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Fragmentation of cesium-carbon cluster anions CsC_n^- $(n \leqslant 10)$

A. K. Gupta[1] and M. Krishnamurthy[2]
[1]*Nuclear Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*
[2]*Tata Institute of Fundamental Research, 1 Homi Bhabha Road, Mumbai 400 005, India*

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We present the fragmentation dynamics of CsC_n^- $(n \leqslant 10)$ in collision with argon at 15 keV impact energy. The propensity for the formation of the fragment ions $C_m^-(m \leqslant n)$ exhibits even-odd oscillations, with the yield being larger when m is even; and this is correlated with the larger electron affinity of the product ion when m is even. We observe C_3 loss in the case of CsC_9^- clusters. We find an unexpected oscillatory pattern in the kinetic-energy release (KER) spectra of C_n^- fragments. The ratio of the width of C_n^- to the parent CsC_n^-, which is a measure of the KER in the center-of-mass (c.m.) frame, shows even-odd oscillation, with the ratio being larger when n is even than when n is odd. The oscillatory pattern is correlated with differences in fragmentation pathways accessed in the Franck-Condon region. Applying the reflection method with model potentials for two different fragmentation paths, we find that the KER in the c.m. frame oscillates if an ion-pair formation pathway is preferred for clusters of even n.

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I. INTRODUCTION

Fragmentation of molecular ions has been a subject of a large number of studies [1,2]. The reaction dynamics of a number of simple systems has been understood by a number of experimental and theoretical methods. A large number of reaction dynamics studies have been carried out with diatomic molecules due to the fact that rigorous computational methods can be applied for better understanding of the dynamics of interaction [3–5]. Ion translational energy spectrometry has been very successfully applied together with both time-dependent wave packet (TDWP) dynamics and reflection methods, to correlate the energy carried away by the fragment ion to the dynamics of collision induced dissociation [4,6]. Such studies have revealed the shapes of the repulsive electronic states that are accessed in the fragmentation. Polyatomic systems are much more difficult to understand, because of the complexity of obtaining accurate information on the multidimensional potential-energy surfaces and the large number of fragmentation pathways that are possible. A better understanding can be achieved by way of simplification in choosing to observe certain fragmentation pathways only and modeling the system as a pseudodiatomic molecule. Model potentials are often used to derive a qualitative understanding of the dynamics of interaction.

Collision induced fragmentation of molecules, for large impact-parameter collisions, is considered to be a two-step reaction. The first involves the collisional excitation of the molecule into an excited electronic state. The second involves the dynamics of the molecular ion in this excited state. If the potential-energy function is purely repulsive, the molecule can roll down the repulsive potential-energy function, giving the excess energy to the fragments in the center-of-mass (c.m.) frame. The width of the kinetic-energy release (KER) in the c.m. frame reflects the slope of the repulsive potential-energy function in the Franck-Condon regime. So, by measuring the KER of the fragment ions, one can use experimental data to simulate the repulsive potential-energy function accessed and, thus, the dynamics of the fragmentation process can be obtained. We have used this method earlier for the fragmentation of simple systems like CO^+ [4] and CO^{2+} [7]. The transition function to the excited state can be computed by the reflection method, wherein the excited state wave function is taken to be a δ function at the classical turning points. We have also used the TDWP method, wherein the excited-state function is computed more rigorously by numerical techniques [6,7].

