IONIC HYDROGEN CLUSTERS: STRUCTURE AND EVAPORATION

S. Marchoud*, R. Fathi, S. Ouaskit
Condensed Matter Physics Laboratory-LPMC,
Faculty of Science Ben M’sik - Sidi Othman, Casablanca, Morocco
*Corresponding author. E-mail : s-marchoud@joymail.com
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Abstract
We report the first account of a hydrogen cluster evaporation study in which we compare three constant rate evaporation models with the experimental cross section of unimolecular dissociation obtained after the collisional reaction between H₂ and accelerated hydrogen cluster H⁺ₙ (n=3 to 21, odd) with incident energy equal to 60kev/amu. The calculations performed in the framework of these three models reproduce remarkably well experimental data.

Keywords: Hydrogen cluster; Evaporation; Molecular structure; Rate constant; Cross section.

1. Introduction
Positive hydrogen cluster ions are of considerable experimental [1-10] and theoretical [11-14] interests since they are probably the simplest example of molecular clustering. The H⁺₅ ion was first identified by Dawson and Tickner in1962 [4] by mass spectrometry. Larger odd mass clusters were afterwards observed by Buckheit and Henkes [1] in TOF mass spectra and by Clampit and Gowland [2] using low-energy electron bombardment on solid hydrogen. Other workers [4] have observed odd mass hydrogen clusters in various mass distributions from low-energy collisional fragmentation studies. Kirchner and Bowers [4] have studied the dynamics of metastable H⁺₅ fragmentation. Directly pertinent to the theoretical studies are experimental measurements [6-7] of the dissociation energies for the following process

\[ H⁺₅ (H₂)ₘ \rightarrow H⁺₄ (H₂)ₘ₋₁ + H₂ \]

with \( m \leq 20 \). From a chemical point of view, the most important experimental paper to date is the one written by Okumura et al [9] on the infrared absorption frequencies measurements. The vibrational spectra of the H⁺₅ cluster (n=3 to 13) have been observed near 4000 cm⁻¹ by vibrational predissociation spectroscopy. In other respects with solid target [10] has been studied recently, giving rise to theoretical development on cluster matter interaction.

Up to now, collisions of ionic hydrogen clusters with solid target [10] has been mostly studied at low velocity (few eV/amu) [4] where molecular scattering is involved inducing mainly unimolecular dissociation of the incident cluster. However, the dissociation of the ionic hydrogen clusters by collisions with argon atoms has been studied at 20 keV/amu for cluster masses less than 25 [15]. At the present time, the availability of hydrogen clusters beams [16] up to 1.55 \( v₀ \) (\( v₀ \) being the Bohr velocity) opens a new field in the collision-induced fragmentation of these clusters. Indeed, in this velocity range, the relative velocity between the projectile and the target atom is around or greater than the velocity of the electrons in the cluster (= the Bohr velocity). Then, the typical time for a collision with a target atom is short enough, compared to the typical time of the motion of the protons in the cluster, so that during the collision the protons can be considered to be stationary in the projectile frame [17]. Moreover, in this velocity range, the collision induces mainly electronic excitation up to ionization. Thus, processes such as the ionization of the incident cluster followed by the dissociation of the transient multi-charged cluster can be involved.

After a brief description of these ionic hydrogen clusters from a theoretical point of view, results on the fragmentation [18] of fast ionic hydrogen clusters H⁺₅ by single collision with helium atoms for various incident cluster masses will be presented.

2. Structure
Among a substantial number of theoretical studies on positive hydrogen clusters, the investigation of Yamaguchi et al [13] (YGRS) for the H⁺₅ species is of great interest. Larger H⁺₅₊₁ species have been studied at both levels of theory, the self-consistent field (SCF) and the configuration-interaction including all single and double excitations (CISD) [11,13]. Another study
of Huber [12] has given near Hartree-Fock energies and structures of $\text{H}_2^{n+1}$ ($n=1$-6) applying the floating orbital geometry optimization (F.O.G.O).

