

DISSOCIATIVE ELECTRON CAPTURE OF H_2^+ INTO H^- FRAGMENTS

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ABSTRACT

Translational energy spectra of H^- ions have been measured for capture dissociation of 6 keV H_2^+ molecular ions in collision with H_2 gas. Voltage separation of the ion spectra has been obtained by the application of a biasing potential to the collision gas cell, allowing the sequence of processes taking place in different regions of the spectrometer to be identified. The energy release distribution of the H^- spectra and a correlation with the corresponding component of the H^+ spectra indicate that the majority of H^- are produced from single electron capture–dissociation of H_2^+ in a double-collision mechanism, $H_2^+ + H_2 \rightarrow H_2^* + [H_2^+]$ and $H_2^* + H_2 \rightarrow H^- + H^+ + [H_2]$, in which high Rydberg states of the H_2^* molecule are involved. The H^- and corresponding H^+ spectral peaks are narrow, with an FWHM of ~ 0.14 eV in the centre-of-mass system for the H^+ and H^- ions released from dissociation of H_2^* , consistent with the suggested mechanism.

INTRODUCTION

Collision-induced dissociation of H_2^+ has been the subject of many investigations. The process can be broadly classified into two main types, direct dissociation, including ionization/dissociation, and electron capture–dissociation.

In direct dissociation, the primary molecular ion H_2^+ in some vibrationally excited state of the ground electronic state $1s\sigma_g$, is collisionally excited to a repulsive electronic state, mainly the $2p\sigma_u$, and dissociates into the ion–neutral pair $H^+–H$



where A represents a target atom or molecule.

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In a violent collision, the molecular ion can be excited to the ionized state $H^+ + H^+$, with the excess energy shared by the two protons in the centre-of-mass frame upon dissociation



$H^+ - H$ and $H^+ - H^+$ fragment pairs resulting from these processes have been measured in coincidence by Meierjohann and Vogler [1,2] in a flight-time-difference experiment. The former process, Eq. (1a), is estimated to have a cross-section of $2.49 \times 10^{-16} \text{ cm}^2$, about 10 times the value for two-proton production.

Electron-capture dissociation can take place via two final separation channels, resulting in the neutral pair $H - H$ or the pair of oppositely charged ions H^+ and H^- .



or



The intermediate step in each process is explicitly given here because the dissociation may not necessarily be spontaneous.

The normal channel for dissociation into two neutral atoms, Eq. (2a), has been thoroughly investigated by Meierjohann and Vogler [1,3] and by de Bruijn et al. [4,5]. Four subsidiary dissociative processes have been distinguished [5] with corresponding translational energy release distributions. The $H - H$ fragments have been detected in coincidence in both sets of experiments. The alternative channel of dissociation, Eq. (2b), into the $H^+ - H^-$ pair has, unfortunately, been largely unexplored. Fournier [6] suggested this dissociation channel as a plausible explanation for the peak-shifts of the observed H^+ spectra and energy release upon formation of the H^+ ions. The suggested mechanism involves electron capture into a high Rydberg state of the hydrogen molecule H_2^* with subsequent spontaneous dissociation via curve-crossing into the ion pair $H^+ - H^-$. The fragment velocity distributions of H^- were measured by Fournier [6] for H_2^+ in collision with a Xe target and the velocity distributions of the $H^+ - H^-$ pair were measured in coincidence by Brouillard et al. [7] for H_2^+ in collision with Xe and Kr. Their results appear to be consistent with the proposed dissociation mechanism. In view of its intrinsic interest as a fundamental process, it is surprising that no further research has been reported in this area. There are still many outstanding questions to be answered and it is in an attempt to answer some of these questions that we have undertaken our present series of experiments. We have endeavoured to identify the dissociation process (2b) without resorting to coincidence techniques. Our measure-

ments have been made using translational energy spectroscopy. By applying a suitable biasing potential to the collision gas cell, one can isolate the possible mechanisms responsible for the observed H^- spectra and, by a process of elimination, identify the mechanism responsible for H^- production with little ambiguity. Correlation with the corresponding H^+ spectra has given us added confidence in our identification. Our observations for 6 keV H_2^+ ions in collision with H_2 gas strongly suggest the predominance of the double-collision process rather than single-collision capture with spontaneous decay



the square brackets indicating lack of knowledge of the states of the product particles.

