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Dissociation channels of multiply charged van der Waals clusters

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We have analyzed the reaction channels for the delayed, unimolecular dissociation of multiply charged clusters made from CO_2 and C_2H_4. The smallest observable triply and quadruply charged clusters feature a large probability for fission into at least two charged fragments. The size distribution of heavy, doubly charged fragments from $(CO_2)_n{}^{3+}$, $109 \lesssim n \lesssim 123$, has been analyzed in detail and shows a strong peak at 92% of the precursor size. Delayed fission of doubly charged clusters, however, does not occur on the time scale of the experiment, which is $10 \lesssim t \lesssim 100$ μs with respect to ionization. A simple model, based on a liquid-drop approximation, is proposed. It allows us to calculate the height of the fission barrier for any given precursor ion and fission channel from readily available bulk data. Calculated critical sizes are presented for two-, three-, and fourfold charged clusters of 28 different van-der-Waals–bound or hydrogen-bonded compounds; they agree reasonably well with experimental values. The model also accounts for the strongly asymmetric fission reaction of triply charged CO_2 clusters, and for the strong size dependence of their fission rate.

I. INTRODUCTION

Recent investigations of dissociation phenomena in free atomic or molecular clusters have been among the most successful approaches in the field of experimental cluster research. Neutral and singly charged clusters are, in general, intrinsically stable, and dissociation would be endothermic.[1] Hence experimental studies have exploited collisions,[2] exothermic ion-molecular reactions,[3] or resonant[4] or nonresonant photon absorption,[5–7] in order to induce decomposition.

Alternatively, the internal excitation energy in the cluster ions may be large enough to cause unimolecular dissociation, if the particles are generated by ion bombardment of solid surfaces in vacuum,[8] or if neutral van der Waals clusters are ionized by electron impact,[9–11] electron attachment,[12] or multiphoton absorption.[13] Vertical ionization of a van der Waals cluster will be followed by structural reorganization and formation of a molecular ion, releasing a large amount of energy which may greatly exceed the binding energy of the individual constituents in the cluster.[14] As energy randomization will normally proceed within less than a nanosecond, the cluster ion is likely to fragment on this time scale, before mass analysis can be accomplished.[13–17] Evaporative cooling, however, will continue to occur microseconds or even milliseconds after ionization.[18] Measured in this time scale, the decay probability of cluster ions $A_n{}^+$ has been found to increase with increasing cluster size.[9–11]

Multiply charged van der Waals clusters, however, behave differently: For small size n, they are intrinsically unstable; dissociation into two charged fragments would be exothermic. An energy of 1 eV, for example, will be released if two elementary point charges of like sign are separated from an initial distance of 14.4 Å to infinity. Thus charged fragments from multiply charged clusters (or molecules) will be imparted a large recoil energy, and the term "Coulomb explosion" has been generally adopted for this phenomenon. For small clusters of light atoms, the process may be taken advantage of in order to determine the geometric structure.[19]

In general, however, the occurrence of Coulomb explosion in a beam of clusters is inferred from mass spectra: Multiply charged clusters $A_n{}^{z+}$ are observed only if their size exceeds a critical value n_c.[20] The concentration of multiply charged clusters rises steeply beyond n_c, and it may become as large as that of singly charged ions of the same size. The critical sizes have been found to be remarkably reproducible for van-der-Waals– and hydrogen-bonded clusters (metal clusters are not a subject of this paper), and some systematic trends in the dependence of $n_c(z)$ on z and on the properties of the material in question have emerged. These topics have been reviewed comprehensively.[21–24]

Direct information about the process of Coulomb explosion, however, has been obtained only recently.[25] We found that triply charged carbon dioxide clusters may undergo "spontaneous" Coulomb explosion on the time scale of 10–100 μs after their formation by electron impact (this process being conspicuously absent in *doubly* charged clusters). The delayed dissociation made possible an analysis of the size distribution of the doubly charged fission fragments; the very asymmetric distribution was found to be at variance with earlier conjectures[26,27] that the size-to-charge ratio of the fragments should be equal to that of their parents (so-called "symmetric" fission). A model, based on the liquid-drop approximation, has been developed that allows us to calculate, for a given parent cluster, the height of the fission barrier as a function of fragment size. Hence the model may be used to predict critical sizes and preferred fission channels for clusters which are not internally excited. In spite of many simplifications, the model can satisfactorily account for the experimental results.

In this paper, we shall present in detail the experimental approach and the results obtained for multiply charged clusters of carbon dioxide and ethylene. Reference will be made to related studies of ammonia and doubly charged carbon dioxide clusters, which have been performed with a different experimental setup.[28,29] The theoretical model will be discussed; its results concerning critical sizes and preferred fission channels will be presented for a variety of materials. Finally, we shall discuss to what extent internal excitation, which obviously drives the delayed, "spontaneous" Coulomb explosion of triply charged clusters, affects the observed critical sizes. A brief account of four findings has been given previously.[25]

II. EXPERIMENT

In brief, clusters of carbon dioxide and ethylene are generated in a supersonic jet. The collimated beam is crossed by a pulsed electron beam; the size-to-charge ratio of the cluster ions is analyzed in a time-of-flight mass spectrometer. Product ions, arising from metastable decay in the field-free drift tube, are identified by energy analysis with a retarding potential analyzer at the end of the drift tube.

A. Generation of clusters

Clusters are grown by homogeneous nucleation in a cw free jet. The gas (CO_2, purity 99.995%, C_2H_4, purity 99.95%) is thermalized in a stagnation chamber, before it expands through a nozzle of diameter 100 μm into vacuum. The stagnation pressure p_0 is of the order of 1000 mbar. In order to promote condensation, the stagnation temperature T_0 is kept close to the saturation limit, i.e., slightly above the boiling point. The jet is collimated beyond its freezing surface. It passes another collimator before it enters the main vacuum chamber. During the experiment, the background pressure in the expansion chamber stays well below 10^{-3} mbar, while the pressure in the main chamber does not exceed 5×10^{-7} mbar. Under these conditions, the contribution of collision-induced dissociation to the large fragment yields being observed in the present study is negligible.

B. Time-of-flight mass spectrometer

At a distance of 10 cm from the nozzle, the collimated cluster beam is intersected by a pulsed electron beam in the first gap of a two-gap ion lens. Under our experimental conditions, formation of multiply charged clusters by successive collisions with *two* primary electrons is negligible. The ion extraction field in the first gap is zero, while the electron beam is on, and ~100 V/cm after the end of the electron pulse. This field accelerates the positive ions from an initial potential $U_0 \sim 2$ kV through the second gap into the grounded drift tube. The ions travel *parallel* to the neutral jet, in order to avoid mass discrimination.

At the end of the drift tube (length ~110 cm), the ions pass an energy analyzer (see below) and hit the conversion dynode of a secondary electron multiplier. Its output, after proper amplification and discrimination, is fed to the stop-input of a home-built time-to-digital converter; its start-input is synchronized with the pulsed electron beam. Time-of-flight mass spectra are accumulated in a multichannel analyzer. Further details may be found in Refs. 12 and 30.

