Search for long-lived doubly charged atomic negative ions

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(Received 9 June 1981)

Using the Argonne 100-in.-radius double-focusing mass spectrometer we have searched for long-lived ($\geqslant 10^{-5}$ sec) doubly charged atomic negative ions with the use of electron impact and Penning ionization sources. Our source operating conditions are similar to those of previous experiments which claim the existence of such ions. In contrast to all previous experiments, our mass resolution is sufficient to absolutely identify any impurity ion from its mass defect, and the machine design is such that artifact peaks (Aston peaks), caused by collisional dissociation of molecular negative ions, do not occur. Using a variety of target gases, we set upper limits for the production of doubly charged or singly charged species in electron bombardment and Penning sources of X^{2-} to $X^- \leqslant 10^{-7}$ to 10^{-8} and X^{2-} to $X^- \leqslant 5\times 10^{-10}$, respectively. These results contrast to those of previous experiments which claim positively identified ratios of X^{2-} to $X^- = 10^{-1}$ to 10^{-2} and X^{2-} to $X^- \approx 10^{-3}$, respectively. We find *no* evidence of any doubly charged atomic negative ion.

I. INTRODUCTION

In recent years there have been several experiments reported which purport to have detected long-lived ($\geqslant 10^{-5}$ sec) doubly charged atomic negative ions.[1–3] Stuckey and Kiser[1] report an intensity ratio of doubly charged or singly charged negative halogen ions of about 10^{-1} using an electron bombardment source in an ion-cyclotron resonance (ICR) spectrometer, using a variety of halogenated hydrocarbons as target gases. These experiments[1] include an observation of both F^{2-} and Cl^{2-} from CF_3Cl in the ratio of F^{2-} to F^- and of Cl^{2-} to Cl^- of 10^{-1}. The interpretation of these experimental results has been criticized by Fremlin,[4] who proposed several mechanisms by which harmonic peaks can occur in ICR-type mass spectra. Beauchamp[5] has pointed out that such harmonic peaks are often observed in ICR spectra and are easily recognized. Attempts by Ahnell and Koski[3] to duplicate the results of Stuckey and Kiser,[1] using an electron bombardment source operating at similar electron beam energies but with a quadrupole mass filter, yielded negative results, except for the observation of F^{2-} (but *not* Cl^{2-}) from CF_3Cl in the ratio of F^{2}– to F^- of 10^{-1}.

Unpublished experiments by Compton[6] and coworkers using electron bombardment and cesium charge exchange ion sources, together with time-of-flight mass analysis (which should be free of artifact structures), have similarly yielded negative results.

The most comprehensively documented experiments reporting the existence of doubly charged atomic negative ions, including O^{2-}, Te^{2-}, Bi^{2-}, F^{2-}, Cl^{2-}, Br^{2-}, and I^{2-}, appear to be those of Baumann *et al.*[2] who observed intensity ratios of double-single charged species of the order 10^{-3} to 10^{-4}, with increasing probability of production of the doubly charged species with increasing mass of the element.

In the experiments of Baumann *et al.*[2] the negative ions were produced in a Penning ion source[7] and extracted through an aperture in the cylindrical anode. The ions were accelerated in a series of lenses and mass analyzed in a 60° magnetic sector. In a magnetic mass analyzer, diatomic negative ions X_2^-, which fragment by collisional dissociation with the background gas after acceleration but prior to mass analysis (yielding the products X and X^-, each having $\frac{1}{2}$ the energy of X_2^-), will give rise to anomalous structures (known as Aston peaks) at an apparent mass of $X^-/2$, i.e., the mass location expected of X^{2-} (which has twice the energy of any primary X^- and X_2^-). Thus, for example, the observation of an ion of mass 63.5 may result from the production of I^{2-} in the ion source, *or* result from I^- which is produced by collisional dissociation of I_2^- as described above. Baumann *et al.*[2] applied an electric deflection analysis technique to their ion beam after mass analysis to separate the two above processes. They conclude that their mass spectra did indeed contain components of X^{2-} produced in their ion source.

