PHYSICAL REVIEW A VOLUME 60, NUMBER 5 NOVEMBER 1999

Experimental verification of the existence of the gas-phase dianions $BeF_4{}^{2-}$ and $MgF_4{}^{2-}$

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(Received 20 January 1997)

Recent calculations of the electron-detachment energies of the alkaline-earth-metal tetrahalides and alkali-metal trihalides yield values between 1.5 and 3.3 eV. If these values are correct, these molecular ions would be the most stable small dianions of any considered so far, and it should be easy to produce them in negative-ion sources. Using a cesium sputter source and accelerator mass spectrometry (AMS), we have detected and identified two multiply charged alkaline-earth-metal molecular-cluster ions, $BeF_4{}^{2-}$ and $MgF_4{}^{2-}$. Using the techniques that we developed earlier to study $C_n{}^{2-}$, we have been able to use AMS to unambiguously identify these dianions. We provide further evidence for their existence in the form of Coulomb explosion images that we produced in the terminal of our tandem accelerator. An unsuccessful search for alkali-metal dianions of the form $MX_3{}^{2-}$ and $M_2X_4{}^{2-}$ ($LiF_3{}^{2-}$ and $Li_2F_4{}^{2-}$) allows us to set an upper limit of 10^{-17} relative to F^- for their production in a Cs sputter source assuming their lifetimes are greater than 10 μs. It seems likely that they are either not formed at all in the sputter source or their lifetimes are considerably shorter than 10 μs.
[S1050-2947(99)08905-2]

PACS number(s): 32.70.Cs, 41.75.Cn, 33.70.Ca, 36.40.Wa

INTRODUCTION

Over the years, singly charged anions in the gas phase have attracted considerable experimental and theoretical attention, an interest stimulated in part by the development of the tandem accelerator. Searches for atomic dianions were initiated when it was recognized that they would allow a significant increase in the total energy of accelerated ions without the expense and complication of higher terminal voltages. Several times during the past 35 years, discovery of an atomic dianion has been claimed [1–4] but none have been confirmed [5–8], and now it appears highly unlikely that any atomic dianion is stable or has a lifetime even approaching 1 μs. Molecular dianions never received the attention of atomic dianions, in part because, from the tandem perspective, they would afford little or no increase in energy. But no one doubted that two electrons could be stable when placed on a molecule, if only the molecule were big enough. The first gas-phase dianions discovered experimentally were moderate-size molecules [9–16]. Not until 1990 were the first dianions consisting of fewer than twenty atoms discovered by Schauer, Williams, and Compton [17]. Theoretical attempts to understand the stability of the dianions already discovered and directed towards finding ever smaller molecules capable of supporting two extra electrons soon followed [18–30]. A summary of the status of these calculations is given in Scheller, Compton, and Cederbaum [31]. To date, the smallest molecular dianions calculated to be stable are alkali-metal halides of the form $MX_3{}^{2-}$ ($M=$Li, Na, or K; $X=$F or Cl), suggested by Scheller and Cederbaum [18] and the alkaline-earth-metal tetrahalides, $MX_4{}^{2-}$ ($M=$Be, Mg, or Ca; $X=$F or Cl), proposed by Weikert and Cederbaum [30]. In both cases, the electron detachment energies are predicted to be greater than 1.5 eV.

Positive identification of double-negative ions is extremely difficult because no combination of electric and magnetic deflecting fields can measure charge or mass alone, only mass to charge ratio. But modern mass spectrometers coupling an electrostatic energy analyzer with a high-resolution magnetic analyzer are immune to many of the mass-to-charge ambiguities caused by fragmentation of molecular ions and energy tails of ions produced in the source that plagued earlier mass spectrometers. Schauer, Williams, and Compton [17] used such a device and a clever trick to identify double-negative carbon clusters of the form $C_n{}^{2-}$, where $n \geqslant 7$. Their technique depends on observing double-negative ions as half-integral mass peaks; in the case of carbon clusters these correspond to molecules of the form ${}^{12}C_{n-1}{}^{13}C^{2-}$. For example, ${}^{12}C_6{}^{13}C^{2-}$ has a mass of 85, but because of its double charge, it behaves in a magnetic mass spectrometer as though its mass were 42.5. While this approach is fairly convincing, our experience with accelerator mass spectrometry (AMS), where spurious weak peaks abound, caused us to be skeptical. It occurred to us that if we accelerated a cluster ion in our tandem, we would be able to determine the number of carbon atoms comprising it by counting them. The number of carbon atoms gives a direct measure of the cluster's mass, and knowing the mass we could deduce its charge.

In this technique, the cluster ion is mass-analyzed twice—first as a negative (dianion) molecule, and then as individual positively charged atomic ions. Between these two analyzes, the negative molecular ion is accelerated to the terminal of a tandem accelerator (set to a voltage in these experiments between 6 and 8 MV) and converted to positive atomic ions by passing it through a gas or thin foil. The terminal voltage is chosen to produce charge states high enough to destroy all molecular bonds, and ensure that only atomic ions leave the stripper. In our case we used a gas stripper to reduce the effects of the Coulomb explosion (see below). After the atomic positive ions are produced, they are accelerated back to ground potential, and a specific mass and charge state are selected by the high-energy beam-transport system. For the

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analysis of $^{12}C_{n-1}{}^{13}C^{2-}$, the probability was ~10% that a ^{12}C would leave in the chosen charge state (3+ was used and the terminal voltage was 6 MV) and arrive at the detector. Because $n-1$ identical $^{12}C^{3+}$ ions are produced in the breakup of $^{12}C_{n-1}{}^{13}C^{2-}$, there was an appreciable probability that one, two, or even all of the identical fragments would arrive at the detector. Thus, we saw peaks corresponding to the arrival of a single carbon from some breakups, two carbons from others, and so on up to $n-1$ carbons. Since we could actually count the number of ^{12}C atoms making up the accelerated molecule, we could infer its mass, and knowing the mass-to-charge ratio of the negative ion (from the injector magnetic settings), we could confirm that the half-integral-mass negative molecules seen while sputtering carbon were indeed double-negative ions.

