Time-of-Flight Measurements of Cesium-Iodide Cluster Ions

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Secondary ions $[(CsI)_nCs]^+$, with n up to ~ 40, were produced by 8-keV Cs^+ bombardment of CsI. The yield of clusters decreased smoothly with n when observed in a time-of-flight mass spectrometer at effective times $\sim 0.2\ \mu s$ after emission. Clusters with $n > 7$ were found to be metastable, with lifetimes $\ll 100\ \mu s$. A large anomaly in the population of the disintegration products was measured at $\sim 70\ \mu s$ after emission, $n = 13$ clusters being favored and $n = 14$ and 15 suppressed.

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Large secondary cluster ions ejected from CsI surfaces by 4.7-keV Xe^+ ion bombardment have recently been observed in a sector-field mass spectrometer.[1-3] Positive ions $[(CsI)_nCs]^+$ were detected up to $n = 70$, and negative clusters $[(CsI)_nI]^-$ up to $n = 4$. For the positive clusters the ion intensity decreased rapidly with increasing n, but superimposed on this general decrease were pronounced anomalies; e.g., the intensity of the $n = 13$ cluster was enhanced by a factor ~ 2, but the clusters with $n = 14$ and 15 lay more than an order of magnitude below the average curve. It was noted that the anomalies were correlated with particularly symmetrical cluster geometries, e.g., $3\times 3\times 3$ at $n = 13$; clusters formed by the addition of CsI molecules to these structures were evidently suppressed, either in the production process or through instability.[1-3] The anomalies were then interpreted[1,4] by a bond-breaking or a cleavage model, under the assumption that they arose in the ion *production* process.

We have observed similar clusters in the Manitoba time-of-flight mass spectrometer[5] when electrosprayed deposits of CsI were bombarded with 8-keV Cs^+ ions. Positive clusters with n up to ~ 40 and negative clusters with n up to ~ 20 were detected (the latter with 28-keV Cs^+ bombardment). Figure 1 shows a positive time-of-flight spectrum. In striking contrast to the results mentioned above, the ion yield varies smoothly with n; no significant anomalies are observed. Figure 2 compares the two measure-

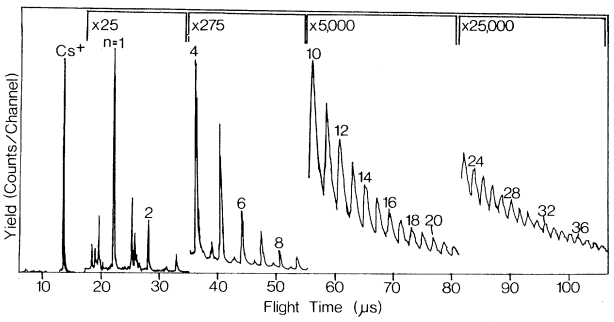

FIG. 1. Time-of-flight spectrum of secondary ions $[(CsI)_nCs]^+$ at primary Cs^+ average current densities of $\sim 2\times 10^{-10}$ A/cm^2 after a total irradiation of $\sim 4\times 10^{15}$ Cs^+ ions/cm^2. The spectrum was taken in three sections (6 to 35, 35 to 55, and 55 to 110 μs) and normalized at $n = 4$ and 10; measurement times were 15, 90, and 120 min. The structures between the main cluster peaks correspond to clusters with replacement of one Cs atom by a Na atom or to replacement of one I atom by a Cl atom.

