Unimolecular Decomposition of Sputtered $Al_n{}^+$, $Cu_n{}^+$, and $Si_n{}^+$ Clusters

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The metastable decomposition of sputtered, mass-selected, cluster ions is investigated under ultrahigh-vacuum conditions. Highly excited $Al_n{}^+$ and $Cu_n{}^+$ cluster ions are found to decompose mainly by evaporation of single neutral atoms, whereas for $Si_n{}^+$ clusters, fission is also observed. The decay rates of $Cu_n{}^+$ clusters are in agreement with calculations presented by Klots. Some consequences of our results for the interpretation of cluster-ion mass spectra produced by other experimental methods are discussed.

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The chemical and physical properties of small gas-phase metal clusters are subjects of great current interest. Much of our knowledge comes from work with neutral clusters for which no reliable method to identify crucial parameters (size, structure, etc.) exists. In general, such identification (for example, by mass spectroscopy) becomes possible only after some more or less violent action is taken on the cluster, e.g., ionization. Striking features of the corresponding mass spectra are strong intensity variations as a function of cluster mass. This raises the question of to what extent an experimental mass spectrum reveals the "true" intensity distribution at the time of production. Extended investigations have dealt with the fragmentation and metastable decay of gas-phase clusters after photon- or electron-impact ionization[1-8] as well as with the fragmentation and metastable decay of sputtered cluster ions.[9,10] Such work shows that cluster-ion intensities alone cannot provide an unambiguous identification of stable cluster structures. In particular, it is often not possible to separate spectral features due to the properties of the parent neutral clusters from those of the daughter ion clusters.

In order to shed more light on the spontaneous behavior of clusters we report in this paper on the time evolution of the unimolecular decomposition of sputtered, mass-selected $Al_n{}^+$, $Cu_n{}^+$, and $Si_n{}^+$ cluster ions. The apparatus is described in detail elsewhere.[11] In short (see Fig. 1), cluster ions are produced by 20-keV Xe^+-ion-beam bombardment (spot diameter 2 mm, 100 $\mu A/cm^2$) of thick metal and silicon targets. Positively charged particles are accelerated to 1.3 keV over a preselected distance d (1.7 or 18.5 mm), and undergo velocity selection while passing a Wien filter (Colutron 600 B). Only those clusters (of specific mass) are selected which do not fragment for at least a time t_0 after they were produced at or immediately in front of the surface, t_0 being the time needed by the cluster beam to reach its final energy of 1.3 keV; t_0 thus varies between 35 nsec (Al^+, $d=1.7$ mm) and 2.7 μsec ($Cu_{21}{}^+$, $d=18.5$ mm). All particles which fragment before acceleration has been completed have smaller energy and are deflected out of the beam by the Wien filter. Then, after a field-free drift, the particles are postaccelerated and detected in a 17-stage CuBe multiplier. Fragmentation during this field-free drift is detected by a simple repeller-grid energy analyzer in front of the multiplier which serves to separate fragment ions from the cluster beam. Intensity steps appear at voltages at which fragments are repelled. Evaluation of these steps uniquely reveals the unimolecular decay of mass-identified cluster ions into defined fragments. The drift length (distance from target to repeller grid) is 2.45 m, corresponding to a flight time typically between 20 and 200 μsec; variation of this drift length from 2.45 to 3.3 m affects the outcome of the experiment only insignificantly.

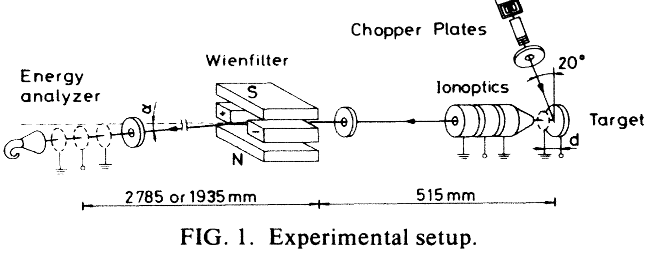

FIG. 1. Experimental setup.