In an attempt to duplicate the experiments of Baumann *et al.*,[2] Frees *et al.*[8] used an identical Penning source together with a 45° magnetic analyzer followed by electric deflection to facilitate species identification in a manner identical to Baumann *et al.*[2] Frees *et al.*[8] also observed a primary ion at mass 63.5, indicative of I^{2-} when using ^{127}I in their ion source. However, when they substituted the radioactive isotope ^{131}I in their ion source, they observed no ion at mass 65.5, but the ion at mass at 63.5 remained. From this, and from radioactivity measurements in their ion collectors, Frees *et al.*[8] conclude that no I^{2-} was produced in their source, and that their (and hence that of Baumann *et al.*[2]) *apparent* I^{2-} signal arose from an unknown impurity ion having nearly the same charge-mass ratio as I^{2-}.

More recently, Hind and Ali[9] have extracted *positive* ions from an rf discharge and charged exchanged these ions with a background gas to give negative ions. Using this arrangement they set limits O^{2-} to O^- of $(0.07 \pm 1.6) \times 10^{-12}$. However, the results of Hind and Ali cannot be compared directly with the experiments of Baumann *et al.*,[2] as it is well known that the generation of a given species of negative ion is critically dependent upon the type of source used.[10]

In a similar manner, the results of theoretical calculations are somewhat ambiguous. While most calculations find the O^{2-} ion to be unbound by as much as 5 eV,[11] another recent calculation[12] points out that it cannot be concluded that O^{2-} is not bound. Although one may intuitively feel that such doubly charged atomic species would not be bound (forming *stable* ions) it has been pointed out by Inghram[13] that long-lived ($>10^{-5}$ sec) multiply excited species, such as a sextet Cl^{2-} $3p^4(^3P)4s4p$ and O^{2-} $2p^3(4s)3s3p^2$, may exist in a manner analogous to He^- $1s2s2p\ ^4P_{5/2}$.

In light of the conflicting experimental results described above, combined with the recent appearance of a lengthy review paper,[14] which concludes that doubly charged negative atomic species definitely exist, we have experimentally reexamined the possible existence of such species under experimental conditions which duplicate as close as possible those experiments which have reported positive observations of doubly charged negative ions.[1–3]

II. APPARATUS

In all of our experiments we have used the Argonne 100-in.-radius double-focusing mass spectrometer.[15,16]

The ultimate resolution of the mass spectrometer,

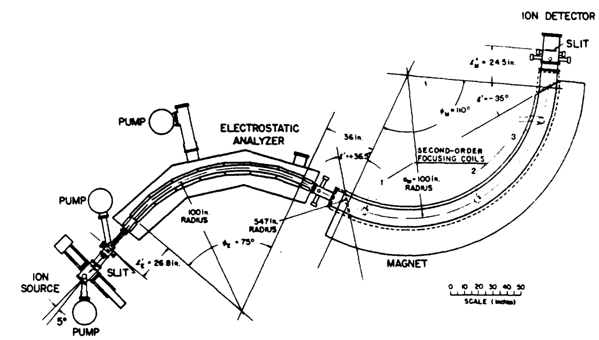

FIG. 1. Schematic diagram of the ANL 100-in.-radius double-focusing mass spectrometer.

shown in Fig. 1, is of the order $m/\Delta m \approx 10^6$. In the present experiments such high resolution is not required, and we typically operate at a resolution $m/\Delta m$ of 2×10^3 to 1.5×10^4, under which conditions the transmission of the mass spectrometer is about 95%, thus ensuring high sensitivity. Even with this degraded resolution, it remains such that we can positively locate, within a few mamu (and hence identify), any impurity ion which may be present. This capability is not present in any previous mass spectrometric study of doubly charged ions.[1–3,8,9]

In all previous measurements of doubly charged negative ions by magnetic analysis spectrometers, whether reporting negative[8,9] or positive[1–3] results, artifact peaks (Aston peaks) have been a complicating issue in interpretation of the data. An important feature of our machine is that artifact peaks do not occur. This is attributed to the use of an electrostatic hemispherical energy analyzer between the ion source region and the magnetic analysis section. The focusing conditions and background pressure ($\sim 10^{-8}$ Torr) in the region between the electrostatic and magnetic sectors are such that any collisionally dissociated species which may occur do not reach the detector, considerably simplifying the interpretation of our results.