Our conclusion is supported by the approximately quadratic pressure dependence of the observed H^- signals and by the behaviour of the voltage separated spectra described below.

EXPERIMENTAL METHOD

The measurements were performed using the ZAB-2F reversed geometry double-focusing mass spectrometer which has been described elsewhere [8]. H_2^+ ions were produced by electron-ionization of H_2 gas in the source of the spectrometer and were accelerated to an energy of 6 keV. Ions were mass selected by the magnetic sector and introduced into the collision cell located near the intermediate focal point of the mass spectrometer. The energy spectra for the H^- ions were obtained by scanning the voltage applied to the electric sector placed after the collision region.

Identification of the plausible collision mechanisms revolved around electrically "floating" the collision gas cell. The entrance and exit apertures were kept at earth potential whilst the collision cell was maintained at + 500 V (Fig. 1). Deflection of charged particles from the main beam could also be achieved by the application of a deflection field to parallel plates placed before and behind the collision cell.

Thus, positive ions would be retarded on entry to the cell and accelerated on exit, whereas negative ions would suffer the reverse consequences. The subsequent scanning of the electric sector would separate the original H^- spectra into several components, enabling us to identify and to eliminate the various H^- -production mechanisms. To facilitate our identification process, we have listed in Table 1 the possible collision mechanisms and sequences; the location of each process, viz. (a) before the collision cell within the

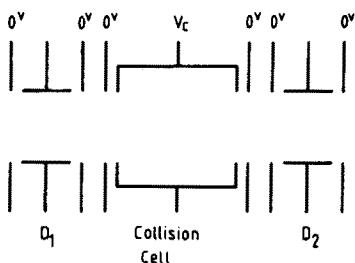


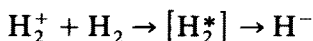
Fig. 1. Schematic diagram of collision cell region for voltage-separated spectra (VSS). D_1 and D_2 are pairs of deflector plates.

second field-free region, (b) in the collision cell, or (c) after the collision cell in FFR2; and the final energies of the detected H^- fragments from the different sequences.

RESULTS

H^- spectra

Results were obtained for the collision-induced production of H^- ions from H_2^+ on H_2 gas



A typical H^- spectrum obtained with the collision cell earthed (normal mode of operation) is shown in Fig. 2. The distribution shows a full width at half maximum (FWHM) of 79 eV in laboratory energy, corresponding to 0.26 eV for the H^- dissociation fragments in the centre-of-mass frame.

To identify the mechanism(s) responsible for the H^- production, we obtained the voltage-separated spectra (VSS) shown in Fig. 3(a) for which the collision cell was maintained at + 500 V. The four peaks can be easily identified by inspection of Table 1. The major peak I appearing at ~ 2.25 keV corresponds to the main process where the reaction under investigation takes place inside the collision cell [Eqs. (3a) and (3b)]. It is conceivable that a certain fraction of the excited neutral molecules resulting from the capture process may undergo spontaneous dissociation



However, our results appear to indicate that the double-collision mechanism cited earlier [Eqs. (3a) and (3b)] is predominant. The nearly quadratic variation with pressure of the H^- signal would support this view (Fig. 4). Further substantiation will be given in later discussions.

TABLE 1

Possible sequential reactions

 $V_c = +500$ V.