Cluster-ion fragmentation has attracted a lot of attention, not only because of the challenge posed by the detailed understanding of the system, but also for applications involving the production of doubly charged anion systems [8,9]. Increase in the number of degrees of freedom does limit the accuracy of the computations that can be carried out and the details of the dynamics that can be obtained from the experimental observations. In spite of the limitations, the ability to produce simple systems such as C_9^{2-} [8] raise questions as to the structural basis of their formation and their stability. The dynamics of the collision process in which these dianions are produced from ‘‘metcar’’ clusters such as CsC_9^-, for example, is an open question that has been partially answered recently [10]. Studies of the fragmentation of such clusters are of interest, as they reveal the electron delocalization in the presence of electropositive atoms. Dynamics of their fragmentation are rather complex due to the formation of the ion-pair excited state. Electron-loss channels are the most prominent in the fragmentation. But those states that lead to the negative-ion products reveal the potential-energy states of the excited negative ion. The repulsive excited state of the negative ions are very difficult to compute theoretically because of the diffuse nature of the atomic wave functions, and it is harder to access experimental information about these due to the larger propensity of the electron-loss channels. The difficulty of producing copious amounts of negative ions and also observe the negative-ion product channels, together with the difficulties in theoretical computations, are perhaps the reason that these studies have attracted very little attention when compared to the studies of

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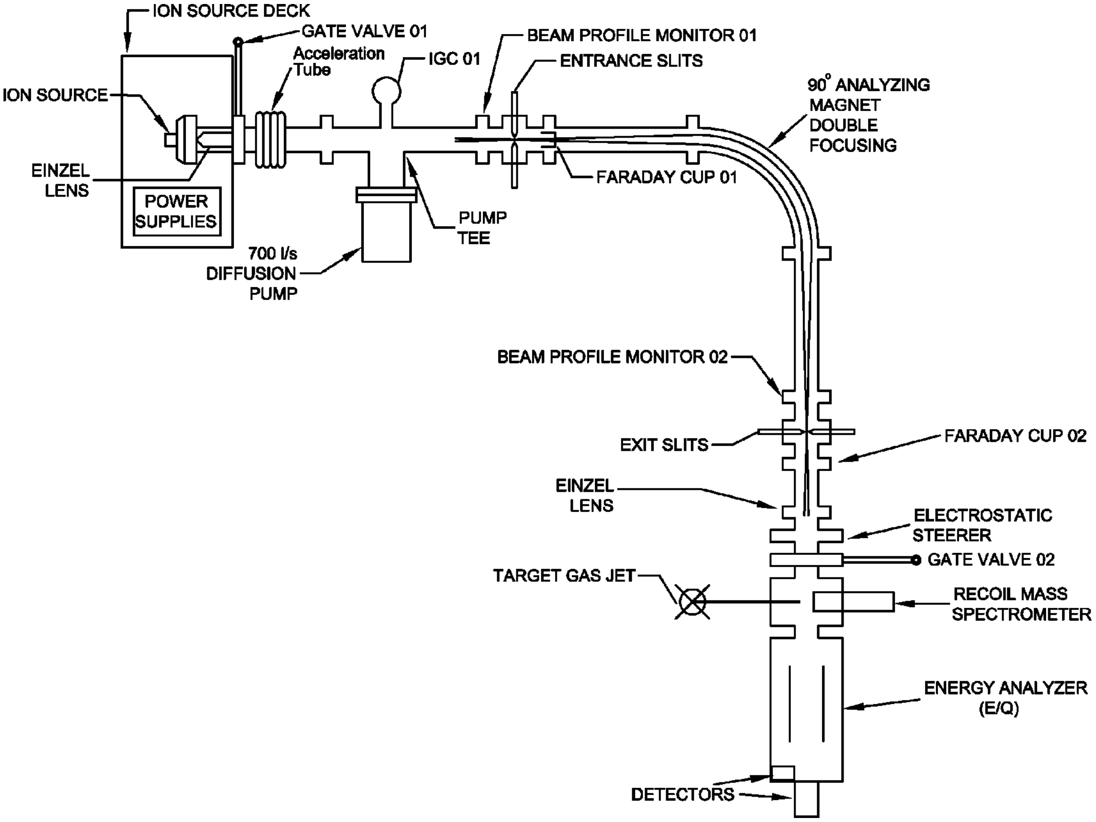

FIG. 1. Schematic layout of the negative-ion beam apparatus used in the experiments.

the fragmentation dynamics of positive ions. In this study, we make an attempt to study the fragmentation dynamics of negative-ion clusters and access the information of the nature of the repulsive potential-energy function of the negative ions.