C. Analysis of unimolecular dissociation

The time-of-flight mass spectrometer has been operated as a tandem mass spectrometer in the following way: a retarding field energy analyzer, consisting of three parallel, closely spaced grids (70 lines per inch, 6 mm distance from each other), is mounted in front of the ion detector. The first and third grid are kept at ground potential, while a retarding potential U_b is applied to the central grid. Hence only those ions which fulfill the condition

$$E_{\text{kin},f} > e_0 z_f U_b \tag{1}$$

will be able to pass to the detector, where $E_{\text{kin},f}$ is the kinetic energy of the ion at this point and $e_0 z_f$ is its charge (the index f refers to "final" values, at the end of the drift tube, while i refers to the "initial" values, at the entrance to the drift tube). $E_{\text{kin},f}$ does, of course, reflect the history of the ion: the initial kinetic energy of an ion $A_{n_i}^{z_i+}$ is[31]

$$E_{\text{kin},i} = e_0 z_i U_0 \tag{2}$$

[the width of the kinetic energy distribution is $\sim z_i \times 50$ eV full width at half maximum (FWHM)]. If the ion decomposes in the drift tube,

$$A_{n_i}^{z_i+} \rightarrow A_{n_f}^{z_f+} + A_{n_i-n_f}^{(z_i-z_f)+} , \tag{3}$$

the kinetic energy of the fragment ion in the laboratory system will be, to a first approximation,[32,33]

$$E_{\text{kin},f} = E_{\text{kin},i} n_f / n_i \ . \tag{4}$$

Combining Eqs. (1), (2), and (4), we find that fragment ions have to fulfill the condition

$$(n_f/z_f)/(n_i/z_i) > U_b/U_0 \tag{5}$$

in order to pass the energy analyzer and be detected. The time of flight of the transmitted ions, however, will be nearly independent of U_b; it will change by 1% at most. Hence, from a series of mass spectra, recorded with different potentials U_b, one may evaluate the intensity and the identity of product ions for any value of n_i/z_i. The initial and final charge states of the ions have, of course, to be determined by some other means (see Sec. III B).

Let us finally consider the possible consequences of a finite recoil energy in more detail.[33] Assume that a metastable cluster decays into two fragments of size m_1 and m_2, releasing a total recoil energy E_{rec} in the center-of-mass system. $\tilde{v}_1$, the velocity of particle 1 in the center-of-mass system, is related to v_i by

$$\tilde{v}_1 = v_i \left[\frac{m_2}{m_1} \frac{E_{\mathrm{rec}}}{E_{\mathrm{kin},i}} \right]^{1/2} , \qquad (6)$$

where $E_{\mathrm{kin},i}$ and the velocity v_i refer, again, to the precursor ion in the laboratory system. For Coulomb explosion, $E_{\mathrm{rec}}/E_{\mathrm{kin},i} \sim 10^{-4}$, and $\tilde{v}_1/v_i$ may become considerably larger than 1% if $m_1 \ll m_2$. Given the inherently low time resolution of a time-of-flight (TOF) mass spectrometer, the corresponding change in the arrival time of the fragment ion might be still acceptable. The fragment ions will, however, recoil in a *random* direction in the center-of-mass system, and hence they may miss the detector. In our case, the resulting discrimination is small as long as $\tilde{v}_1/v_i \lesssim 1\%$.

III. EXPERIMENTAL RESULTS

A. Critical sizes of CO_2 and C_2H_4 clusters

The appearance of multiply charged CO_2 clusters has been studied in detail in a previous publication.[34] The main results are as follows: Doubly charged clusters are detected at half-integer values of n/z above a critical value $n_c/z=22$, provided that the electron energy exceeds ~40 eV. Above ~90 eV, triply charged clusters cause a stepwise increase in the ion intensity beyond $n_c/z \geq 36$. Another step at $n_c/z=54$, observed if the electron energy exceeds ~150 eV, is attributed to fourfold charged clusters. Hence the critical sizes $n_c(z)$ of $(CO_2)_n{}^{z+}$, $z=2,3,4$ are 45, 109, and 216, respectively. Recently, high-resolution mass spectra of CO_2 clusters, recorded with a reflection-type time-of-flight mass spectrometer, have confirmed the appearance of triply charged clusters beyond $n=108$.[35]

The critical sizes of multiply charged ethylene clusters are $n_c(2)=51$, $n_c(3)=108$, and $n_c(4)=192$.[36] The doubly charged clusters have been mass resolved for odd cluster size n, while the identity of clusters in higher charge states has been inferred from their appearance potential in unresolved mass spectra.

It should be kept in mind that mass spectrometers are generally blind to *prompt* dissociation. Rapid decomposition after ionization is likely to occur for van der Waals clusters, because formation of molecular ions and structural relaxation will release a large amount of excitation energy.[13–15] These events will, however, be undetectable if they proceed within much less than 5 μs. (This limiting value may be different for other types of mass spectrometers, or for cluster sizes different from those considered in this paper). The term precursor ion refers to those ions which are present at the *entrance* of the field-free drift tube. Likewise, the values of the critical sizes quoted above denote the size of the smallest multiply charged clusters at this point. The cluster ions being discussed in this paper reach this point approximately 5–10 μs after ionization.

B. Metastable decay of multiply charged CO_2 clusters

Figure 1 displays mass spectra of CO_2 clusters, produced by adiabatic expansion ($p_0=1200$ mbar, $T_0=203$ K), and ionized by electron impact at 150 eV. The top spectrum has been recorded in the conventional mode, without applying a barrier potential U_b to the energy analyzer. Hence all products from metastable decay in the drift tube contribute to the intensity of their precursor ions. The appearance of doubly charged clusters beyond $n_i/z_i=22$ is clearly visible; the second stepwise increase of the intensity, beyond $n_i/z_i=36$, is due to triply charged clusters.

In the two lower spectra, a repelling potential U_b has been applied to the energy analyzer. U_b exceeds U_0, the potential at the point of ion formation. Hence stable ions or any product ions from singly charged clusters will be rejected. Only fragment ions from Coulomb explosion of multiply charged clusters may pass to the detector, if they fulfill Eq. (5). The striking feature in Fig. 1 is the large yield of fragments, arising from decay of precursor ions in the narrow size range $36 \lesssim n_i/z_i \lesssim 41$. The disappearance of the characteristic hump in the bottom spectrum, recorded with $U_b/U_0=1.40$, proves that it is caused by *charged* fragments. The hump completely vanishes upon further increase of U_b. A weak signal of fragments, however, does not respond to U_b, most notably in the size range of small precursors, $n_i/z_i \lesssim 20$. This signal is obviously due to *neutral* products from metastable de-

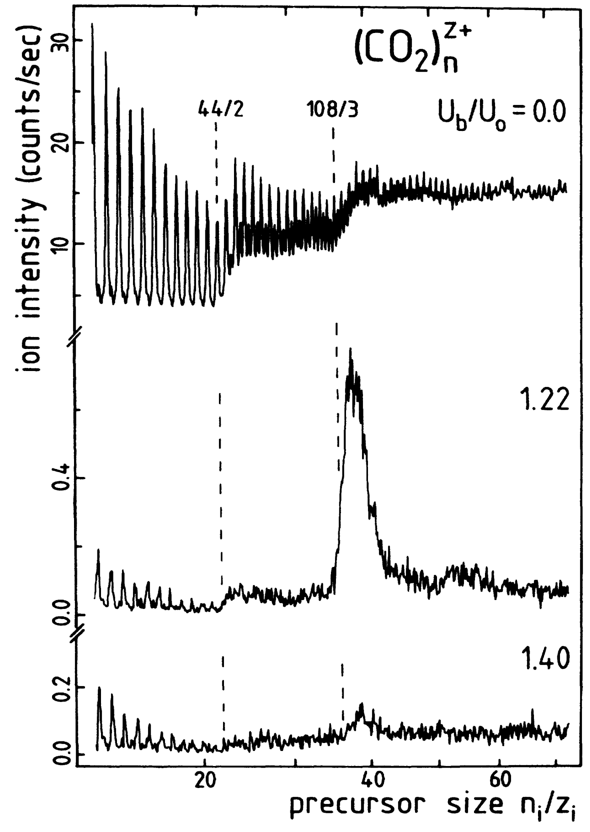

FIG. 1. Time-of-flight mass spectra of multiply charged CO_2 clusters. Top spectrum, conventional mode (no barrier potential applied); bottom spectra, barrier potential $U_b=1.21U_0$ and $1.40U_0$, respectively.

cay, which have a small but finite chance to generate a signal at the detector, which is mounted on axis.

