

# Effect of a localized charge on the stability of Van der Waals clusters

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**Abstract.** The stability of anionic  $(SF_6)_N^-$  clusters (in the range of  $N < 23$ ), generated in a supersonic expansion ion source with electron impact ionization, was investigated by measuring their blackbody induced radiative dissociation (BIRD) rates in an electrostatic ion beam trap (EIBT) at room temperature. The lifetime traces of EIBT-stored clusters were subjected to “master equation analysis” and the activation energies,  $E_a$ , for the evaporation of a  $SF_6$  monomer were extracted. We find that the decay rates of  $(SF_6)_N^-$  anionic clusters are larger than those of cationic  $SF_5^+(SF_6)_{N-1}$  measured previously by the same method, and their corresponding activation energies to be smaller. These observations provide further insight into the effect of localized charge on cluster stability.

## 1 Introduction

What is the effect of a localized charge on the structure and stability of Van der Waals (VdW) clusters? A priori one would expect that the shape of the cluster is determined by the combination of the weak VdW forces between the neutral atoms or molecules in the cluster and the stronger monopole induced-dipole (MID) force between the charged unit and the neutral molecules. Defining the activation energy,  $E_a$ , as the energy needed to evaporate one molecule from the cluster, for neutral VdW clusters  $E_a$  roughly scales with the least number of neighbors of a molecule within the cluster. It is therefore expected that for small clusters  $E_a$  increases monotonically with cluster size until the completion of the first icosahedral shell at  $N = 13$ . Theoretical calculations by Beu et al. [1] of the stability of neutral  $(SF_6)_N$  clusters from  $N = 2$  to 10 confirm this intuition. Following the completion of the first icosahedral shell, one would expect the general trend of  $E_a$  to exhibit a slow variation with cluster size, accompanied with oscillations due to the completion of subshells.

This picture is expected to be very different for charged clusters, due to the influence of the stronger MID force. In this case addition of more units to the clusters has two competing effects – on the one hand an increase in the VdW interaction but also a decrease the MID interaction because of the repulsive induced-dipole induced-

dipole interactions between the neutrals, which effectively screen the central charge. We have previously measured  $E_a$  for the case of cationic  $SF_6$  based clusters and have shown that in this case these two effects seem to be of similar magnitude as  $E_a$  fluctuates around a value of  $\approx 280$  meV [2]. We now extend this work by a comparative study of cationic and anionic  $SF_6$  based clusters.

$SF_6$  is an attractive molecule for such studies since it has a symmetric octahedral structure, that can be roughly modeled as a sphere. Noble gas clusters present an even simpler model system. In charged noble gas clusters, however, the charge is de-localized over several atoms forming linear molecular ions which serve as the cluster core [3]. In charged  $SF_6$  clusters the charge is most likely localized on one cluster unit. This statement is more obvious for cationic  $SF_6$  clusters because upon electron loss the  $SF_6$  molecule also loses one or more fluorine atoms, resulting in  $(SF_M)^+(SF_6)_{N-1}$  clusters, with  $M = 1:5$ . Indeed Hiraoka et al. [4] found that the binding energy of the dimers  $SF_M^+(SF_6)$  is smaller than 10 kcal/mol (0.43 eV), indicating very little charge delocalization. Similarly, the binding energies of the anionic dimers were found to be even lower, less than 2.3 kcal/mole (0.1 eV) [5]. Recently, Luzon et al. provided further evidence [6] that also in anionic  $SF_6$  clusters the charge is localized, by showing that the UV absorption of a  $(SF_6)^-$  monomer is similar to that of  $(SF_6)_N^-$  clusters.

We have therefore set upon measuring the activation energies of anionic  $(SF_6)_N^-$  clusters using blackbody

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induced radiative dissociation (BIRD) and compare it with the activation energies of cationic  $SF_6$  clusters measured previously with the same method and apparatus [2].

