

An Improved Descriptor of Cluster Stability. Application to Small Carbon Clusters

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(Dated: April 26, 2019)

The mass spectra of gas-phase clusters in cluster beams have a rich structure where the relative heights of the peaks compared to peaks corresponding to clusters of neighbor sizes reveal the stability of the clusters as a function of the size N . In an analysis of the published mass spectrum of carbon clusters cations C_N^+ with $N \leq 16$ we have employed the most common descriptor of cluster stability, which is based on comparing the total energy of the cluster of size N with the averaged energies of clusters with sizes $N+1$ and $N-1$. Those energies have been obtained from density functional calculations. The comparison between the stability function and the mass spectrum leaves some experimental features unexplained; in particular, the correlation with the detailed variation of the height of the mass peaks as a function of size N is not satisfactory. We then propose a novel stability descriptor which improves matters substantially, in particular the correlation with the detailed variation of the height of the mass peaks. The new stability index is based on comparing the atom-evaporation energy of the cluster of size N with the averaged atom-evaporation energies of clusters with sizes $N+1$ and $N-1$. The substantial improvement achieved is attributed to the fact that evaporation energies are quantities directly connected with the processes controlling the cluster abundances in the beam.

I. INTRODUCTION

Atomic and molecular clusters, and nanoparticles have enormous interest from both points of view of fundamental science and applications. The properties of clusters are often different from the properties of the macroscopic system, and vary with cluster size^{1,2}. Changing the shape of nanoparticles has been used as a tool to modify their optical properties, for instance the color of the nanoparticles³. Size and shape influence the catalytic properties of clusters and nanoparticles⁴. This means that by playing with their size and shape, clusters and nanoparticles can be tailored for specific functionalities.

Different methods exist for producing clusters¹. In one of the most common methods the solid material is first vaporized, and then the clusters grow by atom aggregation in a cluster beam. Clusters of different sizes are formed in this way, and the analysis of the abundance population as a function of cluster size in the molecular beam is made by mass spectrometry. The relative abundance of clusters with different sizes gives information on the relative stability of the clusters as a function of the cluster size N . In the mass spectrum of clusters X_N , where X indicates the particular chemical element of interest, each cluster of size N yields a peak, and the height of the peak measures the abundance of that size N in the cluster beam. The clusters grow in the condensation chamber mainly by aggregation of new atoms, and this part of the process normally results in a smooth distribution of cluster sizes whose population decreases as N increases. However, the clusters become hot as they grow due to the heat of condensation. Part of this energy can be liberated in collisions with the atoms of a carrier gas (Ar, for instance), but a substantial part of the condensation energy still remains in the cluster and induces the evaporation of one or more atoms. In this way, the size of the cluster shrinks and this evaporative effect leads to an enhancement of the population of the most stable clusters at the expense of the population of the less stable ones.

The final result is a mass spectrum which shows an interesting structure, with peaks of different heights reflecting the abundances of the clusters, related, as indicated above, to their intrinsic stability. In particular, the cluster sizes corresponding to the highest peaks are usually called magic numbers. The specific values of the magic numbers differ in different classes of clusters. For instance, in clusters of inert gases such as Ne, Ar, Kr and Xe, the magic numbers $N = 13, 55, 147, \dots$ reflect the packing of weakly interacting spherical atoms forming icosahedra with an increasing number of shells⁵. Other well-known example corresponds to clusters of alkaline atoms (Na, K, Rb, Cs), in which the magic numbers $N = 8, 20, 40, 58, 92, \dots$ reveal the formation of electronic shells by the delocalized valence electrons confined in the mean-field effective potential well of the cluster⁶⁻⁸.

In addition to the main peaks corresponding to the magic numbers, the mass spectra show a rich structure in between the main peaks. Theoretical modeling and calculations have been of great help to understand the variation of the structure and stability of clusters as a function of size N , and to connect this knowledge with the detailed structure of the mass spectra of the families of clusters mentioned above⁹⁻¹¹, as well as other families. Most theoretical calculations use the density functional formalism, because this method has the potential to give accurate predictions for the atomic structure and the binding energy of the clusters. However, a simple comparison of total binding energies, or binding energies per atom, as a function of cluster size is not sensitive enough to reveal accurately the relative stabilities, and more sensitive stability descriptors have been proposed and used.