What is the charge state of the *precursor ions* causing the hump? The coincidence of its rising edge with the critical size $n_c(3)$ of triply charged clusters already indicates that their charge state might be $z_i=3$. This is confirmed in Fig. 2, displaying the distribution of fragment ions for different electron energies E_e (the other parameters are $p_0=1000$ mbar, $T_0=203$ K, $U_b=1.31U_0$). The hump becomes clearly visible for $E_e \gtrsim 90$ eV. The same appearance energy has been determined for the observability of triply charged CO_2 clusters in conventional mass spectra.[34]

A further confirmation is obtained from the dependence of the fragment ion intensity on the stagnation pressure p_0, see Fig. 3 (recorded with $T_0=203$ K, $E_e=150$ eV, $U_b=1.31U_0$). The stagnation conditions in Fig. 3 (top) are such that cluster ions larger than $n_i \sim 100$ are not present. Hence no triply charged clusters are observed in the conventional spectra, while they are abound if p_0 is doubled.

In summary, the intensity of the hump in the spectra of metastable CO_2 clusters scales with the intensity of triply charged clusters in the conventional spectra. Hence the precursors are triply charged clusters of size $108 \lesssim n_i \lesssim 123$. They are found to undergo delayed Coulomb explosion in the drift tube with a high probability. The shape of the strong fragment signal in Fig. 1 (middle spectrum) may appear strange at first sight; but it is fully consistent with the stepwise onset of triply charged clusters in conventional spectra (Fig. 1, top): The intensity in any conventional spectrum displays the intensity of ions at the entrance to the drift tube, about 9 μs after ionization for $n/z=36$. The intensity of fragment ions, however, is the *product* of this quantity times the probability for decay before the energy analyzer (~ 76 μs). For the 108-mer, the first factor is zero, i.e., $\tau_{108} \ll 9$ μs, while the second factor becomes very small for the 123-mer, hence $\tau_{123} \gg 76$ μs. Thus the lifetimes of triply charged CO_2 clusters increase by at least two orders of magnitude between the 108-mer and the 123-mer.

The size distribution of the fragments may be extracted from the dependence of their intensity on the barrier potential. The intensity stays nearly constant up to $U_b=1.3$ but drops abruptly beyond this value. The relative *change* in intensity, $\Delta I/\Delta U_b$, has been plotted in Fig. 4. This curve reflects the intensity of fragment ions per voltage bin U_b or, according to Eq. (5), their size distribution, if n_i/z_i and z_f are known.

The identity of the precursors is known, but what is the charge state of the detected *fragment ions*? From Eq. (5) we know that z_f is less than $z_i=3$. The following two observations provide convincing evidence that the observed fragments are doubly charged.

(1) Unimolecular dissociation of triply charged *ammonia* clusters has been analyzed recently in a double focusing magnetic mass spectrometer at the University of Innsbruck.[29] The charge state of the fragments, $z_f=2$,

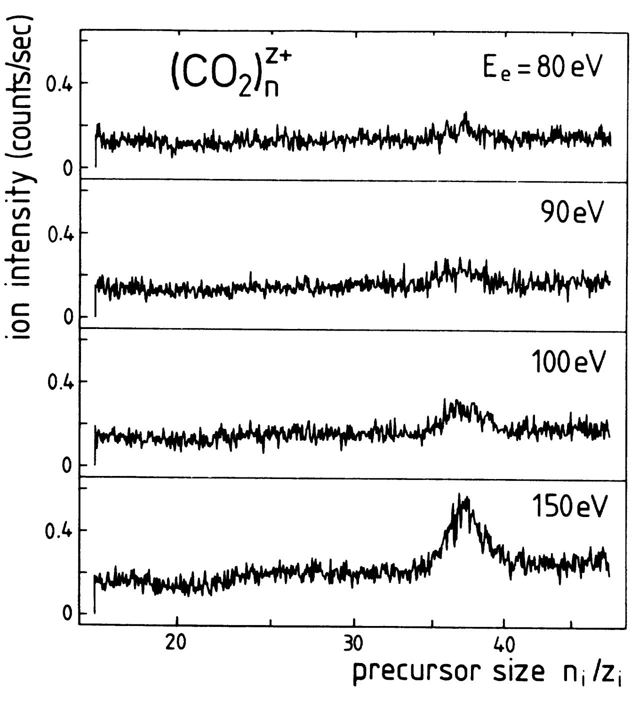

FIG. 2. Mass spectra of fragment ions from multiply charged CO_2 clusters (precursor size n_i/z_i), recorded with $U_b=1.31U_0$, for different energies E_e of the ionizing electrons.

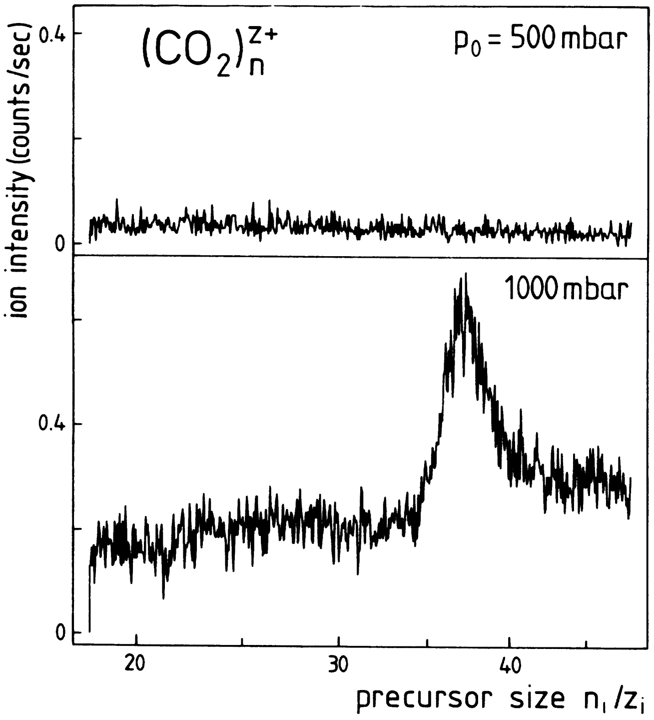

FIG. 3. Mass spectra of fragment ions from multiply charged CO_2 clusters, recorded with $U_b=1.31U_0$, for different stagnation pressures p_0.

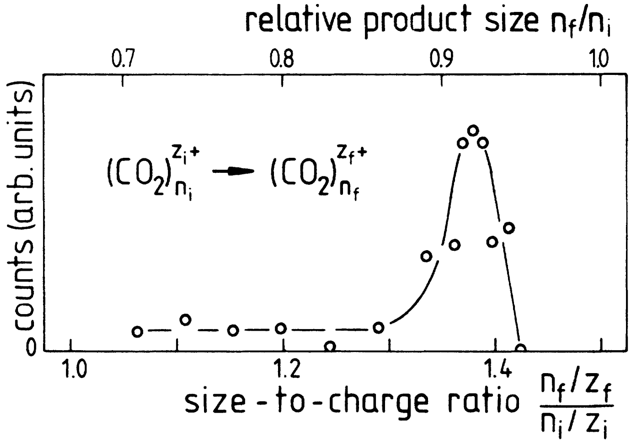

FIG. 4. Size distribution of doubly charged fragments, arising from delayed fission of triply charged CO_2 clusters (precursor size $108 \lesssim n_i \lesssim 120$. The size ratio plotted on the abscissa represents the experimental parameter U_b/U_0.

could be determined unambiguously from the multiplicity of the peaks in the spectrum of product ions.