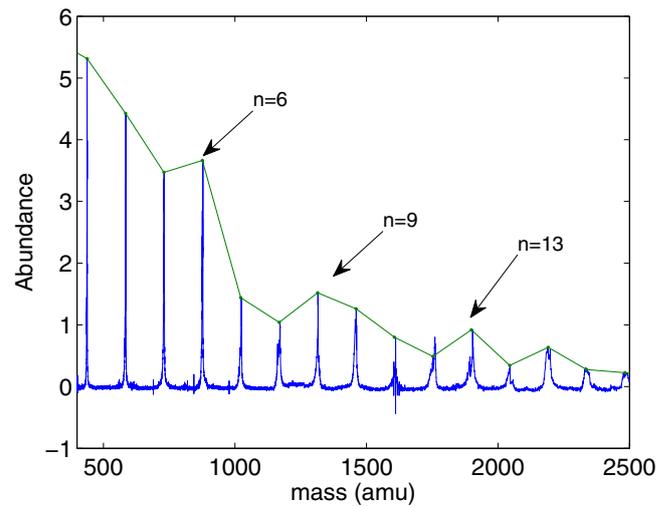
## 2 Experimental setup

The experimental setup has been described in detail in previous publications [2,7]. Briefly, the setup consists of a combination of an Even-Lavie supersonic expansion ion source [8] coupled with an electrostatic ion beam trap (EIBT) [9]. The supersonic expansion ion source is located on a 4.2 kV high voltage platform. A gas mixture of 1%  $SF_6$  in neon is expanded from a pressure of 200 PSI (14 bar) to around  $10^{-6}$  Torr, through a nozzle with an opening time of 20  $\mu$ s. At a distance of 3 mm from the nozzle, the gas jet is ionized by electron impact, and ions, after skimming, are accelerated from the high voltage platform to ground. The ions are then passed through a beam-cleaner to remove the strong neutral component and injected into the EIBT, where they are stored in a pendulating motion between two electrostatic mirrors. The EIBT is operated at room temperature and a pressure of  $\sim 5 \times 10^{-10}$  Torr.

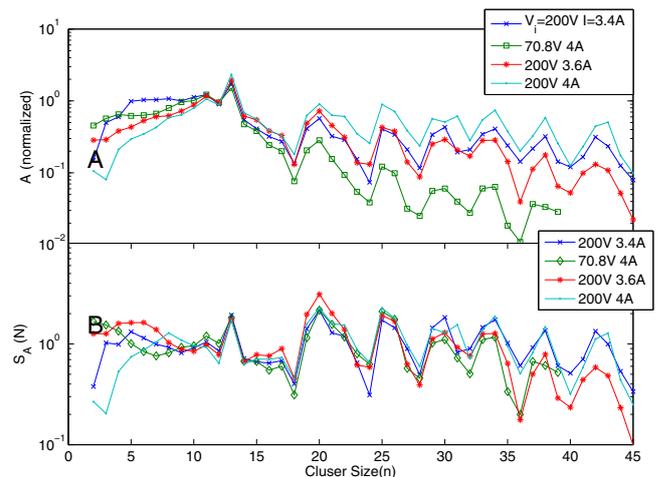
The electrostatic nature of the setup ensures that with the same voltage settings one can store any ion produced in the ion source, regardless of its mass. This makes the setup extremely suitable for scanning cluster series. Operating the EIBT in a self-bunching mode [10], and using pickup-mass spectrometry [11] one can determine the mass distribution of the ions. For a given delay between ion formation and closing of the EIBT entrance mirror, a portion of the ions produced in the source is stored and mass distribution is recorded. By scanning the injection time one can measure the full mass-spectrum. To record the lifetime of a particular cluster size, we use the pickup-lifetime technique [7] in which the ions are stored under normal trapping conditions [10], and the mass of interest is bunched with a small RF field. The pickup signal is measured and analyzed using a windowed Fourier transform.

