# THE FIRST EXPERIMENTAL OBSERVATION OF STABLE $H_4^{\ddagger}$ IONS

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A high pressure, variable temperature ion source is used to generate  $H_5^+$  from ionized  $H_2$ . A mass selected  $H_5^+$  beam is collisionally dissociated and the products mass and energy analyzed. The dominant product is  $H_3^+$  but a significant  $H_4^+$  signal is observed. These ions survived at least  $10^{-6}$  s from the collision cell to the detector and are thus stable to dissociation. Kinetic energy distributions of the  $H_3^+$  and  $H_4^+$  product ions are reported and are significantly different. All experiments were also performed using  $D_5^+$  generated in ionized  $D_2$  with essentially identical results obtained. The mechanism of  $H_3^+$  and  $H_4^+$  formation is discussed.

## 1. Introduction

The reaction of  $H_2^{\dagger}$  with  $H_2$  is the simplest twomolecule reaction and as a consequence it has received considerable attention experimentally [1,2] and theoretically [3]. The reaction proceeds on the  $H_4^{\dagger}$  surface, and one of the important questions is whether or not an  $H_4^{\dagger}$  complex is involved:

$$H_2^+ + H_2 \to (H_4^+) \to H_3^+ + H^-.$$
 (1)

Reaction dynamic studies [2] indicate the dynamics are "direct" even at low energies, suggesting that "stable"  $H_4^{\dagger}$  plays little role in the reaction. This result is well rationalized theoretically [3] where it is suggested [3,4] that the stable form of  $H_4^{\dagger}$  is probably best described as  $H_3^{\dagger}$ ·H<sup>\*</sup>. Hence, the reacting  $H_2^{\dagger}/H_2$ system, which is 39 kcal/mole exoergic <sup>‡</sup>, simply slides through the shallow "bound" region of  $H_4^{\dagger}$  on the way to products.

Recent theoretical calculations [4] give a structure of  $H_4^+$  as triangular  $H_3^+$  bound to a hydrogen atom located 1.6 Å from one of the apex hydrogens in  $H_3^+$ . The best calculations to date indicate this system is stable by  $\approx 4.0$  kcal/mole relative to dissociation to  $H_3^+$  and H<sup>\*</sup>. Hence, according to theory [4,6,7],  $H_4^+$  is as stable as  $H_5^+$  yet  $H_5^+$  is a commonly observed species [8] in ionized  $H_2$  while  $H_4^+$  has never been observed. In fact, in ionized  $H_2$  at high pressures the species  $H_3^+$ ,  $H_5^+$ ,  $H_7^+$ ,  $H_9^+$ , +... are observed but none of the even hydrogen species, except  $H_2^+$ . This occurs, presumably, because of the rapid transformation of  $H_2^+$  to  $H_3^+$  followed by slow, sequential clustering with  $H_2$  molecules.

An effort has been made to observe  $H_4^+$  ions by photoionization of  $(H_2)_n$  neutral clusters [9]. This technique has been successfully used to detect weakly bound clusters of a number of ions with their parent neutral molecules [10]. When  $(H_2)_n$  clusters are formed by adiabatic expansion through a nozzle and subsequently photoionized [9] (or ionized by electron impact [11]) only ions with an odd number of hydrogen atoms are formed (again except for  $H_2^+$ ). Hence, the species  $H_2^+ \cdot H_2$  does not correspond to a minimum on the  $H_4^+$  surface.

The question of interest here, is, then, can stable  $H_4^+$  ions be prepared experimentally to test the theoretical predictions? It appears clear that stable  $H_4^+$  cannot be formed starting from the  $H_2^+/H_2$  part of the  $H_4^+$  surface. We chose to approach the problem from the opposite direction. The idea is to start with larger sized hydrogen clusters ( $H_5^+$ ,  $H_7^+$ , etc.) and attempt to form  $H_4^+$  by collision induced dissociation of these species. The lowest energy theoretical structures of  $H_4^+$  and  $H_5^+$  are similar [4,6,7]

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<sup>&</sup>lt;sup>+</sup> From known heats of formation of H<sup>+</sup><sub>2</sub>, H and H<sub>2</sub> and a proton affinity of H<sub>2</sub> of 101 kcal/mole [5].

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Fig. 1. Schematic view of the instrument used in these studies.



suggesting this procedure has some hope of success. The results of our experiments are presented here.