(2) If Coulomb explosion occurs, a *pair* of ions will be generated. The peak in the size distribution of fragment ions in Fig. 4 occurs at $n_f/z_f = 0.46 n_i$, hence either of the following two fission channels would be compatible with Fig. 4:

$$A_n{}^{3+} \rightarrow A_{0.92n}{}^{2+} + A_{0.08n}{}^{+} , \tag{7}$$

$$A_n{}^{3+} \rightarrow A_{0.46n}{}^{+} + A_{0.54n}{}^{2+} . \tag{8}$$

(The fragment ions may be somewhat smaller, if fission is accompanied by ejection of neutral monomers.) Thus one might distinguish experimentally between these alternative channels if one could determine the size-to-charge ratio of the second fragment ion. We have searched very carefully for these product ions, by varying U_b across the appropriate values. We have not found any statistically significant change in ion intensity in the relevant range of the time-of-flight mass spectra. This negative result may be reconciled with reaction (7), but not with (8): The sensitivity of our experimental method for detection of product ions is reduced considerably if the repelling potential U_b in the analyzer drops below U_0, because in this case *all stable* ions pass to the detector. Nevertheless, we would have been able to identify the expected change in intensity, if it would have been as large as that of the hump displayed in Fig. 1. The absence of a statistically significant change in the appropriate ranges of U_b tells us that some sort of discrimination against the expected fragment ions has occurred in our apparatus. Strong discrimination is, indeed, expected to occur for small fragment ions ejected in Coulomb explosion, because their recoil energy will increase the divergence of the ion beam in the drift tube.

Calculating the recoil energy from Eq. (14) (see below), we estimate from Eq. (6) that the "missing fragment ion" would have changed its velocity by $\tilde{v}_1/v_i \sim 5.7\%$ if reaction (7) applies, or by 1.4% if reaction (8) applies. Hence reaction (7) does indeed predict a very strong suppression of the light fragment ion, while in case of reaction (8), *both* fragments would suffer from a small, but nearly identical degree of discrimination. Summarizing, reaction (7) represents the dominant fission channel: The observed fragments are doubly charged; their size is 92% of the precursor size, with a surprisingly small scatter of only ±2%.

Let us finally present the decomposition channels of *doubly* charged CO_2 clusters. In this case, we do *not* observed fragment ions in the range $U_b > U_0$; cf. Figs. 1–3. A pronounced dependence of the intensity of the mass peaks which are associated with doubly charged precursors does, however, occur slightly below U_0. This is shown in Fig. 5 (recorded with $p_0 = 1000$ mbar, $T_0 = 203$ K, $E_e = 100$ eV). From a comparison of these spectra, recorded with $U_b = 0.93\ U_0$ (top) and $U_b = U_0$ (bottom), we can conclude that dissociation of doubly charged CO_2 clusters in the drift tube is very likely, the size-to-charge ratio of the fragments being slightly less than that of their precursors. The results of a detailed experimental analysis, performed with help of a double-focusing mass spectrometer, have been reported elsewhere.[28] They may be summarized as follows: $(CO_2)_n{}^{2+}$, $n \geq 44$, features a very high probability to lose a neutral monomer by meta-

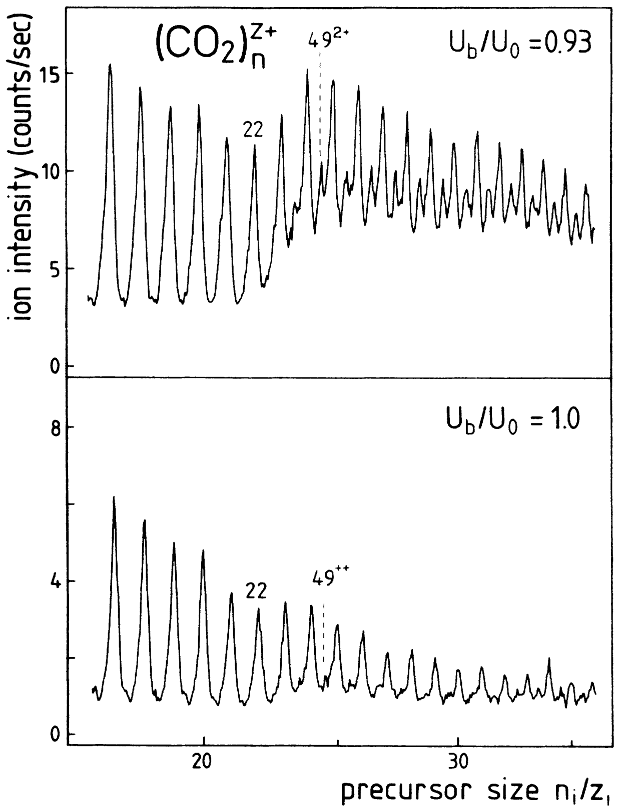

FIG. 5. Mass spectra of singly and doubly charged CO_2 clusters $[n_c(2) = 44]$ for two different barrier potentials U_b, demonstrating the high probability for delayed monomer evaporation from doubly charged clusters.

stable decay. Loss of two monomers is approximately a factor of 10 less likely. *Singly* charged fragment ions from $(CO_2)_n{}^{2+}$, however, are not observed.

C. Metastable decay of multiply charged C_2H_4 clusters

Figure 6 displays a series of mass spectra of ethylene clusters, recorded with different barrier potentials. The experimental conditions ($p_0 = 1500$ mbar, $T_0 = 193$ K, $E_e = 150$ eV) were optimized for the production of triply charged clusters. The upper, conventional spectrum features stepwise increases in the intensity beyond $n_i/z_i = 25$, 36, and ~ 48, indicating the presence of doubly, triply, and quadruply charged clusters, respectively. The other spectra, recorded with $U_b > U_0$, reveal a dominant yield of fragments from Coulomb explosion of triply charged clusters in the size range $108 \lesssim n_i \lesssim 123$, peaking at $n_i \sim 114$. From the dependence of the fragment yield on U_b, we find that the size of fragments is $0.72 \lesssim n_f/n_i \lesssim 0.81$, where we have assumed $z_f = 2$, in analogy to the results obtained for CO_2 and NH_3 clusters. Our measurements for ethylene are not as comprehensive as for carbon dioxide, but it is obvious that the size distribution of fragment ions from $(C_2H_4)_n{}^{3+}$ is not as asymmetric as for CO_2.

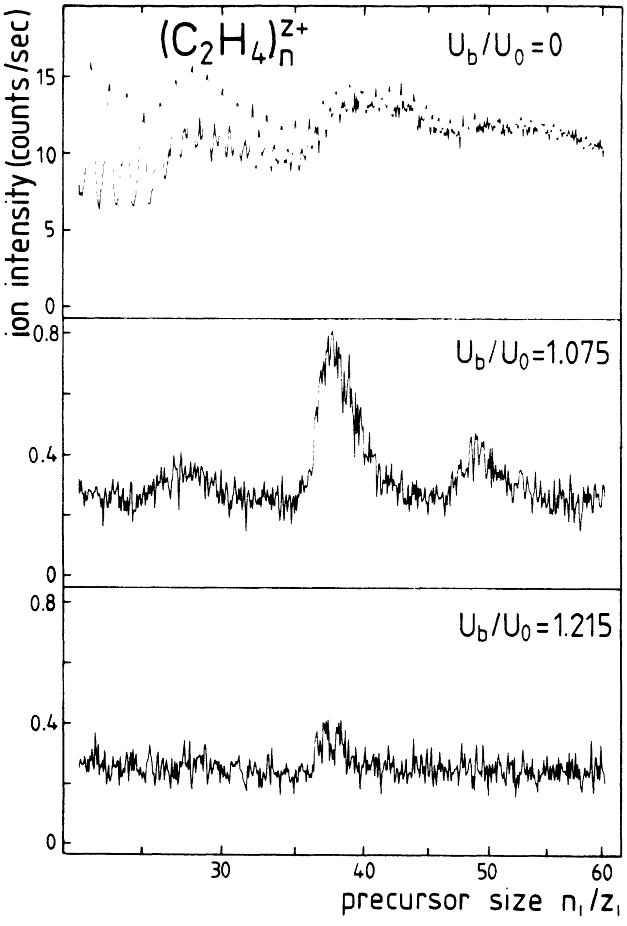

FIG. 6. Mass spectra of multiply charged ethylene clusters. Top spectrum, conventional mode; bottom spectra, barrier potential $U_b = 1.025 U_0$ and $1.215 U_0$, respectively.