Using this technique we confirmed Schauer *et al.*'s identification of carbon dianion clusters. A complete description of the work was reported at the Seventh International Conference on AMS [32]. In another experiment, we attempted to elucidate the structure of the carbon dianions. We placed polycarbonate track detectors at the terminal of the tandem just following a thin carbon foil (we did not use the gas stripper) and used the Coulomb explosion to increase the interatomic spacing in the molecule to give an ''exploded'' view of its structure. The results of these experiments are also included in Middleton and Klein [32].

In the present work, we have used AMS to prove the existence of $BeF_4{}^{2-}$ and $MgF_4{}^{2-}$ ions and to search unsuccessfully for $LiF_3{}^{2-}$ and $Li_2F_4{}^{2-}$. Coulomb-explosion imaging has been used to elucidate the structure of the alkaline-earth-metal dianions. These four ions were selected because all are predicted to have detachment energies greater than 1.5 eV; the prediction for $Li_2F_4{}^{2-}$ is about 3.3 eV.

EXPERIMENTAL PROCEDURE

In an earlier experiment, we readily detected the half-integral-mass peaks corresponding to carbon dianion clusters produced in a high-intensity cesium-sputter source using our home-built magnetic-sector mass spectrometer. We used this same system to search for half-integral-mass peaks corresponding to $^{6}LiF_3{}^{2-}$ and $^{9}BeF_4{}^{2-}$. Lithium fluoride, enriched to 99% in ^{6}LiF, and 99.9% pure commercial BeF_2 were packed into 1.6-mm-diam holes drilled in sputter cathodes made from 99.995% pure molybdenum. No well-defined peaks with an intensity of greater than 10^{-15} A were observed at mass 31.5 ($^{6}LiF_3{}^{2-}$) or at mass 42.5 ($^{9}BeF_4{}^{2-}$) with a $^{19}F^{-}$ current of about 1 μA. However, there was a hint of a peak at mass 42.5 with an intensity of $<10^{-17}$ A that we suspected might be $BeF_4{}^{2-}$.

To further investigate the possibility that $BeF_4{}^{2-}$ was stable, a cathode containing beryllium fluoride was introduced into the tandem accelerator's ion source and mass 42.5 ions were injected. After acceleration through 6 MV, the ions passed through a gas stripper and the resulting $^{19}F^{3+}$ ions were analyzed in our six-anode gas-ionization detector. For a detailed description of the high-energy beam-transport system and the multianode detector, see Fink *et al.* [33].

The high-energy beam-transport system, consisting of two magnetic dipoles and two magnetic quadrupoles (neither velocity selector was used), was set up by accelerating $^{9}BeF_2{}^{-}$ ions at 6.0 MV and detecting the 20.453 MeV $^{19}F^{3+}$ ions in a Faraday cup in front of the detector. After greatly attenuating the current, the beam was admitted into the detector to provide an energy (E) and energy-loss (ΔE_2, measured under the second plate of the multianode detector) calibration for 20.453 MeV $^{19}F^{3+}$ ions.

The various attenuators were removed and the mass 42.5 ions were injected into the tandem at a terminal voltage of 5.925 MV—the voltage calculated to produce $^{19}F^{3+}$ ions from $BeF_4{}^{2-}$ with the same magnetic rigidity as those from $^{9}BeF_2{}^{-}$. This procedure of selecting a terminal voltage to produce $^{19}F^{3+}$ ions of the same energy regardless of the injected ion meant that no changes had to be made to the high-energy beam-transport magnets when switching beams. The energy and energy loss of the ^{19}F ions in the detector were also the same for all injected ions.

The lower half of Fig. 1 shows the energy spectrum of the ions entering the detector. Four equally spaced peaks were observed with intensities decreasing rapidly with energy. The lowest-energy peak corresponds to a single $^{19}F^{3+}$ ion arriving at the detector, while the remaining three are due to two, three, and four $^{19}F^{3+}$ ions (all from a single injected ion) arriving in coincidence. The upper half of Fig. 1 shows a ΔE versus E spectrum. The energy loss of the lowest energy peak is consistent with a single $^{19}F^{3+}$ ion entering the detector and the remaining three peaks show ΔE's that are two, three, and four times as large, as expected from the simultaneous arrival of two, three, and four $^{19}F^{3+}$ ions.

These measurements were made with a $^{19}F^{3+}$ count rate of about 400/s—a rate consistent with almost negligible ''accidental'' pileup. During a 10-min counting period, we observed 201 fourfold coincidences while the accidental pileup during this period was calculated to be 6. To further check the insignificance of pileup, a second 10-min measurement was made with a 20-fold attenuator placed between the ion source and accelerator. Within counting statistics, the ratio of the counts in the four peaks remained unchanged.