The most recent ab-initio SCF calculations [14] have been carried out for $\text{H}_2^{n+1}$ ($n=1$-6) clusters using a triple-zeta plus polarization (TZP) basis set.

This basis set was the author's one including five primitive s functions, contracted to 3 s functions, and p functions with the orbital exponent 0.75. Correlation effects were considered variationally by means of CISD calculation. This CISD method is well known to suffer from the absence of size consistency. To take into account this problem, size consistency corrections (SCC) have been estimated according to Davidson's scheme. Full geometry optimizations have been done, the optimization being stopped when the magnitude of the gradient is below $10^{-5}$ a.u.

Fully optimized structures and energies of $\text{H}_1^{11}$ and $\text{H}_1^{13}$ are presented in Fig.1. These structures can be thought as the addition of $\text{H}_2$ molecules to a weakly deformed $\text{H}_9^+$. Dissociation energies as a function of cluster size follow the pattern established experimentally by Hiraoka and Mori [7]. Nevertheless, our energy results on the biggest clusters suffer from the lack of size-consistency of CISD calculations. Moreover, since some of these potential hyper surfaces are extremely flat in the region of the stationary points, a harmonic vibrational analysis may be required to ascertain the character of each stationary point (local minimum or saddle point). Analytic gradient techniques have been used to locate stationary point geometries and to predict harmonic vibrational frequencies and infrared intensities at the two levels of theory, SCF ($n=1$ to 6) and CISD ($n=1$ to 4) both with TZP basis sets. Of special interest are the new vibrational modes of $\text{H}_1^{11}$ and $\text{H}_1^{13}$, which have no counterpart in the $\text{H}_9^+$ cluster. The predicted frequencies compare fairly well with the experimental results of Okumura et al [9].

![Figure 1](image_url)

*Figure 1*: Fully optimized structures and energies of $\text{H}_1^{11}$ and $\text{H}_1^{13}$.

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3. Unimolecular evaporation

In the macrocanonic statistic ensemble, the probability of an event is given by the ratio between the number in states of the space of phases that realize this event and the total number of accessible states of the system, the number \( \omega_n(E^*) \) of accessible states of the system with internal energy \( E^* \) is the number of manners to distribute \( P \) phonons by \( S \) modes of vibration.

For a system of \( n \) particles (\( S=3n-6 \) degrees of freedom) this number is given by

\[
\omega_n(E^*) = \frac{(E^* + h \nu_0) \times (E^* + 2h \nu_0) \times \ldots \times (E^* + (S - 1)h \nu_0)}{(h \nu_0)^{S-1} (S-1)!}
\]

The number of states corresponding to an energy \( E^* \) distributed on different modes, with energy greater than the dissociation energy \( D_n \) on a given mode, is the number of manners to distribute \( nD \) on the \( S \) modes. So,

\[
\omega_n(E^*, D_n) = \frac{(E^* - D_n + h \nu_0) \times (E^* - D_n + 2h \nu_0) \times \ldots \times (E^* - D_n + (S - 1)h \nu_0)}{(h \nu_0)^{S-1} (S-1)!}
\]

The randomly distributed internal energy \( E^* \) will be localized on one mode of vibration after a lapse of time \( \tau \) which is characteristic of the oscillator system. Then the total energy of this mode will be greater than the bound energy of the dimer, which undergoes dissociation. One will be able to simplify the expression of \( \omega_n(E^*) \) when \( (S - 1)h \nu_0 << E^* \), i.e. when \( h \nu_0 << k_B T \), in these conditions one makes the approximation

\[
\omega_n(E^*) \approx \frac{E^*^{(S-1)}}{(h \nu_0)^{S-1} (S-1)!}
\]

4. Statistical calculation of evaporation probability

4.1 Kassel Model

From two previous expressions of the number

\[
\omega_n^{\text{evap}}(E^*) = n_{\text{ext}} \sigma 8 \pi \nu_0^2 \nu_i = 0 \frac{E^* - D_n}{(3n-7)(3n-8)(3n-9)} \left( \frac{E^* - D_n - \epsilon_i}{E^*} \right)^{3n-10} \frac{(3n-7)}{E^{(3n-7)}}
\]

These calculations have taken into account the kinetic of evaporation molecule. By definition, the dissociation energy \( D_n \) is the necessary energy to extract a molecule from the
cluster and to carry it to infinity with a vanishing kinetic energy.

