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Unimolecular Dissociation of H_{2n+1}^{+} Hydrogen Clusters: Measured Cross Sections and Theoretically Calculated Rate Constants

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ABSTRACT

In this paper, we studied the process of dissociation unimolecular of the evaporation of H_{2n+1}^{+} hydrogen clusters according to size, using the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The rate constants k(E) were determined with the use of statistical theory of unimolecular reactions using various approximations. In our work, we used the products frequencies instead of transitions frequencies in the calculation of unimolecular dissociation rates obtained by three models RRKM. The agreement between the experimental cross section ratio and calculated rate ratio with direct count approximation seems to be reasonable.

Keywords: RRKM; Rice-Ramsperger-Kassel-Marcus; Direct Count Method; Classical Method; Whitten-Rabinovitch Method; High-Energy Cluster Collision; Fragmentation Phenomena; Cluster Fragmentation; Ionic Hydrogen Clusters; Ion-Atom Collisions; Ionic Cluster; Cross Sections; Molecular Dissociation; Size Effect; Metastable States; Hydrogen Ions

1. Introduction

Unimolecular dissociation [1] is a powerful tool to probe experimentally the physical free clusters. It has been used in recent years either to measure thermodynamical properties (dissociation energies [2-9] heat capacity [10]) or electronic properties (photo absorption cross-sections [11-13]).

Since clusters are particles of finite size, one is confronted with the general question of how to detect and/or characterize such a transition in a finite system, a question of interest for many microscopic or mesoscopic systems, for instance, melting and vaporization of metallic clusters, and nuclear liquid-to-gas transition [14-16]. In small systems such as two colliding nuclear or molecular systems fluctuations may wash out the signature of the phase transition [17]. Nevertheless, it has been demonstrated theoretically in Ref. [6] and also experimentally [18-20] that finite systems may indeed exhibit critical behavior to be seen when studying inclusive fragment size distributions, scaled factorial moments, and anomalous fractal dimensions.

Protonated hydrogen clusters present the simplest example for molecular clustering and for decades has attracted experimental and theoretical efforts to clarify their structures and properties.

The fragmentation of atomic and molecular clusters induced by energy deposition represents a fundamental interest for the physics of particle-matter or radiance-matter interactions. Experiences carried out at the IPNL (Institut de Physique Nucléaire de Lyon) demonstrated that this fragmentation is made according to several channels including evaporation, dissociation or multi-fragmentation. These different channels undergo several mechanisms according to the degree of excitation or ionization or multi-ionization that reveal an individual character (Rotational or vibrational excitation of the constituent of the cluster) or a collective character such as the intermolecular reactivity which can explain multi-fragmentation process.

In this paper, we shall study the validity of the RRKM theory, which is based on the Assumption of the internal energy equilibration of the energized molecule and the

dissociation rate constant of the H_{2n+1}^+ hydrogen clusters (n = 1, 2, 3, 4, 5) was calculated by this theory with different approximation method like: classical, Beyer-Swinehart (direct count), and Whitten-Rabinovitch (modified classical).

## 2. Protonated Hydrogen Cluster Structures

The properties of protonated hydrogen clusters H_n^+ (see **Figure 1**) have been studied by means of theoretical [21-31] as well as experimental methods [32-35]. In particular, if n is an odd number the *ab initio* calculations have demonstrated that the cluster structures are basically constituted by an H_3^+ triangular nucleus to which H_2 molecules are bound. For the smaller clusters (or first-shell clusters) H_5^+, H_7^+, and H_9^+, the H_2 molecules are bound to the H_3^+ vertices, with the H_2 axes standing perpendicular to the H_3^+ plane (the equilibrium geometries having C_{2v}, C_{2v}, and D_{3h} symmetries, respectively). In the larger clusters, the H_2 molecules are located above and below the H_3^+ plane, and due to the weak interactions, the high degree of rotational freedom, at finite temperature, may give rise to many isomeric forms.

Several authors have observed that the H_9^+ is markedly more stable than the immediately larger cluster H_{11}^+ [27,30,32-34] favored by a higher symmetry. In the H_{11}^+ case, the fourth H_2 molecule places itself above the H_3^+ plane (C_s symmetry) opening a new ligand shell of H_2 molecules, whose properties, like H-H distance for instance, are distinct from those of the internal molecules.