Before cell		Inside cell		After cell	Energy-to-charge ratio (V) of detected H^-	Channel designation
H_2^+ (6000)	→	→ (5500)	→	$H_2^+ \rightarrow H^-$ (6000)(3000)	3000	IVb
	→	$H_2^+ \rightarrow H_2^*$	→	$H_2^* \rightarrow H^-$	2750	III
	→	$H_2^+ \rightarrow H^+$	→	$H^+ \rightarrow H^-$	3250	
	→	$H_2^+ \rightarrow H$	→	$H \rightarrow H^-$	2750	I
	→	$H_2^+ \rightarrow H^-$	→	→	2250	
	→	$H_2^+ \rightarrow H_2^-$	→	$H_2^- \rightarrow H^-$	2500	
$H_2^+ \rightarrow H_2^*$	→	$H_2^* \rightarrow H_2^+$	→	$H_2^+ \rightarrow H^-$	3250	
	→	$H_2^* \rightarrow$	→	$H_2^* \rightarrow H^-$	3000	
	→	$H_2^* \rightarrow H^+$	→	$H^+ \rightarrow H^-$	3500	
	→	$H_2^* \rightarrow H$	→	$H \rightarrow H^-$	3000	II
	→	$H_2^* \rightarrow H^-$	→	→	2500	
	→	$H_2^* \rightarrow H_2^-$	→	$H_2^- \rightarrow H^-$	2750	
$H_2^+ \rightarrow H^+$	→	→	→	$H^+ \rightarrow H^-$	3000	
	→	$H^+ \rightarrow H$	→	$H \rightarrow H^-$	2500	
	→	$H^+ \rightarrow H^-$	→	→	2000	
$H_2^+ \rightarrow H$	→	$H \rightarrow H^+$	→	$H^+ \rightarrow H^-$	3500	
	→	→	→	$H \rightarrow H^-$	3000	
	→	$H \rightarrow H^-$	→	→	2500	
$H_2^+ \rightarrow H^-$	→	$H^- \rightarrow H^+$	→	$H^+ \rightarrow H^-$	4000	IVc
	→	$H^- \rightarrow H$	→	$H \rightarrow H^-$	3500	
	→	→	→	→	3000	
$H_2^+ \rightarrow H_2^-$	→	$H_2^- \rightarrow H_2^+$	→	$H_2^+ \rightarrow H^-$	3500	
	→	$H_2^- \rightarrow H_2^*$	→	$H_2^* \rightarrow H^-$	3250	
	→	$H_2^- \rightarrow H^+$	→	$H^+ \rightarrow H^-$	3750	
	→	$H_2^- \rightarrow H$	→	$H \rightarrow H^-$	3250	
	→	$H_2^- \rightarrow H^-$	→	→	2750	

A possible mechanism which could contribute to this H^- spectral peak may be identified as dissociation followed by capture



and



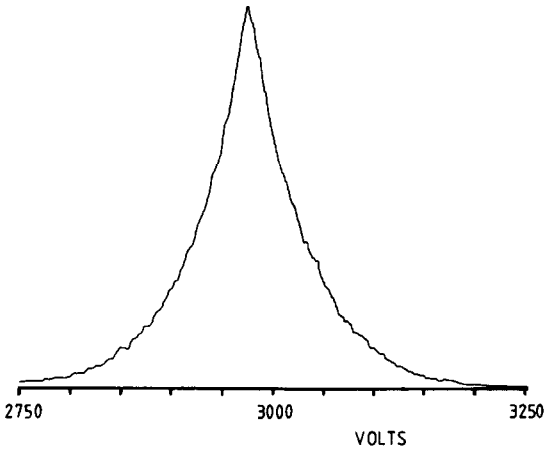
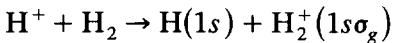


Fig. 2. H^- spectrum obtained under the normal mode of operation with collision cell earthed.

The cross-section for electron capture by H into H^- is extremely small and the combined double-collision shown in Eqs. (5a) and (5b) will result in a relatively minor contribution to the main H^- peak (I). As a consistency check on the order-of-magnitude to be expected from this contribution, we obtained the H^- spectrum shown in Fig. 5 for H^+ in collision with H_2 . The double-peak structure has been explained [9,10] in terms of the sequential collision mechanism for peak A (with energy loss of ~ 22 eV)



and the double-transfer mechanism for peak B (with energy loss of ~ 39 eV)



A smaller central peak [due to double-collision with the photoemission process $\text{H}(2p) \rightarrow \text{H}(1s) + h\nu$ in between] also identified by Durup et al. [11] is not apparent in our H^- spectrum on account of our much lower collision gas pressure ($\sim 3 \times 10^{-3}$ torr).

The intensity of the H^- ions detected from the combined processes (6a) and (6b) amounted to less than 5% of the H^- intensity obtained for the main H^- peak (I) from the dissociation of H_2^+ shown in Fig. 3 (for the same target gas pressure and comparable intensities for the primary ions H^+ and H_2^+). Another argument for dismissing processes (6a) and (6b) is that peak I (in Fig. 3) does not exhibit the characteristic energy spread expected from the dissociation process (5a) [1,2,12].