The probabilities of observing one, two, three, and four $^{19}F^{3+}$ ions in coincidence from the breakup of a single $BeF_4{}^{2-}$ ion at the terminal are given by $4P(1-P)^3$, $6P^2(1-P)^2$, $4P^3(1-P)$, P^4, where P is the probability of a single ion traversing the tandem and leaving the terminal in the desired charge state. In general, the formula is $[n!/k!(n-k)!]P^k(1-P)^{n-k}$, where n is the number of identical particles arriving at the terminal (four in the case of $BeF_4{}^{2-}$), and k is the number detected in coincidence. The upper graph in Fig. 2 shows a histogram of the number of single ions and coincidences observed in a 10-min period and the black dots represent the number calculated with $P=0.127$. Transmissions were estimated by taking the ratio of the counts in the single fluorine peak to the counts in the two-fluorine coincidence [their ratio is given by $2(1-P)/3P$]. The agreement is very good between the calculated count rates in the higher-multiplicity coincidences (three and four) and observation. The transmission of 12.7% is in good agreement with the 10.6% transmission measured while accelerating $^{9}BeF_2{}^{-}$ ions ($^{9}BeF_2{}^{-}$ ions have nearly the same velocity at the terminal as the $BeF_4{}^{2-}$ ions and are expected to have similar transmissions). The transmission of $^{9}BeF_2{}^{-}$ is measured ''through'' the accelerator (transmission

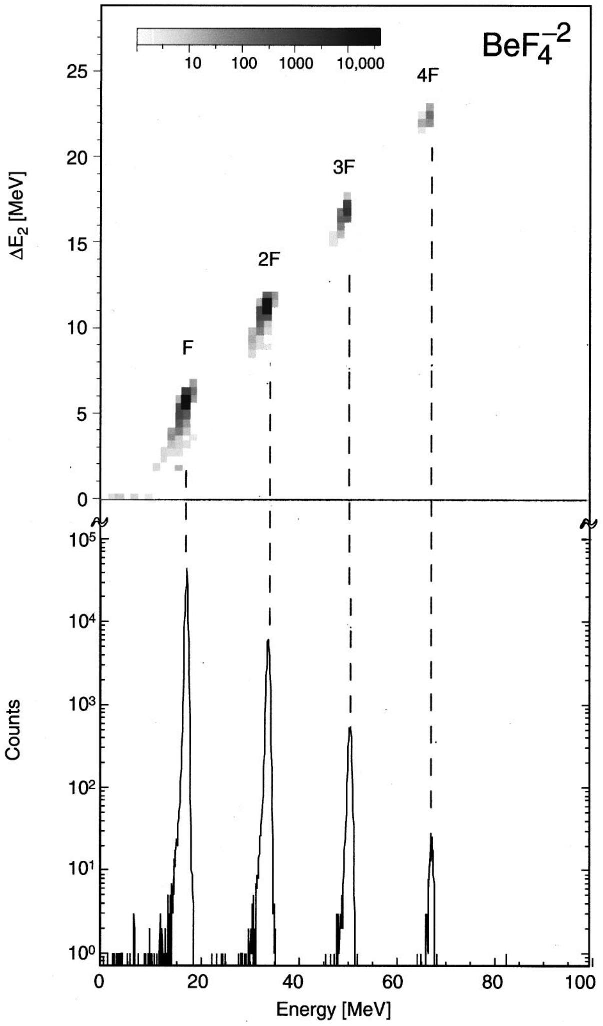

FIG. 1. Positive identification of BeF_4^{2-} in the multianode detector. Upper section: The ΔE_2 versus E (energy loss versus total energy) plot shows the single and coincidence peaks for 20.453 MeV $^{19}F^{3+}$ collected in 10 min from the breakup of BeF_4^{2-}. The $^{19}F^{3+}$ ions lose 2.9 MeV in the window of the detector, 11.9 MeV under the first plate, 5.4 MeV under the second plate (plotted against E_{Total} in the figure), and stop under the third plate. Coincidence peaks result when two or more ions arrive within the detector's resolving time. The resolving time is a function of the ion-collection time in the gas and the shaping constants used in the amplifier; for this experiment, it was approximately 1.0 μs. At these counting rates (several hundred/second), coincidences are likely with fragments from the same molecule, but not with fragments from different molecules. The peaks are equally spaced in both E and ΔE; shading reflects the number of counts in each bin. Lower section: The logarithmically scaled projection of the ΔE versus E plot on the E axis shows clearly the relative intensities of the single and coincidence peaks (see text for relative intensities).

from the low-energy to high-energy Faraday cups) while the transmission calculated from the peak multiplicity is from the stripper foil onward. The transmission through the accelerator includes losses in the low-energy tubes and in the gridded entrance lens (10%), so the transmission determined by the coincidence method should be at least 10% larger than that determined measuring currents.