For the H_{13}^+ case, the results obtained at several theoretical levels indicated that the two H_2 molecules stand at opposite sides of the H_3^+ plane (C_{2v} symmetry) [26,30]. On the other hand, the results from Ref. [27] indicated that it would be energetically more advantageous if the two molecules would stay on the same side of that plane (C_s symmetry). These workers have also proposed equilibrium geometries for clusters from H_{15}^+ to H_{35}^+, based on classical Monte Carlo calculations. More recently, Ignacio and Yamabe [30] presented results of *ab initio* calculations for clusters up to H_{21}^+, and Farizon *et al.* [31] performed density functional calculations (DFT) for the H_{15}^+ cluster. The results of Farizon *et al.* [31] for the H_{15}^+ cluster are favorable to a C_s structure in which the two H_2 molecules are bound one above and the other below the H_3^+ plane. The H_{27}^+ cluster has also been considered [29].

3. Calculations and Description of the Model

The Rice-Ramsperger-Kassel-Marcus theory [36-39] (RRKM) was developed by R. A. Marcus and is based on the RRK theory. The RRKM model takes into account the vibrational and rotational energies of the molecule
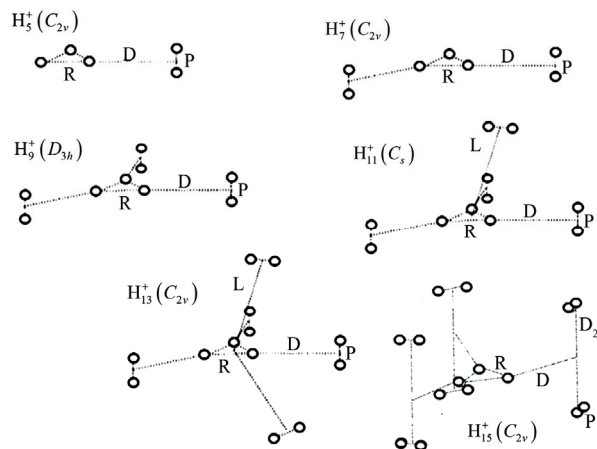
Figure 1. Optimized structures for the H_n^+ clusters with n = 5 - 11.

and uses the transition state concept. As in the RRK theory, the ergodic assumption is made and the RRKM theory can also be described as a micro canonical transition state theory.

In this theory AB is identified as the transition state of the reaction. A transition state is defined as the "dividing surface" between reactants and products, and its location is determined by the condition that every trajectory (flux), which passes this surface, will form the products without recrossing.

There are several ways to calculate sums and densities like:

3.1. Direct Count Method

Beyer and Swinehart (BS) have introduced an extremely efficient, simple, and accurate algorithm [40] which applies to harmonic molecular models. If an energy step is chosen which divides exactly the normal frequencies of the model, the BS algorithm allows the calculation of these functions by "directly counting" all states. The results are therefore exact within the framework of the given theory that determines the states.

The sum of states N(E) can be obtained either by direct numerical integration of the density of states or computed directly by using the Beyer-Swineherd of states N(E). The program calculates N(E) by dividing the energy scale into a series of cells and counting how many vibrational bands are in each cell. The algorithm goes through with the lowest frequency and puts a 1 in each cell where the frequency or its overtone arises. It then goes through with the second frequency and adds one to the cell if the cell is an overtone, or if some combination of the previous frequencies are in the cell. The effect is a complete count of the number of frequencies contributing to the cell.

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If a system consists of s harmonic oscillators with frequencies of $\omega_i = \nu_i/c$ cm^{-1}, where c is the speed of light, each will have a series of equally spaced states located at $E_i = Ni\omega_i$ (Ni = 0, 1, 2···). The zero of energy is the ion's zero point energy and the internal energy is divided into bins of size 1 cm^{-1}.

The direct count of the number of vibrational states of H_{2n+1}^+, up to a total energy of value of energy activation E_0, is split into two tables; in the first one, energies of the lower vibrational states are calculated; in the second, the number of quantum states of H_{2n+1}^+ is calculated.