## 3 Results – cluster abundances

Figure 1 shows a portion of the mass spectrum recorded using pickup mass spectrometry. As opposed to the case of cationic clusters where, under typical source conditions, several clusters of the form  $(SF_6^+)_M(SF_6)_{N-1}$  with  $M = 1:5$  as well as mixed water and  $SF_6$  clusters are seen [2], in the anionic case we observe only one cluster series of pure  $(SF_6)_N^-$  clusters. The abundance distribution,  $A(N)$ , – i.e. the amount of clusters of each size – appears similar to that measured by Ingólfson and Wodtke [12,13] who measured the abundance of neutral  $(SF_6)_N$  clusters using low energy electron attachment time-of-flight mass spectrometry. We define the abundance structure function,  $S_A$  as  $S_A = \frac{A(N)}{\tilde{A}(N)}$  where  $\tilde{A}(N)$  is a smooth fit to  $A(N)$ . Notably, while the distribution of cluster sizes varies considerably



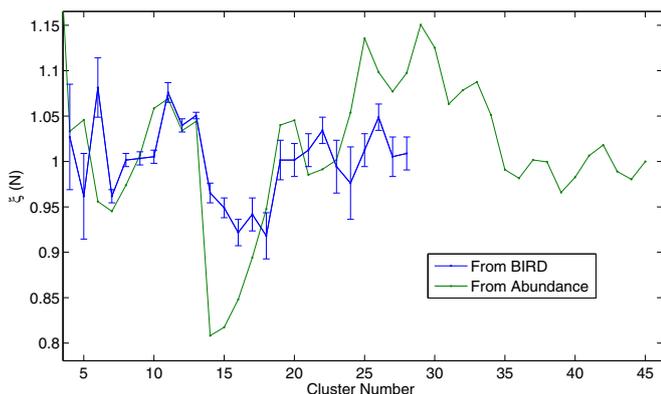
**Fig. 1.** Mass spectrum of anionic  $SF_6$  based clusters. As opposed to the case of cationic  $SF_6$  based clusters, only one prominent cluster series appears here corresponding to  $(SF_6)_N^-$ . The measurements were taken by operating the EIBT under self-bunching conditions, and scanning the delay time between the opening of the Even-Lavie valve and the closing of the trap.



**Fig. 2.** (A) Normalized abundance,  $A(N)$ , of  $SF_5^+(SF_6)_{N-1}$  clusters obtained under different ionization source conditions, including different filament currents, and different electron acceleration voltage  $V_i$ . (B) Abundance structure function.

depending on ion source conditions, the structure function does not, as seen in Figure 2.

The abundance of a cluster gives some indication of the cluster stability. In ion sources, such as the one used here, enhanced stability relative to evaporative precursors will give strongly enhanced abundances [14]. This can be modeled through the evaporative ensemble [15], which assumes that in the first step a smooth broad cluster distribution is formed which then decays statistically, with stable clusters decaying less and thus appearing more abundantly. The comparison with the precursor's stability is important: for example we have shown that although the cationic  $N = 13$  cluster is much more abundant than the  $N = 11$  cluster,



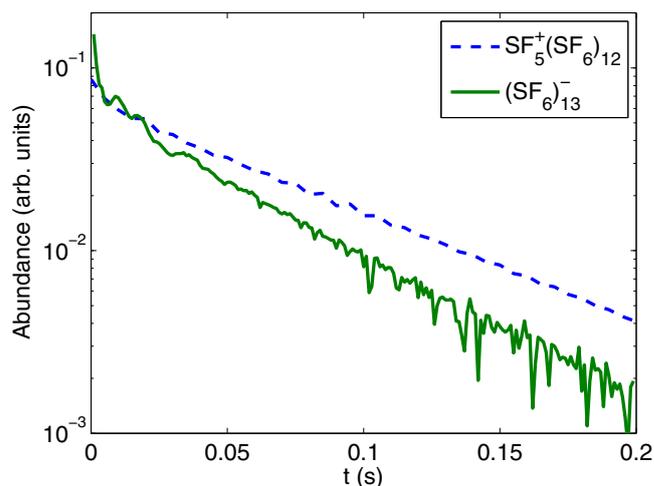
**Fig. 3.** A comparison between the fluctuations in activation energy,  $\xi(N)$ , derived from the abundance measurements shown in Figure 2A, and from BIRD measurements [2,7].

the  $N = 11$  cluster is actually more stable, and the high abundance of  $N = 13$  is a result of a ‘pile-up’ from the weakly bound  $N = 14$  till  $N = 17$  clusters decaying into  $N = 13$ . We define  $\xi(N)$  as the fluctuations in activation energies:  $\xi(N) = \Delta E_a / \bar{E}_a$  where  $\Delta E_a$  is the magnitude of oscillations of  $E_a$  relative to the general trend,  $\bar{E}_a$ . An analysis of cluster abundances which takes into account pile-up effects is explained in reference [14], along with a procedure for determining  $\xi(N)$  based on  $S(N)$ . Notably, as  $\xi(N)$  is an intrinsic property of the clusters, it should not be sensitive to ion source conditions, and indeed it isn’t since  $S(N)$  is not (see Fig. 2).

