred in the combined mechanism for capture-dissociation into the H<sup>+</sup>-H<sup>-</sup> pair is possible.

Fig. 1b displays the H<sup>+</sup>-spectrum for H<sub>2</sub><sup>+</sup> in Kr with the collision cell maintained at ≈ +700 V. Peak I', exhibiting a winged profile, is due to the production of H<sup>+</sup> ions by direct dissociation (4) of H<sub>2</sub><sup>+</sup> inside the collision cell; H<sup>+</sup> formed from the dissociation of the intermediate H<sub>2</sub><sup>+</sup> inside the cell (process (3b)), gives rise to peak II'. Peaks I' and II' correspond to peaks I and II for H<sup>-</sup>, shown in fig. 1a.

To obtain the experimental translational energy loss for the capture-dissociative reionization process ((1), (3a) and (3b)), the H<sup>+</sup>-peak for direct dissociation (4) was first obtained with the collision cell earthed. Application of a deflection field prior to collision cell then allows the detection of the H<sup>+</sup>-peak due to processes (3a) and (3b); the shift of peak positions (fig. 2), as a result of applying the deflection field, corresponds to the energy loss incurred in the combined processes (1), (3a) and (3b). Since each proton carries half the energy loss suffered by H<sub>2</sub> prior to dissociation, the energy loss for the combined capture-dissociation process is equal to twice the measured energy shift. The results of our meas-

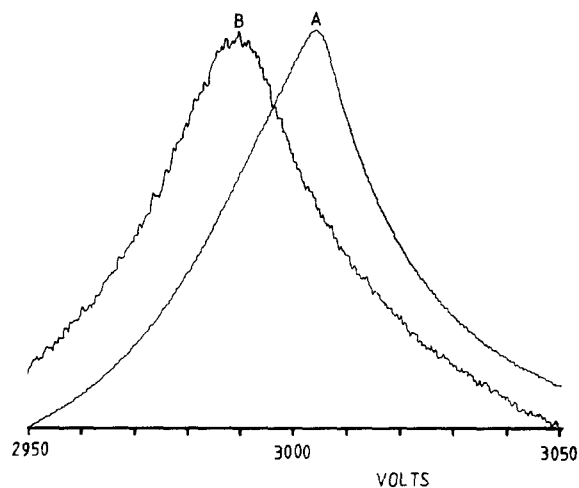


Fig. 2. Translational energy spectra for  $H^+$  fragments from direct dissociation (A) and capture-dissociation (B) of  $H_2^+$ . The shifted  $H^+$  peak B (with deflector field on) relative to the main  $H^+$  peak A (with deflection field removed) establishes the translational energy loss carried by each proton upon dissociation.

urement for the five inert gases are shown in table 1. To facilitate discussion of the theoretical energy loss, we rewrite the double-collision equations for dissociation into  $H^+$  via the  $H_2^*$  intermediate, allowing for the initial, intermediate and final products to exist in various states of excitation,

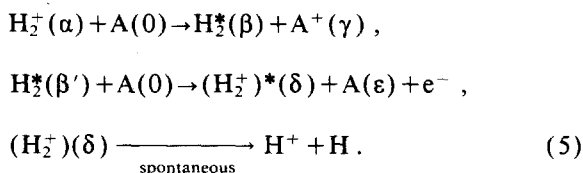


Table 1  
Translational energy loss data.

Collision gas	Experimental value ( $2 \times H^+$ energy loss) (eV)	Theoretical		
		minimum <sup>a)</sup> (eV)	vertical transition <sup>b)</sup>	
			ground state	first excited
He	31 ( $\pm 1$ )	24.6	32	52
Ne	31 ( $\pm 1$ )	21.6	29	45
Ar	27 ( $\pm 1$ )	15.8	23	34
Kr	26 ( $\pm 1$ )	14.0	21	30
Xe	26 ( $\pm 1$ )	12.1	19	27

<sup>a)</sup> Theoretical minimum. See text.

<sup>b)</sup> Theoretical value involving vertical transition to  $2p\sigma_u$  state of  $H_2^+$  from  $v=0$  state of  $H_2^*$  at dissociation limit ( $\sim +7$  eV), with target product in ground state A(0) (first row) and target product in first excited state.

These reactions allow for the possible decay of  $H_2^*(\beta)$  into a different state  $H_2^*(\beta')$  prior to the second collision. If no such decay occurs, the overall energy balance would result in an energy loss  $Q$  given by

$$Q = [E(\delta) - E(\alpha)] + E(\gamma) + E(\epsilon), \quad (6)$$

where  $E(\alpha)$ ,  $E(\delta)$ ,  $E(\gamma)$  and  $E(\epsilon)$  refer to the energy states of the primary  $H_2^+(\alpha)$ , the excited  $H_2^+(\delta)$  prior to spontaneous dissociation, the product ion  $A^+(\gamma)$  and the product atom  $A(\epsilon)$  respectively, relative to the ground state atom  $A(0)$  or molecular  $H_2$ .

The assumption that the target atoms are initially in the ground state  $A(0)$  has been taken for granted. If  $\beta \neq \beta'$ , the energy loss will be increased by  $[E(\beta') - E(\beta)]$ . For minimum energy of excitation leading to dissociation into  $H$  and  $H^+$ , the primary ion  $H_2^+(\alpha)$  is assumed to be populated at the highest vibrational level of its ground electronic state  $X^1\Sigma_g^+(1s\sigma_g)$  [3], the final energy of the molecular ion  $H_2^+(\delta)$  must be formed close to the dissociation limit for  $H^+ + H(1s)$ , and the target atom  $A(\epsilon)$  is left in the ground state. This implies that  $[E(\delta) - E(\alpha)] \approx 0$  and  $E(\epsilon) = 0$ . Accordingly

$$Q = E[A^+(\gamma)], \quad (7)$$

the first ionization potential of the target atom. For dissociation into the  $H^+ - H^-$  channel (process (2b)), the energy loss (7) is further reduced by the electron affinity of  $H^-$  ( $\sim 0.8$  eV).

In arriving at the figures for the minimum theo-

retial energy loss (table 1), we have not allowed for the effect of the Franck-Condon principle. The amount of excess energy required is largely dependent on the vibrational level of the intermediate excited molecule  $H_2^*$ . Lower vibrational levels will require more excess energy to facilitate a vertical transition to the repulsive  $2p\sigma_u$  state which leads to dissociation into  $H^+ + H(1s)$ , on account of the shift of the outer classical turning point of the vibrational level towards smaller internuclear separations. A vertical transition from the  $v=0$  level of  $H_2^*$  in a high Rydberg state will require an extra  $\sim 7$  eV to reach the  $2p\sigma_u$  state of  $H_2^+$ . This excess energy also tends to increase for lower electronic states of the intermediate  $H_2^*$ . Excitation from the ground state  $H_2$  molecule ( $v=0$ ) would require an excess energy of close to 15 eV. The figures shown in table 1 would appear to support the assertion that capture-dissociation of  $H_2^+$  largely involves metastable  $H_2^*$  in the double-collision mechanism. The experimental studies of de Bruin et al. [6] and Meierjohann and Vog-

ler [7] on predissociation of the  $c^3\Pi_u^+$  state of  $H_2$  strongly suggest to us that the metastable  $c^3\Pi_u^-$  state and higher Rydberg states of  $H_2$  may be involved.

We thank the Royal Society and the University College of Swansea for support of this work.

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