This work presents the collisional dissociation of CsC_n^- $(n \leqslant 10)$ cluster anions and attempts to probe their dissociation dynamics. We measure the energy spectrum of the negative fragments formed in the collision of CsC_n^- with Ar at 15 keV. The propensity of the fragment ions $\mathrm{C}_m^-(m \leqslant n)$ shows a preference to produce fragments with even m due to their larger electron affinity. The energy spectra reveal that the ratio of the width of the fragment ion C_n^- to that of the width of the parent CsC_n^- ion shows even-odd oscillations: the ratio is larger when n is even than when n is odd. These experimental observations, which persist for a wide range of n values accessed in the experiment, are correlated to the fragmentation dynamics of the parent ion. We postulate that the fragment ion C_n^- is formed in two different pathways upon collision with Ar, as depicted below.

Fragmentation pathway I (FP-I),

$$\mathrm{CsC}_n^- + \mathrm{Ar} \rightarrow [\mathrm{C}_n^{2-}]^* + \mathrm{Cs}^+ + \mathrm{Ar}, \tag{1}$$

$$[\mathrm{C}_n^{2-}]^* \rightarrow \mathrm{C}_n^- + e. \tag{2}$$

Fragmentation pathway II (FP-II),

$$\mathrm{CsC}_n^- + \mathrm{Ar} \rightarrow \mathrm{C}_n^- + \mathrm{Cs} + \mathrm{Ar}. \tag{3}$$

It is known that the doubly charged negative ion C_n^{2-} is more stable and readily formed when n is even than when n is odd [11]. So FP-I would be preferred when n is even compared to FP-II, and the preference would be converse when n is odd. We formulate the model potential for both of these pathways and use the reflection method to obtain relative KER widths for the two channels. The model calculations show that due to the change in the potential in the Franck-Condon regime, the KER is larger when FP-I is accessed compared to when FP-II is accessed. We correlate the observed oscillation in the KER width to these two different pathways.

II. EXPERIMENTAL METHOD

The present measurements are conducted using a negative-ion beam apparatus that has been described in detail elsewhere [12]. Figure 1 presents a schematic of the experimental setup. Negative ions of interest generated in a source of negative ions by cesium sputtering are extracted and focused into a beam by an Einzel lens. A double focusing 90° analyzing magnet, with a mass-energy product of about 10 amu-MeV, is used for selecting an ion of a particular m/q value. The slits were adjusted so that a unit mass resolution is obtained up to 300 amu. The mass selected ions are made to interact with an inert gas, such as Ar, in a collision cell under single-collision conditions. Post-collision energy analysis of the forward-scattered ions is carried out using a parallel-plate electrostatic deflector that measures the mo-