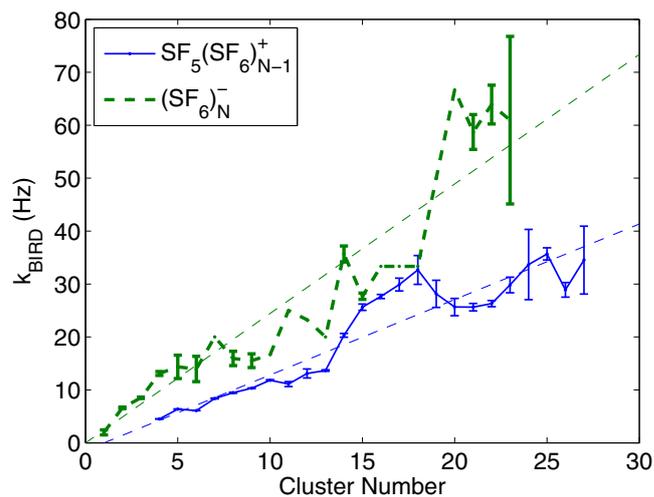
For ionic clusters an alternative activation energy determination can be made through BIRD measurements. This has the advantage that an absolute energy scale is introduced in the problem, to the extent that the photon absorption rate can be estimated. Figure 3 shows a comparison between  $\xi(N)$  determined from abundance measurements and  $\xi(N)$  determined from the activation energies measured with BIRD [2,7] (as explained below). The abundance measurements can be carried out for larger clusters whose abundance is too low for BIRD measurements, and the resulting  $E_a$  structure function does agree reasonably with the BIRD determined structure function. Even the larger activation energy of the  $N = 11$  cluster relative to that of the  $N = 13$  cluster is reproduced, although these kind of minute details depend strongly on the type of smooth fit to the abundances that is used.

## 4 Results – BIRD

Upon storing  $SF_6$  clusters in a room temperature trap, the major loss mechanism is dissociation due to heating by absorption of IR radiation followed by statistical dissociation. This rate of loss will be denoted here as the ‘BIRD rate’,  $k_{BIRD}$ . An example of the measured lifetimes is shown in Figure 4. For  $N > 6$  the lifetimes can be fitted nicely to a two exponent decay. The short time exponent may in practise be a mock-up of several decay curves and will not be interpreted here in detail. We identify the rate of the long exponent with  $k_{BIRD}$ . Notably,



**Fig. 4.** An example of lifetime measurements using the pickup-lifetime technique [7], for the case of the magic  $N = 13$  cluster. The lifetime of the anionic cluster (green) is notably shorter than that of its cationic counterpart (blue), data from [2].

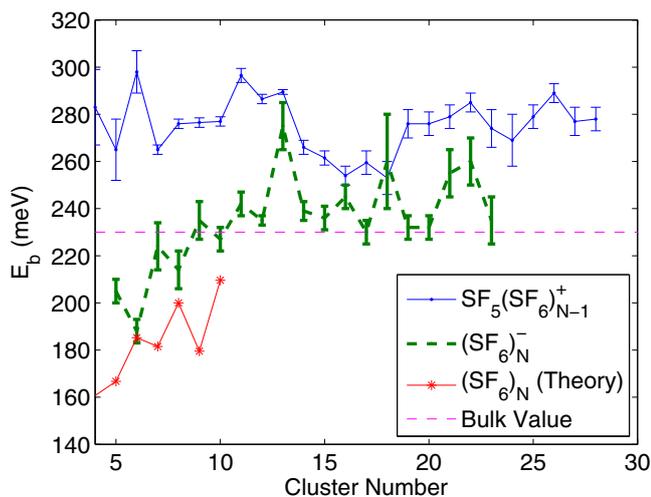


**Fig. 5.** Measured BIRD rates for the anionic  $(SF_6)_N^-$  (green) clusters and compared with those of the cationic  $SF_5^+(SF_6)_{N-1}^+$  clusters (blue) previously measured [2].

the long decay rate makes it essential to use an ion trap for this kind of study rather than single pass techniques.