The mass spectrum in Fig. 6, recorded with $U_b = 1.075$ U_0, also reveals an enhanced intensity beyond $n_i/z_i \sim 48$, obviously arising from delayed Coulomb explosion of quadruply charged clusters. We have not been able, however, to analyze these fragments quantitatively.

IV. LIQUID-DROP MODEL

A. Model

We have developed a model, based on the liquid-drop approximation, in order to calculate the critical sizes as well as the fission channels for Coulomb explosion of van der Waals clusters. The total energy E_t of a multiply charged cluster is written as the sum of a volume term, a surface term, and a Coulomb term,

$$E_t = E_v + E_s + E_c \ . \tag{9}$$

E_v is negative and proportional to the cluster size n. Following the approach of Briant and Burton,[37] which was based on the Tolman expression for the surface energy,[38] E_s can be expressed as

$$E_s = (An^{2/3} + Bn^{1/3}) V_{\rm LJ} \ , \tag{10}$$

where $V_{\rm LJ}$ is the Lennard-Jones energy parameter and $A = 10.3$, $B = -2.7$. The Coulomb energy of the cluster is estimated by assuming that z elementary charges are distributed uniformly within the cluster. Taking the cluster as a countinuous medium with dielectric constant ϵ, one obtains[39]

$$E_c = \frac{\epsilon - 1}{2\epsilon}\frac{z^2 e_0^2}{r} + \frac{3z(z-1)e_0^2}{5\epsilon r} \tag{11}$$

using Gaussian cgs units. The cluster radius r is calculated from

$$r = \left[\frac{3n}{4\pi}\right]^{1/3} \sigma_{\rm LJ} \tag{12}$$

where $\sigma_{\rm LJ}$ is the Lennard-Jones length parameter.

For a given cluster and a given dissociation channel, the difference in total energies before and after fission tells us whether the cluster is intrinsically stable. Even for an exothermic reaction, however, the cluster might have to surpass an energy barrier $E_{\rm bar}$. It is possible to estimate $E_{\rm bar}$ in a simple way from

$$\begin{aligned} E_{\rm bar} = & -E_t(n_i, z_i) + E_t(n_f, z_f) \\ & + E_t(n_i - n_f, z_i - z_f) + E_{\rm rec} \ , \end{aligned} \tag{13}$$

where $E_{\rm rec}$ is the kinetic energy imparted to the recoiling fragments via the Coulomb repulsion after fission and the indices i and f refer to values before and after fission, respectively. $E_{\rm rec}$ may be calculated from the work being needed to bring the spherical fragments from infinity into contact with each other, i.e.,

$$E_{\rm rec} = \frac{z_f(z_i - z_f)e_0^2}{r(n_f) + r(n_i - n_f)} \ . \tag{14}$$

We can now determine the critical size $n_c(z_i)$ from the condition that E_{bar} be zero for the most favorable fission channel, if V_{LJ}, σ_{LJ}, and ϵ are known. These quantities are obtained as follows: For the rare gases, σ_{LJ} and V_{LJ} have been taken from standard values obtained by fitting of second virial coefficients.[40] For the other van der Waals molecules we have estimated σ_{LJ} and V_{LJ} from the approximate relations based on the law of corresponding states:[40]

$$V_{\text{LJ}}=0.77T_c \;, \tag{15a}$$

$$\sigma_{\text{LJ}}=2.44(T_c/p_c)^{1/3} \;, \tag{15b}$$

where T_c and p_c are the critical temperature and pressure (in atm), respectively (numerical values can be found in Ref. 41), V_{LJ} and σ_{LJ} are in K and Å, respectively. For CO_2 the estimated Lennard-Jones parameters give critical sizes which are too large. We obtain better agreement with experiment for $V_{\text{LJ}}=290$ K, this value is close to the value required to fit the bulk sublimation energy of CO_2.

The values of the dielectric constant ϵ have been taken from standard tables.[41–43] Most of these data refer to the pure condensed state at approximately the boiling point. When experimental data were not available, ϵ was calculated from the molecular polarizability α, and the density ρ of the liquid at the boiling point, through the Clausius-Mossotti formula.[40] This procedure neglects, of course, the contribution from the permanent dipole moment μ to the dielectric screening. Table I lists experimental values for ϵ, ρ, α (taken from Ref. 44), and μ (taken from Refs. 41 and 45), together with calculated values of ϵ (denoted ϵ_{CM}). In some cases we had to estimate α from the well-known additivity rule for bond polarizabilities;[46] these values are given in parentheses.

B. Results

We shall start this section with a detailed presentation of results for carbon dioxide clusters, followed by a compilation of results for other compounds. For a given cluster size and charge state, our model allows us to calculate

TABLE I. Experimental (ϵ) and calculated values (ϵ_{CM}) of the dielectric constant. ρ denotes the density of the condensed phase, α the molecular polarizability, and μ the permanent dipole moment of the molecules. For references see text. Numbers in parentheses are estimated values of α obtained from the well-known additivity rule for bond polarizabilities.

Compound	ϵ	ϵ_{CM}	ρ (g/cm^3)	α (Å^3)	μ (Debye)
He	1.05	1.05	0.125	0.206	0
Ne		1.19	1.207	0.397	0
Ar	1.53	1.51	1.395	1.66	0
Kr	1.78	1.67	2.413	2.52	0
Xe	2.00	1.95	3.056	4.11	0
H_2	1.23	1.23	0.0708	0.819	0
N_2	1.45	1.44	0.809	1.77	0
O_2	1.51	1.50	1.141	1.60	0
CO		1.49	0.789	1.98	0.12
NO	2.00	1.70	1.300	1.74	0.15
CO_2	1.60	1.65	1.178	2.63	0
N_2O	1.97	1.80	1.223	3.00	0.17
H_2O	78.54	1.74	0.958	1.48	1.85
H_2S	9.26	2.03	0.915	3.78	0.97
NH_3	25.00	1.87	0.682	2.22	1.47
SF_6		1.52	1.910	4.47	0
CH_4	1.70	1.63	0.423	2.60	0
CHF_3		1.51	1.439	2.80	1.65
CF_3Cl		1.63	1.526	(4.74)	0.50
C_2H_4		1.82	0.568	4.22	0
$C_2H_4F_2$[a]		1.66	1.011	(4.66)	2.27
C_2H_6O[b]	5.02	1.79	0.735	5.16	1.30
C_3H_6[c]	1.87	1.79	0.614	5.64	0.37
c-C_4H_8[d]		1.92	0.641	(8.14)	0.33
t-C_4H_8[e]		1.89	0.626	(8.14)	0
n-C_4H_{10}[f]		1.84	0.601	(8.42)	0
C_5H_{12}[g]	1.84	1.84	0.603	10.36	0
C_6H_6[h]	2.28	2.30	0.899	10.4	0

[a] 1,1-Difluoroethane.
[b] Dimethylether.
[c] Propene.
[d] *cis*-2-Butene.
[e] *trans*-2-Butene.
[f] *n*-Butane.
[g] 2,2-Dimethylpropane.
[h] Benzene.

TABLE II. Calculated critical sizes, $n_c(z)$, of doubly, triply, and quadruply charged van der Waals clusters (experimental values are given in parentheses). $n_c(z)$ is calculated from the Lennard-Jones parameters, V_{LJ} and σ_{LJ}, and the dielectric constant ϵ. ϵ values in parentheses have been obtained from the Clausius-Mossotti relation (cf. Table II). For references see text.