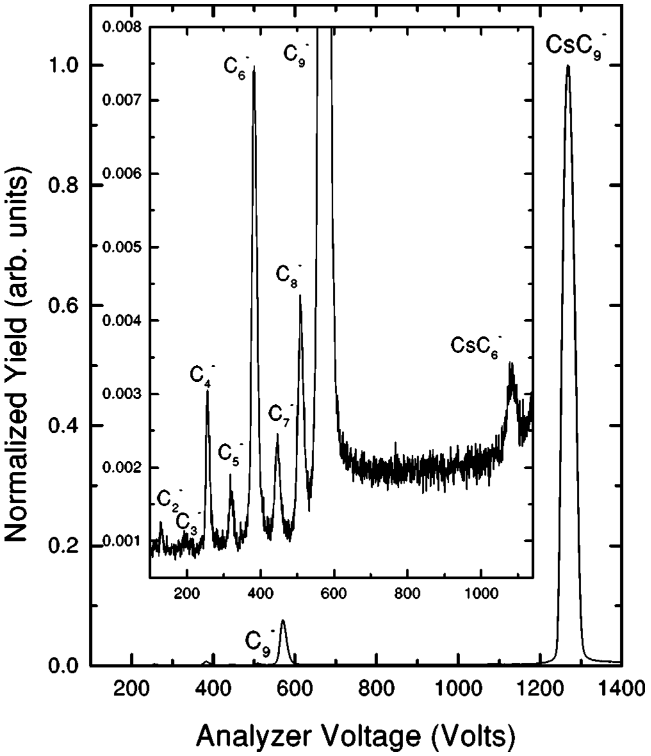

FIG. 2. Mass spectrum of fragment ions formed in collision of CsC_9^- with Ar at 15 keV impact energy. The inset shows the formation of CsC_6^- product ion formed after C_3 loss.

mentum of the ion and is remotely scanned by a computerized data-acquisition card. The size of the slits at the exit of the collision cell and at the entrance of the energy analyzer and the distance between the two are adjusted to ensure that forward-scattered ions are detected with an estimated angular resolution of $\pm 0.01°$. The fragment energy measured by its deflection voltage is a direct measure of its mass, and thus the fragment ion mass spectra along with the energy of the fragment ion is determined. Ion signal detection is with a channel electron multiplier coupled to conventional pulse counting electronics. The recoil mass spectrometer is not used during the course of these measurements.

In the present experiments, Cs^+ ions are made to impinge on a high-purity polycrystalline graphite surface at 5 keV to produce $CsC_n^-(n=1\text{–}10)$ cluster anions. The extracted ions are accelerated to a final energy of 15 keV and made to collide with Ar. All the different fragment ions formed in the collisional event are detected. In this paper we concentrate only on the negative-ion fragments formed in the collision. We measure the propensity of their formation and measure their energy distributions.

III. RESULTS AND DISCUSSION

Figure 2 shows a typical fragmentation spectrum for CsC_n^- in collision with Ar at 15 keV. As can be seen for the case demonstrated with $n=9$, fragment ions with all the possible values of n are observed, with the exception of C^-, which is never positively identified. The general trend in the fragmentation spectra is that of decreasing anion fragment yields with an increasing number of lost atoms. Superposed on this general decrease are strong odd-even oscillations of carbon anion fragments, i.e., $C_m^-(m\leqslant n)$ fragments with even m are more abundant than odd m fragment ions. These oscillations in the yield have some resemblance to the observations in fragmentation of pure C_n^- cluster anions and can be correlated to the differences in the electron affinities of the fragment ions formed. The fragment ions with even carbon atoms are more prominent, as their electron affinities are relatively higher [13]. Apart from the even-odd oscillations, in case of some cluster ions such as CsC_9^- and CsC_7^-, the C_{n-3}^- is the second most prominent product ion. The preference of C_{n-3}^-, which has resemblance to the fragmentation of C_n^-, is once again possibly due to the larger electron affinity of these product ions.

It has been observed that the loss of C_3 is dominant in the fragmentation of small pure carbon clusters C_n^- [14]. In the case of metcar clusters such as CsC_n^-, however, it would be much easier to break a metal carbon bond rather than a covalently bonded carbon-carbon linkage. The observations concur with this argument and C_n^- is the most abundant anion formed in the fragmentation. However, we do also see C_3 loss in the fragmentation spectra for CsC_9^-. The unusual channel of breaking a strongly bound carbon linkage is probably possible in this case due to the exceptional stability of CsC_6^-. The exceptional stability of CsC_6^- is also reflected in its most prolific production through the sputter ion source. A typical spectrum of CsC_n^- cluster anions sputter generated by 5-keV Cs^+ bombardment of the graphite surface is shown in Fig. 3.