Four-stage differential pumping assures ultrahigh-vacuum conditions ($<10^{-8}$ mbar base pressure, and $<10^{-7}$ mbar inside the target chamber during sputtering). No target contamination or collisional relaxation disturbs the unimolecular decay of the sputtered clusters.

Figure 2 gives the total decay probabilities for *aluminum* clusters, i.e., $I(\sum_l Al_l{}^+)/I(Al_n{}^+)$, n and l being the number of atoms in the parent and daughter ions, with $l < n$, and I the intensity of the respective clusters. The upper and lower curves show the results for the short ($d_{\text{short}} = 1.7$ mm) and long ($d_{\text{long}} = 18.5$ mm) acceleration distances. In both cases small $Al_n{}^+$ cluster ions, $n \leq 7$, are practically stable in the time win-

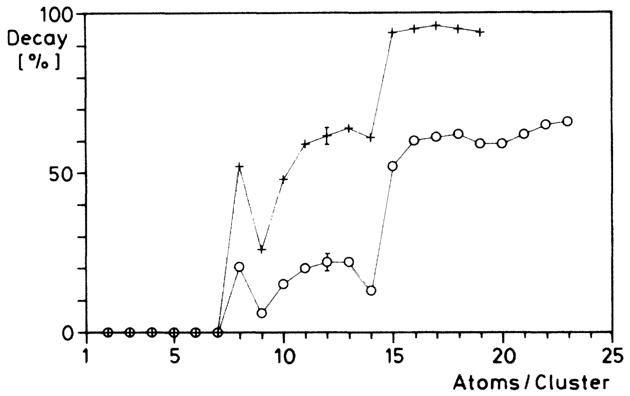

FIG. 2. Integral decay probabilities of mass-selected Al_n^+ clusters, sputtered by 20-keV Xe^+, as function of cluster size. Upper and lower curves, results for acceleration distances of 1.7 and 18.5 mm, respectively.

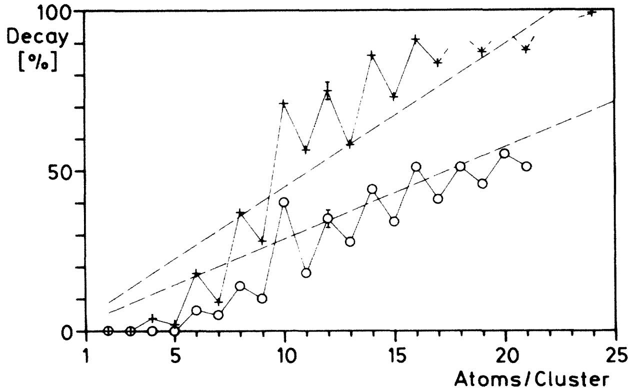

FIG. 3. Integral decay probabilities of sputtered Cu_n^+ clusters. The upper and lower curves correspond to the short ($d = 1.7$ mm) and long ($d = 18.5$ mm) acceleration distances. The dashed lines give the results of the evaporative ensemble model (Ref. 12).

dow between t_0 and detection. Strong decomposition is observed for larger ions, showing an irregular structure with a tendency of an overall increase with n. The decay probability depends strongly on t_0 as is manifested by the gap between the two curves.

The metastable decay of *copper* cluster ions follows a somewhat different behavior, as is shown in Fig. 3. Here the dimers and trimers are also stable, but a significant decomposition is observed for $n \geqslant 4$. A marked even-odd alternation is superimposed on a general increase of the decomposition rate with increasing n, reaching nearly 90% for $n \approx 20$. Corresponding even-odd intensity variations also characterize the mass spectra.[11] These structures have partly been known for a long time,[13] and have been attributed to the increased stability of clusters possessing

TABLE I. Decay probabilities for the unimolecular decomposition of sputtered mass-selected Al_n^+ and Cu_n^+ cluster ions into $n-1$ and $n-2$ singly charged fragments. Values are in percent ($\pm 2.5\%$) for both acceleration distances which correspond to different times t_0 (see text).