Compound	ϵ	V_{LJ} (K)	σ_{LJ} (Å)	$n_c(2)$	$n_c(3)$	$n_c(4)$
He	1.05	6.0	2.63	17092	76895	198966
Ne	(1.19)	35.6	2.75	868	2950	6424
Ar	1.53	119.8	3.41	122 (91)	333 (226)	648
Kr	1.78	171.0	3.60	71 (71)	177 (156)	331
Xe	2.00	221.0	4.10	46 (51)	107 (114)	196 (208)
H_2	1.23	25.6	3.35	863	2824	6014
N_2	1.45	97.2	3.79	145 (99)	411 (215)	814
O_2	1.51	119.2	3.55	120 (92)	330	646
CO	(1.49)	102.6	3.83	131 (98)	364	715
NO	2.00	138.8	3.44	83	195	358
CO_2	1.60	234.2	3.93	54 (45)	143 (109)	274 (216)
CO_2	1.60	290.0	4.10	43 (45)	112 (109)	216 (216)
N_2O	1.97	238.5	3.97	44 (51)	104 (105)	191 (184)
H_2O	78.54	498.4	3.50	10 (35)	20	32
H_2O	(1.74)	498.4	3.50	28 (35)	69	130
H_2S	9.26	287.7	3.94	19 (39)	38 (84)	63
H_2S	(2.03)	287.7	3.94	37 (39)	85 (84)	156
NH_3	25.00	312.4	3.74	15 (51)	30 (121)	50
NH_3	(1.87)	312.4	3.74	38 (51)	91 (121)	169
SF_6	(1.52)	245.4	4.99	44 (39)	121	234
CH_4	1.70	147.1	3.93	78	200	379
CHF_3	(1.51)	230.3	4.52	52 (41)	142 (90)	277 (168)
CF_3Cl	(1.63)	232.6	4.86	44 (43)	114 (87)	218
C_2H_4	(1.82)	218.0	4.33	47 (51)	115 (108)	214 (192)
$C_2H_4F_2$	(1.66)	297.8	4.88	34 (33)	88 (69)	167
C_2H_6O	5.02	308.2	4.80	18 (35)	36 (72)	61
C_2H_6O	(1.79)	308.2	4.80	31 (35)	77 (72)	145
C_3H_6	1.87	281.1	4.85	33 (39)	79 (78)	146
c-C_4H_8	(1.92)	333.6	5.37	25 (31)	60 (63)	109
t-C_4H_8	(1.89)	329.7	5.31	26 (31)	62 (66)	114
n-C_4H_{10}	(1.84)	327.4	5.48	26 (31)	63 (78)	116
C_5H_{12}	1.84	334.0	5.84	24 (30)	58	108
C_6H_6	2.28	432.8	5.51	18 (23)	38 (52)	69 (92)

the height of the fission barrier E_{bar} for all fission channels. A negative value for E_{bar} indicates that there is no barrier against fission. Figure 7 displays E_{bar} for fission of doubly charged (top) and triply charged CO_2 clusters (bottom). It is evident from these curves that the doubly charged 40-mer would undergo spontaneous fission even in the absence of thermal excitation, while the 50-mer would not. Hence the critical size of $(CO_2)_n{}^{2+}$ is $40 < n_c < 50$. Furthermore, we find that the energy barrier against fission of the 50-mer is approximately the same for all fission channels except the most asymmetric ones.

Our model further predicts that the size of the most favorable fission fragment (i.e., the fragment being associated with the lowest fission barrier for a given n_i) will depend on the precursor size. This is illustrated in Fig. 8, displaying the relative size of the preferred fragment from doubly charged CO_2 clusters versus n_i. The most favorable fission channel of small, even-sized clusters, $n_i \leq 30$, would be the symmetric one. For larger clusters, fission would become more and more asymmetric. Experimental verification of these predictions, however, would be difficult. For small precursor sizes, *many* fission channels will be energetically accessible, and energetics may not play the dominant role. For $n_i \sim 40-50$, metastable fission will, in principle, be feasible, but we have not obtained any experimental evidence for the occurrence of this process. Finally, for $n_i \gtrsim 50$, one would have to *induce* fission in order to determine the size distribution of fragments.

Concerning triply charged CO_2 clusters, Fig. 7 predicts a critical size $n_c(3) \sim 110$ and a strong preference for very asymmetric fission into a heavy, doubly charged ion ($\sim 95\%$ of parent mass) and a small singly charged ion. This agrees well with the experimentally determined critical size and size distribution.

From the preceding discussion it is evident that, in general, the critical size of a multiply charged cluster is obtained by calculating E^0_{bar}, the *minimum* of the fission barrier, as a function of precursor size. This is illustrated in Fig. 9 for doubly and triply charged CO_2 clusters. Hence we find $n_c(2)=43$ and $n_c(3)=112$. These numbers specify the smallest cluster in the corresponding charge state that will not undergo spontaneous fission. Strictly speaking, these values should be lower bounds, because our model neglects the excitation energy in the ion which may drive the cluster over a finite fission barrier. This point will be taken up later.

Table II presents calculated critical sizes for 28 weakly bound compounds, including all cases where $n_c(2)$ is known from experiment. The calculations are based on the Lennard-Jones parameters V_{LJ} and σ_{LJ}, and on the dielectric constant ϵ. We have used experimental values of ϵ, wherever possible. Those values which have been calculated from the Clausius-Mossotti relation are marked by brackets. For molecules having a large permanent dipole moment (cf. Table I), ϵ and ϵ_{cm} differ significantly; therefore we have used both quantities for calculating $n_c(z)$.

Experimental values, where known, are included in Table II for comparison. Most of the experimental data have been obtained in our laboratory,[20–22,34–36,47] except for Ar,[48] O_2 and N_2,[49] H_2O,[50] NH_3,[29,50] and benzene.[51,52] The experimental values specify the smallest observable cluster of charge state z. In many cases, however, individual cluster sizes are not resolved in the mass spectra (especially for $z=3$ and 4), and the experimental error of $n_c(z)$ may be as large as $\sim 5\%$.

Table II indicates good agreement between calculated and experimental critical sizes in most cases, given the simplicity of the model and the fact that no parameters were adjusted to fit the data. Concerning quadruply charged clusters, fission may either yield two doubly charged ions, or a singly plus a triply charged ion. The latter reaction features the lower energy barrier, hence the critical sizes given in Table II refer to this channel.

For very weakly bound compounds (Ar, N_2, O_2, and CO), however, our model tends to overestimate the critical size of doubly charged clusters; the agreement is even worse for triply charged clusters. Another serious

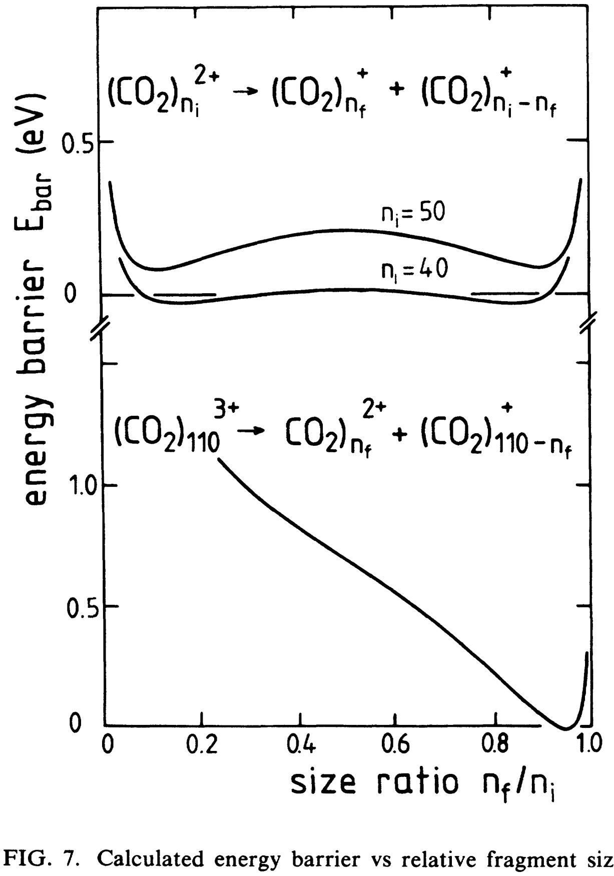

FIG. 7. Calculated energy barrier vs relative fragment size n_f/n_i for fission of doubly charged (size $n_i=40$ and 50, respectively) and triply charged ($n_i=110$) CO_2 clusters.

