# Experimental Search for the Smallest Stable Multiply Charged Anions in the Gas Phase

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An extensive experimental search for the smallest stable gaseous multiply charged anions (MCAs) was pursued. Four penta-atomic dianions, $\mathrm{Pt}X_4{}^{2-}$ and $\mathrm{Pd}X_4{}^{2-}$ ($X = \mathrm{Cl}, \mathrm{Br}$), were found to be the smallest observable using an electrospray ion source. Photodetachment experiments revealed, however, that $\mathrm{PtCl_4}^{2-}$ and $\mathrm{PtBr_4}^{2-}$ are electronically metastable with negative electron-binding energies. $\mathrm{PdCl_4}^{2-}$ and $\mathrm{PdBr_4}^{2-}$ were found to be electronically stable, but thermodynamically unstable against fragmentation. Lifetimes were estimated using an ion-trap technique for the four observed metastable MCAs, providing further insight into their electronic and thermodynamic stability.

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Most atoms and many molecules can form stable singly charged anions. However, until very recently isolated multiply charged anions (MCAs) were rarely known [1–5]. The strong Coulomb repulsion between the excess negative charges makes the most common MCAs in the condensed phases, such as $\mathrm{SO_4}^{2-}$ and $\mathrm{CO_3}^{2-}$, unstable in the gas phase [6]. It is thus still an open question concerning the smallest molecular species that can bind two or more excess electrons with both electronic (against electron detachment) and thermodynamic (against fragmentation) stability. A number of MCAs with relatively large size (more than 10 atoms) have been observed in the gas phase using mass spectrometry and have been well reviewed [1–5]. However, there have been only a few convincing experimental observations of relatively small MCAs in the gas phase, including $\mathrm{C}_n{}^{2-}$ ($n = 7$–$9$) [7], $\mathrm{S_2O_6}^{2-}$ [8], and $\mathrm{S_2O_8}^{2-}$ [8,9]. Thus, the smallest gaseous MCA that has been observed heretofore consists of 7 atoms [10].

Extensive theoretical works have been carried out on small gaseous MCAs [1–4]. Among the MCAs with less than seven atoms, there is now a consensus that no single atom can bind two or more excess electrons [11]. It has also been concluded that no diatomic or triatomic dianions are stable [4,12–14]. The enormous Coulomb repulsion between the two excess charges in these small dianions makes them unstable against electron autodetachment. For tetra-atomic systems, Scheller and Cederbaum predicted some of the smallest electronically stable MCAs consisting of alkali-halides ($MX_3{}^{2-}$) [15]. Boldyrev and Simons predicted that $\mathrm{Mg_2S_3}^{2-}$ is likely to be the smallest electronically stable *linear* dianion [14]. Other penta-atomic MCAs that have been predicted to be electronically stable include alkaline-earth halides ($MX_4{}^{2-}$) [16,17]. Among hexatomic systems, $M_2X_4{}^{2-}$-type of alkali-halides [18] and $\mathrm{Si_2O_4}^{2-}$ [19] have been predicted to be electronically stable. However, none of these relatively small MCAs has been observed experimentally [10].