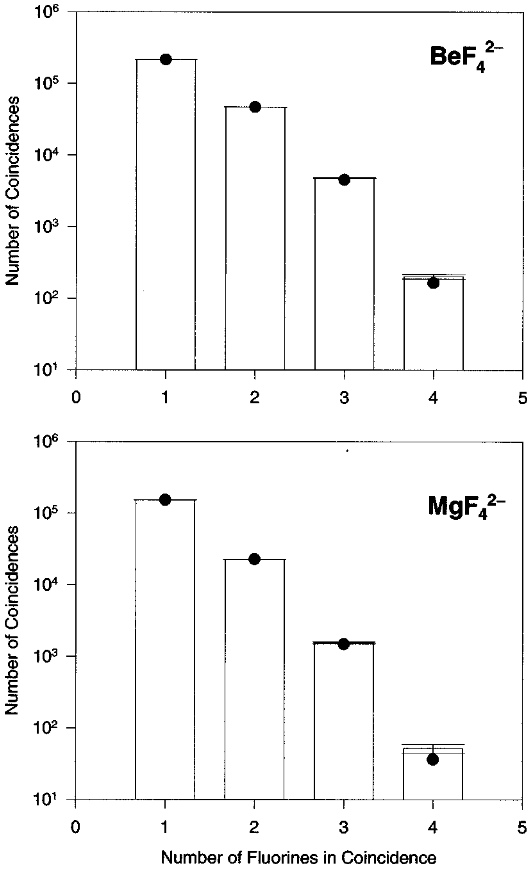

FIG. 2. Comparison of observed coincidences with theoretical predictions for alkaline-earth-metal tetrahalide dianions. Observed coincidences are shown as histograms, calculated values as black circles. ''Accidental'' pileup has been subtracted before plotting observations. The upper histogram shows the same data plotted in Fig. 1 where the total number of counts for the one, two, three, and four fluorine peaks are 215 163, 46 962, 4790, and 207, respectively. Pileup for each peak is calculated to be 0, 85, 18, and 6. Theoretical values (black circles) are calculated using the formula given in the text with an overall transmission for $^{19}F^{3+}$ of 12.7%. The lower histogram shows a similar plot obtained by accelerating MgF_4^{2-}. Here the counts in the one, two, three, and four fluorine peaks are 153 881, 22 690, 1561, and 53, respectively. The pileup is calculated to be 0, 43, 6, and 1, and the transmission through the accelerator was 8.9%. 1σ uncertainties are shown for the measured values as horizontal lines just above and below the top of the histograms.

What sorts of backgrounds are conceivable? The tandem injector has no electrostatic analyzer, so if a $Be_2F_8^-$ ion fragmented between the ion source and the deflection magnet to form a BeF_4^- ion, the BeF_4^- ion would have half the injection energy, and like BeF_4^{2-}, it would be injected into the tandem at a mass of 42.5 amu. Also like BeF_4^{2-}, BeF_4^- could produce four $^{19}F^{3+}$ ions. However, the $^{19}F^{3+}$ ions from BeF_4^- would have an energy of 19.129 MeV, ~6.5% lower than the 20.453 MeV of the $^{19}F^{3+}$ from BeF_4^{2-}. Because the resolution of the positive-ion analyzing magnet of the accelerator is better than 0.3%, $^{19}F^{3+}$ from this source is completely eliminated. Similarly, other possible ions at mass 42.5 amu, even if they contained four fluorine atoms, are easily eliminated by energy analysis at the high-energy end of the accelerator, and other ions that do not contain four fluorine atoms are eliminated in the multianode particle-identifying detector. We conclude that the evidence presented here supports unequivocally the existence of $BeF_4{}^{2-}$ ions with a lifetime that exceeds 25 μs, making $BeF_4{}^{2-}$ the lightest double-negative molecular ion yet observed.

Replacing the beryllium fluoride cathode with a magnesium fluoride cathode, we used a nearly identical procedure to verify the existence of $MgF_4{}^{2-}$. To capitalize on the ease of detection when a half-integral mass is injected into the tandem, we searched for $^{25}MgF_4{}^{2-}$, which is injected at mass 50.5. Since separated magnesium isotopes in fluoride form were unavailable, we used natural magnesium, which contains 10% ^{25}Mg. The reduction in intensity proved inconsequential, and E and ΔE versus E spectra similar to those shown in Fig. 1 were obtained. The lower histogram in Fig. 2 shows the number of $^{19}F^{3+}$ single counts, and the twofold, threefold, and fourfold coincidences obtained in a 20 min period. As in the case of beryllium, the black dots represent the calculated probabilities; this time the calculated transmission was 8.9%. We conclude that $MgF_4{}^{2-}$, like $BeF_4{}^{2-}$, forms a stable double-negative ion with a lifetime greater than 25 μs.

We searched on the tandem for alkali-metal dianions of the form $MX_3{}^{2-}$ and $M_2X_4{}^{2-}$. Using a cathode containing ^{6}LiF, we injected mass 31.5 ions to search for $LiF_3{}^{2-}$, reported by Scheller *et al.* [18,31] to have a detachment energy of about 1.6 eV (a little less than $BeF_4{}^{2-}$), despite not observing a vestige of a negative-ion peak at mass 31.5 on our mass spectrometer. The terminal voltage was adjusted to the calculated value of 5.672 MV. A 20-min counting period produced only 22 single $^{19}F^{3+}$ counts and no coincidences. To ensure that our terminal voltage was adjusted correctly, small excursions were made with little change in count rate. However, when the voltage was decreased to 5.657 MV, the singles count rate increased dramatically and became particularly overwhelming as the injection magnet was reduced towards mass 31, suggesting that these ions arose from the injection of $^6Li_2F^-$. Although it is difficult to place a strict quantitative upper limit on the existence of $LiF_3{}^{2-}$, we estimate that it must be at least four orders of magnitude less abundant than $BeF_4{}^{2-}$, since under identical conditions we detected only 22 $^{19}F^{3+}$ ions when tuned for $LiF_3{}^{2-}$ compared with 10^5 when tuned for $BeF_4{}^{2-}$. Consequently, we conclude either that $LiF_3{}^{2-}$ does not form a stable dianion, or the lifetime of $LiF_3{}^{2-}$ is less than 2 μs (the injection voltage was 28 kV and the distance between the source and the base of the accelerator is about 10 m; the time it takes the ion to travel from the base of the tank to the terminal is only ~10% of the time it takes the ion to travel from the source to the baseplate of the accelerator).