Favoring of the reaction channel $CsC_9^- \rightarrow CsC_6^- + C_3$ indicates that the vertical electron affinity of CsC_6 should be greater than the electron affinity of C_3, since the extra electron is likely to be carried by the species that has the higher electron affinity value. We have made an *ab initio* quantum calculation to compute the vertical electron affinity of CsC_6. The optimized geometry for CsC_9 is computed with Lanl2dz basis by a density-function method, B3LYP, using the GAUSSIAN 92 software system. We obtain a vertical electron affinity of 2.29 eV for CsC_6, which indeed is larger that the electron affinity of C_3, which has been measured to be 1.995 eV [15].

The kinetic-energy release measurements in the fragment ions yield information on the dynamics of the fragmentation process. By measuring the width of the energy release in the fragment ions, one can decipher the nature of the excited state that is the intermediary in the fragmentation mechanism. From the energy width in the laboratory frame, one can obtain the KER in the c.m. frame and use it to obtain the details of the potential-energy function in the Franck-Condon regime. The measured width of the fragment ion energy distribution in comparison to the width of the parent ion energy distribution is thus the measure of the energy release in the c.m. frame. The ratios of the energy width of the fragment ion ($\triangle E_f$) to that of parent ion ($\triangle E_p$) is

$$(\triangle E_f)/(\triangle E_p)\propto m_f/m_p, \tag{4}$$

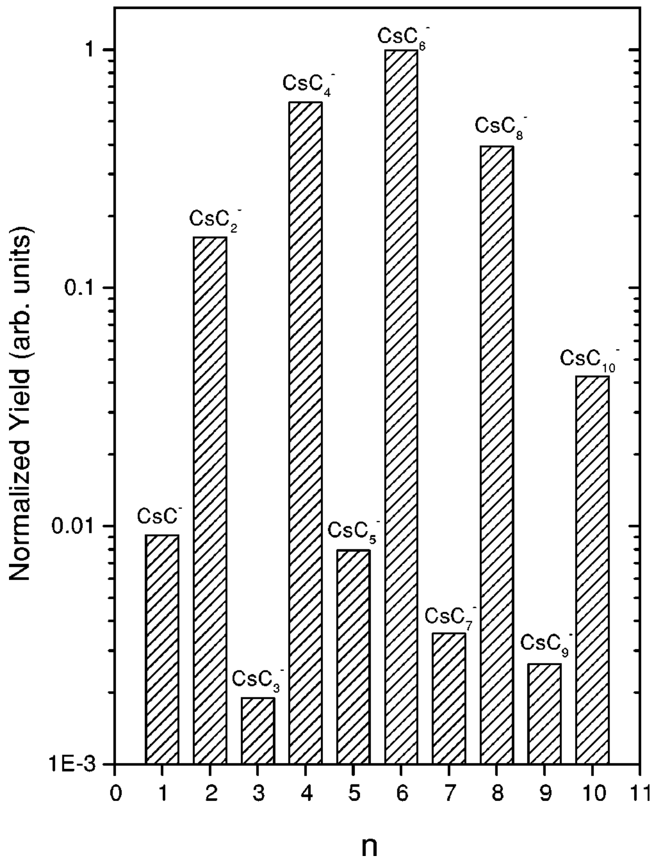

FIG. 3. Yields of CsC_n^- ($n=1$–10) produced in the sputter ion source by the bombardment of 5-keV Cs^+ ions on graphite surface.