There exists a potential barrier in multiply charged ions due to the long-range Coulomb repulsion and short-range binding [1,2,16]. The repulsive Coulomb barrier (RCB) provides dynamic stability against electron detachment in MCAs or molecular fragmentation (Coulomb explosions). Using photoelectron spectroscopy (PES), we have recently observed the RCB directly in a series of stable doubly charged anions [20–22]. In particular, we have shown that the RCB can prevent electron detachment even when the photon energies are higher than the electron-binding energies. Very recently, we have observed a series of stable hepta-atomic MCAs [23], $ML_6{}^{2-}$ ($M = \mathrm{Re}, \mathrm{Os}, \mathrm{Ir}, \mathrm{Pt}$; $L = \mathrm{Cl}, \mathrm{Br}$). Here we present a systematic experimental search for the smallest stable MCAs and report our observations of four penta-atomic MCAs, $MX_4{}^{2-}$ ($M = \mathrm{Pt}, \mathrm{Pd}$; $X = \mathrm{Cl}, \mathrm{Br}$), after screening a long list of candidates and an extensive experimental effort. Surprisingly, we found that $\mathrm{PtCl_4}^{2-}$ and $\mathrm{PtBr_4}^{2-}$ possess negative electron-binding energies; i.e., they are electronically unstable, whereas $\mathrm{PdCl_4}^{2-}$ and $\mathrm{PdBr_4}^{2-}$ are electronically stable, but thermodynamically unstable against fragmentation. Their respective metastability was confirmed by electron-tunneling model calculations and lifetime measurements.

The experiments were performed with an electrospray ionization source (ESI), coupled with ion-trap time-of-flight (TOF) mass spectrometry and photodetachment PES [24]. Two types of small dianions were considered in this study. The first includes the $MX_4{}^{2-}$-type of transition metal complexes ($X = \mathrm{Cl}, \mathrm{Br}$) that are known to exist in solutions [25]. For these species, we typically start with a $10^{-3}$ M salt solution in a water/methanol (10/90) mixed solvent. The second type of dianions involved alkali or alkaline-earth halides species that have no analogs in solutions, but are predicted theoretically to be long-lived in the gas phase [15–18]. To search for these dianions, alkali or alkaline-earth halide salt solutions ($\sim 10^{-3}$ M) in a water/methanol (10/90) mixed solvent were used. Anions produced from the ESI source were accumulated and stored in a quadruple ion trap for 0.1 s before being analyzed by a TOF mass spectrometer. Thus only MCAs with sufficiently long lifetimes (~0.1 s) can be observed in our experiments. For metastable MCAs, we can also estimate their half-lives using the ion trap [24]. Since fluoride compounds have very low solubility in water or methanol, our search of the smaller alkali and alkaline-earth halides MCAs was focused mainly on the chloride and bromide complexes.

We did not observe the anticipated tetra-atomic alkali-halide dianions, $MX_3^{2-}$ ($M$ = Li, Na, K; $X$ = Cl, Br), the smallest dianions predicted to be electronically stable in the gas phase [15]. The hexatomic $M_2X_4^{2-}$-type of alkali halides [18] was also not observed. The current findings are consistent with a previous ESI study of alkali-halide clusters [26] in which the smallest dianion observed contained twelve atoms ($Cs_5Br_7^{2-}$). We also failed to observe the penta-atomic alkaline-earth halide dianions, $MX_4^{2-}$ ($M$ = Mg, Ca; $X$ = Cl, Br), despite their longer predicted lifetimes [10,16,17]. For the transition metal tetrahalide complex dianions, $MX_4^{2-}$ ($X$ = Cl, Br), we searched all the $3d$ and group-10 elements. Much to our surprise, we could not observe any $MX_4^{2-}$ species containing $3d$ elements, although many of these complexes exist in solutions. Our only success came with the two heavier group-10 elements, Pd and Pt. We observed abundant $PtCl_4^{2-}$ and $PtBr_4^{2-}$ dianions. The Pd-containing dianions were barely observable with very weak signals, in particular, for $PdCl_4^{2-}$. We could not search for the $MX_4^{2-}$-type of dianions for the other $4d$ and $5d$ elements because of the lack of appropriate precursor compounds [25]. They all prefer higher oxidation states (>+2), suggesting that the $MX_4^{2-}$-type of dianions probably do not exist for these other $4d$ and $5d$ elements.