Scheller *et al.* [31] predict the molecular dianion $Li_2F_4{}^{2-}$ to be particularly stable with an electron detachment energy of about 3.3 eV. Since the molecule contains even numbers of Li and F atoms, the only way to inject it as a half-integral mass is to accelerate $^7Li^6LiF_4{}^{2-}$ (apparent mass of 44.5). To maximize the formation of the ion, enriched ^{6}Li fluoride was added to natural lithium fluoride to produce a roughly equal isotopic mixture. Measurements were compromised by relatively intense (~2 nA) beams of $^6LiF_2{}^-$ (at mass 44) and $^7LiF_2{}^-$ (at mass 45) flanking the sought after $^7Li^6LiF_4{}^{2-}$ peak at mass 44.5. Even more devastating to the sensitivity of our search, the $^{19}F^{3+}$ from the two anions could be adjusted to have the same magnetic rigidity as the $^{19}F^{3+}$ from the dianion by varying the terminal voltage by as little as ±9 kV. With the accelerator slits closed to their normal settings (±1.25 mm) as used in the previous measurements, the $^{19}F^{3+}$ single count rate was prohibitive, greater than 10^5/s. By closing the slits to ±0.25 mm, introducing our 20-fold attenuator in the negative-ion beam, and defocusing the beam entering the accelerator, the rate was reduced to a satisfactory value of 120/s. A 10 min exposure resulted in 79 300 single $^{19}F^{3+}$ counts, 4222 twofold coincidences, and no threefold or fourfold coincidences. As shown in Fig. 3, there are too few coincidences (two, three, and four) to be consistent with four fluorines arriving simultaneously at the terminal, but as the broken line connecting the black squares shows, the observed count rates are consistent with a difluoride breaking up at the terminal. The best explanation is that the ^{19}F counts were due to either $^6LiF_2{}^-$ or $^7LiF_2{}^-$ and the absence of threefold or fourfold coincidences strongly suggests that $Li_2F_4{}^{2-}$, like $LiF_3{}^{2-}$, either is not formed at all or has a lifetime less than 10 μs. (The limit we can place on the existence of $Li_2F_4{}^{2-}$ is ~10^3 higher than the limit we can place on the existence of $LiF_3{}^{2-}$ because we had to attenuate the output from the ion source.)

COULOMB EXPLOSION STUDIES OF 12 MeV $BeF_4{}^{2-}$ AND $MgF_4{}^{2-}$

We attempted to use Coulomb-explosion imaging (CEI) to determine the molecular structure of the alkaline-earth-metal tetrafluoride dianions, employing the method developed during the study of carbon polyatomic dianions (see Ref. [32]). The difficulty is that the dianions must be given enough energy to leave tracks in an appropriate material, and this means accelerating them in the tandem and imaging them at the tandem's central terminal. After accelerating the dianions through 6 MV, they were imaged with ''Coulomb-explosion films'' located at the position of the gas stripper used to convert the molecular dianion into positive atomic ions in the experiments described in the previous sections. The ''Coulomb-explosion films'' were made by modifying our standard stripper-foil holders (see Fig. 9 in Ref. [32]). These modifications consisted of (i) replacing the standard 5 $\mu g/cm^2$ carbon stripper foil with a much thinner, 1.5–1.6 $\mu g/cm^2$ carbon foil supported on a 90% transmission Ni mesh, and (ii) milling the back of the foil holder so that we could mount a 0.25-mm-thick sheet of track-sensitive polycarbonate plastic[1] without increasing the thickness of the frame assembly. The separation between the ''Coulomb-explosion'' foil and the imaging plastic was 840±50 μm. A dozen CEI ''films'' were made and inserted into the 60-position carousel that holds and changes the stripper foils in the tandem's central terminal. This arrangement allowed us to raise and lower the frames out of and into the negative-ion beam while the accelerator was operating.

Technically, this approach offers several challenges. The greatest inconvenience is that the accelerator's pressure vessel has to be pumped out and the tube vacuum broken both

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[1] PM 355 was obtained from Pershaw Moulding Ltd., Trading Estate, Pershore, Worcestershire, England.