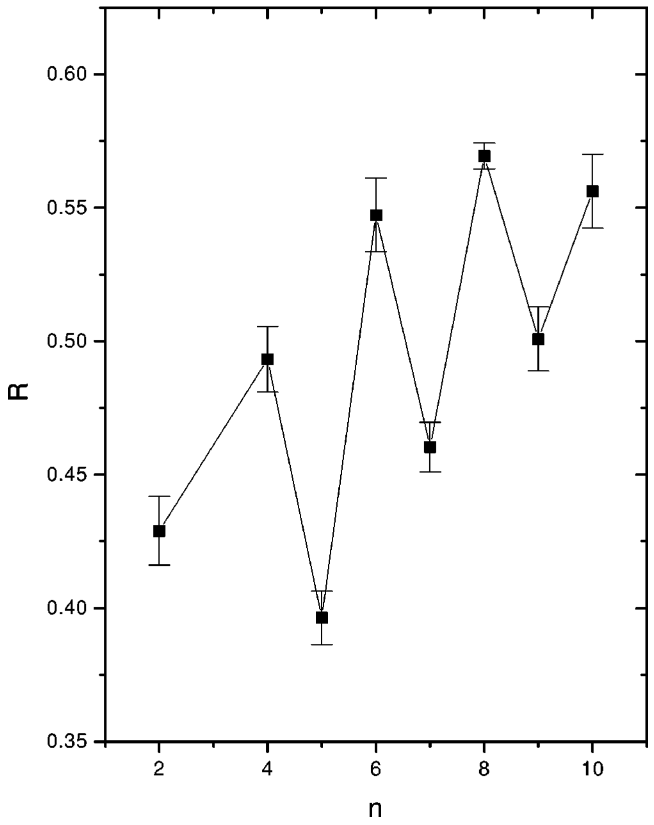

FIG. 4. Ratio R of energy width of product C_n^- ion to the energy width of CsC_n^- parent ion plotted as a function of size n. The line joining the points is to guide the eye.

where m_p and m_f are the masses of the parent and the fragment ion. For clusters of CsC_n^-, as n increases the ratio increases. Figure 4 shows the measured ratio of the width of the fragment ion C_n^- to that of CsC_n^- against the size n, indicating that the ratio does increase with n. However, it is also clear from the figure that the ratio exhibits oscillations, with higher values when n is even and lower values when n is odd. We note that the measurements for $n=3$ could not be made due to low ion signal.

The kinetic-energy width essentially reveals the nature of the repulsive potential-energy function accessed in the Franck-Condon region and suggests therefore, that the fragmentation path for clusters with even n is distinctly different from that for clusters with odd n.

We model the collision reaction based on the following two different pathways presented in the earlier section. In the first pathway (FP-I), the excited state is characterized by the ion-pair formation involving metastable C_n^{2-}. The other pathway is a repulsive state that is essentially characterized by the ion-induced dipole interaction. It has been shown experimentally for clusters with $n \geqslant 7$ that the propensity of producing C_n^{2-} with even n can be two to three orders of magnitude larger [16]. These experimental results are correlated with the theoretical computations of electron affinities for C_n^- for n as small as 2 [11]. The electron affinities are larger when n is even compared to when n is odd and, therefore, the propensity of forming a dianion with even carbons is much larger than with odd carbons. Based on the higher stability of the C_n^{2-}, when n is even we propose that FP-I, which involves the dianion intermediate, is preferred. We compute the KER for the model potentials for the two fragment pathways and test if the KER is larger when FP-I is accessed.

We use the reflection principle [4,17] in modeling the kinetic-energy release formed in the two fragmentation pathways. The molecule is excited from the ground electronic state to the excited state and depending on the nature of the excited potential-energy state, fragmentation occurs, giving the excess energy to the fragment ions in the center-of-mass frame. The transition probability for the excitation of the molecular ion is given to be

$$P_{i,f} \propto |\langle \psi_i \phi_i | M_{if} | \phi_f \psi_f \rangle|^2, \tag{5}$$

where ϕ_i and ϕ_f are the electronic wave functions of the initial and final state, respectively, ψ_i and ψ_f are the wave functions for the nuclear motion in the initial and final state, respectively, and M_{if} is the multipole operator for the transition. Following the Franck-Condon approximation, we can take the electronic transition operator μ_{if},

$$|\mu_{i,f}|^2 \propto |\langle \phi_i | M_{if} | \phi_f \rangle|^2, \tag{6}$$

to be slowly varying with the nuclear coordinate and get

$$P_{i,f} \propto |\mu_{i,f}|^2 |\langle \psi_i | \psi_f \rangle|^2. \tag{7}$$

In the reflection method, the initial nuclear wave packet or the vibrational wave function of the molecule in the ground electronic state (ϕ_i) is evolved on the excited potential-energy curve by taking the excited-state nuclear wave function ψ_f to be a δ function, as the classical turning point,