## 2. Experimental

The experiments were carried out on a V.G. analytical ZAB-2F mass spectrometer [12] using a specially designed high pressure ion source that can be cooled to liquid nitrogen temperature [13]. This source forms relatively large abundances of  $H_5^+$  and higher order clusters. No signal corresponding to ions at m/z = 4 in  $H_2$ or m/z = 8 in  $D_2$  is observed. The ions are extracted from the source, accelerated to 8 kV, mass selected by passing through a magnet, and passed through a collision cell for collisional excitation. The collision products are mass and energy analyzed by a high resolution electrostatic analyzer, detected by single-ion counting techniques and stored in a multichannel analyzer. A schematic of the instrument is given in fig. 1.

High resolution spectra were taken to ensure only a single-mass component was present in the  $H_5^+$  main beam. At mass 5 the possible peaks are  $H_5^+$ , HeH<sup>+</sup> and  $D_2H^+$ . Great care was taken to eliminate the trace amounts of HeH<sup>+</sup> and  $D_2H^+$  present at m/z 5. In the data reported here these impurities were not present, a result confirmed by high resolution studies. There are no potential impurities at m/z 10. High resolution studies indicated that the m/z 10 beam from ionized  $D_2$  was pure  $D_5^+$ . All experiments were run using both  $H_5^+$  and  $D_5^+$  main beams with essentially identical results in all cases.

# 3. Results and discussion

The CID spectrum of a mass selected beam of  $H_5^+$  created in a high pressure ion source cooled to 80 K is given in fig. 2a with the relative intensities listed in table 1. A comparable spectrum for  $D_5^+$  is given in fig. 2b. The data in fig. 2 are plotted as the logarithm of the ion intensity versus ion mass so that all product ions can be conveniently shown on the same graph. A number of things are immediately evident from the data. First and most important for this paper, is the presence of a significant peak at mass 8 corresponding to  $H_4^+$ , and a similar peak at mass 8 corresponding to  $D_4^+$ . The flight time from the collision cell to the detector is of the order of  $10^{-6}$  s. Any quasibound  $H_4^+$  ions would have decayed at times short relative to  $10^{-6}$  s and hence the signal at mass 4 corresponds to stable  $H_4^+$ .

The second feature immediately evident from the data is that  $H_3^+$  is overwhelmingly the preferred reaction product. Hence, the weak  $H_3^+ \cdot H_2$  bond ( $D^0 \approx 5$  kcal/mole) [6] breaks preferentially relative to the  $H_4^+ \cdot H$  bond ( $D^0 \approx 100$  kcal/mole).

A third feature is the apparent broadness of the  $H_3^+$  peak relative to the  $H_4^+$  peak. To some extent this apparent broadness is due to the way the data is plotted. The  $H_3^+$  peak actually is composed of a strong narrow peak with a weak but broad base, while the  $H_4^+$  product exhibits a narrow overall peak shape.



Fig. 2. Collision induced dissociation spectra of  $H_5^+$  (a) and  $D_5^+$  (b). The vertical axis is the  $\log_{10}$  of the signal intensity and is plotted versus the ion kinetic energy passed by the electric sector. This energy is directly proportional to ion mass and hence each peak is characteristic of the fragment ion indicated. Differences in peak shape and intensity between the two spectra are in part due to different collision cell gas pressures used in the two experiments.

The differences in the two product channels can be better seen in the product kinetic energy distributions given in fig.  $3^{\ddagger}$ . The H<sup>+</sup><sub>4</sub> distribution peaks at  $\approx 0.03$  eV and falls smoothly to zero at  $\approx 0.35$  eV. Such a distribution is consistent with the dissociation of H<sup>+</sup><sub>5</sub> on a repulsive surface. On the other hand, the

<sup>‡</sup> These distributions are from H<sup>↓</sup><sub>4</sub> and H<sup>↓</sup><sub>3</sub> peaks obtained under high (≈ 10000) energy resolving power. The method for deriving these center of mass kinetic energy distributions from the laboratory peaks has been previously described [14].

Table 1 Experimental collision induced dissociation spectra for H<sub>5</sub><sup>+</sup> and  $D_5^+a$ )

H <sup>+</sup> <sub>5</sub>	Relative b) intensity	D <sub>5</sub> <sup>+</sup>	Relative b) intensity
Hả	0.011	Då	0.014
н	0.883	$D_{1}^{2}$	0.867
нţ	0.092	D,	0.104
н <sup>∓</sup>	0.014	D‡	0.015

a) Hc collision gas, 8 keV  $H_5^+/D_5^+$  main beam.

b) Integrated intensities normalized by the sum of the fragment ion peak areas.