Figure 5 shows the BIRD rates as a function of cluster size for both the anions and cations. Similar to BIRD measurements in water clusters [16] we expect a linear general trend of  $k_{BIRD}$  with cluster size because the rate of IR heating is linear with the number of IR absorbers, i.e. with the number of molecules within the cluster. On top of the general trend  $k_{BIRD}$  fluctuates with cluster size due to the fluctuations in the activation energies of the clusters. Notably, the BIRD rates of the anionic clusters are faster than those of their cationic counterparts indicating that the anionic clusters are less bound.

To extract the activation energies of the anionic clusters we have modeled the BIRD process of IR heating



**Fig. 6.** Activation energies,  $E_a$  which were determined from the BIRD rates for the anionic (green) cationic (blue)  $SF_6$  based clusters. Also shown are the activation energies for neutral  $(SF_6)_N$  clusters (red) which were calculated by Beu et al. [1].

and statistical fragmentation, as explained in detail in reference [2] Section B, except that we assume that the IR heating rate of the ionic core –  $(SF_6)^+$  is similar to that of a neutral  $SF_6$  molecule (whereas the heating rate of  $SF_5^+$  is slower). The resulting activation energies are shown in Figure 6. Also shown in the figure are  $E_a$  for the cationic  $SF_5^+(SF_6)_{N-1}$  clusters which were measured in reference [2], and the  $E_a$  values computed by Beu et al. [1] for neutral  $(SF_6)_N$  clusters.

## 5 Discussion and conclusions

In the present work the stability of  $(SF_6)_N^-$  clusters has been studied based on the decay of their population in electrostatic ion beam trap induced by dissociation due to absorption of blackbody radiation. We measure decay times in the range of 16–500 ms. The characteristic decay rates  $k_{BIRD}$  were found to scale linearly with the number of cluster units,  $N$ , and to be faster than the decay rates of cationic  $SF_5^+(SF_6)_{N-1}$  clusters [2]. Using master equation analysis we determine the activation energies for fragmentation of the clusters. We find that the activation energies of the anionic clusters  $(SF_6)_N^-$  increase with cluster size up until the completion of the first cluster shell at  $N = 13$ , and subsequently fluctuate around a constant value of  $\approx 240$  meV which is close to the bulk value of  $\approx 230$  meV. The values of  $E_a$  are found to lie in between the experimentally determined values of the cationic  $SF_5^+(SF_6)_{N-1}$  clusters, and theoretically calculated values for the neutral clusters. These observations can be explained by a model in which the negative charge in the anionic clusters is de-localized over the entire cluster. However, since photo-absorption measurements suggest that the charge is localized on one cluster unit [6], we conclude that the MID force is smaller for anionic clus-

ters than for their cationic counterparts. This is to be expected as the MID force scales inversely with the fourth power of the distance, and the  $SF_5^+$  is physically smaller than the  $SF_6^-$  anion. Defining  $d_{SS}$  as the distance between two  $S$  atoms in a dimer, Hiraoka et al. [4] calculated it to be  $\sim 4.5$  Å, in the  $SF_5^+(SF_6)$  dimer, and Beu et al. [1] calculated  $d_{SS}$  to be around 5 Å for the neutral dimer. Since the  $S - F$  distance in  $SF_6^-$  is  $\sim 10\%$  larger than that in  $SF_6$ , the  $d_{SS}$  in the  $(SF_6)_2^-$  dimer is expected to be  $>5.1$  Å, explaining part of the difference observed in Figure 6. Assuming that the MID force is in fact smaller for the anionic case, the rise in  $E_a$  for small cluster sizes in the anionic case can be explained by the gain in VdW interaction between neighboring neutral units to be larger than the decrease in MID potential energy due to screening. Of further interest is the fact that there is a significant difference in activation energies between anionic and cationic clusters even in the second shell region ( $N > 13$ ) where we expect the interaction with the ionic core to be less significant.

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