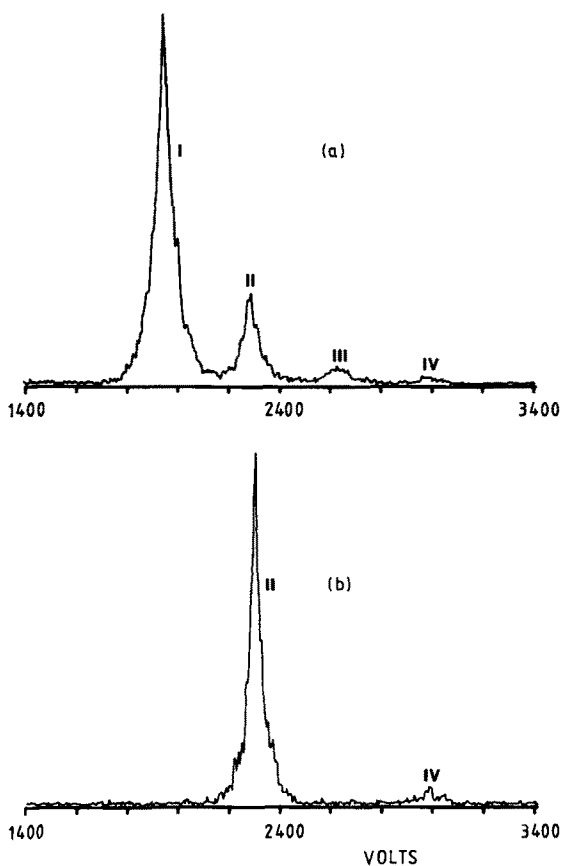


Fig. 3. (a) Voltage-separated spectra for H⁻ with the collision cell maintained at $V_c \approx +700$ V. Note that the choice of V_c was only approximate and the peak locations do not correspond exactly to the values given in Table 1. (b) As (a) with additional deflection field applied before the collision cell.

The second H⁻ peak, (II) in Fig. 3(a) centred around 2.5 keV, can be identified with the correspondingly designated (II) sequence of processes shown in Table 1. The relatively high intensity of this peak appears to indicate that a substantial fraction of H₂⁺ ions has undergone electron capture to some metastable excited states of H₂^{*} in FFR2 before the collision cell and that a substantial fraction of these H₂^{*} molecules survives to the target region to participate in collision-induced dissociation [process 3(b)]. The collisional dissociation cross-section for H₂^{*} would appear, not surprisingly, to be large.

H⁻ peak III (with corresponding designation in Table 1) results from H₂^{*} production in the collision gas cell [Eq. 3(a)] with subsequent collision-in-

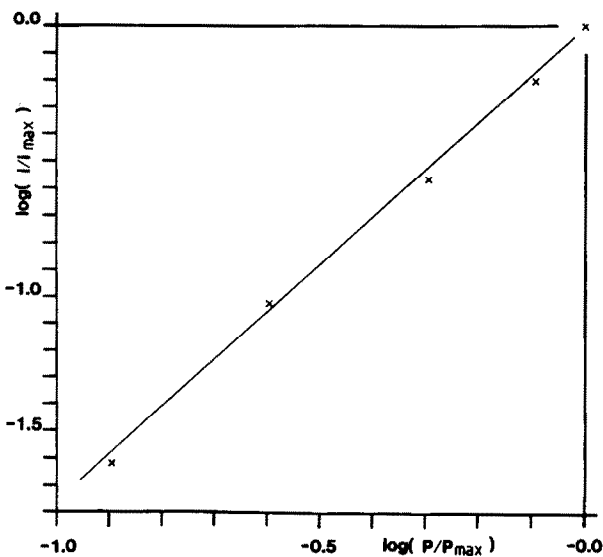


Fig. 4. Pressure (P) dependence of H^- intensity (i). Maximum pressure in the gas cell was $P_{\max} \sim 4 \times 10^{-3}$ Torr. Slope ≈ 1.75 .

duced dissociation of the H_2^* into H^+ and H^- in the region after the collision cell. The only likely competing process again involves $H + H_2 \rightarrow H^- + H_2^+$, which has been dismissed. It should also be noted that this process could not make any contribution to the major peak I in Fig. 3.