The formula giving the energies is:

$$E\left(\text{cm}^{-1}\right) = \sum_{i=1}\sum_{j=1}^{s} n_i\nu_j, \, n_i = 1, 2, 3\cdots \quad (1)$$

The direct count of the number of states gives rise to combinatorial problem for the counting of degenerate states. The number of ways to accommodate n quanta in q oscillators is given by:

$$w\left(E\right) = \frac{(n+q-1)!}{n!(q-1)!} \quad (2)$$

A simple program can calculate these functions. Although the required programming is very simple, it does have several draw-backs. First, it is the most time consuming approach, which becomes a problem when dealing with large ions. Second, in most calculations one is interested in the density or sum of states at a few energies that are well above the minimum energy for dissociation. However, in the exact count method one is obliged to calculate these functions from 0 up to the maximum energy of interest. Third, each frequency is treated separately so that frequencies cannot be bunched to save time in calculations. For these reasons, it is generally worthwhile to invest the additional programming time required for the following two approximate methods.

A description of the original BS algorithm in [40], the original BS algorithm treats all the vibrations separately regardless of degeneracy. It is obvious that reduction in computation time may occur if a method to treat degenerate vibrations all at the same time can be devised. In the grouped-frequency direct counting mode of RRKM calculation used before the advent of the BS algorithm, this was achieved by taking advantage of the fact that the number of ways to distribute j vibrational quanta into g degenerate

3.2. Classical Method

The classical mechanical RRKM k(E) takes a very simple form, if the internal degrees of freedom for the reactant and transition state are assumed to be harmonic oscillators. The classical sum of states for s harmonic oscillators is [41].

The most general expression for the RRKM reaction rate constant is given by:

$$k\left(E\right) = \frac{G^{\#}\left(E\right)}{hN\left(E\right)} \quad (3)$$

where $G^{\#}(E)$ represents the sum of states for the active degrees of freedom in the transition state and $N(E)$ denotes the density of states for the active degrees of freedom in the reactant. For the calculation of the RRKM reaction rate constant, the classical expressions for the sum and density of states can be used:

$$G^{\#}\left(E\right) = \frac{E^s}{s!\prod_{i=1}^{s} h\nu_i} \quad (4)$$

where s represents the number of oscillators, E denotes the energy of the activated complex and ν_i is frequency of the oscillator i. The density $N(E) = dG^{\#}(E)/dE$ is then

$$N\left(\text{E}\right) = \frac{E^{s-1}}{(s-1)!\prod_{i=1}^{s} h\nu_i}. \quad (5)$$

The reactant density of states in Equation (2) is given by the above expression for N(E). The sum of the transition state is

$$G^{\#}\left(E - E_0\right) = \frac{\left(E - E_0\right)^{s-1}}{(s-1)!\prod_{i=1}^{s-1} h\nu_i^{\#}} \quad (6)$$

Inserting Equation (5) and Equation (6) into Equation (3) gives

$$k\left(E\right) = \frac{\prod_{i=1}^{s}\nu_i}{\prod_{i=1}^{s-1}\nu_i^{\#}}\left(\frac{E - E_0}{E}\right)^{s-1} \quad (7)$$

3.3. Whitten-Rabinovitch Method

The Whitten-Rabinovitch [42] method is based on the classical sum of states calculation. The equation for calculating the sum of states is

$$G^{\#}\left(E - E_0\right) = \frac{\left(E - E_0 + \alpha E_z\right)^{s-1}}{(s-1)!\prod_{i=1}^{s-1} h\nu_i^{\#}} \quad (8)$$

where E is the energy, E_0 is the activation energy, h is Planck's constant, ν_i are the vibrational frequencies, s is the number of frequencies, and α is a constant which varies from 0 to 1 as the energy goes from 0 to infinity. The parameter α, β, and w are empirically set to approximate the exact quantum mechanical count. They are

$$\alpha = 1 - \beta\omega$$

$$\log\left(\omega\right) = -1.0506\left(\text{E}/E_z\right)^{0.25}, \text{ for } E > E_z$$

$$\omega = \left[5.00\left(\text{E}/E_z\right) + 2.73\left(\text{E}/E_z\right)^{0.5} + 3.51\right]^{-1}, \quad (9)$$

$$\text{for } E < E_z, \, \beta = \frac{s-1}{s}\times\frac{\left\langle\nu^2\right\rangle}{\left\langle\nu\right\rangle^2}$$

and E_Z is the zero point energy given by:

$$E_z = \frac{1}{2}\sum_{i=1}^{s} h\nu_i \qquad (10)$$

4. Experimental Approach

Mass selected hydrogen cluster ions with an energy of 60 keV/amu are prepared in a high-energy cluster ion beam facility consisting of a cryogenic cluster jet expansion source combined with a high performance electron ionizer and a two-step ion accelerator (consisting of an electrostatic field and a RFQ post-accelerator).

