Size and Temporal Dependence of the Average Kinetic-Energy Release during the Evaporation of Sputtered $Cs(CsI)_n{}^+$ Clusters

Hyun Jin Hwang, Dilip K. Sensharma, and Mostafa A. El-Sayed[(a)]
Department of Chemistry and Biochemistry, University of California,
Los Angeles, California 90024-1569

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The average kinetic-energy release is measured for the evaporation of CsI and $(CsI)_2$ molecules from sputtered $Cs(CsI)_n{}^+$ clusters ($n=2$–17) in two different time windows. The size and temporal (temperature) dependence of the average kinetic-energy release is found to be in reasonable agreement with the predictions of the evaporative ensemble model, except for evaporation processes involving the cluster with magnetic number $n=13$. Agreement can be obtained for the latter if the assumption of the independence of the heat of evaporation on the cluster size in the model is removed.

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In recent years, a growing number of groups have studied the fragmentation and the metastable decay of various gas-phase cluster ions produced either by photoionization[1-4] or electron-impact ionization[5-9] of a neutral cluster beam or by sputtering[10-12] of a bulk surface. Such studies have provided not only valuable implications for studies on neutral clusters but also information for the energetics and the mechanisms of dissociation of ionized clusters. However, most of the studies have been limited to rather qualitative observations, in part due to the lack of theoretical data for the energetics associated with the dissociation and also in part due to the fact that cluster ions are frequently formed with an ill-defined broad range of internal energy.

In the present work, we examine the evaporative ensemble model (EEM) by comparing the model predictions of the size and temporal (temperature) dependence of the average kinetic-energy release (KER) with the experimental results measured for the evaporation of ionic clusters, e.g., the evaporation of CsI and $(CsI)_2$ from sputtered $Cs(CsI)_n{}^+$ clusters in two different time windows. Klots has developed the EEM[13-15] based on the statistical unimolecular reaction theory to describe the evaporation process of an ensemble of unstable clusters. The main underlying assumption is that the sequential evaporation of monomer units dominates the metastable decay of a collection of hot clusters and that each cluster has evaporated at least one monomer unit. Under this assumption, the evaporation of hot clusters is treated as a statistical unimolecular decay of a canonical ensemble at a temperature T through a transition state at which the canonical ensemble has a temperature $T^{\neq}$. Various experimental results are found to be in reasonable agreement with the model predictions,[15] e.g., the temperature[15] and the kinetic-energy release[5] of rare-gas and molecular clusters as well as the decay probabilities of rare-gas[6,7] and $Cu_n{}^+$ clusters.[11,14]

From the EEM, the following relationship can be derived for the average KER ($\bar{\epsilon}_t$) associated with the evaporation of CsI and $(CsI)_2$ molecules from $Cs(CsI)_n{}^+$ clusters:[15]

$$\bar{\epsilon}_t/\Delta = 3/2\gamma(k) - 3k_B/4c(2n+1)\,, \tag{1}$$

where Δ is the heat of evaporation, k_B is the Boltzmann constant, and $c(2n+1)$ is the heat capacity for a cluster of a given size n with c being the heat capacity per atom. The Gspann parameter $\gamma(k)$ is defined as[15,16]

$$\gamma(k) = \Delta/k_B\bar{T}(k)\,, \tag{2}$$

where $\bar{T}$ is the arithmetic average of T and $T^{\neq}$, and k denotes the microcanonical rate constant whose value can be determined from the experimental time window.[17] To obtain Eq. (1), we have used the relation $\bar{\epsilon}_t = \frac{3}{2}k_BT^{\neq}$ instead of $\bar{\epsilon}_t = 2k_BT^{\neq}$ which is used in the original treatment of Klots.[15] This modification is based on the Langevin collision model in which the relationship between $\bar{\epsilon}_t$ and $T^{\neq}$ is determined by the form of the long-range attractive potential[18] (i.e., the evaporation is adiabatic with no reverse activation energy). The former relationship is more appropriate for the present case since the KER distributions for the evaporation of both CsI and $(CsI)_2$ are found[19] to be fitted by the polarization potential rather than the hard-sphere potential assumed by Klots.[15]

The Gspann parameter $\gamma(\kappa)$ is predicted to be nearly independent of the cluster size and to depend weakly on time.[14,15] This is true if one assumes that Δ is independent of the cluster size (as in the continuum-based calculations[13,14]) since $\bar{T}$ is predicted to be constant for a given time window.[15] Furthermore, from the empirical results of Gspann[16] for the relation between the heat of sublimation and the measured temperatures of various rare-gas clusters and also from the Klots evaporative-ensemble-model calculations[14] for various clusters, it has also been suggested that the Gspann parameter is nearly independent of the constituent of the cluster, implying the scaling of the cluster temperature by its evaporation energy.