Among these, the most popular one is the stability function $\Delta_2(N)$, which measures the total energy of a cluster of size N with respect to the average of the total energies of clusters with sizes $N-1$ and $N+1$. In a plot of $\Delta_2(N)$ as a function of N , specially stable clusters are characterized by positive values of $\Delta_2(N)$, whilst less stable clusters are characterized

by near-zero or negative values of $\Delta_2(N)$. The higher the value of $\Delta_2(N)$, the more stable is the cluster of size N with respect to adjacent clusters with sizes $N + 1$ and $N - 1$.

Nonetheless, some classes of clusters are more complex than inert gas clusters or clusters of simple metals, and $\Delta_2(N)$, although useful, does not explain the full richness of the experimental mass spectra. In addition, the mass spectrum may depend on whether the clusters are born neutral or charged.^{12,13} We propose herein an improved stability index. Since the process of evaporation cooling is important in building the abundance distribution of clusters in the cluster beam, the new stability index $\Delta_2^v(N)$ is derived from the evaporation energies. Specifically, $\Delta_2^v(N)$ is constructed in a way similar to $\Delta_2(N)$, but with evaporation energies instead of total cluster energies. We apply this new stability index to understand the experimental abundance of carbon clusters with sizes up to $N = 16$ measured by mass spectrometry¹⁴.

The evolution of the geometrical structure of small carbon clusters is complex¹⁵⁻¹⁹, and an accurate description of the structures is required to calculate evaporation energies. In section 2 we briefly present the computational methodology, and give a description of the geometrical, energetic and electronic properties of the different C_N and C_N^+ ($N \leq 16$) gas-phase clusters obtained within our theoretical framework as compared with the broad available experimental and theoretical literature in this field. In Section 3 we apply the most common and extensively used stability descriptors, such as the evaporation energy and the stability function, in order to compare this theoretical analysis with the experimental mass-spectrometric information on cluster abundances. As a step forward beyond the standard stability descriptors, in Section 4 we propose a new descriptor of the relative stability of clusters that we test by comparing with the time-of-flight mass spectrum of carbon cluster cations C_N^+ with $N \leq 16$. The values of the new stability descriptor as a function of cluster size N provide an accurate correlation with the cluster abundances, reproducing all the details found in the mass spectrum and providing a substantial improvement over the performance of previous descriptors. Finally, we conclude in Section 5 summarizing the conclusions extracted from this study.

II. COMPUTATIONAL APPROACH AND ATOMIC STRUCTURE OF C_N AND C_N^+ ($N \leq 16$)

The structure of neutral C_N and cationic C_N^+ carbon clusters with $N \leq 16$, and the corresponding electronic structures have been optimized by using the GAUSSIAN09 atomistic simulation package²¹. The density functional level employed was the hybrid B3LYP method^{22,23} with cc-pVQZ basis²⁴. As the starting geometries used as input for the structural optimization we have considered, for each cluster-size, different isomers reported in the literature lying within a total energy window of 0.5 eV. Those isomers had been obtained by accurate molecular orbital calculations (CCSD(T)/cc-pVQZ, CCSD(T)/PVTZ, CCSD(T)/275cGTOs, among others¹⁵). Besides, for all the isomers studied we have analyzed the two lowest-lying electronic spin states. Performing a detailed dis-