In our experiments we have used both electron impact and Penning ionization ion sources in order to duplicate as closely as possible the experimental conditions of those who do report positively the existence of doubly charged negative ions.[1–3] Our Penning ion source is geometrically identical to the commercial Penning sources used on accelerators,[7] and used by Baumann *et al.*,[2] except that we have replaced the plasma confining electromagnet with a permanent magnet of field strength about 500 G. Our conditions of ion flight time and electric field strengths during acceleration do not differ significantly from those of earlier work[2] so as to invalidate the results of our experiments.

III. EXPERIMENTAL TECHNIQUE

The sensitivity of our machine is such that the ratio X^{2-} to X^- is very small, typically 10^{-7} to 10^{-10}, which is well outside the dynamic range of our detection system without changing electron-multiplier voltages, etc. Thus we usually determine the ratio for X^{2-} to X^- in two stages as follows.

First, we choose an arbitrary negative ion, Y^-, whose mass lies close to that of the particular doubly charged ion X^{2-} we are looking for. These negative ions Y^- are produced from impurities in the ion source region from earlier experiments. The sensitivity of the machine is such that small signals corresponding to negative ions can be observed at most mass numbers. The intensity of these impurity ions Y^- is necessarily small, but still sufficiently large they can be measured on the output of the electron-multiplier with an electrometer. The ratio for Y^- to X^- is measured on electrometers by applying different voltages to a calibrated electron-multiplier tube.

Next, operating in a pulse counting mode, multiple alternate scans of Y^- and any possible X^{2-} are stored in a multichannel analyzer. Mass ranges are changed by switching the acceleration voltage and electrostatic analyzer voltages automatically. The mass scale of our machine is sufficiently well calibrated that up to four mass ranges[17] can be scanned sequentially with the zero point of any particular mass scan being accurately known to within about 1 or 2 mamu. The ratio of X^{2-} to Y^- is thus obtained, which together with the ratio of Y^- to X^- determined above gives the ratio X^{2-} to X^-.

IV. RESULTS

In the electron bombardment ion source we have operated at incident electron energies between 20 and 80 eV, electron beam currents of 100 μA to a few mA, and target gas pressures between 5×10^{-5} and 2×10^{-3} Torr. These experimental conditions lie within the range of previous experiments using electron impact sources[1,3] which purport to have observed doubly charged negative ions.

Using the Penning ionization source our gas pressures have been typically in the range 2×10^{-4} to 5×10^{-3} Torr, with discharge currents between 100 μA to a few mA. Thus in our experiments, the gas pressures are about an order of magnitude lower and discharge currents about a factor of 30 lower than previous Penning source experiments[2] which claim to have detected doubly charged negative ions.

A typical example of our data obtained from a Penning discharge in HI is shown in Fig. 2. In Fig. 2, channels 0–200 show the mass scan around mass 63.5, the expected location of any I^{2-} (the most intense doubly charged ion observed by Baumann *et al.*[2]) and channels 200–400 show a mass scan around mass 64 (S_2^- and SO_2^-, which we use as the intermediate ions in this case to determine the ratio of I^{2-} to I^-). Note that S_2^- and SO_2^-, which have nominally the same mass (separated by only 18 millimass units), are completely resolved in our apparatus. In this scan $m/\Delta m \approx 12\,800$, which together with our ability to set our mass range to 1 or 2 mamu, gives us absolute identification of any ion from its mass defect, a feature absent in other machines.[1–3,8,9] Furthermore, it is obvious from Fig. 2 that no ions

TABLE I. Electron impact ionization source.

Target gas	Ratio X^{2-} to X^- previous data	Ratio X^{2-} to X^- present data
CF_3I		I^{2-} to $I^- \leq 1.3 \times 10^{10^{-7}}$
CF_3I		F^{2-} to $F^- \leq 2.1 \times 10^{-7}$
CF_3Cl	F^{2-} to $F^- \approx 10^{-1}$ [a,b]	F^{2-} to $F^- \leq 4.6 \times 10^{-8}$
CF_3Cl	Cl^{2-} to $Cl^- \approx 10^{-1}$ [a]	Cl^{2-} to $Cl^- \leq 1.15 \times 10^{-7}$
O_2	O^2 to $O^- \approx 10^{-3} \rightarrow 10^{-4}$ [c]	O^2 to $O^- \leq 1.0 \times 10^{-7}$
CCl_4		Cl^{2-} to $Cl^- \leq 2 \times 10^{-8}$
I_2		I^{2-} to $I^- \leq 1.0 \times 10^{-8}$
	Penning ionization source	
HI I_2 H_2+I_2	I^{2-} to $I^- \approx 10^{-3}$ [c]	I^{2-} to $I^- \leq 5.0 \times 10^{-10}$

