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**DOUBLY CHARGED CLUSTER OF 1,1-DIFLUOROETHYLENE;
OBSERVATION OF AN ANOMALOUS CRITICAL SIZE**

by

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Doubly Charged Clusters of 1,1-Difluoroethylene:

Observation of an Anomalous Critical Size

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We present in this communication the first observation of a critical size (n_2) of 9 for doubly charged clusters of 1,1-difluoroethylene. This is a highly unusual result in that it is the lowest critical size measured so far (the previous record was $n_2 = 21$ for SO_2). In addition, this is the first example of a doubly charged cluster where its critical size is not predicted by the Echt scaling law (that the critical size of the doubly charged cluster is proportional to the inverse of the product of T_c and $v^{1/3}$, where T_c is the critical temperature and v is the molecular volume). This suggests that the doubly charged CH_2CF_2 clusters are packed in a non-spherical arrangement (ie, chains, rings, or stacking of the ethylene planes).

A field of growing interest is the observation of doubly charged molecular cluster ions (M_n^{2+}) generated through electron impact ionization¹. Current work indicates that these cluster ions are composed of two separate cations generated via two sequential single ionization events of one incoming electron². These doubly charged cluster ions can then be detected through mass spectroscopy, if their size, n , is larger than n_2 , a critical value where the coulombic repulsion is offset by the cohesive forces of solvation. These critical sizes have been observed to range from $n_2 = 99$ (for $M = \text{N}_2$)³ to as small as $n_2 = 21$ (for $M = \text{SO}_2$)⁴. Echt⁵ has recently proposed, on the basis of a liquid drop model, that the appearance size of a doubly charged cluster should obey a scaling law ; $(n_2)(v^{1/3}) \propto 1/T_c$ where v is the molecular volume and T_c is the critical temperature. This simple relationship has done a remarkable job in describing critical sizes over a wide variety of systems⁵.

In this communication we report the first observation of a critical size of 9, for doubly charged clusters of 1,1-difluoroethylene. Not only is this critical size significantly smaller than any other system previously studied, it also represents the first significant deviance from the Echt scaling law.

The molecular beam apparatus has been described before⁶ and consists of a Campargue type beam source⁷ where the source chamber is pumped by a $1000\text{m}^3/\text{h}$ roots blower package. The cluster beam is generated by a neat, adiabatic expansion of CH_2CF_2 (Linde, purity > 99%) at 3 atm stagnation pressure (source chamber pressure = 50 mtorr) through a 250 μm nozzle which

is kept at 253K by a circulating chiller, as measured by a thermocouple within the nozzle.

Following collimation by a 5 mm diameter skimmer 20 mm from the nozzle, the cluster beam passes into a differentially pumped chamber ($p = 1 \times 10^{-5}$ torr). The cluster beam then travels through a second collimating skimmer before entering the differentially pumped mass spectrometer chamber ($p = 5 \times 10^{-7}$ torr). The collimating and mass spectrometer chambers are each pumped by a 360 l/s turbo pump and the two chambers are separated by an electromagnetic gate valve which also serves as a beam flag.

The skimmed beam enters into the mass spectrometer chamber in a direction collinear with the ion optic axis. The electron impact ionizer of the mass spectrometer is located 22 cm from the nozzle. The mass spectrometer is an Extrel C-50, (200 watt, 3/8" diameter rods, open design ionizer) which is capable of unit mass resolution up to $m/z = 1400$. Mass scale calibration was accomplished through the use of a standard (PFTBA) as well as an Ar cluster beam. The electron emission current and electron energy for these experiments were kept respectively at 1 mA and 100 eV. Ions formed in the source are mass filtered and detected by an off-axis channeltron. The amplified signal from the channeltron is then averaged for 200 scans by a LeCroy 9400 digital oscilloscope.

Figure 1 shows raw mass spectra of a sequence of CH_2CF_2 cluster peaks. At low n , these three peaks represent singly charged fragment cluster ions where the intensities of these peaks drop monotonically with increasing cluster size. However at $m = 288$ we see an abrupt increase in intensity of the fragment ion at m , as well as the appearance of a new peak at 288.5. These peaks we assign as due to doubly charged clusters with a critical size of $n_2 = 9$. That is, most of the intensity of the peak at 288 is due to $(\text{M}_9)^{2+}$ and the peak at 288.5 is solely due to $(\text{M}_9\text{H})^{2+}$.