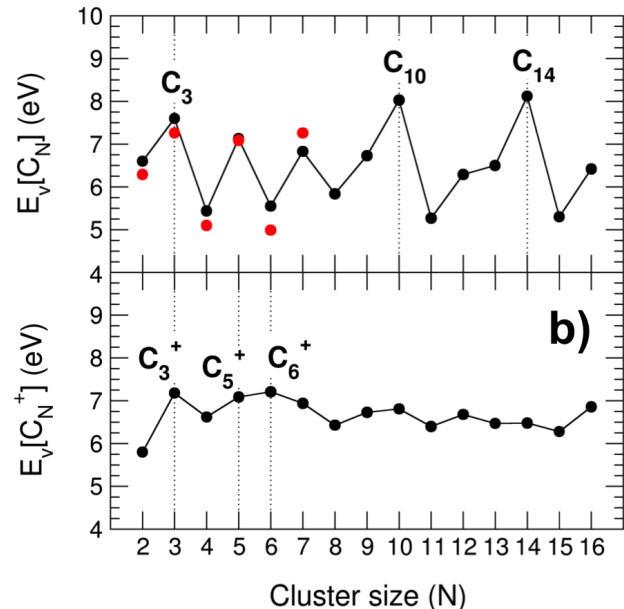


FIG. 1. Calculated evaporation energies $E_v(N)$, in eV, of: (a) neutral C_N clusters (red dots: experimental values for C_2 – C_7 extracted from Ref.²⁰); and (b) positively charged C_N^+ clusters.

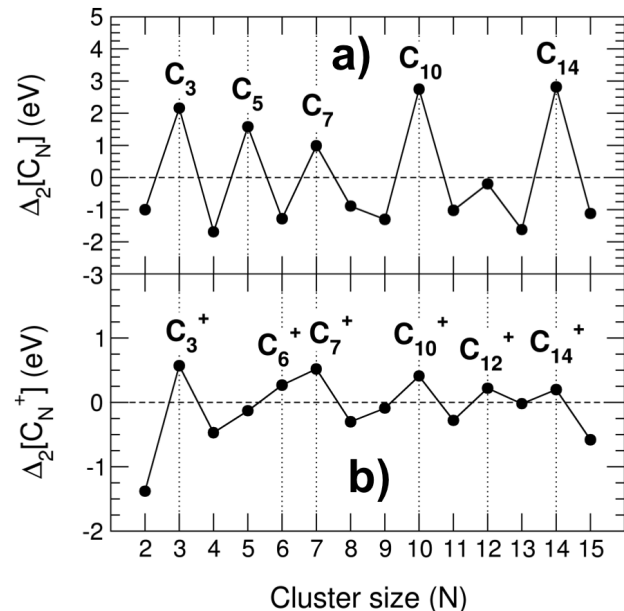


FIG. 2. Computed stability function $\Delta_2(N)$, in eV, of: (a) neutral C_N clusters; and (b) positively charged C_N^+ clusters.

cussion of the geometric and electronic structure of these clusters is not our intention here, given the extensive work already reported in the literature. Our goal herein just consists in carrying out an analysis of the ground-state structures of the C_N and C_N^+ ($N \leq 16$) clusters within the mentioned B3LYP formalism, in order to obtain their global energetic map within

an accurate and unified computational framework allowing us to test the new stability descriptor.

Extensive information exists on small neutral and cationic carbon clusters obtained from accurate spectroscopic investigations, astronomical observations and theoretical calculations (see, for instance, the excellent review by Van Orden and coworkers¹⁵ and the referees therein). The ground state and low lying structures that we have obtained for C_N and C_N^+ ($N \leq 16$) clusters with the B3LYP method and cc-PVQZ basis are in excellent agreement with the established structures. Our calculations predict that the lowest energy structures of C_3 , C_4^+ , C_5 , C_5^+ , C_7 , C_7^+ , C_9 and C_9^+ , besides the obvious C_2 and C_2^+ , are cumulenic linear structures with nearly equivalent bond lengths (contrary to acetylenic bonding exhibiting alternating bond lengths). In agreement with other works the electronic ground states are of type $^1\Sigma_g^+(^3\Sigma_g^-)$ for the odd(even)-numbered neutral chains, and $^2\Sigma_u^+(^4\Sigma_u^-)$ for the odd(even)-numbered cation chains²⁵⁻³². Also in agreement with the reported literature^{15,33-36}, $C_{11} - C_{16}$ and $C_{11}^+ - C_{16}^+$ clusters exhibit monocyclic-ring structures with 1A_g and $^2A''$ electronic ground-states, respectively. This behavior of clusters larger than C_{10} forming monocyclic rings is due to the reduction in angular strain as the radius of the ring increases and to the added stability arising from an additional C-C bond compared to the chains^{28,35,36}.

