Observation of Sequential Decay Series in Metastable Ar Clusters: $Ar_n^{+*} \rightarrow Ar_{n-1}^{+*} \rightarrow Ar_{n-2}^{+}$

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The first experimental observation of sequential decay of metastable cluster ions is reported herein. Ar cluster ions are produced by electron-impact ionization of a supersonic Ar cluster beam. Some of these ions are observed to decay via sequential decay series in the microsecond time scale, i.e., $Ar_n^{+*} \rightarrow Ar_{n-1}^{+*} \rightarrow Ar_{n-2}^{+*}$ (with $n \geq 7$), evaporating a single monomer in each of these successive decays. Conversely, the dominant metastable decay of $Ar_4^{+*} \rightarrow Ar_2^{+}$ proceeds predominantly via a single-step fissioning process leading to the simultaneous evaporation of two neutral Ar monomers.

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Recently a number of studies have reported the metastable decay of singly and multiply charged cluster ions in the *microsecond* time regime.[1] In most of these studies the evaporation loss of only *one* monomer was observed and investigated.[1] Although, several investigators have reported also the occurrence of metastable dissociations involving the loss of *two* monomers,[1-12] it was not possible in these studies to determine whether the observed loss of two monomers was simultaneous *(single-step fissioning process)*, i.e.,

$$Ar_n^{+*} \xrightarrow{k_{n,n-2}} Ar_{n-2}^{+} + 2Ar, \tag{1}$$

or sequential *(successive multiple evaporation)*, i.e.,

$$\begin{array}{l} Ar_n^{+*} \xrightarrow{k_{n,n-1}} Ar_{n-1}^{+*} + Ar \\ \qquad\quad \Big\downarrow k_{n-1,n-2} \\ \qquad\quad\; Ar_{n-2}^{+} + Ar. \end{array} \tag{2}$$

In order to gain more insight into the metastable dissociation mechanism and the concomitant evolution of cluster ion spectra, it is of great interest to answer this question (see discussions in Refs. 4–6, and 11).

In this Letter we present direct experimental evidence that metastable argon cluster ions (produced by electron-impact ionization of a neutral-argon-cluster beam) which lose two monomers in the microsecond time-region decay via sequential decay series if their size is equal to or larger than Ar_7^{+}. Conversely, the strong metastable decay of Ar_4^{+*} into Ar_2^{+} proceeds predominantly via a single-step fissioning process. These findings were made possible by the innovative use of a double-focusing sector field mass spectrometer (reversed geometry). We have also studied quantitatively the kinetics of these sequential decay series for cluster sizes including $n=4$ and $7 \leq n \leq 10$.

The supersonic beam-electron impact ionization mass spectrometer system used has been described in detail previously.[6] In short, neutral argon clusters are produced by expanding neat Ar gas at $\simeq -130\,^{\circ}C$ and pressures up to $\simeq 2.5$ bars through a 20-μm nozzle. The ensuing supersonic beam passes a skimmer (differential pumping stage[6]) and is crossed downstream at right angles by an electron beam of variable energy. Cluster ions thereby produced are (i) extracted at right angles from the ionization region, (ii) accelerated by an acceleration potential (typically to 1, 2, or 3 kV), analyzed in a 90° magnetic sector field followed by a 90° electric sector field, and (iii) detected with a CuBe conversion dynode followed by a channel electron multiplier.

Essential to the present measurements (which go beyond the usual mass-to-charge analysis and simple metastable ion detection) is the existence of a first field-free region between the end of the acceleration region and the beginning of the magnetic sector field (length: 41 cm) *and* of a second field-free region between the end of the magnetic sector field and the beginning of the electric sector field (length: 25 cm). A possible metastable decay of an ion m_1^{+} (produced in the ion source) into m_2^{+} can be detected according to Cooks *et al.*[13] either (i) in the first field-free region by tuning the magnetic sector field to a nominal mass $m^{*}=m_2^2/m_1$ and the electric sector field to an electric field $E^{*}=m_2E/m_1$, or (ii) in the second field-free region by tuning the magnetic sector field to m_1^{+} and the electric sector field to $E^{*}=m_2E/m_1$ (with E being the correct sector field to detect m_1). This corresponds to the usual operating mode for the detection of metastable decay of polyatomic ions. In the present study we employed an additional experimental procedure in order to discover and study the occurrence of successive metastable decay series. In this alternative mode of operation we detect a possible metastable decay of m_1^{+} into m_2^{+} in the first field-free region followed by a metastable decay of this m_2^{+} into m_3^{+} in the second field-free region. This is accomplished by tuning the magnetic sector field to a nominal mass $m^{*}=m_2^2/m_1$ and the electric sector field to an electric field $E^{*}=m_3E_1/m_1$. In this case only those m_3^{+} ions will arrive at the detector of our mass spectrometer which stem from two successive decays in the first and

second field-free regions, respectively.