As we go up in cluster size, to where the singly charged unimolecular fragments are negligible, we see that the doubly charged clusters are composed of a sequence of three peaks, each separated by 1/2 amu. These peaks are assigned as due to the parent peak p (M_n^{2+}) composed of two singly charged cations. The other two peaks correspond to either one (peak 1) or two (peak 2) of the cations reacting to form protonated cations. This protonation reaction is also observed within singly charged clusters, and on the basis of ICR data⁸, is assumed to first go by a unimolecular fragmentation



where the fragment ion can now react with a neutral within the cluster via the exoergic reaction (-156 kJ/mole)



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Recently it has been shown for doubly charged water clusters⁹ and ammonia clusters⁶, the same ion-molecule chemistry which occurs within a singly charged cluster can also occur at the separate cation centers, within a multiply charged cluster.

To further secure the identity of the doubly charged peaks we measured the appearance potential (Figure 2) and contrasted it with the appearance potentials of a variety of singly charged clusters. All singly charged clusters of CH_2CF_2 exhibited appearance potentials in the range of 15-17 eV while the doubly charged cluster has an appearance potential of ~ 28 eV. We interpret the result that $\text{AP}(\text{M}_9\text{H}^{2+}) \sim \text{AP}(\text{M}_5\text{H}^+) + \text{AP}(\text{M}_5^+)$ as evidence² that the peak at 288.5 amu is due to a doubly charged cluster which was formed via sequential electron collision processes.

It is interesting to note that the critical size predicted by the Eght relationship⁵ is approximately 25 to 30 (assuming $T_c = 303.2\text{K}$ and $v^{1/3} = 6.34\text{\AA}$)^{4,10}. This predicted critical size exceeds the experimental value reported herein by a factor of three. This apparent breakdown of the Eght relationship merits further discussion.

Eght's scaling law is derived from a liquid drop model which is based on two key assumptions: first, the charge within the cluster is uniformly distributed over the cluster surface; and second, molecules within the cluster assume an orientation which minimizes total surface energy. A doubly charged cluster is stable if the potential energy it gains by constraining two like charges within close proximity is offset by the potential energy it loses by maintaining its ensemble of molecules within the configuration of lowest surface area (i.e., a packed sphere). We feel that this model fails to predict the behavior of the CH_2CF_2 system because the second key assumption is in this case inappropriate; that is, the potential energy of the doubly charged cluster is not minimized by reducing surface area, and a packed sphere is therefore, not adopted. Rather, the CH_2CF_2 doubly charged cluster adopts some alternative geometry, perhaps a prolate rod shape, or a stacking of the olefinic planes. While the repulsive part of such an interaction is still dependent upon separation of two like charges, the attractive part is now due to the maximization of intermolecular forces within the cluster, and should dominate in the limit where n_2 is small. We are currently investigating other olefinic systems to determine the general applicability of this model.

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Figure Captions

Figure 1) Raw data of electron impact mass spectra of doubly charged 1,1-difluoroethylene cluster ions taken at 100 eV electron energy (note: scaling of ion intensity changes as a function of m). In the low mass range the spectrum is composed of unimolecular fragments (with loss of CFH being most prominent). In the high mass range the spectrum is dominated by doubly charged clusters which are assigned as follows: $\mathbf{p} = (M_n)^{2+}$, $\mathbf{1} = (M_nH)^{2+}$ and $\mathbf{2} = (M_nH_2)^{2+}$, where $M = CH_2CF_2$. The onset of the doubly charged clusters, is noted by the appearance of a ion peak at a half integer mass, between the singly charged fragment ions.

Figure 2) Ion current vs. uncorrected electron energy close to threshold for:
a) doubly charged cluster (M_9H^{++}) and singly charged clusters produced via;
b) unimolecular fragmentation (M_3CHF^+), c) simple ionization (M_5^+), and
d) ion-molecule reaction within a cluster (M_5H^+), where $M = CH_2CF_2$.

Ion Intensity (arb. units)