	Al_n^+ clusters				Cu_n^+ clusters			
	1.7 mm		18.5 mm		1.7 mm		18.5 mm	
n	$n-1$	$n-2$	$n-1$	$n-2$	$n-1$	$n-2$	$n-1$	$n-2$
2	0		0		0		0	
3	0	0	0	0	0	0	0	0
4	0	0	0	0	3	0	0	0
5	0	0	0	0	2	0	0	0
6	0	0	0	0	18	0	7	0
7	0	0	0	0	5	5	2	3
8	52	0	21	0	37	0	14	0
9	26	0	6	0	28	0	10	0
10	48	0	15	0	71	0	40	0
11	59	0	20	0	11	46	0	18
12	62	0	22	0	75	0	35	0
13	64	0	22	0	52	6	26	2
14	61	0	13	0	86	0	44	0
15	94	0	52	0	67	6	34	0
16	52	43	60	0	87	4	51	0
17	61	35	61	0	72	12	41	0
18	64	31	62	0	...	...	...	...
19	63	31	59	0	77	10	46	0
20	...	...	59	0	...	...	...	...
21	...	...	62	0	67	21	51	0
22	...	...	65	0	...	...	...	...
23	...	...	66	0	...	...	...	...

spin-paired binding electrons.

In order to get further insight into the decay process we have determined the branching ratios for the decay of each parent cluster into defined positive daughter ions. Table I gives the results for $\mathrm{Cu}_n{}^+$ and $\mathrm{Al}_n{}^+$. Particularly for d_{long} the dominant daughter ion is in most cases the $n-1$ fragment: After some initial cooling time t_0, sputtered metal cluster ions apparently lose further excess energy mainly by evaporation of single neutral atoms. If the initial cooling time t_0 is reduced (d_{short}), two-atom decomposition becomes more prominent; the experimental situation does not allow one to decide whether two single atoms leave the cluster independently or as a dimer. This behavior is particularly noticeable for $\mathrm{Al}_n{}^+$, $n \geqslant 16$; for copper the situation is similar except that the emission of two neutral atoms is even less probable, and the role of some stable cluster ions is more dominant than in the case of aluminum.

The fractional decay for $\mathrm{Cu}_n{}^+$ clusters has been calculated by Knots.[12] A collection of clusters, following some initial "big bang," start to shed both matter and energy by evaporation of single neutral atoms. Collisions and radiative losses are supposed to be negligible. The results for the metastable decomposition, calculated with this "evaporative ensemble" model, are given by the dashed lines in Fig. 3. The difference between the slopes is merely generated by application of the appropriate time windows as defined by the experimental situation (d_{short} and d_{long}). It should be noted that no fit parameter is involved in this model. The calculation is in reasonable agreement with the *mean* slopes of the experimental results for $n \geqslant 7$. These findings again support the assumption that excited copper cluster ions evaporate single neutral atoms, cool down, and gain stability. Deviations between the theoretical slopes in Fig. 3 and the measurements might be partly due to deviations from continuum-based heats of formation.[12] For example, by modulation of the heat of formation by about 0.05 eV the even-odd alternation of the measured decay can be roughly reproduced.

In addition to the even-odd alternation, a pronounced increase in the decay probability is seen after $\mathrm{Cu}_9{}^+$ (see Fig. 3). A special stability of $\mathrm{Cu}_9{}^+$ appears in the one-electron shell model of Knight *et al.*,[14] in which an accumulation of eight electrons (here, the valence electrons of $\mathrm{Cu}_9{}^+$) results in a filled $1p$ level. As this level is followed by a large energy gap until the next level is filled this cluster is relatively tightly bound. The mass spectra[11] show corresponding intensity drops after $n=9$ (and also 21, 35, and 41) in agreement with the shell model.