$$\psi_f \propto \delta(r-r_e). \tag{8}$$

The reaction system is essentially modeled as the fragmentation of a pseudodiatomic system Cs-C$_n$. The potential-energy curves for the two-fragment pathway are modeled taking the attractive component of the potential to be the Coulomb interaction of the ion pair in FP-I and the ion-induced dipole interaction for FP-II. The repulsive part of the potential is modeled by an $1/r^{12}$ potential. The initial state ψ_i is modeled to be a simple Gaussian function that depicts the molecule in the initial vibrational state of the ground electronic state. Here we are making an assumption that, irrespective of the size of the cluster, the vibrational state of the molecule remains close to the harmonic-oscillator solution for the vibrational motion, even though the electronic state itself may differ in nature. The peak position of the ground-state wave function, which essentially denotes the bond distance of the pseudodiatomic system Cs-C$_n$, is chosen such that the kinetic-energy release in the center-of-mass frame peaks around zero, to correlate with the measured fragment ion spectrum. The change in the width of the ground-state Gaussian function or the peak position are parameters that do not influence the conclusions based on this model calculation. Figure 5(a) shows the model potentials for the two pathways and Fig. 5(b) shows the computed transition function for the two potentials. This directly gives the KER in the c.m. frame for the two fragmentation pathways. The KER is essentially dependent on the variation in the slope of the potential-energy function in the Franck-Condon region. As can be seen from the figure, a change in the binding part of the potential from the Coulombic attraction to the ion-induced dipole interaction does change the KER in the center-of-mass frame and that KER width is larger for fragmentation with FP-I [potential $V_1(R)$] compared to that with FP-II [potential $V_2(R)$].

The energy of the fragment ion peak in the laboratory frame is given to be

$$E_{f,lab}=\frac{m_f}{m_p}E_p+\frac{m_f}{m_p}E_{c.m.}\cos^2\theta\pm\frac{m_f}{m_p}(E_{c.m.}E_p)^{1/2}\cos\theta, \tag{9}$$

where $E_{f,lab}$ is the fragment ion energy in the lab frame, $E_{c.m.}$ is the kinetic-energy release of the fragment ion in the center-of-mass frame, E_p is the projectile ion energy as measured in the lab frame, θ is the angle of orientation of the molecular axis with respect to the projectile ion beam axis, m_f and m_p are the masses of the fragment ion and projectile ion, respectively. This equation, which is obtained by the vector addition of the velocities, shows that small values of energy release in the center-of-mass frame will appear as a large change in the lab frame energy, when the projectile ion energy is very large. In the past, this apparent *kinematic energy amplification* has been used even to probe the rotational excitation of the molecular ion in the collision induced dissociation [18]. Thus, even though the model calculation shows a very small difference in $E_{c.m.}$, it would be significant for the energy widths measured in the lab frame.

