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Study on H_3^+ formation by synchrotron radiation

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Abstract. A molecular beam experiment on the formation of H_3^+ has been carried out by using tunable vacuum ultraviolet (VUV) synchrotron radiation. Reflectron time-of-flight mass spectrometer is applied to detect the signal of H_3^+. The ionization energy (IE) of H_2 and the appearance energy (AE) of H_3^+ are determined to be 15.41 eV and 14.61 eV, respectively, by measurements of photoionization efficiency (PIE) curves. Additionally, two most likely H_3^+ formation ways, $(H_2)2 \rightarrow H_+^3 + H$ and $(H_2)_3 \rightarrow H_3^+ + H + H_2$, are discussed by *ab initio* calculations at CCSD(T) and MP2 level with aug-cc-pVQZ basis set and compared with the experimental result. The optimized geometries of species involved in the dissociative photoionization channels are also determined at MP2/aug-cc-pVQZ level.

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Key words: H_3^+, photoionization, synchrotron radiation, *ab initio* calculation

1 Introduction

H_3^+ ion was first found by Thomson in 1912 [1]. Subsequently, a lot of experimental and theoretical works have been devoted to the study of hydrogen clusters since they are perhaps the simplest example of molecular clusters [2-12]. It has established that H_3^+ is a very stable molecule having an equilateral triangular structure [3]. Meanwhile, many theoretical works predicted the geometrical structures of various H_n^+ clusters are composed of a triangular H_3^+ core with surrounding H_2 molecules weakly bound to the core [2-6], whereas recent studies showed the energy of H_6^+ cluster with H_2^+ core is lower than

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that with H_3^+ core [7-9]. The H_3^+ ion also plays an important role in the chemistry of interstellar clouds as an efficient protonator of neutral molecular [13]. Given all this interest it is not surprising that H_3^+ has been the subject of numerous theoretical and experimental studies [2, 10, 11]. However, the details of the mechanism for H_3^+ formation from neutral clusters are still unclear and the appearance energy of H_3^+ is also controversial [11, 12].

The H_3^+ ion can be usually generated by two methods. One method is that it can be easily formed by passing electron beam through molecular hydrogen gas [4]. It believes that H_3^+ is produced by ionic-molecular reaction,

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{1}$$

The large exothermicity of 1.72 eV makes this reaction easily occur, and then larger clusters are subsequently formed in the reaction between H_3^+ and its neighboring neutral molecule. These ionic hydrogen clusters have already been found which included not only the odd-membered ionic clusters but also the even-membered ionic clusters in 1986 by Nicholas and Michael [4]. The other method does not via the ionic-molecular reaction. The ionic hydrogen clusters are formed by ionization of the neutral clusters in a supersonic expansion beam. For example, H_3^+ can be produced by dissociative photoionization of the neutral cluster H_4. The first observation of cluster formation in free jet expansion was by Becker et al. [14] in 1956. They observed the intensities, velocities and speed ratios of H_2, N_2, and Ar beams with changing stagnation temperatures and pressures. Then a lot of experiments for neutral hydrogen clusters have been extensively explored [11, 12, 15-17]. They are almost detected using electron impact ionization mass spectrometers. Because of the unavoidable fragmentation and other disadvantages, such as the appearance energies of fragments obtained in this ionization method is inaccurate [12], photoionization is considered a more accurate measurement in studying of hydrogen clusters. Anderson et al. [11] has carried out the hydrogen cluster research with a light source of a capillary discharge lamp. However, because of the low light intensity, they hardly picked any of the anticipated small autoionzation "peaks" out of the base line in the photoionization efficiency curves of H_3^+ and the AE of H_3^+ they obtained is 0.39 above the theoretical value.