Nonetheless, as in previous works we predict a few exceptional cases deviating from the general trend. C_3^+ which exhibits a bent configuration³⁷⁻³⁹ (C_{2v} symmetry) with a bond angle of 71° (to be compared with an angle of 68° reported in literature³⁷) and a 2B_2 electronic ground state, 0.19 eV lower in energy than the perfect linear isomer (to be compared with the value of 0.3 eV obtained in an accurate Configuration Interaction (CI) calculation.³⁷)

For the neutral C_4 , C_6 and C_8 , some accurate molecular orbital calculations have found cyclic isomers as low-energy structures, isoenergetic or in some cases even lower in energy than their linear counterparts^{28,35,40-43}. However, these cyclic isomers have been extremely difficult to detect using spectroscopic techniques, while their linear forms have been observed in most experimental studies. Within our B3LYP/cc-PVQZ calculations we have found the linear cumulenic forms as the most stable structures, with the cyclic isomers lying within an energy range of 0.15 eV.

For the ground state structure of the cation C_6^+ we found a slightly non planar distorted hexagon (D_{3h} -symmetry) with an $^2A''$ electronic ground-state, practically isoenergetic with its linear form. This feature is reproduced by most high-accuracy molecular orbital methodologies, and it has been also confirmed by ion-mobility measurements^{32,44}. The same occurs for the C_8^+ , for which we have found a cyclic ground-state configuration and a low lying linear isomer nearly degenerate in energy, both with $^2A''$ electronic ground-states. The structures are again confirmed by experiment³².

In agreement with previous work²⁸, we found C_{10} as the size for which the transition from linear cumulenic chains to monocyclic rings occurs (allowing for the exceptions discussed above). Our calculation yields a D_{5h} monocyclic ring as the ground-state configuration, with an 1A_g electronic

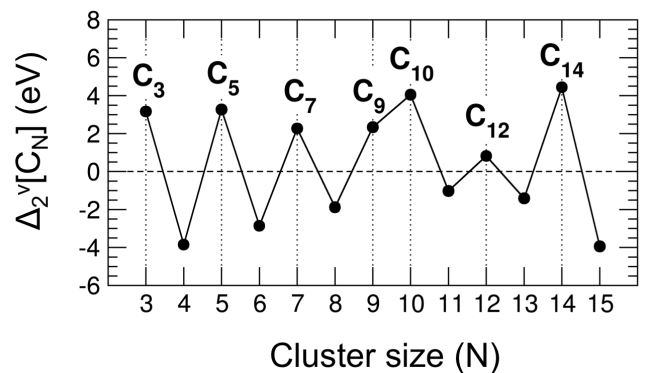


FIG. 3. Computed stability function, $\Delta_2^v(N)$, (in eV) obtained from evaporation energies of neutral C_N clusters.

ground-state. Finally, we found a cyclic ground state configuration for C_{10}^+ , with a $^2A''$ electronic ground-state, again in agreement with previous work³².

III. STABILITY DESCRIPTORS AND CORRELATION WITH THE MASS SPECTRUM

The evaporation energy of a carbon cluster with N atoms, $E_v(N)$, is the energy required to detach an atom from the N -atom cluster:

$$E_v(N) = E(N-1) + E(1) - E(N), \quad (1)$$

where $E(N)$ is the total energy of an N -atom cluster. Correspondingly, $E_v(N+1)$ is the energy to remove an atom from the cluster C_{N+1} :

$$E_v(N+1) = E(N) + E(1) - E(N+1). \quad (2)$$

$E_v(N+1)$ can also be viewed⁴⁵ as a capture energy, $E_c(N)$, that is, the energy released when C_N captures an atom and becomes C_{N+1} :

$$E_c(N) = E_v(N+1). \quad (3)$$

In the case of positively charged carbon clusters C_N^+ the evaporated atom is neutral while the charge remains in the cluster C_{N-1}^+ . The computed evaporation energies of neutral and charged carbon clusters are plotted in Figures 1a and 1b (black dots), respectively. Differences can be observed between the two figures. The largest evaporation energies occur at C_3 , C_{10} and C_{14} for the neutrals, and at C_3^+ , C_5^+ and C_6^+ for the cations. Additionally, for sake of comparison, Figure 1a also shows (red dots) the experimental values of the evaporation energies for the neutral clusters C_2-C_7 extracted from Ref.²⁰. The agreement between the computed and experimental values for C_N up to $N=7$ is excellent.