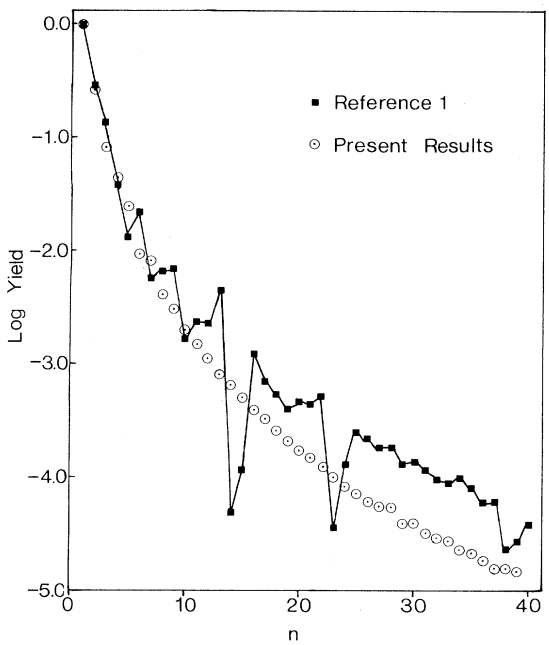

FIG. 2. Relative yields of $[(CsI)_nCs]^+$ clusters in the present measurements and in the previous measurements (Refs. 1–3), both normalized to $n = 1$. The slope of our yield function varied for different targets but was always a smooth curve. Neither measurement is corrected for spectrometer or detector efficiency, but these corrections are expected to vary smoothly with n.

ments.

Methods of target preparation and conditions of ion bombardment were somewhat different in the two cases. However, we believe that the most significant difference between them lies in the time scales of the observations, an important factor if the clusters are unstable. In the sector-field spectrometer[6] a cluster ion with $n = 13$ (mass ~ 3500 u) and energy 0.3 keV requires ~ 750 μs to traverse the instrument; if the ion decomposes within that time it is not observed, at least not at its original mass. By contrast, an ion in a time-of-flight spectrometer need survive only long enough to be fully accelerated in order to appear at its original mass number; subsequent decays simply increase the width of the peak since the velocity of the center of mass remains constant.[5,7,8] Thus the ion fragments are still detected at the approximate position of the parent ion. In our case the $n = 13$ cluster ion is accelerated to its full energy of 10 keV in 0.17 μs, and so our measurement yields the population of $n = 13$ ions 0.17 μs after their production.

In order to investigate the stability of the CsI clusters, we have inserted a set of three grids (each 90% transmission at 1.3 cm spacing) in front of the detector at the end of the 1.6-m flight tube.[7,8] The detector was maintained at ground potential as before, so that the energy of the ions striking it was unchanged. The entrance grid was also kept at ground, but a retarding potential V_R was applied to the central grid. Under these conditions the time of flight of neutral fragments is unchanged, but charged particles are delayed. The delay is larger for a charged fragment (mass m_f) than for the parent ion (mass m_p), since the fragment has only a fraction ($\approx m_f/m_p$) of the parent energy; if the energy of the fragment is too low, it will be reflected. This enables us to examine the mass spectrum at the time the ions arrive at the detector (~ 70 μs after emission for $n = 13$ and 10 kV accelerating potential).

Time-of-flight spectra were measured for various retarding potentials between 7 and 10 kV applied to the central grid. For clusters $[(CsI)_n\text{-}Cs]^+$ up to $n = 4$, the parent ions were predominant, but for $n > 4$ fragmentation increased rapidly. Above $n = 7$, no parent ions could be observed, only fragments. The measurements were taken at a pressure of ~ 10^{-7} Torr; an increase in pressure by a factor of 3 gave no observable change in fragmentation. Thus collisions in the flight tube play no important role in the process. On the other hand, the results are consistent with metastable decay; evidently the larger clusters acquire enough internal energy during emission to make them unstable on a time scale $\ll 100$ μs.