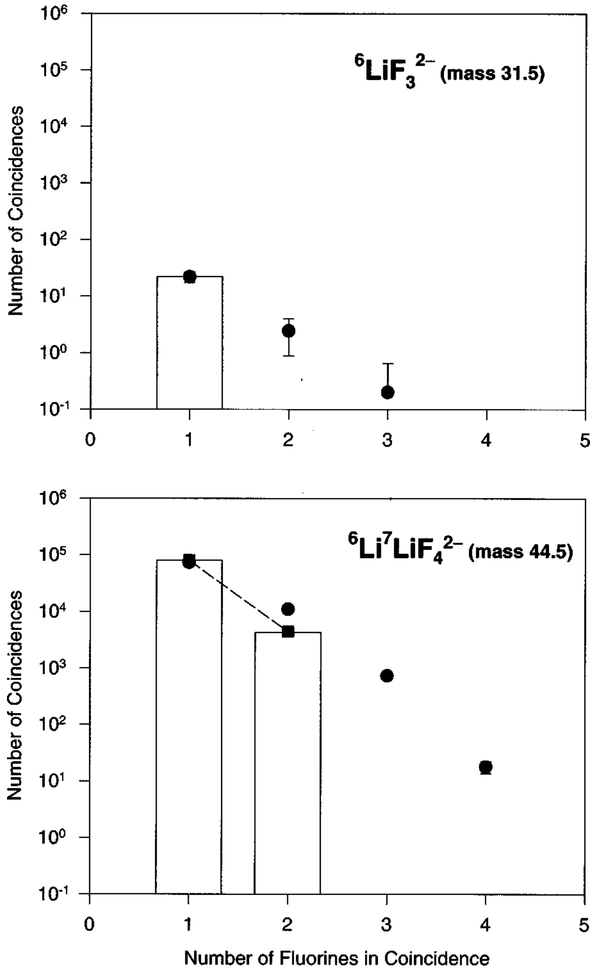

FIG. 3. Comparison of observed and calculated peaks for alkali-metal dianions. Neither panel shows evidence for alkali-metal dianions. The upper panel shows the observed coincidences (only 22 singles, no coincidences) while injecting mass 31.5 ($^6LiF_3^{2-}$). The error bars on the theoretical predictions (black dots) are 68% confidence intervals calculated from the square root of the number of expected counts. The low counting rate is also good evidence that the double–negative-ion does not exist: compare the 22 counts observed in 20 min with the 10^5 observed in 10 min for the BeF_4^{2-} and MgF_4^{2-}. Lower panel: Similar figure for the injection of mass 44.5. No evidence was seen for $^6Li^7LiF_4^{2-}$ although there were strong single- and double-coincidence peaks. The higher-order coincidences are missing (the black dots show their expected number of counts) and the single- and double-coincidence peaks are completely explained as arising from the injection of the tails of the $^6LiF_2^-$ (mass 44) or $^7LiF_2^-$ (mass 45). The black squares joined by the broken line show the expected values for the single-and double-coincidence peaks assuming a transmission of 10% (the average value of the transmissions observed throughout this experiment) and a negative ion containing only two fluorines arriving at the terminal.

before the experiment and after to install and remove the foils. Another major problem is estimating the proper ''exposure'' for the Coulomb-explosion films. For the carbon experiments, we were able to estimate the exposure fairly accurately from the analyzed beam since the injected beam was almost entirely composed of the carbon dianions. For this experiment, we were plagued by the injection of contaminant beams at neighboring masses. Because the dianion–negative-ion current was too small to measure, we attempted to determine the arrival rate of ions at the foil by observing the count rate of the $^{19}F^{3+}$ ions in our multianode detector. Using the estimated transmission (see the preceding section) we calculated the time required to yield about 10 counts per mm^2 in the plastic. But this technique provided no means of determining the number or the species of ions that were simultaneously injected but rejected by the positive-ion analysis system. Because of the lack of an electrostatic analyzer on the tandem's injector, these ions proved to be much more copious than expected. As a result, our five or six exposures made while injecting BeF_4^{2-} and $^{25}MgF_4^{2-}$ ions were grossly overexposed by ions consisting of three atoms (rather than the expected five). Carefully scanning almost the entire exposed area of plastic, we were able to find a few reasonably isolated events.

Figure 4(a) shows four BeF_4^{2-} breakup events. The track left by the Be ion is easily distinguishable from the larger diameter tracks produced by the F ions. In three of the events, the Be track lies outside of the space occupied by the four F tracks, and in the fourth it just fails to do so. In all cases, the figures have been oriented to place the Be track at the bottom. Figure 4(b) shows four similar figures produced by the breakup of 12 MeV $^{25}MgF_4^{2-}$ ions. Once again, the track left by the Mg ion is distinguishable from the tracks of the F ions, this time by its larger diameter. As in the case of the CEI's of BeF_4^{2-}, the alkaline-earth-metal ion lies outside the space occupied by the four fluorines.

Originally, we hoped to use the CEI's to deduce structural information about the dianions. We expected that the results would have to be analyzed statistically because the images would be affected by the random orientation of the molecules as they impinged on the stripper foil, variations in the charge states of the ions after the stripper foil, and multiple scattering. Unfortunately, because of the overwhelming background from the tails of the neighboring peaks, we were not able to analyze enough images of the dianions to make definitive statements about structure. But even from the few images we have analyzed, we can make the following observations. (i) The average separation between the fluorine ions in both Figs. 4(a) and 4(b) is about 9 μm, which corresponds to an explosion angle (measured with respect to the initial trajectory) of 5 mrad. This angle is considerably larger than the calculated multiple-scattering angle (0.7 mrad for 2.68 MeV fluorine ions, 0.14 MeV/amu, in charge state 4+) and consequently suggests that the images we see reflect structure. (ii) The average separation between the fluorine atoms is relatively constant from one image to another. (iii) In nearly all images, the Be and Mg lie outside of the quadrilateral formed by the four fluorine atoms.

The major destabilizing force in dianions is Coulomb repulsion between the extra two electrons. Although in principle a linear structure might minimize Coulomb effects by providing the most separation between the electrons, it is hard to conceive of how such a structure could be built from monovalent fluorine atoms. If MX_4^{2-} is a symmetric molecule, only two structures are possible: a tetrahedron with the alkaline-earth-metal ion in the center and a quadrilateral-based pyramid with the alkaline-earth metal at the apex. An elongated tetrahedral structure is preferred from a theoretical basis [30]. Weikert and Cederbaum calculate the distance