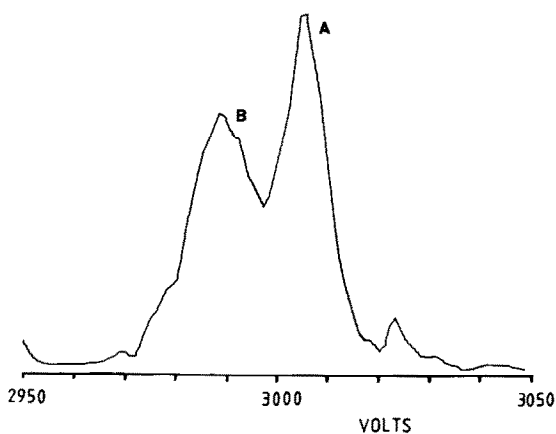
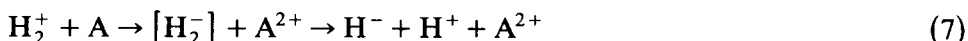


Fig. 5. H^- spectrum from electron capture by H^+ in collision with H_2 gas. Peak A corresponds to the double-collision mechanism of Eq. (6a) and peak B corresponds to the double-transfer mechanism of Eq. (6b).

Peak IV (at ~ 3 keV in Fig. 3) is a minor structure. The competing processes are listed in Table 1. Process IVa again features the main capture–dissociation process (3a) and (3b), this time taking place in the second field-free region after the collision cell.

It was pointed out by Fournier [6] that experiments were needed to distinguish single-capture dissociation [(3a) and (3b)] from the double-capture dissociation process



Our voltage-separated spectra (Fig. 3) would again appear to preclude the possibility of any significant contribution from such a process. In the first instance, no H_2^- ions have been detected. This could happen if H_2^- ions were short-lived and decayed spontaneously into $\text{H} + \text{H}^-$ ($\leq 10^{-8}$ s). In that case, however, one would have expected a linear dependence of peak I intensity on collision gas pressure, instead of the nearly quadratic dependence observed (Fig. 4), if double capture had indeed been a dominant process. Furthermore, Peak II (Fig. 3) could only result from production of H^- by neutral beam particles in the collision cell, excluding all possibilities of process (7). A convincing demonstration follows from the application of a deflection voltage on the parallel plates in front of the gas cell to remove charged particles from the main beam. The resulting H^- spectrum is shown in Fig. 3(b). Peaks I and III [Fig. 3(a)], which involve processes with charged primary particles in the region before the collision cell, are completely removed. Peak II is essentially unchanged, substantiating the arguments that it represents the second step of the capture–dissociation process (3b) and no other process. Peak IV is reduced in size because processes IVb and IVc (Table 1) have been removed.

Correlation with H^+ spectra

A similar scan of the electric sector can be made for the H^+ spectra with the collision cell maintained at a positive potential relative to the entrance and exit apertures or with deflection field applied prior to the gas cell. The normal H^+ spectra from H_2^+ dissociation display symmetrical wings (cf. ref. 12) from the kinetic energy release, as shown in Fig. 6. The wings extend to beyond 300 eV on either side of the central peak in the laboratory frame. H^+ ions produced from the various dissociation processes (1)–(3) all reside within this central distribution. Neutral H atoms released from dissociation process (1a) would be expected to exhibit a similar energy distribution, thus any H^- or H^+ ions which result from electron transfer or reionization of these neutral atoms should inherit this spectral profile.

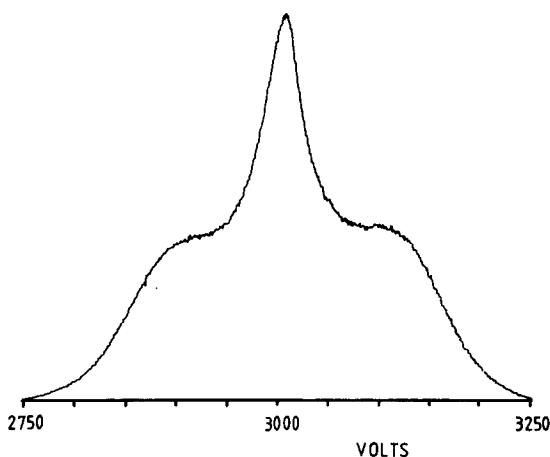
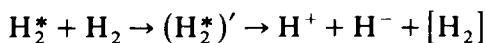
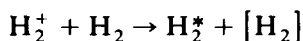


Fig. 6. A typical H^+ spectrum from direct dissociation of H_2^+ under normal mode of operation.