Most of the charged fragments observed from these decays correspond to ejection of one or more CsI molecules from the parent clusters. Decay of the clusters above $n = 13$ was investigated in some detail. Figure 3 shows time-of-flight spectra for retarding voltages of 8.0 and 8.4 kV. Here the $n = 16$ cluster is prominent at $V_R = 8.0$ kV ($\approx 62\%$ of its original yield), but has disappeared at $V_R = 8.4$ kV. This is consistent with decay of ~ 60% of the $n = 16$ parent to $n = 13$ in the flight tube since the potential required to stop this fragment is

$$V_R \approx (10\text{ kV})\,\frac{(13\times 260)+133}{(16\times 260)+133} \approx 8.2\text{ kV}.$$

Similar measurements at different retarding potentials gave the yields of fragments from parent ions with $n = 14$ to 18. The results are shown in Table I. We note that disintegrations which yield fragments with $n = 13$ are strongly favored and fragments with $n = 14$ and 15 have very low yields. Thus our cluster distribution also exhibits an anomaly near $n = 13$, but only at times $\gg 1$ μs after emission; the anomaly is a result of the pattern of metastable decay, not a consequence of the production process.[9]

The peaks in the spectra of parent ions include

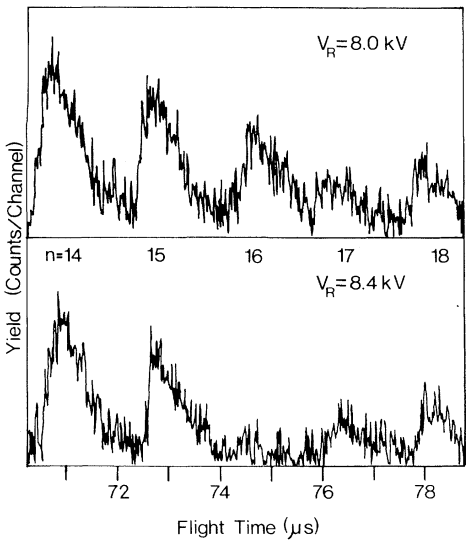

FIG. 3. Yields of $[(CsI)_nCs]^+$ clusters above $n = 13$ for retarding potentials $V_R = 8.0$ and 8.4 kV on the grid in front of the detector. Here background (the spectrum at $V_R = 9.5$ kV) has been subtracted.

TABLE I. Yield of fragments from CsI clusters measured at ~70 μs after emission, both parent and fragment having structures $[(CsI)_nCs]^+$. Each column lists the percentage yield of fragments with various values of n, i.e., the number of fragments detected per 100 detected events in the parent peak. The last row gives the percentage yield of neutral fragments (measured at V_R=9.5 kV). Estimated errors in these numbers are ± 5 or less.

Fragment \ Parent n=	14	15	16	17	18
n=11	6	6	5	1	0
12	24	22	2	11	0
13	40	40	62	45	26
14	0	0	0	0	6
15		0	0	8	11
16			0	20	19
17				0	22
18					0
Neutrals	17	17	19	16	15

neutral as well as charged fragments, indicated in Table I. Some of these neutral fragments are CsI molecules ejected in the decays discussed above. Their number may be estimated from the number of charged fragments observed if it is assumed that the efficiency of the microchannel plate detector is proportional to the number of atoms in the fragment[10]; for example, the number of neutral fragments in the n = 15 parent peak corresponding to the charged daughter n = 13 would then be $(2/13)\times 40 \approx 6.2$. For n = 15 to 18, the calculated sums of the neutral fragments corresponding to the charged daughters observed account for most, if not all, of the neutral fragments detected. Instead of emitting one or more CsI molecules, the parent ion might decay by emission of small charged fragments, e.g., Cs^+. The large neutral fragments produced in this process would be detected with high efficiency. Since the neutral fragments observed are already accounted for, it appears that this mode of decay is relatively improbable.

We conclude the following:

(1) Our measurements give no evidence for anomalies in secondary-ion *production*. Such anomalies if present would contradict the smooth variation with n predicted by thermal or statistical models.[11] Cluster yields in the present case decrease smoothly with n when they are measured at sufficiently short times ($\ll$1 μs) after emission.