In the present study, the beam of mass selected $H_3^+(H_2)_m$ cluster ions (m = l, 14) is crossed perpendicularly by a helium target beam effusing from a cylindrical capillary tube. The undissociated primary $H_3^+(H_2)_m$ cluster projectile ion or the neutral and charged fragments resulting from reactive collisions, are then passing a magnetic sector field analyzer and detected with a multi detector device consisting of an array of passivated implanted planar silicon surface barrier detectors located at different positions at the exit of the magnetic analyzer With this instrument we are able to record for each event simultaneously the number of each mass-identified fragment ion resulting from the interaction (for more experimental details, see [19,20,43]).

Thus this experimental approach is able to analyze on an event-by-event basis the identity of all correlated fragments produced in a single collision event between the $H_3^+(H_2)_m$ cluster ion and the He target atom, the fragmentation reactions having the general form.

$$H_3^+(H_2)_m + He \rightarrow aH_3^+(H_2)_k + bH_3^+ + cH_2^+ + dH^+$$
$$+eH_2 + fH, \text{ with } a-f = 0,1\cdots \qquad (11)$$
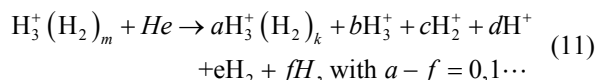
Several processes of fragmentation of clusters ionized hydrogen $H_3^+(H_2)_{(n-3)/2}$ (n = 5 - 35 see Equation (13)) were studied by S.Louc and M. Farizon *et al.* [44-48] using the same experimental situation (see **Figure 2**): the fragmentation of the clusters is induced by collision with a helium atom at high speed (60 keV/u).

Measurements of the total destruction cross sections SIGMA of the hydrogen clusters $H_3^+(H_2)_m$ with $0 \leq m \leq 16$ were done by S. Louc with the size of the cluster and reported in the first row in **Table 1**.

$$H_3^+(H_2)_m + He > H_3^+(H_2)_{m-1} + H_2 \qquad (12)$$
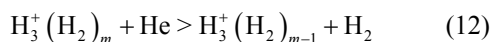
5. RRKM Calculations Results

The dissociation of H_{2n+1}^+ occurs if the energy of vibration along the reaction coordinate exceeds the activation energy, *i.e.*, the barrier height (or the heat of reaction, if the reaction does not have a distinct transition state, see **Figure 3**). The probability of this event can be calculated
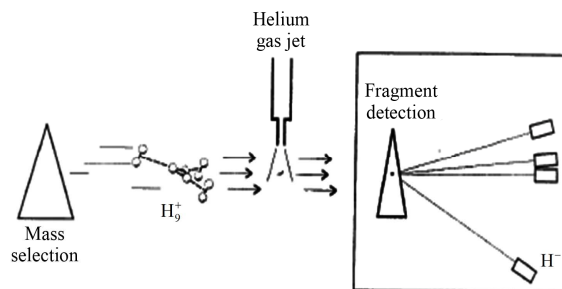
Figure 2. Experimental set-up.
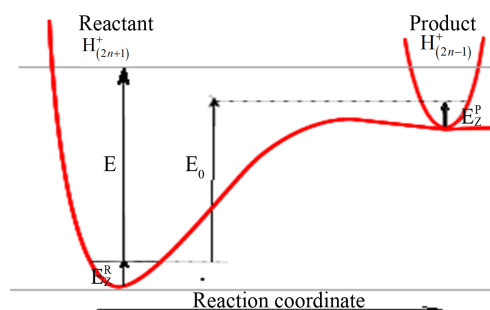
Figure 3. Reaction coordinate for a dissociation with a very low barrier. The active energy E is measured from the zero point energy of the reactant well. The critical energy E_0 is the zero point energy difference between the product well and the reactant well.

using the statistical approach of the RRKM theory.

For the parent H_{2n+1}^+ ion, the available internal energy is the part of the excitation energy beyond the ionization threshold, which is converted to vibration energy. After dissociation, the internal energy of secondary fragments is less than the energy of the parent molecule, because of the fact that the excess energy is distributed among the product species and can be approximated as being proportional to the ratio of internal degrees of freedom of the fragment and the parent molecule. The reaction coordinate should be excluded from the total numbers of internal degrees of freedom, because the kinetic energy along the reaction coordinate is supposed to be close to the barrier's height and is already subtracted from the total internal energy.