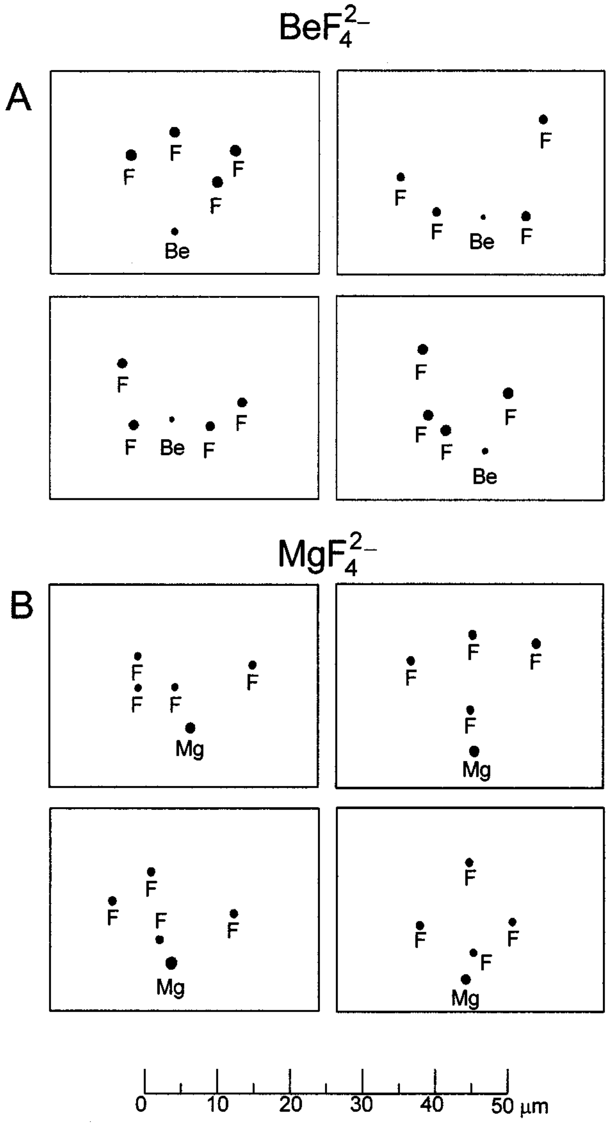

FIG. 4. Coulomb-explosion images of BeF_4^{2-} and MgF_4^{2-}. Photocopies of photomicrographs of tracks in polycarbonate plastic produced by the Coulomb explosion of BeF_4^{2-} (a) and MgF_4^{2-} (b) in 1.5–1.6 μg/cm^2 carbon foils. The dianion energy was 12 MeV and the separation between the polycarbonate and carbon foil was about 0.8 mm. Each box represents a single photograph that has been oriented so that the track left by the alkaline-earth-metal ion, readily distinguishable from the fluorine ion, is at the bottom.

between the apex fluorine and the alkaline-earth-metal atom is about 70% longer in the case of BeF_4^{2-} and about 90% longer in the case of MgF_4^{2-} than the distance between the alkaline-earth-metal atom and the three fluorines forming the triangular base. Our data from the Coulomb-explosion images are much too limited to allow us to make any definitive statements about structure. However, results from a very limited Monte Carlo simulation suggest that for the structure proposed by Weikert and Cederbaum, the majority of CEI's should have the alkaline-earth-metal ion within the confines of the quadrilateral formed by the four fluorines. We find that the alkaline-earth-metal ion is found always outside the four fluorines. Unless our results are simply a consequence of low statistics, they suggest the ions are oriented before they strike the foil, or that the structure of the dianions is really a pyramid with the alkaline-earth-metal atom at its apex. Unfortunately, more data are needed to distinguish between these possibilities.

CONCLUSIONS

Accelerator mass spectrometry provides a useful and rigorous method of positively identifying molecular dianions. Unlike conventional mass spectrometry that permits only the charge-to-mass ratio to be measured, AMS effectively allows an independent determination of mass and thereby determines, without ambiguity, charge. We have used this method to experimentally verify the existence of a theoretically predicted small dianion.

AMS techniques have been used to search for four small molecular dianions, LiF_3^{2-}, $Li_2F_4^{2-}$, BeF_4^{2-}, and MgF_4^{2-}, for which Scheller and Cederbaum [18] and Weikert and Cederbaum [30] report electron detachment energies of greater than 1.5 eV. The alkali-metal fluorides, LiF_3^{2-} and $Li_2F_4^{2-}$ were not observed. We place an upper limit on their formation rates in a sputter source of 10^{-20} and 10^{-17} that of $^{19}F^-$, respectively. Calculations of the Cederbaum group rather definitively argue for the stability of LiF_3^{2-} and $Li_2F_4^{2-}$. Our inability to observe these dianions suggests that the alkali-metal dianions either are not formed or, if formed, have lifetimes less than 10 μs. If the latter is the case, it could be that the short lifetimes of these ions are an artifact of producing them in a sputter source. It is certainly the case that sputter sources are very effective in producing small dianions, in fact all small dianions to date have been produced in Cs sputter sources. But it is also known that sputter sources produce ions in high states of excitation. Perhaps the vibrational excitations of LiF_3^{2-} and $Li_2F_4^{2-}$ are sufficient to destabilize them. If this is the case, then heavier dianions in the class MX_3^{2-} and $M_2X_4^{2-}$ formed in a sputter source might have longer lifetimes. We plan to look in the near future for KF_3^{2-} and $K_2F_4^{2-}$.

Earlier investigators [34] using a CAMECA IMS-4f ion microprobe were unable to detect the alkaline-earth-metal tetrafluoride dianions; we now present definitive evidence for their existence based on identification using AMS. If these dianions are not stable, they must have lifetimes greater than ~20 μs. However, they are only weakly formed in a cesium sputter source with intensities about 10^{-16} that of $^{19}F^-$; they are two to five orders of magnitude less intense than the dianions composed of carbon clusters [32].