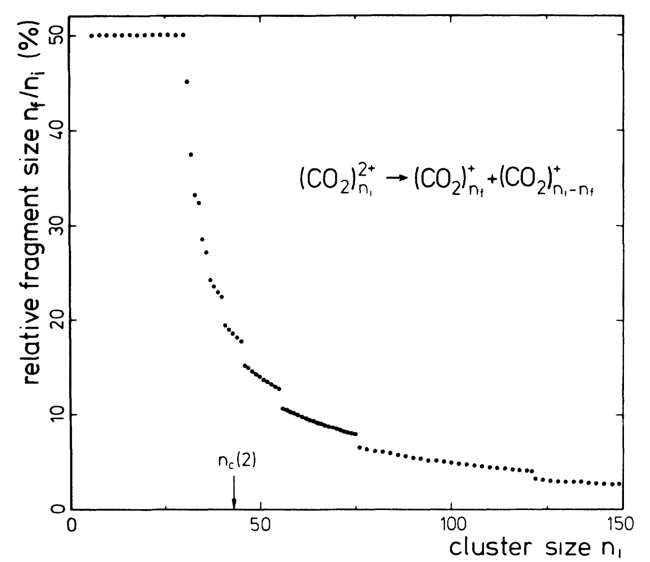

FIG. 8. Relative fragment size, n_f/n_i for fission of doubly charged CO_2 clusters across the minimum energy barrier, plotted vs precursor size n_i.

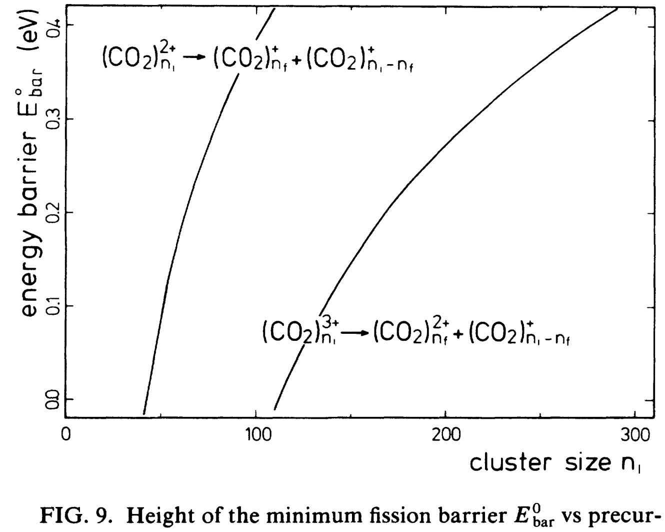

FIG. 9. Height of the minimum fission barrier E^0_{bar} vs precursor size for doubly and triply charged CO_2 clusters.

discrepancy occurs for strongly polar molecules (H_2O, H_2S, NH_3, and C_2H_6O). The theory underestimates $n_c(z)$ if experimental values for the dielectric constant are used. A possible explanation for this result can be found in the approximations made in our model. Firstly, the determination of the Lennard-Jones parameters V_{LJ} and σ_{LJ} from Eq. (15) is strictly valid for nonpolar molecules only. Secondly, for large dielectric constants the spherical shape assumed for the clusters will be a bad approximation. In this case, most of the excess charge in the cluster will be distributed over the surface. Hence the Coulomb barrier can be reduced significantly by an increase of the surface area; and the critical size would be larger and its dependence on ϵ would be weaker than predicted by our model. Thirdly, our model does not take into account the mutual induction of image charges in the separated fragments.

We have also calculated the critical sizes from ϵ values obtained from the Clausius-Mossotti equation, i.e., neglecting the contribution from the permanent dipole moment to the dielectric screening. This procedure results in surprisingly good agreement between theory and experiment. It may be justified by the assumption that the molecular dipoles do not reorient with respect to the excess charges because fission is too fast or, more realistically, because the influence of the cluster surface on the dipole orientation is too strong.[53] Nevertheless, a calculation which accounts for possible deformations of the cluster is necessary to better understand the role played by the permanent dipole moment in the fission process of clusters from polar molecules. Results of a more elaborate model for doubly charged clusters have been published recently.[54]

Let us finally point out that our model predicts an essentially linear dependence of critical sizes on the quantity $(V_{LJ}\sigma_{LJ})^{-1}$. In fact, it has been shown recently that the experimentally determined critical sizes of doubly charged clusters follow remarkably well an equivalent scaling law, namely, $n_c(2) \sim [T_{\text{boil}}(v)^{1/3}]^{-1}$ where T_{boil} is the boiling temperature, and v denotes the molecular volume determined from the bulk density.[21,55]

V. DISCUSSION

The absence of z-fold charged clusters below $n_c(z)$ clearly indicates that these species undergo fission into at least two charged fragments before mass analysis can be accomplished experimentally, i.e., within $t \ll 10^{-5}$ s in our apparatus. There is no doubt that the initial ionization event by a single, energetic electron (or by some other kind of radiation of sufficient energy) will produce z-fold charged clusters for *all* sizes n_i. In fact, several mechanisms favor the ejection of more than one secondary electron from a cluster,[56] hence the yield of multiply charged clusters in the observable size range $n_i > n_c$ is, in general, enormous.[21,48,52,57,58]

Small multiply charged clusters of weakly bound compounds, however, will be intrinsically unstable, i.e., they will undergo spontaneous fission independent of the initial excess energy in the ion. (This statement may become invalid for metal clusters,[59] covalently bonded "van der Waals" dimers like $He_2{}^{2+}$, or other strongly bound species.[60] Hence, the appearance of a positive fission barrier above some cluster size will be mathematically well defined; we have attempted to determine this critical size within a simple, static liquid-drop approximation.

The experimental situation is, of course, much more complicated, because the initial excess energy in the multiply charged clusters is unknown. The introduction of holes into a van der Waals cluster will be followed by the formation of dimer ions or larger charged complexes within the cluster;[14,61] structural relaxation of the neutral monomers around the localized charges will also release excitation energy. Furthermore, the initial separation between the holes will also control the total excess energy. In spite of this, the experimentally determined critical sizes are very well defined. The intensity of doubly charged clusters, e.g., typically rises from "unobservable" to its maximum value within $\Delta n/n \sim 10\%$. Neither the energy of the ionizing radiation,[48] nor the type of radiation,[52] nor the parameters of the cluster source, affect the values of the critical size.