We further measured the photoelectron spectra for $PtCl_4^{2-}$ and $PtBr_4^{2-}$ at three photon energies ($h\nu$)—193, 266, and 355 nm, and for $PdCl_4^{2-}$ and $PdBr_4^{2-}$ at 266 nm only. Photoelectron kinetic energies (KE) were measured using a magnetic-bottle TOF electron analyzer [24]. The electron-binding energies (BE) were determined from the Einstein's photoelectric equation, $h\nu = \mathrm{BE} + \mathrm{KE}$. Figure 1 shows the 266 nm spectra for the four observed dianions. Surprisingly, $PtCl_4^{2-}$ and $PtBr_4^{2-}$ showed negative electron-binding energies, suggesting that they are electronically unstable (or metastable), whereas $PdCl_4^{2-}$ and $PdBr_4^{2-}$ gave positive electron-binding energies, suggesting that they are electronically stable species. The photon-energy-dependent spectra for $PtCl_4^{2-}$ and $PtBr_4^{2-}$, not shown here, were consistent with the dianion nature of these species. In order to confirm the electronic metastability of $PtCl_4^{2-}$ and $PtBr_4^{2-}$, we further measured their lifetimes using the ion trap. We used a mechanical chopper to load the ion trap for a predetermined period of time. The trapping time was then varied systematically while the ion intensity was monitored with the TOF mass spectrometer. We could estimate approximately the half-lives for metastable species by carefully calibrating the trapping efficiency with stable molecular ions. Within our experimental sensitivity, we estimated roughly a half-life of ~0.2 s for $PtCl_4^{2-}$. Similar measurements showed that $PtBr_4^{2-}$ has a much longer half-life of about ~60 s. We were also able to measure the lifetime of $PdBr_4^{2-}$, and were surprised to find that it was short-lived with a half-life of only ~8 s, suggesting that this dianion is actually *thermodynamically* unstable against fragmentation. The $PdCl_4^{2-}$ signal was too weak for us to perform any lifetime measurements. We thus attributed the very weak $PdCl_4^{2-}$ signal to its thermodynamic instability. From our experimental time scale, we inferred that its half-life should be less than 0.1 s.

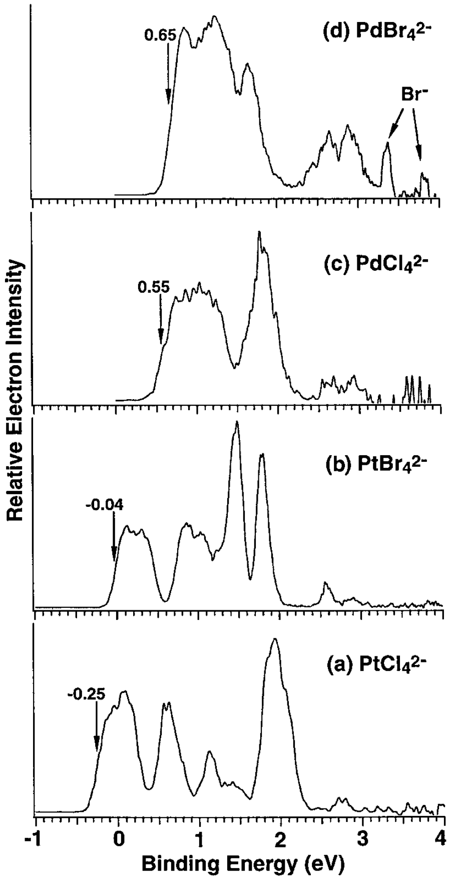

FIG. 1. Photoelectron spectra of (a) $PtCl_4^{2-}$, (b) $PtBr_4^{2-}$, (c) $PdCl_4^{2-}$, and (d) $PdBr_4^{2-}$ at 266 nm (4.661 eV). The numbers and arrows indicate the estimated adiabatic electron-binding energies with an uncertainty of ±0.05 eV. Note the negative binding energies revealed for $PtCl_4^{2-}$ and $PtBr_4^{2-}$.

