Collision-Induced Coulomb Fragmentation in Mass-Selected $(CO_2)_n{}^{2+}$ Clusters

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Using the supersonic expansion technique in conjunction with a double-focusing mass spectrometer, Coulomb explosion in mass-selected $(CO_2)_n{}^{2+}$ clusters has been promoted through collisions with a background gas. Extensive fragmentation to a range of different-sized singly charged clusters is observed. However, the kinetic-energy release associated with fragmentation is less than that predicted from an estimate of the Coulomb repulsion energy.

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Many multiply charged clusters exhibit a cutoff in minimum size, below which they are unstable because repulsion between the positive charges is greater than the binding energy between the constituent atoms or molecules.[1,2] Thus no argon doubly charged clusters are observed below $Ar_{91}{}^{2+}$,[3] and the lower limit for benzene clusters is $(C_6H_6)_{23}{}^{2+}$.[4] The term "Coulomb explosion" has frequently been used to describe the process responsible for the cutoff[1] and, although such a label suggests that comparatively large energy releases are involved, evidence to that effect in clusters has not been forthcoming.

Echt and co-workers have presented the results of several investigations into the fragmentation routes of multiply charged clusters,[5-7] and have reported evidence of charge separation in triply charged carbon-dioxide and ammonia clusters. Similar experiments on large doubly charged clusters have been singularly unsuccessful, with the evaporation of neutral molecules being the only observed decay step.[6,8] However, Lezius and Mark[9] have shown that the intensities of singly charged ions are influenced by the rapid decay of unstable doubly charged argon clusters in the ion source of a mass spectrometer.

The ideal experiment should involve mass selecting a doubly charged cluster at the observed cutoff limit, i.e., $(CO_2)_{43}{}^{2+}$ (see below), and monitoring the loss of a single molecule. As a consequence of this decay process, the cluster should become unstable and "explode." In practice, such experiments are very difficult to perform. The smallest observed doubly charged cluster ions often have very low intensities, and it is frequently the case that the decay products are in fact stable ions. In a typical cluster-ion mass spectrum, only the odd-sized doubly charged clusters can be assigned with certainty; the presence of even-sized clusters is frequently obscured by very intense signals from singly charged ions. Thus, $(CO_2)_{43}{}^{2+}$ (see below) and $Ar_{91}{}^{2+}$ are the smallest observed clusters, however, $(CO_2)_{42}{}^{2+}$ and $Ar_{90}{}^{2+}$, respectively, can be detected as their stable fragmentation products.[10] Two recent experiments on doubly charged clusters have provided evidence of decay steps involving charge separation. Brechignac *et al.*[11] have detected the asymmetric fragmentation of "hot" sodium clusters, $Na_n{}^{2+}$, and provisional results by Stace[12] suggest that $Ar_{92}{}^{2+}$ may undergo symmetric decay. Theoretical support for the possibility of asymmetric fragmentation in doubly charged clusters is provided in calculations by Gay and Berne[13] on $Xe_{51}{}^{2+}$.

It is clear that a significant advance in the study of Coulomb explosion will only be made if instability in multiply charged clusters can be created through the promotion of multiple evaporations. Our intention in this Letter is to present the first results of such experiments on large molecular clusters. Mass-selected $(CO_2)_n{}^{2+}$ clusters have been subjected to single collisions which have induced the loss of sufficient molecules as to render the clusters unstable. A broad range of singly charged decay products are observed.

The experiments have been performed on an apparatus which combines a supersonic nozzle system with an ultrahigh-resolution, double-focusing, reverse-geometry mass spectrometer (VG Instruments Inc., ZAB-E).[14] Figure 1 shows a schematic diagram of the apparatus. Under typical operating conditions, the pressure in the ion source is approximately 1×10^{-6} mbar and in the flight tube of the mass spectrometer the pressure remains

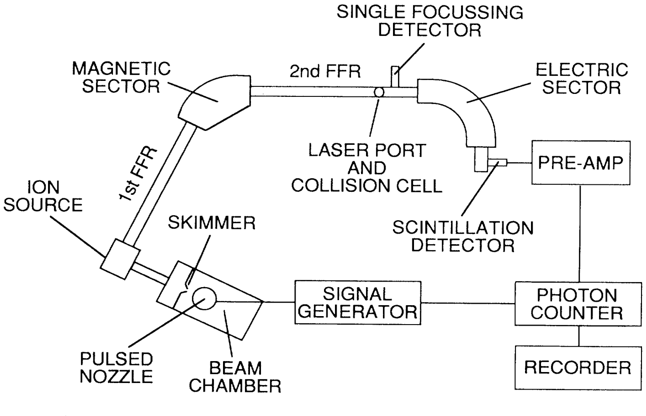

FIG. 1. Schematic diagram of the apparatus. The collision cell is located in the second field-free region (FFR) at the focal point between the magnetic and electric sectors.

below 6×10^{-9} mbar. This latter value is sufficiently low as to ensure that there is no detectable level of collision-induced fragmentation during the normal operation of the apparatus.[15] Collision-induced dissociation (CID) is promoted in a collision cell situated in the second field-free region (FFR) at the focal point of the magnetic and electric sectors. Gas is bled into the cell via a needle valve and the pressure is read from an ion gauge situated approximately 10 cm away. Because of the separation between the cell and the gauge, quoted pressures are to be considered as lower limits.