(2) Secondary-ion clusters $[(CsI)_nCs]^+$ produced by 8-keV Cs^+ ion bombardment are predominantly metastable for $n>7$, with lifetimes $\ll 100$ μs. Decay of the clusters occurs mainly by emission of one or more CsI molecules. The distribution of decay products, observed at times ~70 μs after emission, exhibits a striking anomaly; product clusters with n = 13 are favored, and clusters with n = 14 and 15 are suppressed. This appears to be consistent with the results of Martin's calculations,[12] which indicate that charged alkali-halide clusters with a high degree of cubic symmetry should be particularly stable, and additions to these structures should have low binding energies.

(3) The present measurements give no direct information on the production of neutral clusters. However, we note that sputtering yields of molecules and neutral clusters have necessarily been measured at times $\gg$1 μs after emission, and these yields have normally been interpreted as giving the actual distribution of particles ejected in the sputtering process. Our results suggest that such interpretations should be accepted with some caution.

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[9]In the sector-field measurements (see Refs. 1–3 and 6), an ion with $n=13$ spends $\sim 50\,\mu$s within the extraction lens before entering the spectrometer, and so it appears likely that many of the large clusters observed were disintegration products originating from regions close to the target. The same comment may apply to some of the clusters observed earlier in a quadrupole mass spectrometer [see F. Honda, G. M. Lancaster, Y. Fukuda, and J. W. Rabelais, J. Chem. Phys. 69, 4931 (1978)].

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Interference Effects in the Quasimolecular *K* X-Ray Production Probability for 10-MeV Cl^{16+}-Ar Collisions

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The impact-parameter dependence of the quasimolecular K x rays emitted in collisions of 10-MeV Cl^{16+} with Ar has been measured. The coincidence spectra show a clear impact-parameter–dependent structure. The results are in good agreement with dynamical calculations which take into account the interference between the $1s\sigma$ decay amplitudes in the incoming and the outgoing halves of the trajectory.

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Quasimolecular x rays have been the subject of many studies over the past years,[1] not only for their intrinsic interest, but also because they potentially can be used to study transient molecular orbitals formed during ion-atom collisions. However, in practice this has been more difficult than expected partly because, as a result of the collision broadening,[2] the observed x-ray spectra exhibit a structureless shape[3-6] with a nearly exponential falloff essentially independent of the impact parameter.[6]

In the present experiment we have substantially and radically improved the experimental conditions used for the study of quasimolecular K x rays. These improvements have resulted in a strong impact-parameter–dependent structure in the noncharacteristic x-ray spectrum and have allowed the first comprehensive comparisons with theoretical calculations of transition probabilities. The essential and new improvement that has been made is the use of low-velocity hydrogenlike ions produced by the tandem acceleration-deceleration method[7] which made it possible for the first time to bring a K vacancy into the collision. As a result of the low velocity, the collision broadening (which is proportional to the velocity^2) is reduced, and the adiabaticity condition[8] is better fulfilled. Furthermore, with decreasing velocity the collision time increases and thus the decay rate of $1s\sigma$ vacancies increases. In nearly symmetric collision systems, the presence of a K vacancy in the projectile gives a probability close to 0.5 for production of a vacancy in the $1s\sigma$ orbital. These conditions are expected to produce a considerable increase in the quasimolecular radiation cross section.[9]

Finally, another important effect is expected when a $1s\sigma$ vacancy is brought into the collision. The vacancy can decay with equal probability in the incoming or the outgoing half of the trajectory. Dynamical calculations[10-13] predict interference structures in the x-ray spectrum, which result from the coherent sum of the two corresponding amplitudes, and which could be observable through measurements as a function of impact parameter.

For convenience the experiment was carried out with a Cl^{16+} beam on Ar at 10 MeV. Although the K vacancy is in the lower-Z collision partner, the binding energy of K electrons in a H-like Cl ion is comparable to the binding energy of the K electrons in a neutral Ar atom. There is therefore a probability of $\sim 50\%$ to transfer the vacancy into the $1s\sigma$ orbital as a result of the K-vacancy sharing[14] in the incoming part of the trajectory.

The 10-MeV Cl^{16+} beam was obtained at the