Because the reaction occurs via transition state, the initiating energy for this reaction is the barrier's height at TS. The energy difference between the barrier's and the energy of products is converted to kinetic energies of the fragments.

In our work we neglect the energy difference between the barrier's and the energy of products then the available internal energy of the H_2. Because the assumption that the energy difference between the barrier's and the energy of products is converted to the kinetic energies of the fragments is very crude, and energy difference be-

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Table 1. Comparison of dissociation unimolecular rates for H_2 atom loss predicted by three Models (Classical, BS and the WR) at E = 8 kcal/mol excitation energy.

	H_3^+	H_5^+	H_7^+	H_9^+	H_{11}^+	H_{13}^+
SIGMA	0.36	0.46	0.37	0.59	0.66	0.82
Rate Eun J BS	4.17E+10	4.23E+10	6.79E+09	1.30E+11	1.59E+11	2.58E+11
Rate Eun J WR	1.11E+10	4.28E+10	9.04E+09	3.11E+11	1.46E+12	3.26E+11
Rate Eun J CL	2.17E+11	1.82E+12	6.24E+11	5.67E+13	1.94E+13	3.55E+14
Rate Rita BS	1.36E+10	3.77E+10	2.76E+10	3.86E+10	5.23E+10	6.27E+10
Rate Rita WR	8.20E+09	3.28E+10	2.98E+10	3.59E+10	1.20E+11	1.02E+11
Rate Rita CL	4.33E+10	4.04E+12	2.29E+12	1.41E+12	1.94E+13	2.26E+13

tween the initiation energies of the H_{2n+1}^+ and H_{2n-1}^+ dissociation is small, in other words, The internal energy value of $E = E_0$ is sufficient to initiate the H_{2n+1}^+ ion dissociation, which is sufficient for the H_2 loss reaction to occur. The H_2 elimination reaction passes through transition state TS with a low barrier of value $E = E_0$ and produces the H_{2n+1}^+ ion.

In our work, we consider that the active energy E is measured from the zero-point energy of the reactant well. The critical energy E_0 is the difference between the zero-point energy and the product and the reactant well.

The originality of our work is the use of products frequencies instead of frequencies of transitions to calculate the unimolecular dissociation rate according to three models of RRKM, *i.e.* we calculate the rate constant using:

1) The dissociation energies E_0 published in [31] by farizon, and the fundamental frequencies of vibration of parent H_{2n+1}^+ and vibrational frequencies of product H_{2n-1}^+ published in [49] by Eun-Jung In.

2) The dissociation energies E_0 published by Hireoka in [50-52] and the fundamental frequencies of vibration of parent H_{2n+1}^+ and vibrational frequencies of product H_{2n-1}^+ published in [53] by Rita.

First we launched our simulation program by varying the excitation energies between 5.7 and 9 kcal/mol.

For hydrogen ion aggregates, at E = 8 kcal/mol, we present in **Table 1** the results calculations of the unimolecular rate constant $K(E)$ obtained by three models with values of (Rita and Hireoka) and Eun-Jung In are compared with each other, with experimental results of cross sections of dissociation.

Then we shall Use The ratio $k(E)/k(E)$ min of the RRKM unimolecular rate constant, which will be compared with The ratio σ diss/σ dissmin of cross sections previously measured (see **Table 2**).

Then we draw in **Figure 4** both the curves of the ratio of cross sections of unimolecular dissociation that found experimentally and the ratio of evaporation rates constant

Table 2. The ratio of rate constant of unimolecular dissociation (kdiss [H_n^+]/kdiss [H_5^+]) obtained by Classical, BS and the WR Methods for Rita and Hireoka and Eun-Jung In and the ratio of cross sections of unimolecular dissociation (σ[H_n^+]/σ[H_5^+]) that found experimentally.