The metastability of $PtCl_4^{2-}$ and $PtBr_4^{2-}$ could be either electronic (autodetachment) or thermodynamic (molecular fragmentation) in origin. The electronic contribution could be evaluated using a simple electron-tunneling model through a Coulomb potential [Fig. 2(a)]

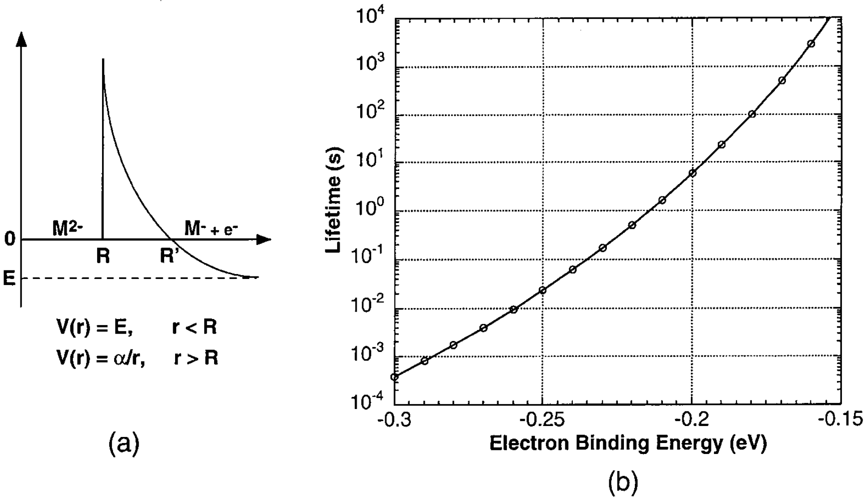

FIG. 2. (a) The model potential used to evaluate the electron-tunneling lifetimes of metastable dianions with a negative electron-binding energy, $E$. Here the short-range potential is modeled as a square well; the negative electron-binding energy, $E$, is measured from the threshold of the photoelectron spectra; $R$ is the equilibrium distance between the two charges in the dianion (for $\mathrm{PtCl_4}^{2-}$, $R$ is assumed to be the diagonal Cl-Cl distance, 4.75 Å, of the planar molecule, which was obtained from both crystal structures and theoretical calculations [29]). The value of $\alpha$ is 14.4 $(e^2/4\pi\varepsilon_0)$ if we adopt eV for energy and Å for distance. (b) The calculated lifetimes using the WKB formalism based on the model potential in (a) as a function of the negative electron-binding energy [27,28]. The calculated lifetime for $\mathrm{PtCl_4}^{2-}$ is in good agreement with the measured value, considering the uncertainty of ±0.05 eV on the binding energy.

developed for $\alpha$ decay in nuclear physics [27]. The potential energy between the outgoing electron and the singly charged anion is determined by their Coulomb repulsion at long range and the electron-binding energy at short range. The exact shape of the short-range interaction needs a more rigorous quantum treatment. Since our focus here is to obtain a qualitative understanding of the lifetime of the metastable dianions, we used a very simple model potential, as shown in Fig. 2(a), which is analogous to the nuclear potential used in the $\alpha$-decay theory [27]. The calculated lifetimes as a function of the unbound electron energy are given in Fig. 2(b) [28], which shows that the range of calculated lifetimes corresponding to the binding energy of $\mathrm{PtCl_4}^{2-}$ $(-0.25 \pm 0.05$ eV) is in good agreement with our experimental observation, confirming the electronic nature of its metastability. On the other hand, a much longer electron-tunneling lifetime was obtained for $\mathrm{PtBr_4}^{2-}$ due to its small negative binding energy, as can be inferred from Fig. 2(b). Thus we concluded that the observed relatively short lifetime of $\mathrm{PtBr_4}^{2-}$ could not be attributed to its electronic metastability, suggesting that even $\mathrm{PtBr_4}^{2-}$ was thermodynamically metastable.