The detection system consists of a modified Daly scintillation detector, originally developed by VG Instruments Inc., but subsequently modified to enable photon-counting techniques to be used in addition to phase-sensitive detection. Ion counting is achieved using a fast photomultiplier (EMI 9324) at a cathode voltage of -1 kV in conjunction with a gated photon counter (Stanford Research SR 400). Neutral carbon-dioxide clusters were generated by an expansion of the pure gas through a 200-μm-diam pulsed conical nozzle operating at approximately 20 Hz. The stagnation pressure behind the nozzle was typically 1500 mbar.

To study CID processes, the MIKE (mass-analyzed ion kinetic-energy) technique has been used.[16] The magnet is set to transmit cluster ions of a single mass, and the electric sector voltage is then scanned in such a way that any ions which fragment in the second FFR can be detected and identified. The following equation[16]

$$E^* = (m_2 z_1 / m_1 z_2) E_0 \qquad (1)$$

provides a means of identifying fragment ions from the magnitude of the electric sector voltage necessary to transmit them. It is normal practice to consider the electric sector as a kinetic-energy analyzer and, therefore, to discuss fragmentation in terms of changes in the ion kinetic energy.[16] In Eq. (1), E_0 is the initial parent-ion netic energy (8000 eV in the present experiment), E^* is the kinetic energy after fragmentation, m_1 and z_1 are, respectively, the mass and charge on the parent ion, and m_2 and z_2 are the mass and charge on the fragment ion.

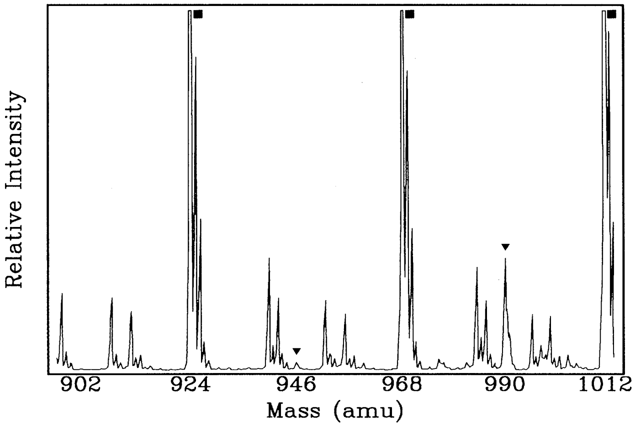

FIG. 2. Typical mass spectrum showing the region where the cutoff in doubly charged clusters occurs. $(CO_2)_{43}{}^{2+}$ (946 amu) and $(CO_2)_{45}{}^{2+}$ (990 amu) are shown (▼), and singly charged cluster ions are also shown (■). Other minor peaks can be identified as fragment ions arising from the decomposition of CO_2 cluster ions.

Figure 2 shows a typical mass spectrum recorded in the region where the cutoff in the doubly charged cluster-ion signal occurs. A very weak signal for $(CO_2)_{43}{}^{2+}$ is evident, which is two molecules lower than the limit previously identified.[17] In Fig. 3, the magnet has been set to transmit $(CO_2)_{47}{}^{2+}$ and a series of MIKE scans were performed. In each case, the scans were started below 8000 eV in order to avoid saturating the detection system with the comparatively intense parent-ion signal. Figure 3(a) was recorded in the absence of any gas (air) in the collision cell, and the two intense peaks correspond to a unimolecular loss of one and two CO_2 molecules from the parent ion. Figure 3(b) shows the effect of increasing the (air) pressure in the collision cell to approximately 3×10^{-7} mbar. It can be seen that a series of new peaks appear in the mass spectrum, and each of them is very much broader (FWHM$\simeq$150 eV) than the unimolecular peaks (FWHM$\simeq$15 eV). In addition, it should be noted that