To determine AE of H_3^+ and to explore the mechanism for its formation, we carried out a molecular beam study of H_3^+ using tunable vacuum ultraviolet synchrotron radiation as ionization source for its great advantage. The IEs of H_2, AE of H_3^+ are measured by the PIE curves. Furthermore, with the help of ab initio calculations, two most likely dissociative photoionization channels, $(H_2)_2 \rightarrow H_3^+ + H$ and $(H_2)_3 \rightarrow H_3^+ + H + H_2$, are discussed, and the theoretical IE of H_2, AE of H_3^+ are obtained. In addition, geometry optimizations are also obtained by Gussian 09 at the MP2 levels with the aug-cc-pVQZ basis set.

2 Experimental and apparatus

The experiments are performed at the Atomic and Molecular Physics Beamline (U14-A) station at the National Synchrotron Radiation Laboratory of Heifei. The apparatus has been described in detail elsewhere [20]. It consists of a cluster source and a reflectron time-of-flight mass spectrometer. The cluster source composed of a 10 mm diameter, 16-cm-long stainless steel tube which is cooled by liquid nitrogen around the tube with the temperature of about 80 K. The cooling method can refer the work of Han et al. [21] Neutral clusters are produced by adiabatic expansion of hydrogen through an orifice of 50 μm diameter. Typical stagnation pressures are 2 bar.

At a distance of 25 mm from the nozzle, the molecular beam passes through a skimmer with 2 mm diameter, 80 mm further downstream the beam is crossed perpendicular by a VUV synchrotron radiation from the electron storage ring. The ions produced here are analyzed with the reflectron time-of-flight mass spectrometer mounted in a direction perpendicular to the plane defined by molecular and photon beam. A microchannel plate (MCP) detector serves for the collection and detection of the ions formed in ionization region. Signals from the detected ions are counted with a multiscaler P7888 counter (FAST Comtec, Germany) after they are amplified with preamplifier VT120C (EG&G, ORTEC) and transferred to a computer for further processing.

The photoionization mass spectrum of hydrogen clusters can be obtained when it's excited by using fixed photon energy above its ionization threshold. The PIE curves are measured while the monochromator is scanned from 13.0 eV to 16.0 eV with the energy increment of 30 meV. To normalize the ion signals, the photon intensity is monitored simultaneously with a silicon photodiode (SXUV-100, International Radiation Detectors, Inc.). In the study, we use the rare-gas (Ar) harmonic filter to reduce higher-order harmonics, and the pressure of the gas filter is about 5 Torr with the efficiency of above 99.9 % [22].

3 Theoretical methods

In the theoretical study, the geometry optimizations of neural hydrogen clusters and ionic hydrogen clusters are done at the MP2 level with aug-cc-pVQZ basis set, and harmonic vibrational frequencies are also computed analytically at the same level in order to characterize the optimized geometries as potential minima or saddle points. The relative energies are obtained at the CCSD(T) and MP2 level based on the optimized geometries at aug-cc-pVQZ basis sets. All *ab initio* calculations, performed with the GAUSSIAN 09 program, are carried out on the Supercomputing Center of University of Science and Technology of China.

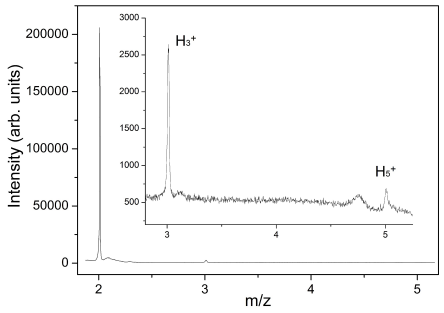

Figure 1: Photoionization mass spectrum of hydrogen clusters at 15.7 eV.