From equations (1) and (2) the following relations are immediately obtained:

$$\begin{aligned} E_v(N) - E_v(N+1) &= E_v(N) - E_c(N) = \\ E(N+1) + E(N-1) - 2E(N) &= \Delta_2(N). \end{aligned} \quad (4)$$

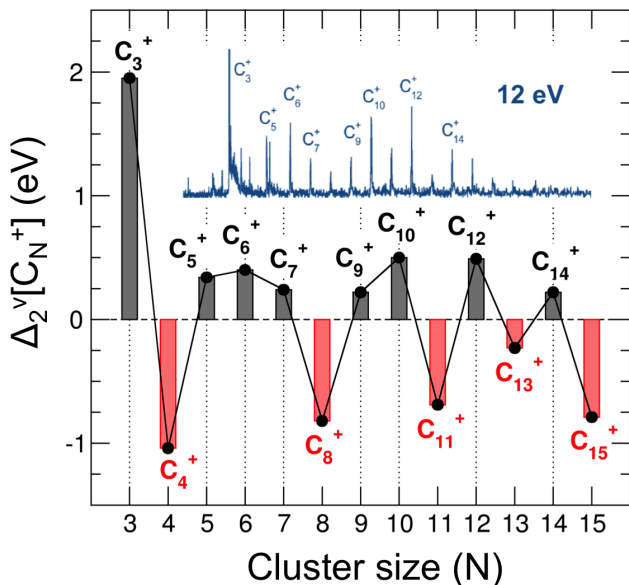


FIG. 4. Computed stability function, $\Delta_2^v(N)$, (in eV) obtained from evaporation energies of positively charged C_N^+ clusters. For comparison, the experimental mass spectrum of carbon cluster cations obtained at an ionization energy of 12 eV¹⁴ is shown as an inset.

$\Delta_2(N)$ is the “stability function” often used to analyze the relative stability of clusters as a function of size, and to interpret the abundance mass spectrum of clusters obtained by gas aggregation techniques. Clusters with large values of $\Delta_2(N)$ are highly stable compared with clusters of neighbor sizes, and the experiments show that those clusters are more abundant. This can be readily understood from equation (4). A large value of $\Delta_2(N)$ results from the combination of a large value of $E_v(N)$ and a small value of $E_c(N)$. This means that for that special cluster, both the tendency to grow by capturing one atom and the tendency to shrink the size by evaporating one atom are feeble, so its abundance is enhanced when hot larger clusters evaporate atoms, because that evaporation chain practically stops at the special C_N cluster.

The quantity given in (4) is the atomic parallel of the electronic hardness used in chemistry to quantify the reactivity of a chemical species⁴⁶. A high chemical hardness is indicative of low chemical reactivity. Here we call $\Delta_2(N)$ of eq. (4) the “atomic hardness”⁴⁵ because a high value of this quantity indicates a low predisposition of the cluster to change its size. Figures 2a and 2b show $\Delta_2(N)$ for C_N and C_N^+ clusters, respectively. The peaks at C_3 , C_5 , C_7 , C_{10} and C_{14} observed for the neutrals indicate that these clusters are more stable than the others. For charged clusters $\Delta_2(N)$ reveals that C_3^+ , C_6^+ , C_7^+ , C_{10}^+ , C_{12}^+ and C_{14}^+ are the most stable cationic clusters.

The stability peaks of neutral or cationic clusters do not show a clear correlation with their corresponding ground-state geometries, since we find a variety of conformations among them: for instance, in the cationic clusters a bent C_{2v} structure for C_3^+ , a distorted D_{3h} hexagon for C_6^+ , a cumulenic linear form for C_7^+ and monocyclic rings for C_{10}^+ , C_{12}^+ and C_{14}^+ . It is noticeable that the peak at $N = 3$ is not the highest