Application of a deflection field prior to the gas cell prevented all charged particles from entering the cell, leaving a resolved H^+ spectral peak (Fig. 7) which could arise only from collision-induced dissociation of H_2^* in the collision-cell. This has been verified from the voltage-separated spectra in a similar manner to the H^- spectra. This H^+ peak is remarkably symmetrical and well-defined. Spectra obtained for two different collision gas pressures did not reveal any noticeable difference in energy profile [Fig. 7(a) and (b)]. It prompted us to measure the width of the distribution at various heights to obtain a correlation with the corresponding distribution (II) for the H^- ions (Fig. 8). The results are displayed in Table 2. Conversion to centre-of-mass energy is obtained using a well-known formula given by Cooks et al. [13]. The notable absence of the spectral wings characteristic of the direct dissociation processes (1a) and (1b) in the H^+ and H^- peaks is indicative of the insignificant contribution to the detected ions arising from neutral H atoms produced from process (1a). H^+ ions resulting from re-ionization and H^- ions from electron capture would inherit the spectral characteristics of the parent neutral H atom.

An estimate of the energy loss incurred in the combined capture–dissociation processes



can be obtained by determining the relative positions (Fig. 9) of the main H^+ peak with the prior-deflector “on”, and H^+ peak II' due to the second

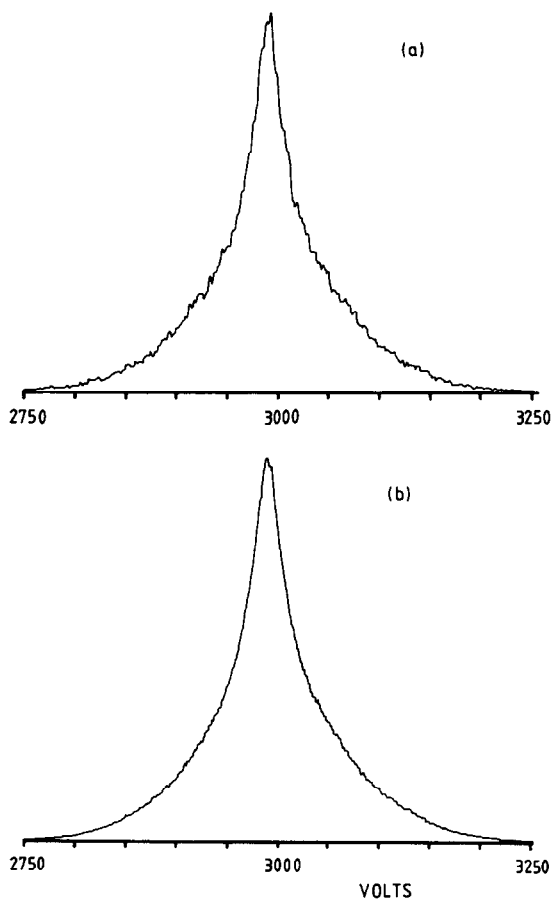


Fig. 7. H^+ spectra resulting from collision-induced dissociation of H_2^* with deflection field applied before the collision cell, at two gas pressures (a) $\sim 1 \times 10^{-3}$ Torr and (b) $\sim 4 \times 10^{-3}$ Torr.

TABLE 2

Correlation between H^+ and H^- spectra

Pressure $\sim 4 \times 10^{-3}$ Torr.