4 Results and discussion

The photoionization mass spectrum of hydrogen clusters at 15.7 eV is shown in Fig. 1. In the graph, the H_2^+ ($m/z=2$), H_3^+ ($m/z=3$) and H_5^+ ($m/z=5$) peaks can be distinguished clearly. Moreover, the intensity of H_3^+ peak is about 1% of the intensity of H_2^+ peak and the intensity of H_5^+ peak is even smaller. The PIE curves for H_2^+ and H_3^+ are shown in Fig. 2 (a) and (b), respectively. The general trend of the increase of the photoionization efficiency as a function of photon energy is some similar for the H_2^+ and H_3^+. They all have a dramatic change near the ionization energy of H_2. However, there are significant differences between them. For the PIE curve of H_2^+, it easily establishes the IE of H_2 is 15.39 eV, and below the energy of 15.36 eV, the curve is almost a straight line. But for the curve of H_3^+, above the energy of 14.6 eV, the curve still has some signal peaks at some energies points.

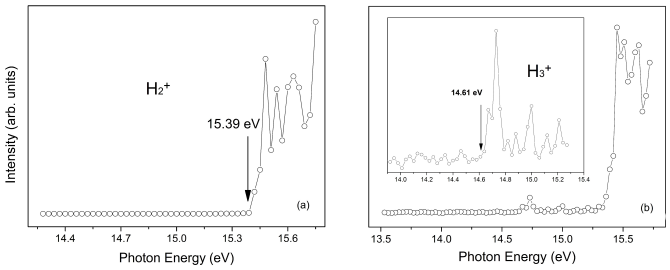

Figure 2: PIE curves for H_2^+ (a), and H_3^+ (b).

Compared our experimental result with Anderson's [11] PIE curve of H_3^+ which obtained by photoionization with a light source of a capillary discharge lamp. Our experimental value of AE for H_3^+ is 14.61 eV whereas their experimental value is 14.09 eV.

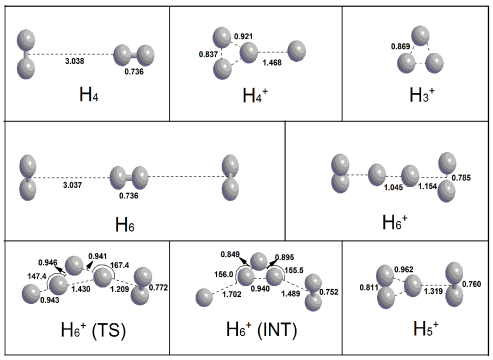

Figure 3: Optimized geometries at the MP2/aug-cc-pVQZ level. Bond lengths in Å and angles in degree.

Moreover, the Anderson's PIE curve of H_3^+ is in a process with decreased continuously and gradually until it arrives at 14.09 eV. But in our experiment it has obvious inflexion point at the energy which closes to the ionization energy of H_2. It is maybe caused by the large energy interval for signal collection in our experiment.

Unfortunately, the even-membered ionic clusters were not observed in our experiment, such as H_4^+ and H_6^+. The absence of H_4^+ from the photoionization of the H_4 has been attributed to the absence of barrier at ground state surface going down from $H_2{\cdot}H_2^+ \rightarrow H_3^+$ + H [23, 24]. Many experiments also conformed this result that it's hard to observe even cluster ions by ionization neutral hydrogen clusters [11, 12]. Because we have not found more larger ionic hydrogen clusters, the ion H_3^+ is most probably produced by dissociative photoionization of the neutral molecular clusters $(H_2)_2$ or $(H_2)_3$. The relative theoretical works are explored base on this assumption.

Neutral clusters can form in a supersonic expansion. Ionic clusters can be produced by disscociative ionization of the neutral clusters. In our experiment, the H_3^+ produced from $(H_2)_2$ or $(H_2)_3$ can be via three pathways as follows

$$(H_2)_2 + h\nu \rightarrow (H_2)_2^+ + e \rightarrow H_3^+ + H + e \tag{2}$$

$$(H_2)_3 + h\nu \rightarrow (H_2)_3^+ + e \rightarrow H_4^+ + H_2 \rightarrow H_3^+ + H \tag{3}$$

$$(H_2)_3 + h\nu \rightarrow (H_2)_3^+ + e \rightarrow H_5^+ + H \rightarrow H_3^+ + H + H_2 \tag{4}$$