[a] Reference 1. [b] Reference 3. [c] Reference 2.

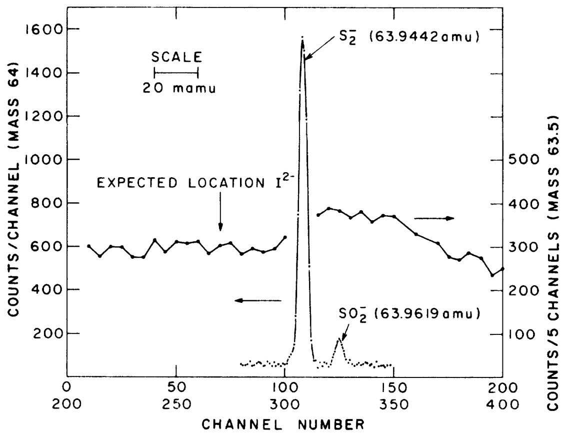

FIG. 2. Mass spectra of negative ions produced in a Penning ionization source containing HI in the region of mass 64 (SO_2^- and S_2^- produced from background impurities, channels 200→400) and in the mass region any I^{2-} would be expected to appear (mass 63.5, channels 0→200). From the ratio of I^{2-} to S_2^- and S_2^- to I^- measured in an electrometer, we set limits of the ratio I^{2-} to $I^- \leq 4.5\times10^{-10}$ in this experiment. Note that our resolution is such that 200 channels correspond to approximately 200 millimass units, i.e., $m/\Delta m \sim 12\,800$.

are detectable above noise level in the region of mass 63.5. This demonstrates that not only are no I^{2-} ions being detected, but also the complete lack of any artifact peaks arising from collisional dissociation of I_2^-, which is certainly being produced in copious quantities in our ion source. From Fig. 2 and electrometer measurements of I^- to S_2^-, we establish limits of I^{2-} to I^- produced in a Penning discharge of HI to be $\leq 4.5\times10^{-10}$ in this particular experiment.

A summary of our experimental results is shown in Table I where we list an upper bound on the production of X^{2-} to I^- for a variety of target gases and ion sources operating under the highest pressures and currents listed above. Under no experimental conditions did we observe *any* doubly charged negative atomic ion.

V. CONCLUSIONS

In the experiments described in this paper we have searched for long-lived doubly charged negative atomic ions under ion source conditions which duplicate,[1,3] or come close to duplicating,[2] previous experiments which claim to have positively identified such ions. However, our experiments have been carried out under conditions which, for the first time, allow for an aboslute identification of any ions which may result in false signals caused by impurities,[8] and in which aritfact peaks do not occur. Using electron impact ionization sources we set upper limits of X^{2-} to X^- for various ions to be of the order 10^{-7}, whereas earlier experiments[1,3] claim ratio values of X^{2-} to X^- of 10^{-1} to 10^{-2}. In our Penning source measurements we set upper limits X^{2-} to X^- of $\approx 5\times10^{-10}$, whereas previous experiments[2] claim ratio values X^{2-} to $X^- \sim 10^{-3}$. Although our Penning source pressures and currents were smaller than in a previous experiment[2] (by 10 and 30, respectively), it is difficult to conceive of any multiple collision process necessary to explain the difference of X^{2-} to $X^- \sim 2\times10^6$ in these experiments. We must conclude, contrary to a recent review,[14] that there is *no* convincing evidence in the literature at the present time for the existence of long-lived doubly charged atomic negative ions. Such observations as have been reported probably arise from impurity ions of similar e/m to doubly charged species, or from Aston peaks, or both.

This work was performed in part under the auspices of the U.S. DOE.

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