% Height	H^+ ions (eV)		H^- ions (eV)	
	Lab.	C.m.	Lab.	C.m.
90	12.5	0.01	17.5	0.01
75	27.5	0.03	25	0.03
50	60	0.15	52.5	0.11
25	145	0.88	105	0.46
10	292.5	3.56	207.5	1.79

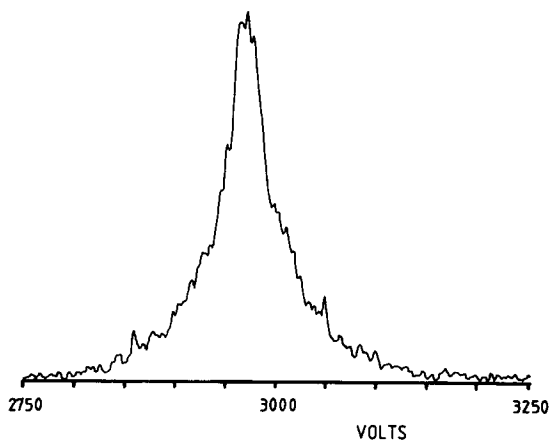


Fig. 8. H^- spectrum from collision-induced dissociation of H_2^* at $\sim 4 \times 10^{-3}$ Torr [cf. Fig. 7(b)].

of the above processes with the deflector “off”. The position of the main H^+ peak [from processes (1a) and (1b)] is used as an energy marker. The peaks are broadened and their positions cannot be measured with a high degree of accuracy. Nevertheless, a reliable shift of $14 (\pm 3)$ eV has been obtained for the proton peak, corresponding to an energy loss of $28 (\pm 6)$ eV for the capture–dissociation process, since each proton carries half the energy loss

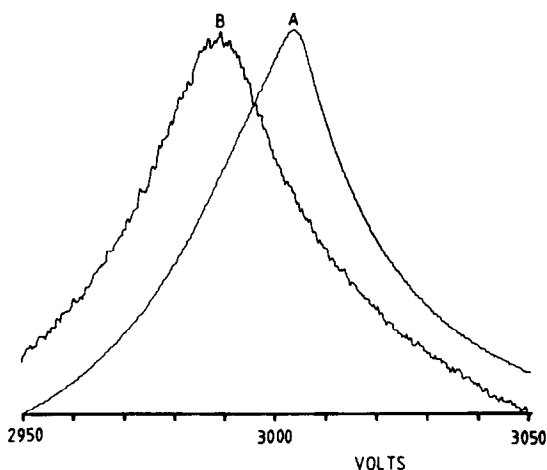
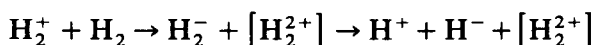


Fig. 9. Determination of translational energy loss from capture dissociation of H_2^+ . The shifted H^+ peak B (with deflector “on”) relative to the main H^+ peak A (with deflector “off”) establishes the energy loss carried by each H^+ upon dissociation.

of the parent H_2 molecule. The minimum energy required for capture–dissociation into H^- – H^+ has a theoretical value of ~ 15 eV, based on the assumption that the initial H_2^+ ion is produced in the highest vibrational level of the $1s\sigma_g$ state and that the target particles in the two steps are left in the lowest vibrational levels of their ground electronic states after impact. The minimum theoretical value for the energy loss incurred in the double-capture process



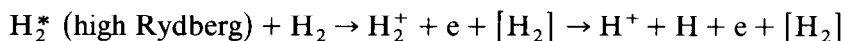
is ~ 40 eV from a Franck–Condon transition and cannot account for the measured value.

CONCLUSION

We have attempted to explore the remarkable channel for capture–dissociation of H_2^+ into H^+ and H^- , one with an escape window of perhaps less than 0.8 eV represented by the dissociation limits of the $\text{H}^+ + \text{H}^-(1s^2)$ and $\text{H}^+ + \text{H}(1s)$ systems. Nonetheless, the cross-section appears significant and a further elucidation of the mechanisms involved is of fundamental interest. In our present work, we have obtained translational energy spectra for both H^+ and H^- ions from collision-induced dissociation of H_2^+ . By separation of the spectra into components corresponding to sequences of processes occurring in the different sections of the mass spectrometer, we are able to identify with a high degree of confidence the predominant process(es) leading to the production of H^- ions. The results indicate that a double-collision mechanism, Eqs. (3a) and (3b), is largely involved (with collision gas in the 10^{-3} to 10^{-2} torr region). The relatively high intensity of the H^- peak II in Fig. 3 implies, without ambiguity, that a large fraction of highly excited H_2^* molecules is produced in the region before the collision cell, with a sufficiently long lifetime to survive in abundance to the collision cell. One may conjecture that a significant portion of these H_2^* molecules is formed in the metastable $C^3\Pi_u^-$ state, which is known to have a mean lifetime of 0.1–1.0 ms [14–18]. The predissociation of the $C^3\Pi_u$ state, of which only the half with negative parity $C^3\Pi_u^-$ is metastable, has been studied in careful detail by Meierjohann and Vogler [3] and de Bruijn et al. [5] for H_2^* in capture–dissociation of H_2^+ into the H – H neutral pair. The metastable half of this state with negative parity is presumably formed with similar vibrational populations under various capture conditions with different collision partners. The insight gained from the predissociation of the $C^3\Pi_u$ state [and higher Rydberg states converging onto the $\text{H}^+ + \text{H}(1s)$ dissociation limit] provides valuable clues for capture–dissociation into the H^+ – H^- channel under consideration. Recent measurements by Tischer and Phelps