Optimized geometries for species involved in the pathways are depicted in Fig. 3. As shown in Fig. 3, $(H_2)_2$ was optimized to be two hydrogen molecules perpendicularly in a plane with the bond length of 3.038 Å, and the neutral cluster $(H_2)_3$ was optimized to be a complex which two hydrogen molecules are weakly bound to the H_2 core in a three-dimensional space with the bond length of 3.037 Å, and each of the hydrogen molecule is perpendicularly. The bond length between hydrogen molecule in $(H_2)_2$ is almost the same with the one in $(H_2)_2$, it is likely that $(H_2)_3$ is formed by $(H_2)_2$ attaches a hydrogen molecule by the same way as the $(H_2)_2$ formed. H_3^+ is an equilateral triangular structure. H_4^+ and H_5^+ are optimized to be a hydrogen atom and a hydrogen molecule

weakly attach to the H_3^+ core with the bond lengths of 1.468 and 1.319 Å respectively. The optimized geometry of H_6^+ with minimum energy is a H_2^+ core attached two hydrogen molecules. The geometry of H_6^+ is likely the neutral cluster H_6, the most change is the distance between the core H_2^+ and the around H_2.

Total energies of the optimized geometries for species involved in the pathways are listed in Table 1. The energies are calculated at the CCSD(T) and MP2 level with aug-cc-pVQZ basis set, and the ZPE is estimated at the MP2 level. Potential energy diagrams for H_3^+ formation are presented in Fig. 4. In the figure are given the values for energy estimated at the CCSD(T) and MP2 level with aug-cc-pVQZ basis set. The zero point of energy is set to be the energy of neutral cluster H_4 or H_6.

Table 1: Total energies and zero-point vibrational energies (ZEP) for the MP2/aug-cc-pVQZ geometries (Hartree).

Species	CCSD(T)	MP2	ZPE
H	-0.4999483	-0.4999483	0
H_2	-1.1738458	-1.1667398	0.010286
H_2^+	-0.6025356	-0.6025356	0.005290
H_3^+	-1.3431425	-1.3357099	0.020823
H_4	-2.3478588	-2.3336220	0.021277
H_4^+	-1.8519254	-1.8436336	0.023173
H_5^+	-2.5306561	-2.5157200	0.035603
H_6	-3.5218725	-3.5005040	0.032111
H_6^+	-3.0415825	-3.0230907	0.037550
H_6^+(TS)	-3.0301474	-3.0099621	0.033266
H_6^+(INT)	-3.0355166	-3.0201032	0.037781

For the H_3^+ formation pathway described in (2), ionic hydrogen cluster H_4^+ is produced by losing an electron of neutron cluster H_4. The energy for H_4^+ formation is 13.55 eV in CCSD(T)/aug-cc-pVQZ level and 13.38 eV in MP2/aug-cc-pVQZ level respectively. When the energy is above this value, the H_4^+ will dissociate by losing the hydrogen atom around the H_3^+ core. The least energy for this process is 13.72 eV in CCSD(T)/aug-cc-pVQZ level and 13.53 eV in MP2/aug-cc-pVQZ level respectively.

For the H_3^+ formation pathway described in (3), H_6^+ ion can be formed by H_6 absorbing a photon with the energy above 13.22 eV in CCSD(T)/aug-cc-pVQZ level and 13.14 eV in MP2/aug-cc-pVQZ level. If remain energy in H_6^+ is strong enough, one side hydrogen molecule of H_6^+ will throw away, H_6^+ decompose to H_4^+ and H_2, then H_4^+ will decompose to H_3^+ and H as illusion of (3). The least energy for this process is 13.71 eV in CCSD(T)/aug-cc-pVQZ level and 13.53 eV in MP2/aug-cc-pVQZ level by our calculations.