In several aspects, $Cs(CsI)_n{}^+$ clusters are good candidates to test more rigorously the predictions of the EEM shown in Eq. (1) and thus to investigate the evaporation dynamics of hot clusters. First, as implied by the observed cluster yield[20,21] and metastable decay probability[22] of sputtered $Cs(CsI)_n{}^+$ clusters, the evaporation energy (i.e., the stability of these clusters) shows a strong size dependence, which is not considered in the EEM described above. Moreover, the theoretical data for the evaporation energetics of these clusters, which agree well with the various experimental data (e.g., the cluster yield distribution,[20,21] the metastable decay probability,[22] and the branching ratio between the two main evaporation channels[22]), are available from the polarizable-ion model calculations.[23,24] Second, our results on the shape of the KER distribution[19] suggested that the loss of two CsI molecules involves a direct fission of a $(CsI)_2$ molecule with a near-zero dipole moment, rather than a sequential loss of two CsI molecules which is assumed in the EEM. Third, the observed correlation between the theoretical evaporation energies[23,24] and the measured branching ratios between the two main evaporation channels[22] [i.e., the evaporation of CsI and $(CsI)_2$ molecules] suggested that most likely both processes are adiabatic, in accordance with the EEM.

In this study, the average KER for evaporation of CsI and $(CsI)_2$ from sputtered $Cs(CsI)_n{}^+$ clusters is measured in two different time windows. The experimental conditions and instrumentation are described in more detail elsewhere.[19,22] $Cs(CsI)_n{}^+$ clusters are produced by sputtering a CsI bulk surface with 7-keV Xe atoms and analyzed by a VG Instruments Inc. Analytical ZAB-SE mass spectrometer (reverse geometry) at the acceleration voltage $V_a^0 = 8.1$ kV. Ion kinetic-energy spectra for the parent ion m_1^+ and the resulting metastable ion m_2^+ (corresponding to the loss of one or two CsI molecules) are taken in both the first and the second field-free region.[25] In the first field-free region, the magnetic sector field is tuned either to the mass of the parent ion m_1 or to the nominal mass of the metastable ion $m^* = m_2^2/m_1$, and the acceleration voltage is scanned. In the second field-free region, the electric sector voltage is scanned after tuning the magnetic sector field to the mass of the parent ions.

The average KER is determined from the widths of the ion kinetic-energy spectra, assuming that both the parent and metastable ion peaks are Gaussian.[19] For the Gaussian peak profiles, the corrected width W_t of the metastable peak due to kinetic-energy release ϵ_t is obtained using the following relation:[26]

$$W_t^2 = (\Delta V_m / V_m)^2 - (\Delta V_p / V_p)^2 . \tag{3}$$

The widths of ΔV_m and ΔV_p and the central positions V_m and V_p for the metastable and parent ion peaks, respectively, are measured in units of the acceleration voltage in the first field-free region and in units of the electric sector voltage in the second one. Kinetic-energy release ϵ_t associated with a unimolecular reaction $m_1^+ \rightarrow m_2^+ + m_3$ is related to the corrected width W_t by the following relation:[25]

$$\epsilon_t = (m_2/16 m_3) V_a^0 W^2 \text{ eV} . \tag{4}$$

For the first field-free region, the average KER is calculated from the widths of the parent and metastable peaks at 22.3% peak height[27] using Eqs. (3) and (4). For the second field-free region, the widths are measured at 50% peak height due to the very low signal level, and thus the average KER is approximated by multiplying[19] the KER value calculated from these widths by 2.16.

The experimental time windows estimated from the acceleration voltage and the dimension of the instrument are as follows. In the first field-free region, the starting time t_0 and the residence time Δt change from ~0.44 and ~24.6 μsec for the $n = 2$ cluster to ~1.2 and ~65.0 μsec for the $n = 17$ cluster, respectively. The second field-free region is estimated to be t_0 and Δt changing from ~44.6 and ~41.2 μsec for the $n = 4$ cluster to ~77.3 and ~71.3 μsec for the $n = 13$ cluster, respectively. These two time windows are expected to induce about tenfold change in the rate of evaporation.[17]

Figure 1 shows the size dependence of measured and predicted average KER for the first field-free region. The circles and crosses denote experimental $\bar{\epsilon}_t/\Delta$ values determined for the evaporation of CsI and $(CsI)_2$ mole-