Using these experimental techniques, we were able to detect and measure metastable abundance fractions of a specific cluster ion Ar_n^+ (up to $n=10$ in the present study[14]) as a function of cluster size for the following dissociation reactions:

$$Ar_n^{+*} \xrightarrow{k_{n,n-1}(I)} Ar_{n-1}^+ + Ar, \quad (3)$$

in the first field-free region,

$$Ar_n^{+*} \xrightarrow{k_{n,n-1}(II)} Ar_{n-1}^+ + Ar, \quad (4)$$

in the second field-free region,

$$Ar_n^{+*} \xrightarrow{k_{n,n-2}(I)} Ar_{n-2}^+ + 2Ar, \quad (5)$$

in the first field-free region, or alternatively,

$$Ar_n^{+*} \xrightarrow{k_{n,n-1}(I)} Ar_{n-1}^{+*} + Ar \quad (5a)$$
$$\xrightarrow{k_{n-1,n-2}(I)} Ar_{n-1}^+ + Ar,$$

$$Ar_n^{+*} \xrightarrow{k_{n,n-2}(II)} Ar_{n-2}^+ + 2Ar, \quad (6)$$

in the second field-free region, or alternatively,

$$Ar_n^{+*} \xrightarrow{k_{n,n-1}(II)} Ar_{n-1}^{+*} + Ar \quad (6a)$$
$$\xrightarrow{k_{n-1,n-2}(II)} Ar_{n-2}^+ + Ar,$$

$$Ar_n^{+*} \xrightarrow[\text{(first field-free region)}]{k_{n,n-1}(I)} Ar_{n-1}^{+*} + Ar \xrightarrow[\text{(second field-free region)}]{k_{n-1,n-2}(II)} Ar_{n-2}^+ + Ar + Ar. \quad (7)$$

Some of the reactions occurring in the first field-free region are contaminated by collision-induced dissociations due to the presence of background gas.[15] However, by studying these unimolecular dissociations as a function of pressure in the first field-free region (in the range from 4×10^{-6} Torr up to 2×10^{-5} Torr), it is possible to distinguish between truly metastable dissociations and collision-induced dissociations leading to the same fragment ion. Figure 1 shows as an example some of these pressure dependences for the dominant dissociation reactions of Ar_{10}^+.

Careful analysis of this pressure dependence yields the metastable abundance fractions (for details see Ref. 6; a simple linear extrapolation is shown in Fig. 1). It is found that all dissociation reactions mentioned above [processes (3) to (7)] show metastable abundance fractions for cluster ions $7 \le n \le 10$. In contrast, Ar_4^+, which exhibits a particular strong loss of two monomers in the first field-free region [i.e., $k_{n,n-2}(I)$ is approximately 1800 s^{-1} compared to $k_{n,n-1}(I)=100$ s^{-1}], does not show any metastable decay signal via reaction (7). *Of particular interest, however, is the observation of reaction* (7) for cluster ions $7 \le n \le 10$. This constitutes the first *experimental evidence for the occurrence of sequential decay of metastable cluster ions.* In view of the fact that several molecular-dynamics calculations have shown such multiple decay reactions to occur in the picosecond time regime[16,17] directly following the ionization event, it is especially intriguing that these sequential decay series are observed here in the microsecond time regime.

With use of the appropriate kinetic rate equations (coupled differential equations) it is possible to derive corresponding metastable dissociation rates k. Figure 2 shows as an example calculated (with the derived reaction rates) ion currents as a function of time within the apparatus for Ar_{10}^{+*} decaying via the sequential decay reaction (7) (for more details and consistency checks see Ref. 6 and a forthcoming full paper). Table I gives the