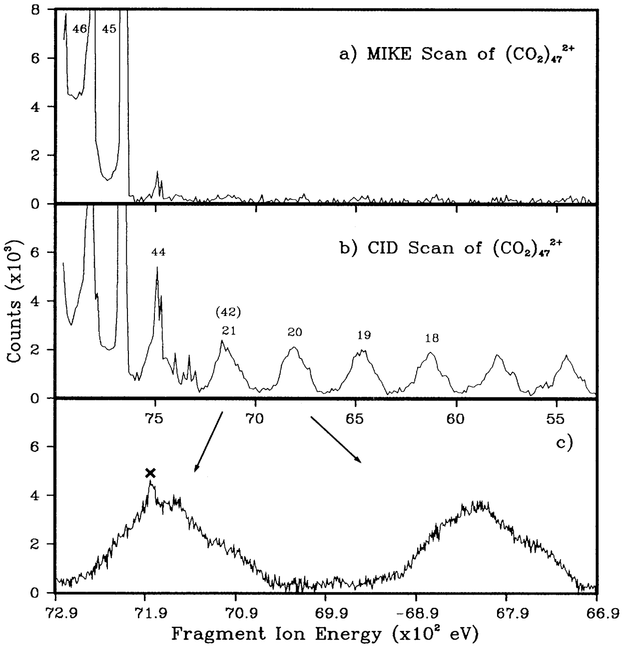

FIG. 3. MIKE spectra of $(CO_2)_{47}{}^{2+}$. (a) Unimolecular decay pattern; the fragment peaks are labeled. (b) Collision-induced dissociation, with the singly charged fragment ions labeled. (c) Expanded scan of two of the fragment peaks shown in (b). The peak marked as × is thought to be an artifact (see text).

the energy spacings between the new CID peaks are twice that of the unimolecular peaks. Finally, Fig. 3(c) is an expanded section of 3(b) showing two of the broad peaks in greater detail. Each of Figs. 3(b) and 3(c) took approximately 10 h to record.

It is clear that the introduction of collision gas leads to a new series of fragment-ion peaks; to identify their origin(s), it is necessary to first consider possible sources of interference. Because we are dealing with ions which have very low intensities, it is quite possible that the mass spectra (MIKE) scans may be dominated by accidental mass coincidences with other (unspecified) singly or doubly charged ions. There are two possible sources of interference: (i) artifact peaks[14] and (ii) overlap with a singly charged ion with the same *m/z* value. Because all the appropriate artifacts are going to be doubly charged,[18] they should behave in precisely the same manner as those ions we have nominally mass selected. In order to evaluate the effect interference from a singly charged ion might have, the above experiments were repeated for $(CO_2)_{18}\cdot O^+$. The latter ion is frequently observed in the mass spectrum of CO_2 clusters[19] and it has an intensity comparable to $(CO_2)_{47}{}^{2+}$. The unimolecular and CID fragmentation patterns of $(CO_2)_{18}\cdot O^+$ are shown in Fig. 4. Although the introduction of collision gas has quite a profound effect on the decay pattern, the most important factor as far as the present experiments are concerned is that the fragment peaks remain narrow. Figure 5 shows the results of three further CID experiments on different-sized doubly charged CO_2 clusters. In each case it can be seen that the broad fragment peaks begin to dominate the MIKE scans at ions kinetic energies beyond where either $(CO_2)_{43}{}^{2+}$ or $(CO_2)_{45}{}^{2+}$ should appear, i.e., the Coulomb cutoff. That the energy difference between adjacent broad peaks is twice that appropriate for doubly charged fragments can be explained if the peaks are due to those singly charged ions which have been identified in Figs. 3 and 5. Because the CID of singly charged ions gives only narrow fragment peaks, it must be concluded that the broad peaks seen in Figs. 3 and 5 are due to singly charged ions produced by the collision-induced Coulomb explosion of doubly charged ions.

For any decay process in the field-free region of a mass spectrometer, the relationship between kinetic-energy release T and peak width ΔE in a MIKE spectrum[16] is given by

$$T=\frac{z_2^2 m_1^2 eV}{16 z m_1 (m_1-m_2)}\left(\frac{\Delta E}{E}\right)^2 . \tag{2}$$

Most of the terms have been defined previously for Eq. (1); V is the ion-source accelerating voltage. As a mechanism for promoting Coulomb explosion, CID is not particularly discrete. As Fig. 4 shows, ten or more molecules can be removed as a result of a single collision. A lower limit to the energy transferred in such processes has been calculated as $\simeq 200\ \mathrm{cm}^{-1}$;[20] an upper limit could be $\simeq 20$ eV.[21] From Eq. (2) we would conclude that a FWHM (ΔE) in the laboratory frame of ≤ 20 eV (as given in Fig. 4) indicates that collisional excitation makes only a small additional contribution to the instrumental peak width ($\simeq 10$ eV). In turn, this implies that collisions transfer very little internal energy to the clusters. In contrast, a FWHM of $\simeq 150$ eV (Fig. 3) suggests that partitioning of the repulsive Coulomb barrier imparts a substantial kinetic-energy release to the fragment ions.