[19] indicate that $H_2^*(C^3\Pi_u)$ has an unusually large cross-section for quenching by thermal H_2 molecules. At our collision energy of 6 keV, it is possible that collisional excitation to high Rydberg states of the system could occur, with subsequent transfer to the repulsive $b^3\Sigma_u^+$ state via rotational coupling. The $H^+ + H^-$ state is “mixed” with the ground $X^1\Sigma_g^+$ state at short internuclear distances. If transition to the $b^3\Sigma_u^+$ curve takes place at an energy above the dissociation limit for $H^+ + H^-(1s^2)$, corresponding to an internuclear separation of $\lesssim 0.6 \text{ \AA}$, H^+H^- pairs could indeed result. Transition to a lower point on the $b^3\Sigma_u^+$ curve would simply lead to dissociation into 2 ground-state H atoms in the normal channel. It is to be noted that spin-orbit coupling in H_2 is small, so that this projected transition may not be very likely. Another possible mechanism for dissociation into the ion pair involves rotational/vibrational excitation of the H_2^* molecule in a high Rydberg state to a continuum energy in the same state beyond the H^+H^- dissociation limit and a transition takes place to that channel at a curve crossing at large separation. The dissociation limit for $H^+ + H^-(1s^2)$ is only $\sim 0.754 \text{ eV}$ [20,21] below that for $H^+ + H(1s)$, to which the Rydberg series $H(1s) + H(nl)$ converge. If only Rydberg states belonging to this series are responsible for the charge transfer resulting in the H^+H^- pair, the dissociation energies carried by the H^- and H^+ ions would be limited to $\lesssim 0.38 \text{ eV}$ if not for excitation to continuum energies. The main bulk of the H^- ions detected in this experiment satisfies this criterion. Part of the higher energy tail observed may have been caused by diverse factors such as collisional broadening, instrumental effects, and other mechanisms of capture-dissociation, including involvement of excited states of H_2^* beyond the dissociation limit for $H^+ + H(1s)$ [e.g. $H(nl) + H(n'l')$ with $n \geq 2$, $n' \geq 2$] or capture of a second electron by H_2^* into a repulsive state of H_2^- .

H^+ ions monitored in the “voltage-separated spectra” mode also enable us to identify the H^+ spectral component complementary to the H^- ions. The energy distribution of the H^+ ions shows similar profiles and are devoid of the spectral wings which are characteristic of H^+H^- pairs produced from direct dissociation, Eq. (1a). This component of H^+ ions is produced from collision-induced dissociation of H_2^* molecules. Apart from the H^+H^- dissociation channel, H^+ ions could also be produced from re-ionization of the H_2^* molecules, which are already populated at energies close to the $H^+ + H(1s)$ limit



It is not possible, in our present experiment, to distinguish between protons produced by these two different mechanisms, but similarity of the H^- and H^+ spectral profiles is perhaps indicative of a similarity in the two dissociation mechanisms.

While a certain insight has been gained from our present investigation in capture-dissociation into the H^+-H^- channel, many outstanding questions remain to be answered. Coincidence experiments similar to those of de Bruijn et al. [4,5] and Meierjohann and Vogler [3], but designed specifically to study the collision-induced dissociation of highly excited H_2^* molecules produced from charge transfer, would be invaluable in probing the exact states involved in the dissociation mechanisms.

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