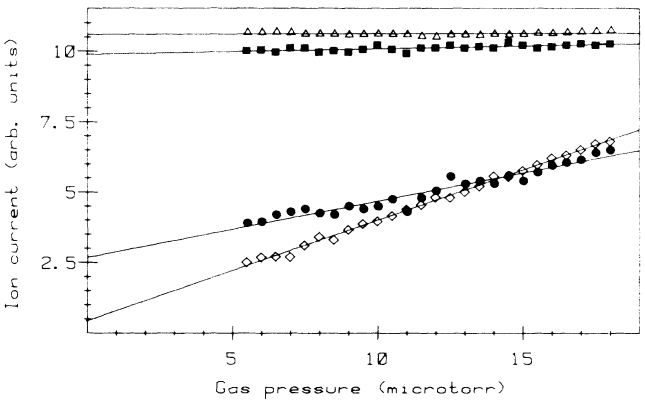

FIG. 1. Precursor (Ar_{10}^+, designated by triangles) and fragment (Ar_9^+,Ar_8^+) ion currents as a function of uncorrected gas pressure in the first field-free region for the unimolecular reactions $Ar_{10}^+ \rightarrow Ar_9^+$ (first field-free region), designated by squares and multiplied by 20; $Ar_{10}^+ \rightarrow Ar_8^+$ (first field-free region), designated by lozenges and multiplied by 300; and $Ar_{10}^+ \rightarrow Ar_9^+ \rightarrow Ar_8^+$ (first and second field-free regions, respectively, see text), designated by circles and multiply by 15000. Stagnation pressure: 2.5 bars Ar, stagnation temperature: −130 °C, electron energy: 180 eV, electron current: 0.3 mA, acceleration voltage: 3 kV. Lines drawn through the experimental points have been obtained from least-squares fits, and metastable fractions obtained by extrapolating to zero pressure are statistically significant nonzero values.

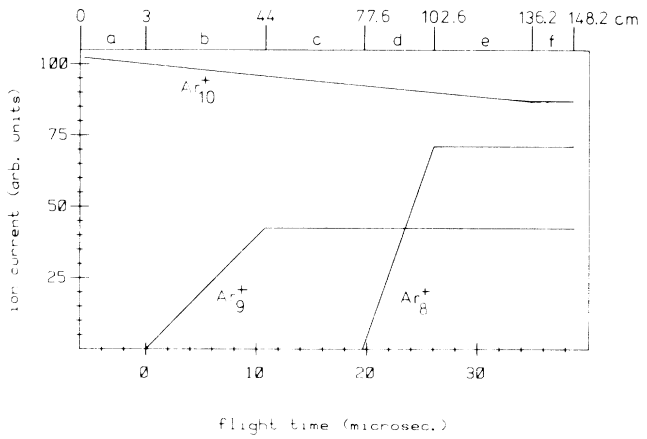

FIG. 2. Calculated ion currents in the mass spectrometer (see upper scale) as a function of flight time (lower scale) for parent ion Ar_{10}^+, fragment ion Ar_9^+ (produced by a metastable dissociation $Ar_{10}^{+*} \rightarrow Ar_9^+$ in the first field-free region) and fragment ion Ar_8^+ (produced via the sequential decay $Ar_{10}^{+*} \rightarrow Ar_9^{+*}$ in the first field-free region and $Ar_9^{+*} \rightarrow Ar_8^+$ in the second field-free region) using the derived reaction rates (see Table I) $k_{n,n-1}=4030\ s^{-1}$ and $k_{n-1,n-2}=65\ s^{-1}$, respectively [without taking into account the recently discovered dependence of k on time (Ref. 12)]. It is interesting to note that the respective ion current ratios Ar_9^+/Ar_{10}^+ and Ar_8^+/Ar_{10}^+ present at the end of the flight time are in excellent agreement with the experimental data (zero pressure ratios in Fig. 1). Curve designated Ar_9^+ multiplied by ten and curve designated Ar_8^+ multiplied by 40000. Note: The calculational model includes the successive dissociation reaction $Ar_{10}^{+*} \rightarrow Ar_9^+ \rightarrow Ar_8^+$. These decay reactions occur at any time during the flight of these ions through the mass spectrometer with the derived reaction rates given above. The curves calculated and shown, however, illustrate the situation for the three operational modes, i.e., (i) normal mass analysis of Ar_{10}^+, (ii) detection of Ar_9^+ produced by metastable decay from Ar_{10}^+ in the first field-free region, and (iii) detection of Ar_8^+ produced by metastable decay in the second field-free region from Ar_9^+ which has been produced before by metastable decay from Ar_{10}^+ in the first field-free region. *a*: acceleration region (3 cm), *b*: first field-free region (41 cm), *c*: magnetic sector field (33.6 cm), *d*: second field-free region (25 cm), *e*: electric sector field (33.6 cm), and *f*: third field-free region before detector (12 cm).