The strongest support for the applicability of our static model, however, comes from the observation of delayed, thermally activated fission. This phenomenon indicates that clusters being slightly larger than $n_c(z)$ feature a finite, but rather small barrier E^0_{bar} against fission. The height of this barrier may be estimated as follows: Fission has to compete with monomer evaporation. For most compounds we may safely assume that the initial excess energy in the cluster has been randomized over all vibrational modes on the time scale of the experiment.[15] The rate for the competing decay channels may be estimated from the Arrhenius expression, $\nu = \nu_0 \exp(-E_a/kT)$. The "attempt frequency" ν_0 is $\sim 10^{12}$ s^{-1} for evaporation of neutral monomers, but somewhat lower for ejection of a massive fragment in the fission reaction. Gay and Berne, from their molecular dynamics simulation, estimate $\nu_0 = 2 \times 10^{10}$ s^{-1} for fission of $Xe_{51}{}^{2+}$ into $Xe_{15}{}^{2+} + Xe_{36}{}^{2+}$.[62] What is the activation energy for monomer evaporation E_a and what is the internal temperature of the cluster? There is ample evidence that E_a for a charged cluster of size $n \gtrsim 30$ will be close to the bulk sublimation energy.[6,63] The temperature T will be controlled by E_a and, hence, by the Lennard-Jones parameter V_{LJ}. Based on electron diffraction, Farges *et al.* have estimated $kT \sim 0.35 V_{LJ}$ for van der Waals clusters,[64] in reasonable agreement with computer simulations[65] and thermodynamic arguments.[18,66]

Summarizing, a large rate of thermally activated fission is expected to occur for those clusters that feature a minimum fission barrier E^0_{bar}, being somewhat smaller than the heat of sublimation of the bulk material. (Clusters with an even lower barrier would, of course, feature a higher rate, but they are not amenable to experimental analysis). For CO_2, in particular, we have $T \sim 110$ K from electron diffraction,[64] and the effective rate of fission in our time window is $\sim 2.5 \times 10^4$ s^{-1} for triply charged clusters of size $n_i \sim 114$ (see Sec. III B). Assuming $\nu_0 = 10^{11}$ s^{-1} for the attempt frequency, we obtain $E^0_{\text{bar}} = 0.14$ eV. This may be compared with the heat of sublimation of bulk CO_2 (0.25 eV), or with the heat of monomer evaporation from small CO_2 cluster cations (0.16 eV), as deduced from photodissociation data.[63,6]

Clearly, our liquid-drop model will systematically underestimate the experimental critical sizes, because it neglects thermally activated fission over a finite barrier. We may, however, estimate the corresponding error in $n_c(z)$ from the calculated dependence of the fission barrier E^0_{bar} on the size n_i. The data plotted in Fig. 9 indicate that, for triply charged CO_2 clusters, the error for n_c will be $\sim 25\%$. A systematic correction of the calculated critical sizes would therefore *deteriorate* the apparent agreement between experiment and theory. In other words, the agreement is, to some extent, fortuitous, due to cancellation of errors introduced by the various simplifying assumptions inherent to our model.

In the experimental section we have found that the rate of thermally activated fission increases by approximately two orders of magnitude in going from $(CO_2)_{108}{}^{3+}$ to $(CO_2)_{123}{}^{3+}$. This implies an increase in the height of the fission barrier by 0.044 eV, if we assume $T = 110$ K (see above) and a constant preexponential factor. This value agrees well with the calculated slope of E^0_{bar} versus n_i (Fig. 9).

Our present results disagree with a previous postulation that the specific size-to-charge ratio of fragment ions would be equal to that of their precursors[26] ("symmetric" fission). This statement, however, was supported only indirectly by the experimentally determined ratio of critical sizes, $n_c(4){:}n_c(3){:}n_c(2)$. The average value of this ratio is 4.1:2.2:1.[21] This is quite close to the ratio 3.67:2.31:1, predicted by Bennemann and co-workers on the *assumption* that fission proceeds "symmetrically."[27] Note, however, that Rayleigh's theory on the charge limit of a spherical droplet[67] already predicts a ratio of 4.0:2.25:1, in even better agreement with experiment. This ratio was derived without any *a priori* assumption on the size distribution of fragments. According to our model, the ratio of critical sizes will slightly depend on the input parameters ϵ, V_{LJ}, and σ_{LJ}; cf. Table II.

In a qualitative picture, we may relate the asymmetry of the fission process to the fact that ejection of a small singly charged ion tends to minimize the number of bonds that have to be broken (or, in other words, the increase in surface area). A naked monomer ion, however, will not be ejected because the bond strength between the ion and its immediate neighbors is strongly enhanced by the ion-induced dipole interaction.

Let us now turn to a discussion of doubly charged clusters, which, within the sensitivity of our apparatus, do *not* undergo delayed fission. The temperature of these ions, however, is still high enough to cause monomer evaporation with a large rate (cf. Fig. 5). An explanation for the absence of delayed fission may be derived from an early, very illuminating molecular dynamics study of $Xe_n{}^{2+}$ by Gay and Berne:[62] Vertical ionization of a cold neutral xenon cluster in a low-energy configuration introduces a large amount of excitation energy. A significant portion of this initial excess energy, however, is concentrated in a single vibrational mode: The repulsion between the like charges will deform the cluster and excite a collective vibration which is favorable for surpassing the fission barrier. Hence, if the initial energy in this mode exceeds the fission barrier, instantaneous (prompt) fission will take place as observed in the computer simulation for the 51-mer. If, on the other hand, fission is not instantaneous (as for the 55-mer), the excess energy in this particular mode will dissipate and merely increase the "temperature" of the ion. In this case, the probability for overcoming the barrier against fission will decrease with increasing time, because thermal excitation of the cluster will decrease upon evaporation of neutral monomers.

The possibility that a doubly charged cluster may become self-trapped in its metastable state by *reducing* its size might appear strange. If, however, the initial size of the cluster was well above n_c (where the barrier would vanish), this process is possible. How large exactly the initial size would have to be will, of course, depend on the initial nondirected excess energy in the cluster.

Accepting the preceding arguments, we are left with the task of explaining why triply charged clusters *do* undergo delayed fission. In this case, the instantaneous excitation of a suitable collective vibrational mode is less likely than for doubly charged clusters. If the initial location of the holes is such that it minimizes the excess energy (symmetry D_{3h}), a symmetric stretching mode would be excited; this mode correlates with a rather high fission barrier. Further differences in the behavior of doubly and triply charged clusters arise from their different sizes: The larger clusters feature a lower barrier against deformations, because their ratio of surface energy versus Coulomb energy is lower. Furthermore, the cooling rate of a large (triply charged) cluster is likely to be smaller than that for a small (doubly charged) one; hence the role of thermal activation in the experimental time window will be more important for triply charged clusters.

In any case, a theory including cluster deformations and dynamical effects will be necessary. Our improved model for doubly charged clusters, introduced recently,[54] does indeed confirm the qualitative explanation given above.

VI. CONCLUSION

Our experiments have shown that triply charged clusters of carbon dioxide and ethylene feature a high probability for delayed, unimolecular fission. The rate for this process rapidly decreases with increasing cluster size. Hence the yield of observable fragment ions in the experimental time window ($10 \lesssim t \lesssim 100$ μs with respect to ionization) strongly peaks at a size slightly above the "critical size" $n_c(3)$, which denotes the smallest triply charged cluster being detectable. Because of this delayed fission, $n_c(3)$ will slightly depend on the time scale of the mass analysis.

The occurrence of delayed fission makes possible an analysis of the size distribution of fission fragments. The preferred channel for $(CO_2)_n{}^{3+}$ is very asymmetric, the doubly charged fragments carrying approximately 92% of their parent's mass. Delayed fission of triply charged ethylene clusters is less asymmetric. Evidence is obtained for the occurrence of delayed fission in quadruply charged clusters, too; but more refined experimental techniques will be needed in order to determine the corresponding size distributions of fission fragments.

We have presented a liquid-drop model which allows us to calculate the height of the fission barrier for a given size and charge state of precursor and fragment ion from easily obtainable bulk properties. In spite of its rather crude simplifying assumptions, this model appears to catch many of the essential features of the fission process. In particular, it predicts critical sizes which reasonably agree with experimental values; its prediction for the most favorable size distribution of triply charged CO_2 clusters also agrees well with the experiment. The amount of systematic errors introduced by the model due to its omission of dynamical and thermally activated processes have been discussed in detail.

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