The minimal kinetic energy to extract a molecule to the parent is therefore included in the energy of dissociation, and $\varepsilon_i$ is the kinetic energy of the molecule at infinity. Fig. 2 presents result of our calculations of evaporation rate in the framework of Kassel and Weisskopf models.

![Figure 2a](image)

**Figure 2a:** Rate of unimolecular evaporation from $H_n^+$ clusters obtained by Kassel.

![Figure 2b](image)

**Figure 2b:** Rate of unimolecular evaporation from $H_n^+$ clusters obtained by Weisskopf.

Fig. 3 shows the variation of the dissociation cross section according to the size $n$ of the incident clusters. The most stable clusters $H_n^+$ are those of the weakest $\sigma_{n-2}$.

5. Comparison of $K_{ev}$ to $\sigma_n$

Theoretical curves show that the rate of evaporation follows the same variations as the dissociation cross section for values of ($n=7,9,11,\ldots, 19$).

For the cluster $\sigma(H_3^+)$ one observes that $\sigma(H_5^+)$ > $\sigma(H_3^+)$ while $Kev(H_5^+) < Kev(H_3^+)$. This is due to the fact that the production of $H_2$ from the dissociation of $H_5^+$ comes only from evaporation $H_5^+ + H_e \rightarrow H_3^+ + H_2$ and $H_5^+ + H_e \rightarrow H_5^0 + H_2$.
Figure 3: Unimolecular dissociation cross section $\sigma_{n-2} = f(n)$ (in $10^{-16}$ cm$^2$).

This second way of production of H$_2$ by electronic capture of an electron out of the collision can be estimated from the cross section of the reaction: $H_3^+ + e^{-} \rightarrow H_2^0 + H_1^+$, which is of the order $\sigma (H_3^+ \rightarrow H_2^0) = 4.10^{-17}$ cm$^2$ and will contribute less than one percent to the measured cross section.

Fig. 4 shows a great correlation between experimental data of unimolecular dissociation cross section and the predicted values of the constant rate of evaporation ($H_n^+ \rightarrow H_{n-2}^- + H_2$).

Figure 4: Schematic comparison between the evaporation rate and the cross section for the Kassel and the Weisskopf models.

We can see that $\sigma_{\text{dis}}$ and $K_{\text{ev}}$ exhibit the same maxima for $H_{11}^+$ and $H_{17}^+$ and the same minima for $H_6$ and $H_{15}$.

These results are in agreement with the experimental data of A. Van Lumig and J. Reuss [19]. These authors measured the dissociation cross section of hydrogen clusters with $H_e$ target at low energy while the evaporation was predominant and suggested the particular stability of $H_6^+$, $H_{15}^+$, $H_{19}^+$ and $H_{29}$.

On the other hand, the recent (H.F) and (DFT) structure calculations of B. Farizon et al [20] have shown that the stability of the $H_{2N+1}$ Clusters Series can be thought as a result of the interaction of a given number of hydrogen molecules with a core consisting in $H_{15}^+$ nucleus which itself
consists of a $\text{H}_3^+$ nucleus formed by $\text{H}_3$ core surrounded by three $\text{H}_2$ molecules.

6. Conclusion

The reported results show a good agreement between the normalized data of the evaporation rate constant $k_{\text{evap}}$ derived from weisskopf model and the experimental results of evaporation cross section.

When the cluster size is small $n\leq 16$, Fig. 4 shows a large deviation between kassel model predictions and experimental data. This is due to the fact that, this model considers a statistical population of harmonic oscillators which take only account of vibrational excitations, while rotational excitations play an important role in evaporation mechanism of cluster hydrogen.

References