	H_3^+	H_5^+	H_7^+	H_9^+	H_{11}^+	H_{13}^+
Ratio of SIGMA	1.00	1.28	1.03	1.64	1.83	2.28
Ratio of Rate EunJ BS	1.00	1.01	0.16	3.11	3.81	6.19
Ratio of Rate EunJ WR	1.00	3.85	0.81	27.98	131.47	29.35
Ratio of Rate EunJ CL	1.00	8.38	2.88	261.32	89.58	1635.32
Ratio of Rate Rita BS	1.00	2.78	2.04	2.85	3.86	4.63
Ratio of Rate Rita WR	1.00	4.00	3.63	4.38	14.68	12.44
Ratio of Rate Rita CL	1.00	93.39	52.92	32.65	448.09	523.24
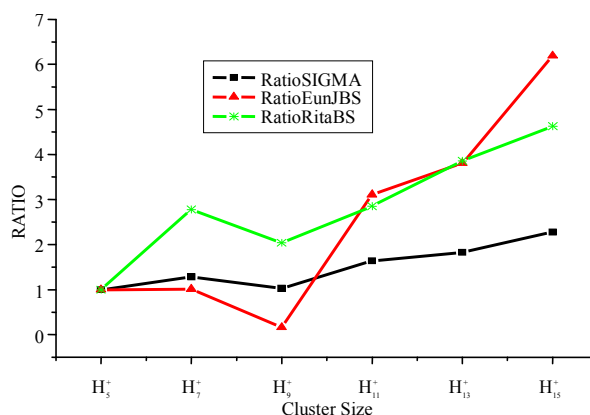
Figure 4. Comparison of the ratio of evaporation rates constant for the Direct count Method or Beyer and Swinehart (BS) model according to the RRKM theory of clusters H_{2n-1}^+ following the loss of a neutral H_2 molecule with the cross section of unimolecular dissociation that found experimentally.

calculated using different models of RKKM.

In this figure, we note that both theoretical curves for the ratio of rate dissociation rates present the same shape as the curve with the experimental results relative to cross sections; we also note the presence of two parts,

- In the first part, clusters of zone H_9^+, H_7^+ and H_5^+ where these three aggregates report rate dissociation of Eun-Jung In are slightly lower than those of RITA and Hireoka due to the fact that the values of dissociation energies E_0 of Rita and Hireoka are higher than those of Eun-Jung In;

- In the second part where are the unimolecular dissociation of clusters H_{11}^+, H_{13}^+ and H_{15}^+, the two theoretical curves for the ratio of dissociation rates have the same shape as the curve with the experimental results the reports of cross sections, but they have differences which are due to low values of the energy of dissociation from the high excitation energy given to the aggregate and that the values of the ratios of rates are slightly higher compared to the experimental factor 3, while those of Eun-Jung In are slightly elevated with a factor 5.

The theoretical curves show that the evaporation rate using fundamental frequencies follows the same variations as the cross section for dissociation values ($n = 5, 7, 9, 11, 13, 15$) and The two curves are indistinguishable except for the aggregate H_{11}^+ and H_{15}^+ a slight shift is observed. But there is a wide gap curves for the aggregate H_{13}^+.

In both **Figures 5** and **6** we note the presence of two parts:

- In the first one, concerning the unimolecular dissociation of the clusters H_9^+, H_7^+ and H_5^+ we note how these three aggregates report rate dissociation of Eun-Jung In are slightly lower than those of Rita and Hireoka due to the fact that the values of dissociation energies E_0 of Rita and Hireoka are higher than those of Eun-Jung In, but in this part, the evaporation rates are slightly lower than those of Rita and Hireoka because the values of the dissociation energies E_0 of Rita and Hireoka are slightly higher than those of Eun-Jung In.

- In the second part, the two theoretical curves for the ratio of the dissociation rate on unimolecular dissociation of clusters H_{11}^+, H_{13}^+ and H_{15}^+ have the same shape as the curve related to the experimental results of cross sections, but they have differences which are due to lower values of the dissociation energies relative to the excitation energy E given to the aggregate to dissociate, and the fact that both the two formulas are empirical.