The unimolecular decay pattern of *silicon* cluster ions (see Table II) shows for small n a behavior resembling that of $\mathrm{Cu}_n{}^+$ and $\mathrm{Al}_n{}^+$: no decomposition of small clusters in the experimental time window between t_0 and detection, and increasing decomposition with increasing n. Noteworthy is the decomposition of $\mathrm{Si}_9{}^+$ whose main fragment is $\mathrm{Si}_6{}^+$. This decomposition seems to proceed via fission of $\mathrm{Si}_9{}^+$ since no decay of $\mathrm{Si}_8{}^+$ into $\mathrm{Si}_6{}^+$ is observed. We note that photofragmenttation yields a similar decay pattern of $\mathrm{Si}_n{}^+$ ions except that significant decay of $\mathrm{Si}_8{}^+$ into $\mathrm{Si}_6{}^+$ is reported.[8] This difference could be caused, e.g., by different time scales or by fragments reacting with the laser field.

From the above discussion we may draw a few more general conclusions. Firstly, sputtered Cu, Al, and Si cluster-ion decay probabilities and mass spectra are qualitatively the mirror image of one another; we may suspect that this result is also applicable to photon- or electron-impact ionization. In other words, *the relative ion abundances,* i.e., the cluster mass spectra, *reflect the stability of the charged particles.* The decisive influence of the metastable decay and of the stability of cluster decay products on the observed cluster-ion mass spectrum appears to be of rather general nature. Current investigations in our laboratory of the metastable decomposition of a large variety of sputtered metal clusters show a decay behavior similar to that of $\mathrm{Al}_n{}^+$ and $\mathrm{Cu}_n{}^+$. For example, $\mathrm{Pb}_n{}^+$ clusters with $n \geqslant 15$

TABLE II. Same as Table I, except for sputtered $\mathrm{Si}_n{}^+$ (errors ± 3%).

	1.7 mm				18.5 mm			
n	$n-1$	$n-2$	$n-3$	Σ	$n-1$	$n-2$	$n-3$	Σ
2	0			0	0			0
3	0	0		0	0	0		0
4	0	0	0	0	0	0	0	0
5	6	0	0	6	4	0	0	4
6	6	0	0	6	0	0	0	0
7	22	0	0	22	9	0	0	9
8	48	0	0	48	22	0	0	22
9	13	6	17	36	3	2	12	17

decompose at a rate of 100%. As a consequence no parent masses with $n \geqslant 15$ reach the detector. This is a particularly striking example of a mass spectrum which is (for $n > 15$) completely determined by the metastable decay.

Secondly, it is obvious that the concept of *temperature* is not adequate for describing a beam of sputtered metal cluster ions: Successive evaporation steps cool the clusters further, the decay rates varying with n. Consequently, there is not only no uniform temperature for all clusters, but even clusters having the same mass differ widely in their temperatures, depending on the cluster's origin and the time between production and detection. For example, from the "evaporation ensemble" model[12] we can estimate a temperature of 1880 K for Cu_{20}^+ and 3000 K for Cu_5^+, which is necessary to sustain an evaporation rate constant of 10^5 sec^{-1} (a typical value in our experiments). It should be mentioned that experiments on sputtered sulfur[15] and alkali-metal dimers[16] resulted in vibrational temperatures between 1000 and 1500 K, much lower than those of copper clusters. This discrepancy could be a consequence of the fact that the internal energy distributions have been measured by laser-induced fluorescence[15] or laser ionization.[16] Both methods are sensitive to the *density* of molecules in the observed states. Since, however, the kinetic energy distributions of sputtered ions and neutrals is very broad (from thermal energies up to about 60 eV for $Cu_2^{+\,17}$), mainly the slow clusters are recorded by these techniques. Furthermore, these laser experiments investigate the beam some millimeters away from the target where the clusters have already had a chance to cool, partly being fragments of larger clusters. Apparently, conclusive information about the sputtering process by the study of vibrational and rotational excitation may not be gained without due regard of the appropriate time scales.

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