dissociation rates obtained for Ar_n^+ cluster ions with $n=4$ and $7 \leq n \leq 10$ for fragmentations in the first field-free region [reaction (3)] and successive fragmentations in the first and second field-free region, respectively [i.e., reaction (7)]. Several conclusions and points follow from these data:

(1) It can be seen that $k_{n,n-1}(\mathrm{I})$ [reaction (3)] is for all cluster ions smaller than $k_{n,n-1}(\mathrm{I})$ deduced for reaction (7). This is caused by assuming in the analysis that Ar_{n-1}^+ ions produced in the first field-free region via reaction (3) are stable for the rest of the flight time. Hence, previous analyses of such data, which have neglected the additional decay [i.e., as evidenced by reaction (7)], give too low values of the decay rates.

(2) The metastable decay rates in the sequential decay of reaction (7) are very different, i.e., $k_{n,n-1}(\mathrm{I}) \gg k_{n-1,n-2}(\mathrm{II})$. This is a result of the cooling which accompanies each decomposition (leading to a lowering of the rate for further evaporation) and is in accordance with a theoretical prediction of Klots.[18]

(3) Finally, it is interesting to note that we have also observed the loss of two monomers only within the first field-free region [reaction (5) and/or (5a)] and also only within the second field-free region [reaction (6) and/or (6a)]. In this case it is not possible to distinguish in the experiment between a simultaneous decay [reaction (5) and reaction (6), respectively] or a sequential decay [reaction (5a) and reaction (6a), respectively]. It is possible, however, to use the derived reaction rates $k_{n,n-1}(\mathrm{I})$, $k_{n,n-1}(\mathrm{II})$, and $k_{n,n-2}(\mathrm{II})$ and to simulate possible ion current evolutions in our mass spectrometer assuming either simultaneous and/or sequential decay. Comparison between calculated ion current ratios at the end of the mass spectrometer and the corresponding measured ratios indicates that the loss of two monomers of Ar_n^{+*} (with $7 \leq n \leq 10$) occurs predominantly via a sequential decay series. It is interesting to note that Polymeropoulos, Löffler, and Brickmann[19] found evidence in recent computer simulations of the dissociation dynamics of argon ion clusters that only single-particle dissociation are observed. This is in agreement with the present observation that the dominant channel is sequential evaporation of single monomer units. Moreover, charac-

TABLE I. Metastable reaction rates $k(s^{-1})$ for the reactions (3), and (7) (see text) as a function of cluster size. t_1: time at which the ions enter the first field-free region, $\Delta t(\mathrm{I})$: sampling time window in first field-free region, $\Delta t(\mathrm{II})$: sampling time window in second field-free region, and t_2: total flight times from ionization to detection. Acceleration voltage: 3 kV.

Cluster ion	t_1 (μs)	$\Delta t(\mathrm{I})$ (μs)	$\Delta t(\mathrm{II})$ (μs)	t_2 (μs)	Reaction (3) $k_{n,n-1}(\mathrm{I})$	Reaction (7) $k_{n,n-1}(\mathrm{I})$	Reaction (7) $k_{n-1,n-2}(\mathrm{II})$
Ar_{10}^+	5.8	10.8	6.6	41	3900 ± 120	4030 ± 200	65 ± 15
Ar_9^+	5.5	10.2	6.2	39	700 ± 35	1250 ± 60	180 ± 30
Ar_8^+	5.2	9.6	5.9	36.5	650 ± 35	940 ± 50	110 ± 20
Ar_7^+	4.8	9.0	5.5	34	490 ± 30	890 ± 40	150 ± 30
Ar_4^+	3.6	6.8	4.2	100 ± 20	Not observed		

teristic adsorption difference spectra of N_2 cluster ions (produced by secondary-ion mass spectroscopy[4]) and of other polymer ions have been rationalized on the grounds that repeat units are lost sequentially.[20]

In conclusion, we have found that the evaporative loss of *two* monomers from Ar_n^+ clusters observed in the microsecond time range proceeds predominantly via sequential dissociations of single monomers if $n \geq 7$. Conversely, for Ar_4^+ the loss of two monomers appears to be a single fissioning process. We want to emphasize that this discovery strengthens the view that magic numbers observed in mass spectra are due to a sequence of monomer evaporations[16,17,21] occurring after the ionization event. Surprisingly, these evaporation sequences extend from a first evaporation at around 10^{-10} s[16] into the microsecond time regime.

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