 $H_3^+$  distribution peaks at  $\approx 0.004 \text{ eV}$ , falls rapidly to  $\approx 0.15 \text{ eV}$  and then falls slowly to zero at  $\approx 0.8 \text{ eV}$ . This distribution is due either to two dissociation me-



Fig. 3. Kinetic energy distributions of the product ions (a)  $H_4^+$  and (b)  $H_3^+$  from collision induced decomposition of  $H_5^+$ , taken under high energy resolving power (10000). The inset in (b) gives the low energy portion of the H<sub>3</sub> kinetic energy distribution.



Fig. 4. Schematic reaction coordinate diagrams for formation of  $H_3^+$  and  $H_4^+$  from CID of  $H_5^+$ . The proposed  $H_5^+$  collisional energy deposition function is given by the solid line on the vertical axis. The dashed curve on the vertical axis is a hypothetical collisional energy deposition function for H5 assuming Franck-Condon factors are not important (see text).

chanisms or to an unusual  $H_5^+$  excitation mechanism. In any case it is apparent that the  $H_5^+$  dissociation mechanisms for formation of  $H_4^+$  and  $H_3^+$  are different.

Table 2	
Heats of	formation

$\Delta H_{f,298}^{0}$ (kcal/mole)		
366 a)		
51.5a)		
354 a)		
0		
255 b)		
300 c)		
250 d)		
	$\Delta H_{f,298}^{0} (kcal/mole)$ 366 a) 51.5 a) 354 a) 0 255 b) 300 c) 250 d)	

a) Ref. [15].

b) From the experimental proton affinity of  $H_2$  [5]. c) From the  $H_3^+$  H<sup>+</sup> bond dissociation energy of  $H_4^+$  [4].

d) From the  $H_3^* \cdot H_2$  bond dissociation energy of  $H_5^*$  [6,7].

The  $H_2^+$  and  $H^+$  peaks in the  $H_5^+$  CID spectra are relatively weak and relatively broad. These products are the consequence of high energy, sequential dissociation. Discussion of the possible mechanism of formation of these species will be deferred to a future publication.

It is useful to discuss the formation of  $H_4^{\dagger}$  (and  $H_3^{\dagger}$ ) from collisional excitation of H<sup>+</sup><sub>5</sub> using the diagram in fig. 4. The appropriate heats of formation are given in table 2. Kim and McLafferty [16] have argued that the energy deposition function for high energy ion beams colliding with thermal neutral atoms has the general qualitative shape given by the dashed line in fig. 4. The model of Kim and McLafferty was developed for large ions with essentially continuous state densities. In addition, Franck-Condon factors were assumed not to be important. If this model is applied to  $H_{5}^{+}$ , Franck-Condon factors must be included. Hence, for  $H_5^{+}$ , it is expected that the energy deposition will be clustered about the H<sup>+</sup><sub>5</sub> ground state and excited electronic states. A qualitative energy deposition function is shown as the solid line on the vertical axis in fig. 4.

The sketch given in fig. 4 suggests the following interpretations for formation of  $H_4^+$  and  $H_3^+$  from  $H_5^+$ CID. The principal excitation is low energy vibrational excitation of  $H_5^+$ . The only exit channel available at these energies is  $H_3^+/H_2$  and hence  $H_3^+$  is the principal ionic product as observed. The unusual kinetic energy distribution for the  $H_3^+$  product ions could be a reflection of the shape of the energy deposition function at these low energies.

The  $H_4^+/H$  exit channel becomes energetically accessible at  $H_5^+$  internal energies of  $\approx 4.5$  eV. The  $H_5^+$  system samples  ${}^{3}A_1$  repulsive surface leading to dissociation and stable  $H_4^+$  product  $\ddagger$ . The  $H_4^+$  ions formed are probably vibrationally excited; specifically the  $H_3^+ \cdot H$  bending modes should be activated by vertical transitions of ground state  $H_5^+$ . Theory predicts [4] the  $H_4^+$  well should support several vibrational quanta. A certain percentage of the  $H_4^+$  ions may be excited above their dissociation limit and may subsequently dissociate to  $H_3^+/H^-$ . This dissociation pathway could contribute to the shape of the  $H_3^+$  kinetic energy distribution.

## 4. Conclusion

The  $H_4^{\pm}$  ion is not observed as a stable species either in reactions in ionized hydrogen or in reactions of ionized neutral  $(H_2)_n$  clusters. However, the  $H_4^{\pm}$  ion is theoretically predicted to be stable to dissociation by  $\approx 4.0$  kcal/mole. We have succeeded in forming stable  $H_4^{\pm}$  ions by collisionally dissociating  $H_5^{\pm}$ . The theoretical structures of  $H_5^{\pm}$   $(H_3^{\pm} \cdot H_2)$  and  $H_4^{\pm}$   $(H_3^{\pm} \cdot H)$  are similar and hence the stable portion of the  $H_4^{\pm}$  surface can be accessed in the CID process. Kinetic energy distributions of both  $H_3^{\pm}$  and  $H_4^{\pm}$  ions, arising from  $H_5^{\pm}$  CID, are obtained. These distributions are analyzed in terms of qualitative reaction coordinate diagrams and a collisional energy deposition function.