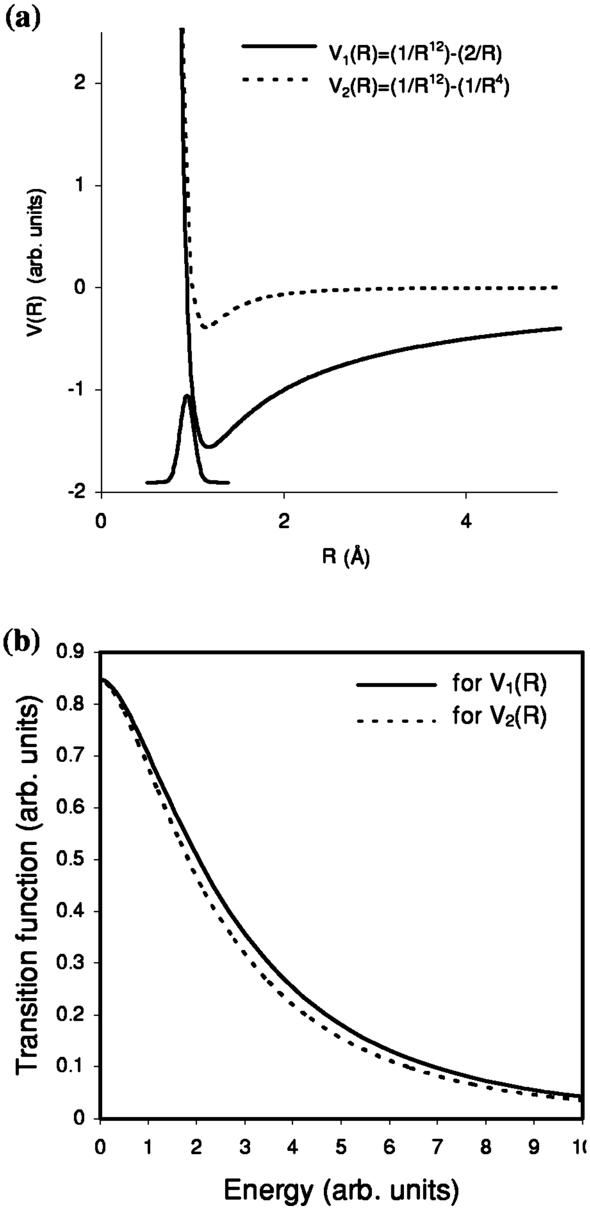

FIG. 5. (a) Model potentials for the two fragmentation pathways. Attractive Coulomb interaction [$V_1(R)$] for FP-I and ion-induced dipole potential [$V_2(R)$] for FP-II. (b) Transition function for the two potentials $V_1(R)$ and $V_2(R)$ computed using reflection method.

So if CsC$_n^-$, with even n access the ion-pair intermediate in their fragmentation (FP-I), which is likely based on the favorable electron affinities, the KER in the c.m. frame would be larger. This would result in the experimental observations that the ratio of energy width of the C$_n^-$ fragment to that of the parent ion (C$_n^-$/CsC$_n^-$) is larger for even n. We thus correlate the experimental observations presented in Fig. 4 with the different fragmentation pathways accessed by the molecule with even n as compared to odd n.

The model calculations presented here only qualitatively explain the measured observations. To make a quantitative comparision, we require information of the potential-energy surface of the excited negative-ion clusters. It is difficult with even the most advanced quantum chemsitry computations to obtain information on the excited states of the diatomic negative ions and nearly impossible to obtain the same for polyatomic negative-ion clusters.

IV. CONCLUSIONS

We have studied fragmentation of $CsC_n^-(2 \leqslant n \leqslant 10)$ clusters in collision with Ar at 15 keV impact energy. The anion fragmentation spectra mainly consist of $C_m^-(m \leqslant n)$ ions exhibiting an odd-even oscillatory pattern, i.e., fragments with even m are produced with higher yields. The oscillations are ascribed to the alternating electron affinities of carbon clusters. C_3 loss is observed in the case of CsC_9^- fragmentation due to the large stability of CsC_6^-, which is also recorded as the most abundant cesium-carbon anion species produced in the sputter ion source. We observe an unexpected oscillatory pattern of the ratio of width of C_n^- and width of CsC_n^-, which is a measure of the kinetic-energy release in the center-of-mass frame and reflects the nature of the potential-energy function accessed in the fragmentation. We model the reaction to occur in two distinct pathways, one involving an ion-pair formation and the other involving an ion-induced dipole potential. The former is preferred by the cluster with even n due to larger stability of the C_n^{2-} with n even. The two potentials result in different KER in the center-of-mass frame as shown by the model calculation, and the observed oscillatory pattern in the KER observed is correlated to be due to the preference of the ion-pair pathway when n is even.

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