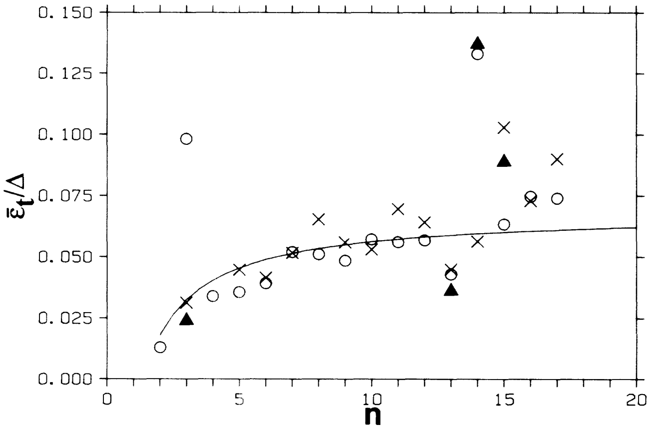

FIG. 1. Comparison of the measured and the predicted $\bar{\epsilon}_t/\Delta$ values in the first field-free region. The circles and the crosses denote experimental values for the evaporation of CsI and $(CsI)_2$ from clusters of different sizes, respectively. These values were reproducible within ±6%. The solid curve represents the predicted values of Eq. (1) with $\gamma(k) = 22$ and $c = 3k_B$. The filled triangles show the predicted values when the Gspann parameter in Eq. (1) is corrected to take into account the fact that the heat of evaporation involving clusters with magic numbers has a strong dependence on the cluster size.

cules, respectively. Δ values are obtained from the theoretical total energies of $Cs(CsI)_n{}^+$, CsI, and $(CsI)_2$ predicted from the polarizable-ion model.[23,24] The solid curve represents the predicted size dependence calculated from Eq. (1), assuming c equal to $3k_B$. The Gspann parameter $\gamma(k)$ is taken[14] to be 22 which corresponds to k equal to 10^5 sec^{-1} as is estimated[17] for the first field-free region.

As shown in Fig. 1, the predicted values agree well with most of the measured values. The sharp increase in the small cluster region and the asymptotic approach in the large cluster region are observed for both the measured and the predicted values and are in quantitative agreement for most reactions. The measured values, however, are smaller than the predicted ones for the reactions $n=13 \rightarrow 12$ and $13 \rightarrow 11$ and larger for the reactions $n=3 \rightarrow 2$, $14 \rightarrow 13$, and $15 \rightarrow 13$. Notice that except for one reaction all of these reactions involve the most stable cluster with the magic number $n=13$.

In Fig. 2, the experimental results obtained in the second field-free region are compared with the predicted values. The time window for the second field-free region corresponds[17] to k equal to $\sim 10^4$ sec^{-1}. According to the Klots calculation,[14] a tenfold change of k induces about 20% change in the Gspann parameter. Thus, $\gamma(k)$ is taken to be 27. Since the clusters examined in the second field-free region are expected to be colder than those in the first one, the high-frequency vibrations would become ineffective, resulting in a decrease[28] in c. Without having any specific information about the dependence of c on time, we have chosen two somewhat smaller values of c compared to the first field-free region. The solid and the dashed curves correspond to c equal to $2.5k_B$ and $1.5k_B$, respectively. As shown in Fig. 2, the measured and the predicted values are in reasonable agreement, except for the reactions $n=13 \rightarrow 12$ and $13 \rightarrow 11$ which show negative deviations from the predicted values as observed in the first field-free region.