Further studies of structure and stability are being contemplated. Improving structure determinations using the Coulomb-explosion method would require many more observations (on the order of 100), but such a large number of images is not possible with our current injector because of interferences from contaminant ions injected along with the BeF_4^{2-} and MgF_4^{2-} ions. Adding an electrostatic analyzer to the injector would reduce the tails of the neighboring peaks and perhaps make such a large number of measurements possible. Electron affinity measurements would establish the stability of these ions. However, electron affinity measurements on dianions are extremely difficult because of the low intensity of dianion beams and the added difficulty, when dealing with molecular ions, of insuring that they are in their ground states (no vibrational or rotational excitation). So far, we have established limits on the electron affinity of only one double-negative ion [35]; the alkaline-earth-metal dianions would be much more difficult because they are much weaker in intensity. It is possible that the ions we observe are metastable. So far we have only been able to establish limits on the lifetimes of several dianions [32,36], although we hope in the future that such measurements could be improved using the recently developed ion traps [37].

ACKNOWLEDGMENTS

We wish to thank the NSF for supporting this work under Grant No. PHY 94-17364 and, Harry White, who assisted in all phases of this work.

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[1] K. Bethge, E. Heinicke, and H. Baumann, Phys. Lett. **23**, 542 (1966).
[2] W. K. Stuckey and R. W. Kiser, Nature (London) **211**, 963 (1966).
[3] H. J. Kaiser *et al.*, Z. Phys. **243**, 46 (1971).
[4] I. H. Bauman *et al.*, Nucl. Instrum. Methods **95**, 389 (1971).
[5] L. Frees, E. Heinicke, and W. S. Koski, Nucl. Instrum. Methods **159**, 105 (1979).
[6] D. Spence, W. A. Chupka, and C. M. Steven, Phys. Rev. A **26**, 654 (1982).
[7] K. H. Chang *et al.*, Phys. Rev. A **35**, 3949 (1987).
[8] W. Kutschera *et al.*, Nucl. Instrum. Methods Phys. Res. A **220**, 118 (1984).
[9] R. C. Dougherty, J. Chem. Phys. **50**, 1896 (1969).
[10] J. H. Bowie and B. J. Stapleton, J. Am. Chem. Soc. **98**, 6480 (1976).
[11] K. Leiter *et al.*, Int. J. Mass Spectrom. Ion Processes **68**, 341 (1986).
[12] A. P. Bruins, T. R. Covey, and J. D. Henion, Anal. Chem. **59**, 2642 (1987).
[13] W. P. M. Maas and N. M. M. Nibbering, Int. J. Mass Spectrom. Ion Processes **88**, 257 (1989).
[14] P. A. Linbach *et al.*, J. Am. Chem. Soc. **113**, 6795 (1991).
[15] R. L. Hettich, R. N. Compton, and R. H. Ritchie, Phys. Rev. Lett. **67**, 1242 (1991).
[16] A. T. Blades and P. Kebarle, J. Am. Chem. Soc. **116**, 10 761 (1994).
[17] S. N. Schauer, P. Williams, and R. N. Compton, Phys. Rev. Lett. **65**, 625 (1990).
[18] M. K. Scheller and L. S. Cederbaum, J. Chem. Phys. **99**, 441 (1993).
[19] M. K. Scheller and L. S. Cederbaum, J. Chem. Phys. **100**, 8934 (1994).
[20] M. K. Scheller and L. S. Cederbaum, J. Chem. Phys. **101**, 3962 (1994).
[21] M. K. Scheller and L. S. Cederbaum, J. Phys. B **25**, 2257 (1992).
[22] A. I. Boldyrev and J. Simons, J. Chem. Phys. **97**, 2826 (1992).
[23] A. I. Boldyrev and J. Simons, J. Chem. Phys. **98**, 4745 (1993).
[24] M. Guerra, Chem. Phys. Lett. **197**, 205 (1992).
[25] J. F. Liebman and A. Skancke, THEOCHEM **99**, 67 (1993).
[26] T. Sommerfeld, M. K. Scheller, and L. S. Cederbaum, J. Chem. Phys. **103**, 1057 (1995).
[27] T. Sommerfeld, M. K. Scheller, and L. S. Cederbaum, J. Chem. Phys. **104**, 1464 (1996).
[28] J. D. Watts and R. J. Bartlett, J. Chem. Phys. **97**, 3445 (1992).
[29] H. G. Weikert *et al.*, Z. Phys. D **18**, 299 (1991).
[30] H. G. Weikert and L. S. Cederbaum, J. Chem. Phys. **99**, 8877 (1993).
[31] M. K. Scheller, R. N. Compton, and L. S. Cederbaum, Science **270**, 1160 (1995).
[32] R. Middleton and J. Klein, Nucl. Instrum. Methods Phys. Res. B **123**, 532 (1997).
[33] D. Fink *et al.*, Nucl. Instrum. Methods Phys. Res. B **47**, 79 (1990).
[34] H. Gnaser and H. Oechsner, Nucl. Instrum. Methods Phys. Res. B **82**, 518 (1993).
[35] D. Berkovits, J. Klein, and M. Paul (unpublished).
[36] R. Middleton and J. Klein, Nucl. Instrum. Methods, Phys. Res. B (to be published).
[37] D. Zajfman *et al.*, Phys. Rev. A **55**, R1577 (1997).