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#### References

- M.T. Bowers, D.D. Elleman and J. King Jr., J. Chem. Phys. 50 (1969) 4787;
   R.H. Neynaber and S.M. Trujillo, Phys. Rev. 167 (1968) 63;
   W.A. Chupka, M.E. Russell and K. Refaey, J. Chem. Phys. 48 (1968) 1518;
   J. Durup and M. Durup, J. Chem. Phys. 46 (1967) 386;
   J.J. Leventhal, T.F. Moran and L. Freedman, J. Chem. Phys. 46 (1967) 4666;
   C.F. Giese and W.B. Maier H, J. Chem. Phys. 39 (1963) 739.
   J.R. Krenos, K.K. Lehman, J.C. Tully, P.M. Hierl and
- G.P. Snuth, Chem. Phys. 16 (1976) 109;
   W.R. Gentry, D.J. McClune and C.H. Douglass, Rev. Sci. Instrum. 46 (1975) 367;
   A. Henglein, J. Phys. Chem. 76 (1972) 3883.
- [3] R.D. Poshusta and D.F. Zetik, J. Chem. Phys. 58 (1973) 118;
  J.R. Stein and J.T. Muckerman, J. Chem. Phys. 68 (1977) 185, and references therein.
- [4] L.R. Wright and R.F. Borkman, J. Chem. Phys. 77 (1982) 1938.
- [5] J.A. Burt, J.L. Dunn, M.J. McEwan, M.M. Sutton, A.E. Roche and H.I. Schiff, J. Chem. Phys. 52 (1970) 6062; D.H. Aue and M.T. Bowers, in: Gas phase ion chemistry, Vol. 2, ed. M.T. Bowers (Academic Press, New York, 1979) ch. 9, and references therein.

In fig. 4 it is assumed that the surfaces associated with recombination of ground state H<sup>+</sup><sub>3</sub> · H<sup>\*</sup> with ground state H<sup>\*</sup> are similar to those of H<sup>\*</sup>/H<sup>\*</sup> recombination.

Volume 106, number 1,2

67 (1977) 4235.

- [6] R. Ahlrichs, Theoret. Chim. Acta 39 (1975) 149.
- [7] Y. Yamaguchi, J.G. Gaw and H.F. Schaefer III, J. Chem. Phys. 78 (1983) 4074.
- [8] N.A. Kulazhenkava, I.K. Lavin and V.L. Tal'rose, Dokl. Phys. Chem. 207 (1972) 915;
   S.L. Bennett and F.H. Field, J. Am. Chem. Soc. 94 (1972) 8669.
- [9] S.L. Anderson, T. Hiroaka, P.W. Tiedemann, B.H. Mahan and Y.T. Lee, J. Chem. Phys. 73 (1980) 4779.
- [10] C.Y. Ng, Advan. Chem. Phys. 52 (1983) 263;
  C.Y. Ng, B.H. Mahan and Y.T. Lee, J. Chem. Phys. 65 (1976) 1956;
  C.Y. Ng, P.W. Tiedemann, B.H. Mahan and Y.T. Lee, J. Chem. Phys. 66 (1977) 3985;
  C.Y. Ng, D.J. Trevor, P.W. Tiedemann, S.T. Ayer, P.L. Kronebusch, B.H. Mahan and Y.T. Lee, J. Chem. Phys.

- [11] A. van Lunig and J. Reuss, Intern. J. Mass Spectrom. Ion Phys. 27 (1978) 197.
- [12] R.P. Morgan, J.H. Beynon, R.H. Bateman and B.N. Green, Intern. J. Mass Spectrom. Ion Phys. 28 (1978) 171.
- [13] P.A.M. van Koppen, P.R. Kemper, A.J. Illies and M.T. Bowers, Intern. J. Mass Spectrom. Ion Phys., to be published.
- [14] M.F. Jarrold, A.J. Illies and M.T. Bowers, Chem. Phys. 65 (1982) 19.
- [15] H.M. Rosenstock, K. Draxl, B.W. Steiner and J.T. Herron, J. Phys. Chem. Ref. Data 6, Suppl. No. 1 (1977).
- [16] M.S. Kim and F.W. McLafferty, J. Am. Chem. Soc. 100 (1978) 3279.