Different from ordinary molecules or singly charged anions, the stability of MCAs is entirely determined by the Coulomb repulsion between the excess charges. In order for a doubly charged anion to be stable, the Coulomb repulsion must be smaller than the electron affinity of the corresponding singly charged species (electronic stability) and the chemical bond strength against charge separation fragmentation (thermodynamic stability). To meet *both* conditions is difficult in small molecular species, requiring a delicate balance among the electron binding strength, chemical bond strength, and molecular structures. This is clearly illustrated in the current observations, as shown in Fig. 1—despite the fact that Cl has a higher electron affinity than Br, the bromide complexes exhibit higher electronic and thermodynamic stabilities due to its slightly larger size (reduced Coulomb repulsion).

The order of stability that we observed for the four metastable MCAs is as follows: $\mathrm{PdCl_4}^{2-}$ $(<0.1$ s) $<$ $\mathrm{PtCl_4}^{2-}(\sim 0.2$ s) $<$ $\mathrm{PdBr_4}^{2-}(\sim 8$ s) $<$ $\mathrm{PtBr_4}^{2-}$ $(\sim 60$ s), among which the lifetime of $\mathrm{PtCl_4}^{2-}$ was mainly electronic in origin, that of $\mathrm{PtBr_4}^{2-}$ was mainly thermodynamic in origin, whereas that of the Pd complexes was purely thermodynamic in origin. The $MX_3{}^{2-}$-type of alkali and $MX_4{}^{2-}$-type of alkaline-earth halide dianions are predicted to be electronically stable [15–17]. But they are unstable thermodynamically against loss of a halide ion, due to the relatively weak metal-ligand bonding, which is essentially ionic in nature. Their lifetimes are determined by the magnitude of the RCB along the fragmentation coordinate. The relatively weak bonding in the small alkali and alkaline-earth halide systems suggests that the RCB is small in these dianions. A recent detailed lifetime calculation on $\mathrm{LiF_3}^{2-}$ [10], which has a relatively small RCB of ~0.2 eV, indicates that although it has a lifetime of $>10^{17}$ s at temperatures $<20$ K, the lifetime falls below $10^{-5}$ s at 80 K. The ESI ion source produces ions around or slightly above room temperature, which sets a practical limit for the observability of metastable dianions with small RCBs. The current results suggest that even the enhanced metal-ligand bonding strength in the 3*d* $MX_4{}^{2-}$ dianions is not enough to render these dianions observable under our experimental conditions. It takes the bond strength of a 4*d* metal-ligand system to make the $MX_4{}^{2-}$-type of dianions to be sufficiently long-lived to be observed. Although the four penta-atomic MCAs observed in the current experiments are metastable after all, they set a practical lower size limit for the smallest *stable* dianions in the gas phase. The Pd-complex dianions set the limit of thermodynamic stability while the Pt-complex dianions set the limit for electronic stability.

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$$T = \exp\left\{-\frac{2}{\hbar}\left|\int_R^{R'}\sqrt{2m[E - V(r)]}\,dr\right|\right\}, \tag{1}$$

where $R$ and $R'$ define the tunneling barrier width, as shown in Fig. 2(a), $m$ is the mass of the electron, and $\hbar$ is the Planck constant. Using the model potential of Fig. 2(a), Eq. (1) can be reduced to

$$T = \exp\left\{-\frac{2}{\hbar}\alpha\sqrt{\frac{2m}{E}} \times \left[a\cos\sqrt{\frac{ER}{\alpha}} - \sqrt{\frac{ER}{\alpha}\left(1 - \frac{ER}{\alpha}\right)}\right]\right\}. \tag{2}$$

The lifetime $\tau$ thus can be estimated as

$$\tau = \frac{1}{\text{rate}} = \frac{2R}{\nu T}, \tag{3}$$

where $\nu$ is the velocity of the electron at kinetic energy $|E|$, as determined by

$$\nu = \sqrt{\frac{2E}{m}}. \tag{4}$$

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