one in the plot for neutral clusters, and the height of the peak at C_3^+ is similar to that of C_7^+ and only a bit larger than that of C_{10}^+ . The two stability plots can be compared to the experimental abundance spectrum. Experimental mass spectra obtained by Belau *et al.*¹⁴ for carbon cluster cations photoionized at 10 and 12 eV yield that, at both ionization energies, the even-numbered clusters in the higher size range ($N=9-15$) are more prominent than the odd-numbered clusters. The most interesting spectrum obtained by Belau and coworkers¹⁴ is the one measured at the ionization energy of 12 eV (see inset in Figure 4), sufficiently large to ionize C_N clusters of all the relevant sizes. In fact, at that ionization energy, new peaks are detected, and C_3^+ becomes the largest peak in the spectrum. In the zone of small clusters, the most abundant ones are C_3^+ , C_5^+ , C_6^+ and C_7^+ , that is, odd-size clusters, with the addition of C_6^+ . In that plot Belau *et al.* mark C_3^+ , C_5^+ , C_6^+ , C_7^+ , C_9^+ , C_{10}^+ , C_{12}^+ and C_{14}^+ as abundant clusters. In fact, the peaks at C_4^+ , C_8^+ , C_{11}^+ , C_{13}^+ and C_{15}^+ are clearly small compared to adjacent cations with $N + 1$ and $N - 1$ atoms. Although the abundance of C_5^+ is smaller than that of C_6^+ , the cluster C_5^+ can be considered abundant, and then very stable, because it is not flanked by more abundant neighbors on both sides. The same applies to C_7^+ and C_9^+ . Some of the sizes corresponding to abundant clusters are reproduced by the stability functions $\Delta_2(N)$ of Figures 2a and 2b. However, $N = 6$ and $N = 12$ are missing in Figure 2a ($\Delta_2(N = 12)$ is a negative number) and $N = 5$ and $N = 9$ are missing in Figure 2b. Besides the missing peaks, the trend displayed by the relative peak heights in the experimental mass spectrum (inset of Figure 4) is not reproduced well in Figures 2a and 2b.

IV. NEW DESCRIPTOR OF STABILITY

We have seen above that $\Delta_2(N)$ provides a rationalization of a number of features seen in the experimental spectrum, but not all features. With the aim of improving the theoretical description and the prediction of all the features in the experimental spectrum, herein we introduce a new stability descriptor. For that purpose we write the evaporation energies for clusters with $N + 1$, N and $N - 1$ atoms:

$$E_v(N + 1) = E(N) + E(1) - E(N + 1), \quad (5)$$

$$E_v(N) = E(N - 1) + E(1) - E(N), \quad (6)$$

$$E_v(N - 1) = E(N - 2) + E(1) - E(N - 1). \quad (7)$$

From these equations:

$$E_v(N) - E_v(N + 1) = \quad (8)$$

$$E(N + 1) + E(N - 1) - 2E(N) = \Delta_2(N).$$

and

$$E_v(N - 1) - E_v(N) = \quad (9)$$

$$E(N) + E(N - 2) - 2E(N - 1) = \Delta_2(N - 1).$$

Subtracting (9) from (8), we obtain $2E_v(N) - E_v(N+1) - E_v(N-1)$, which, by comparing with eq. (4), is an stability descriptor defined from the evaporation energies. That is,

$$\Delta_2^v(N) = 2E_v(N) - E_v(N+1) - E_v(N-1) = \Delta_2(N) - \Delta_2(N-1), \quad (10)$$