Equation (2) can be used to estimate the center-of-mass (c.m.) energy release for possible decay routes. Assuming, for example, $(CO_2)_{47}{}^{2+}$ loses seven molecules through a collision which is then followed by a sym-

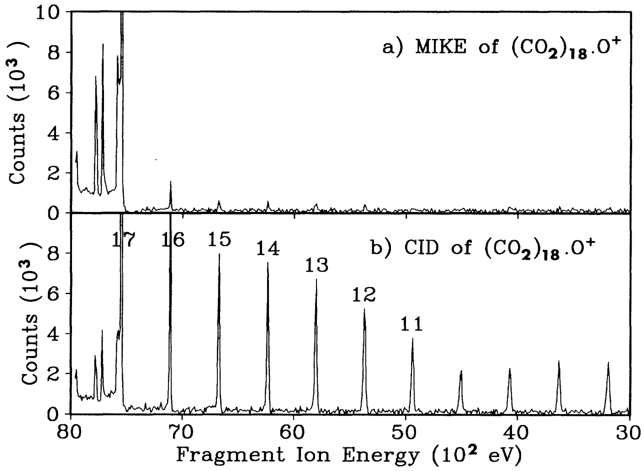

FIG. 4. MIKE spectra of $(CO_2)_{18}\cdot O^+$. (a) Unimolecular decay pattern. (b) CID fragments.

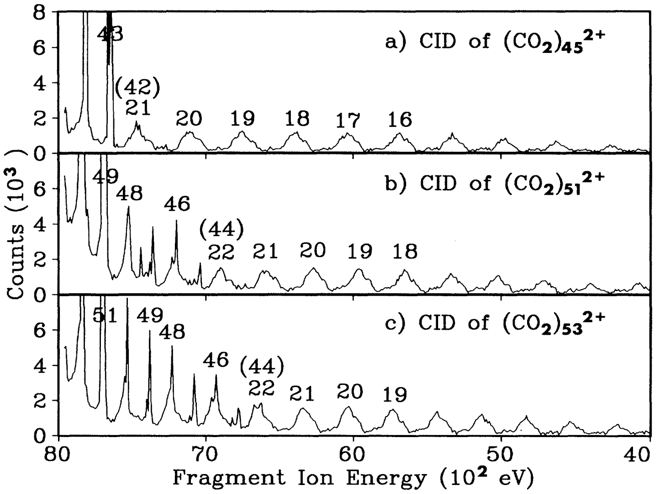

FIG. 5. MIKE spectra of the fragments arising from the CID of doubly charged CO_2 clusters; both doubly and singly charged fragments are labeled. (a) $(CO_2)_{45}{}^{2+}$, (b) $(CO_2)_{51}{}^{2+}$, and (c) $(CO_2)_{53}{}^{2+}$.

metric explosion, a laboratory frame energy of 150 eV would transform into a c.m. kinetic-energy release of 0.35 eV. Even the introduction of a slight asymmetry into the fission process does not lead to a significant increase in T. However, using the fragment $(CO_2)_{20}{}^+$ as an example, Eq. (1) suggests a limit to the degree of asymmetry in the fission process; if $m_2z_1/m_1z_2 > 1$, then we would expect to observe fragment ions in a MIKE scan at energies greater than that of the parent,[7] i.e., 8000 eV, and that is not the case. The energy release calculated above is substantially below that estimated for the Coulomb repulsion between two like charges separated by a distance R; $T = e_0^2/4\pi\epsilon_0 R \simeq 14.39/R$ eV, which for a large carbon-dioxide cluster gives T a value of 1-1.5 eV.[7]

The fact that the experimental measurements are yielding values for the energy release which are below the Coulomb estimate can be attributed to the possibility that charge separation (fragmentation) is accompanied by simultaneous internal excitation.[22] As the two fragments move down the Coulomb barrier some fraction of the repulsive energy, E_c, is transformed into intermolecular and intramolecular vibrational energy. One possible mechanism for such behavior would be for each fragment to be anisotropically polarized by the opposing positive charge.[12] Comparisons can be made with chemical processes where the energy associated with large repulsive barriers is partitioned to the reaction fragments; both experiments[23] and calculations[24] suggest that less than 50% of the repulsive energy appears in the form of fragment kinetic energy. Additional evidence to support the possibility of internal excitation comes from experiments on other doubly charged cluster systems.[18] Thus, observed fragment peak widths go in the order $Ar_n{}^+ \gg (CO_2)_n{}^+ > (C_6H_6)_n{}^+$; i.e., the greater the number of internal degrees of freedom, the smaller the kinetic-energy release. Finally, the sequential decay of singly charged benzene cluster fragments has also been observed,[18] suggesting that the internal excitation is eventually dissipated through molecular evaporation.

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Note added.— Following the submission of this paper, we became aware of work by Saunders[25] on the collision-induced fission of small doubly charged gold clusters. Although a range of singly charged fragments are identified, no analysis of their kinetic energies is presented.[25]

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