For the H_3^+ formation pathway described in (4), the process is somewhat complicated as shown in Fig. 4(c). H_5^+ is formed by H_6^+ dissociation, and H_3^+ is produced by H_5^+ losing

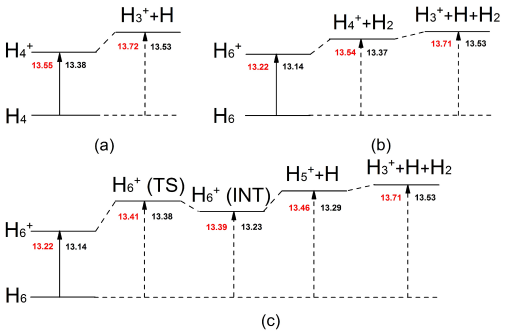

Figure 4: The energetics systems of the H_3^+ formation from H_4 (a), and H_6 (b), (c). Numerical values in red font on the left of arrows are calculated at the CCSD(T)/aug-cc-pVQZ level; numerical values on the right of arrows are calculated at the MP2/aug-cc-pVQZ level. The unit is eV. The energy of neutral cluster H_4 or H_6 is defined to be zero.

a hydrogen molecule. The structure of H_5^+ is a H_3^+ core around by a hydrogen molecule which depicted in Fig. 3. Compared with H_6^+, the structure of H_5^+ is greatly different. From the work from Kurosaki and Takayanagi [7], we know there is a transition state H_6^+ (TS) before H_6^+ decomposing. The intrinsic reaction coordinate also defines this result which calculated at the MP2/aug-cc-pVQZ level. H_6^+ will isomerize into transition state H_6^+ (TS) and intermediate H_6^+ (INT) subsequently dissociates a hydrogen atom to form H_5^+, then H_3^+ is formed by H_5^+ losing a hydrogen molecular. The relative energies are shown in Fig. 4. The final threshold for this process is 13.71 eV in CCSD(T)/aug-cc-pVQZ level and 13.53 eV in MP2/aug-cc-pVQZ level.

From our calculation, the threshold energy for H_3^+ formation are 13.72 eV in CCSD(T)/aug-cc-pVQZ level and 13.53 eV in MP2/aug-cc-pVQZ level which are greatly different with our experimental value 14.61 eV. In Anderson's [11] experiment which also studied by photoionization, the experimental appearance energy of H_3^+ was estimated 14.09 eV which was 0.39 eV larger than the theoretical threshold value. They thought the low density of Rydberg levels at the H_2^+ threshold, coupled with low light intensity and low detection sensitivity causing the error between theory and experiment. In Fiegele's [12] experiment which used electron impact ionization, the appearance energy obtained for H_3^+ is 15.16 eV and they ascribed this difference for the drastic structural rearrangement which occurs after vertical ionization of the neutral dimer. For the advantage of our light source, we should get better result. The difference between our experiment and theory is most likely caused by the low density of neutral hydrogen cluster in the molecular beam and the low detection sensitivity.

5 Conclusions

A molecular beam experiment on the formation of H_3^+ has been carried out by using tunable synchrotron vacuum ultraviolet (VUV) radiation in conjuction with reflectron

time-of-flight mass spectrometer. The ionization energy of H_2 and the appearance energy of H_3^+ are determined to be 15.41, and 14.61 eV, respectively. Additionally, two most likely dissociation photoionization channels, $(H_2)_2 \rightarrow H_3^+ + H$ and $(H_2)_3 \rightarrow H_3^+ + H + H_2$, are discussed by ab initio calculations at CCSD(T) and MP2 level with aug-cc-pVQZ basis set and compared with the experimental result. The geometries and energies of species involved in the dissociative photoionization channels have also been determined by optimizing at MP2/aug-cc-pVQZ level. The experimental appearance energy for H_3^+ is 14.61 eV which is about 1.0 eV above the theoretical value.

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