6. Discussion

A comparison of methods for calculating the ratio of rates
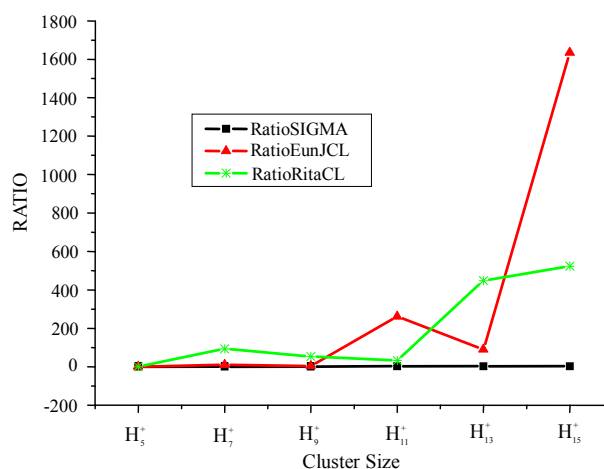
Figure 5. Comparison of the ratio of evaporation rates constant for the classical model according to the RRKM theory of clusters H_{2n+1}^+ following the loss of a neutral H_2 molecule with the cross section of unimolecular dissociation that found experimentally.
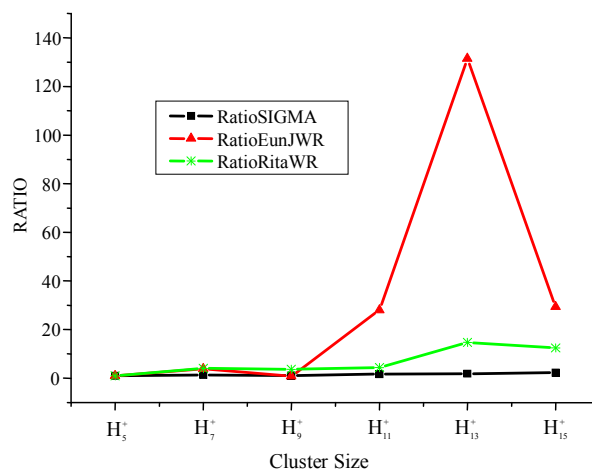
Figure 6. Comparison of the ratio of evaporation rates constant for the Semi classical or Whitten-Rabinovitch (WR) model according to the RRKM theory of clusters H_{2n+1}^+ following the loss of a neutral H_2 molecule with the cross section of unimolecular dissociation that found experimentally.

constant for H_{2n-1}^+ clusters following the loss of a neutral H_2 molecule, it will be shown that the results of the unimolecular dissociation obtained from RRKM theory with the three models: Classical (CL), Beyer-Swinehart (BS), and Whitten-Rabinovitch (WR). Using the vibrational frequencies of products are better, than that from the experimental data.

The curves obtained by the three modes, particularly that of the method (BS) have the same shape as that of the curved cross-section which shows the results obtained experimentally.

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To assess and compare the rate of unimolecular dissociation of clusters H_n^+, we have provided a value of exciting energy E ($E = 8$ kcal/mol) greater than all the values of the dissociation energies E_0 of all clusters, we see that all the theoretical curves for the three approximations have qualitatively the same shape as the curve of the ratio of the cross section, whereas aggregates H_{13}^+ and H_{15}^+ only the theoretical curves based on direct calculation (BS) that keeps the same pace as experimental, but other like approximations classical (CL) or semi-classical (WR) where the calculation of rate constant is based on empirical formulas and where the values of the dissociation energies E_0 of clusters are very small compared to the exciting energy E, it gives some errors on the values of the dissociation rate.

7. Conclusions

In this paper we have presented different way of calculating rate constant of unimolecular dissociation of clusters with RKKM model. This model takes into account the frequencies of products instead of the frequencies of transition state.

We conclude that the comparison between the normalized unimolecular dissociation cross sections obtained experimental and normalized rates constants calculated using different models, showing that the RRKM model is qualitatively consistent with the experimental data.

- Generally in the three methods exposed in this work, we note that Rates constants calculated by using input parameters according to Rita and Hireoka (high dissociation energies) are too high for those reported by Eun-Jung In (low dissociation energies).
- The curves obtained by the three methods especially that of the Beyer-Swinehart method present the same shape as that of the cross section curve obtained experimentally. In addition we observe that Beyer-Swinehart is a good approximation method in analyzing the experimental data of unimolecular reactions.
- The curves of the other models (WR) and (CL) have almost the same shape as the experimental curve but quantitatively the normalized rates constants are far from the normalized cross sections.
- RRKM model can serve as theoretical base of interpretations of the dissociation of internally excited molecular ions, either in thermal collision in gas or for experience of collision inducing dissociation.

The validity of the RRKM based on direct count method or Beyer-Swinehart. Using the frequencies of vibration of the products instead of vibration frequencies of the transition complex is entirely acceptable with regard to the behavior of the rate constant as a function of the excitation energy.

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