which is the difference between the ‘‘atomic hardness’’ of the clusters with N and $N-1$ atoms. One may notice the change in the relative order of the quantities pertaining to N , $N+1$ and $N-1$ compared to eq. (4). The reason is that total energies $E(N)$ are negative, but evaporation energies $E_v(N)$ are positive. The interpretation of eq. (10) is that a cluster of size N is very stable if its evaporation energy is larger than the average of the evaporation energies of the clusters with adjacent sizes $N+1$ and $N-1$. Another way to interpret eq. (10) is that a cluster is very stable, and abundant, if its atomic hardness is high and the hardness of clusters with size $N-1$ is low. In this way, the tendencies of clusters of size N to grow or to shrink are feeble, and at the same time the population of clusters of size N can easily grow in the cluster beam when clusters of size $N-1$ capture one atom. Very stable clusters are characterized by positive values of $\Delta_2^v(N)$. Results obtained with this descriptor of cluster stability for neutral and cationic clusters are plotted in Figures 3 and 4, respectively. An improvement is noticed in Figure 3 compared to the results for the standard stability index $\Delta_2(N)$. Now the only missing feature in comparison to the experimental spectrum is the peak at C_6 . However, the relative heights of the peaks do not correlate with the heights of the peaks in the experimental mass spectrum. This suggests the need of accounting for the charge of the cluster and Figure 4 confirms this expectation. $\Delta_2^v(N)$ separates the cations in two groups: C_3^+ , C_5^+ , C_6^+ , C_7^+ , C_9^+ , C_{10}^+ , C_{12}^+ and C_{14}^+ have positive values of $\Delta_2^v(N)$, and C_4^+ , C_8^+ , C_{11}^+ , C_{13}^+ and C_{15}^+ have negative values of $\Delta_2^v(N)$, indicating that the first group is formed by the more stable (and then more abundant) cationic clusters, in full agreement with experiment. A remarkable observation is the correlation between the heights of the peaks in Figure 4 and the corresponding heights in the experimental spectrum. C_3^+ appears as the largest peak in the spectrum. Also, the trends in the two groups (C_5^+ , C_6^+ , C_7^+) and (C_9^+ , C_{10}^+ , C_{12}^+ , C_{14}^+) are well reproduced.

To justify the clear improvement obtained by using the new stability index $\Delta_2^v(N)$ instead of $\Delta_2(N)$ we notice from eq. (4) that $\Delta_2(N)$ is constructed from the total energies of clusters with sizes $N+1$, N and $N-1$. On the other hand $\Delta_2^v(N)$ is constructed from evaporation energies of clusters with sizes $N+1$, N and $N-1$. Evaporation energies are more relevant quantities in the processes controlling the relative cluster abundances in the beam, so it is reasonable that $\Delta_2^v(N)$ provides a better correlation with the mass spectrum of carbon cluster cations.

V. SUMMARY AND CONCLUSIONS

The abundance mass spectrum of gas-phase atomic clusters measured in cluster beams has a rich structure that arises from a complex process of growth by atom addition and evaporation when the clusters become hot due to the heat of condensation. The most popular stability descriptor, usually called ‘‘stability function’’, is based on comparing the total energy of clusters of size N with the averaged total energy of clusters with neighbor sizes $N+1$ and $N-1$. Those total energies have to be obtained by laborious calculations of the atomic and electronic structures of the clusters using powerful theoretical methods, usually the density functional theory. This index explains the main features of the experimental mass spectra, but application to carbon cluster cations C_N^+ ($N \leq 16$) leaves some secondary features, and in particular the detailed behavior of the height of the experimental abundance peaks, unexplained. In this work we have introduced a novel stability descriptor which is based on comparing the evaporation energy of clusters of size N with the averaged evaporation energies of clusters of sizes $N+1$ and $N-1$. Application to carbon cluster cations C_N^+ ($N \leq 16$) reveals a perfect correlation with the experimental mass spectrum, and in particular with the detailed variation of the height of the abundance peaks as a function of size N . The success is attributed to the fact that the normal stability index is constructed from total cluster energies, while the new index is constructed from atom–evaporation energies, which are quantities more directly connected with the processes controlling the abundances in the beam. We expect that the new stability index will be useful in the analysis of the mass spectra of all kinds of clusters. The index is based on the energies involved in the processes of evaporation and capture of atoms by the clusters forming and flying in the molecular beam. A part of the condensation energy of the clusters is removed by collisions with a cool inert carrier gas. Another part is removed by evaporation of atoms from the hot clusters. For the detailed variations of the abundance population with cluster size to develop, abundant evaporation events are required, and this is usually the case in cluster formation experiments in the gas phase.

ACKNOWLEDGEMENTS

We acknowledge funding from the Spanish MINECO (Grants MAT2017-85089-C2-1-R and RYC-2015-17730), Junta de Castilla y Le3n (Grant VA021G18), University of Valladolid (Grupo de F3sica de Nanoestructuras), and the EU via the ERC-Synergy Program (Grant ERC-2013-SYG-610256 NANOCOSMOS) and EU Horizon 2020 Research and Innovation program (Grants 696656 – Graphene Flagship Core1 – and 785219 – Graphene Flagship Core2 –). We also thank the computing resources from CTI-CSIC.

The authors declare no competing financial interests.

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