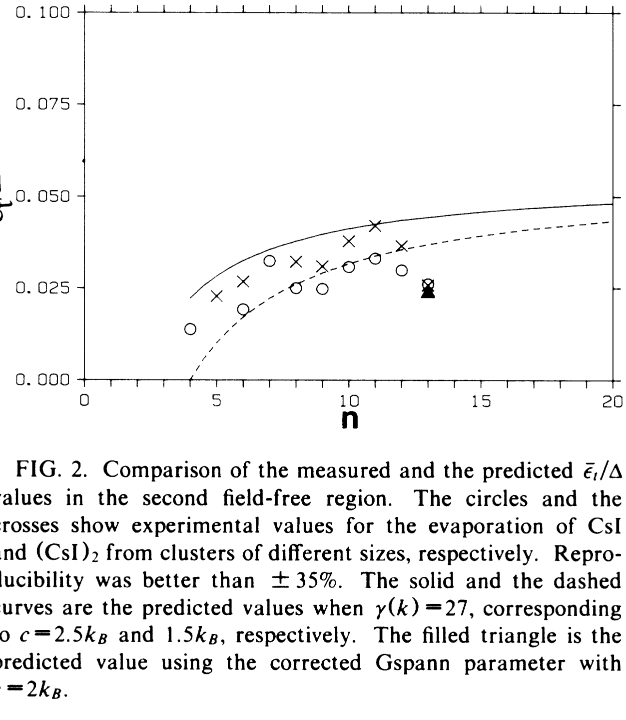

FIG. 2. Comparison of the measured and the predicted $\bar{\epsilon}_t/\Delta$ values in the second field-free region. The circles and the crosses show experimental values for the evaporation of CsI and $(CsI)_2$ from clusters of different sizes, respectively. Reproducibility was better than ± 35%. The solid and the dashed curves are the predicted values when $\gamma(k)=27$, corresponding to $c=2.5k_B$ and $1.5k_B$, respectively. The filled triangle is the predicted value using the corrected Gspann parameter with $c=2k_B$.

The strong deviations observed above are found for the evaporation channels involving the cluster with the magic number $n=13$, except for one case. The evaporation energies for these reactions are quite different from all the others and one expects that the assumption made in the EEM that Δ is a very weak function of the cluster size is not correct for these reactions. Below we correct this assumption. In each time window, $\bar{T}$ is predicted to be constant.[15] If we use an average Δ of 1.5 eV (taken from the other clusters), we can get $\bar{T}$ for each time window from the Gspann parameter used for each window (found to be ~ 790 K in the first and ~ 640 K in the second field-free region). Using the evaporation energies predicted from the polarizable-ion model[23,24] and the values of $\bar{T}$ estimated above, a new Gspann parameter is estimated according to Eq. (2) for the evaporation processes that showed deviations. New values of the Gspann parameters are found to be ~ 33 for the reactions $n=13 \rightarrow 12$ and $13 \rightarrow 11$, ~ 10 for $n=14 \rightarrow 13$, ~ 15 for $n=15 \rightarrow 13$, and ~ 25 for $n=3 \rightarrow 2$ in the first field-free region; but equal to ~ 40 for the reactions $n=13 \rightarrow 12$ and $13 \rightarrow 11$ in the second field-free region.

Using these new values of the Gspann parameter, Eq. (1) is used to calculate the values of $\bar{\epsilon}_t/\Delta$ for these processes. The results are given by the solid triangles shown in Figs. 1 and 2. Good agreement for the reactions $n=13 \rightarrow 12$, $13 \rightarrow 11$, $14 \rightarrow 13$, and $15 \rightarrow 13$ is obtained in both time windows. The new predicted value for the reaction $n=3 \rightarrow 2$ still deviates from the observed value. This can be interpreted as evidence for the existence of reverse activation energy[24] or for the involvement of either electronic predissociation or tunneling through a centrifugal barrier.[29]

From the above results, we reach the following conclusions: (a) The EEM[14,15] can be used to describe the evaporation from the strongly bound ionic clusters when the Gspann parameter is modified to take into account the dependence of Δ on the structure of clusters involving those with magic numbers; (b) the polarizable-ion model calculations[23,24] for the evaporation energetics are very accurate; and (c) the evaporation of CsI and $(CsI)_2$ molecules from the $Cs(CsI)_n{}^+$ clusters is statistical and adiabatic except perhaps for the evaporation of a CsI molecule from the $Cs(CsI)_3{}^+$ cluster. The latter two conclusions are consistent with our previous results.[19,22]

Our results imply several important aspects regarding the statistical evaporation process of hot clusters which is observed for $Cs(CsI)_n{}^+$ clusters in the present study and also for ionized alkali clusters recently by Bréchignac *et* *al.*[4] The scaling of the cluster temperature $\bar{T}$ by the evaporation energy Δ is not perfect when Δ is not a weak function of the cluster size. Nevertheless, for the evaporation processes not involving magic-number clusters, the average value of the Gspann parameter is found to be constant [e.g., $\gamma(k) \sim 22$ for $k = 10^5$ sec^{-1}] and is suggested to be transferrable to other media. This should be useful particularly for studying larger clusters.

The assumption in the EEM that the evaporation is dominated by the sequential loss of monomer units does not seem to be necessary in formulating the evaporation process of hot clusters. The evaporation of a CsI dimer from $\mathrm{Cs(CsI)}_n{}^+$ clusters is found to have comparable evaporation energies to the evaporation of a monomer.[19,22] The fact that the EEM is found to describe the evaporation of the dimer with equal success to that for the monomer suggests that the model could be modified to assume the requirement of the evaporation of at least one of the stable units that are dominant in the evaporation process (i.e., involving the least-energy evaporation channel). This then implies that the predictions of the EEM are more general and that agreement with the EEM does not provide evidence for the evaporation mechanism, i.e., sequential evaporation of monomers or fission of a larger stable unit.

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[a] Author to whom correspondence should be addressed.

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