

Electron Scattering on Centrosymmetric Molecular Dianions $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$

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Electron scattering on stored $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ centrosymmetric molecular dianions has been performed at the electrostatic storage ring ELISA. The thresholds for production of neutral particles by electron bombardment were found to be 17.2 and 18.7 eV, respectively. The relatively high thresholds reflect the strong Coulomb repulsion in the incoming channel as well as a high energetic stability of the target electrons. A trianion resonance was identified with a positive energy of 17.0 eV for the $\text{Pt}(\text{CN})_4^{2-}$ square-planar complex, while three trianion resonances were identified for the $\text{Pt}(\text{CN})_6^{2-}$ octahedral complex with positive energies of 15.3, 18.1, and 20.1 eV.

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The existence and stability of small multiply charged anions (MCAs) in the gas phase have attracted great attention among both experimentalists and theoreticians since these species behave quite differently from their neutral and singly charged counterparts [1,2]. In MCAs the electron correlation is of the utmost importance, and a proper description calls for advanced theoretical models. Of special interest are their electronic properties and stability. Even when the electron-binding energy is negative, the lifetime of a MCA may be long enough (microseconds or even seconds) for the ion to be detected in a mass spectrometer. This, at first a surprising result, is due to the repulsive Coulomb barrier (RCB) that prevents immediate electron autodetachment [1,2]. In the present work we are concerned with the dynamical properties of dianions in interactions with low-energy electrons as well as the formation and stability of small gas-phase trianions which represent systems of highly correlated electron motion.

When the separation between an anion and a free electron is large, the potential is dominated by the Coulomb repulsion. At shorter distance, the electron also feels the attractive potential of the nuclei. The combination of the short-range and long-range forces gives rise to the RCB. A typical potential for the interaction between an electron and a dianion is shown in Fig. 1. The height of the Coulomb barrier is determined by the size of the molecule and the angular momentum of the electron in the orbital it occupies behind the barrier. Thus, in the absence of dissociation, the lifetime of the MCA is determined by the tunneling probability through the barrier. The existence of the RCB was experimentally proven by Wang and co-workers [3] from photoelectron spectroscopy experiments. In their pioneering work they found that the photodetached electron from a tetra-anionic metal complex had a kinetic energy higher than the photon energy, which is possible only if the initial electronic state is in the continuum [3].

States in the continuum are conveniently studied by electron scattering experiments [4]. The first scattering experiments of electrons on monoanions in the 1970s

showed indications of short-lived doubly charged negative atomic hydrogen [5] but it was shown later in the 1990s by experiments at storage rings [6–8] and by theory [9] that such states do not form for atomic hydrogen and other atoms like oxygen [7]. Since then, however, a number of dianion resonances were discovered for diatomic [10] and triatomic [11,12] molecular anions. Although several resonances in the electron-detachment cross section of monoanions were found, their existence is still a challenging issue and energy calculations are non-trivial. Recently it was shown that the energy of the NO_2^{2-} dianion ground state [11] is indeed stabilized by the attachment of single water molecules to the target NO_2^- monoanion prior to electron scattering, thus supporting the proposed origin of these resonances [13].

Concerning the overall shape of the electron-detachment cross section near threshold, it is found that there is an effective classical threshold (tunneling effects neglected), E_{th} , which scales as [6,7]

$$E_{\text{th}} = 1.03\sqrt{E_{\text{det}}/a} = 1.23(E_{\text{det}})^{3/4} \quad (1)$$

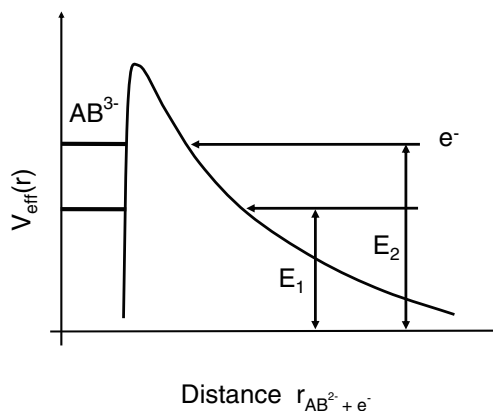


FIG. 1. Schematic drawing of the electron scattering process against a repulsive Coulomb barrier of a dianion AB^{2-} . Two trianion resonances at energies E_1 and E_2 are located behind the barrier. The abscissa is the distance between the dianion and the electron.

(we use atomic units unless otherwise specified). E_{det} is here the vertical detachment energy and a is the extension of the binding potential which is related to the detachment energy as $a \sim 1/\sqrt{2E_{\text{det}}}$ [14]. The classical approach, developed for spherically symmetric potentials, gives quite accurate threshold values for atomic and diatomic anions [4].

A basic understanding of electron scattering on monoanions therefore seems to emerge. If electrons, however, are scattered on *doubly charged* anions, it is unknown what the energy threshold is for the electron-detachment process; i.e., does it follow Eq. (1)? It is also unknown whether trianions at certain electron energies may be formed as fragile species of positive energy in the scattering event. Hence, a natural step is to extend the experimental investigations to include the scattering of electrons on molecular dianions. In particular, it is interesting to see what effect the *additional* Coulomb repulsion has on the energy threshold of the detachment process and for the possible existence of trianion resonances.

The electronic binding of PtBr_4^{2-} and PtCl_4^{2-} has been studied by photoelectron spectroscopy [15] and the PtCl_4^{2-} dianion was found to be metastable against electron ejection with a lifetime in the order of seconds, whereas PdCl_4^{2-} and PdBr_4^{2-} are essentially stable [16]. In this work we have carried out electron scattering on $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ complexes using the electrostatic ion-storage ring ELISA. Thus we demonstrate the stability of these dianions (on the several seconds time scale) and investigate their stability when bombarded by free electrons of well-defined energy. These dianions represent classic examples of square-planar and octahedral centrosymmetric complexes being textbook examples in, for example, inorganic chemistry. Importantly, they can be formed in large abundances in the gas phase by electrospray ionization [17], and trianion states may be favored for such transition metal complexes compared to complexes of, for example, alkali-earth metals since platinum can attain several oxidation states.

The experimental setup is described in detail elsewhere [18]. Briefly, $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ dianions were formed by electrospray of $\text{K}_2\text{Pt}(\text{CN})_4$ and $\text{K}_2\text{Pt}(\text{CN})_6$ salts dissolved in water-methanol solutions and accumulated in a 22-pole ion trap for 2.3 s. The dianions were then accelerated to a kinetic energy of 44 keV, mass and charge selected by a magnet, and injected into ELISA. In the ring, the dianions were crossed with a beam of nearly monoenergetic electrons from an electron target, ETRAP, located in the first arm of ELISA (see Fig. 2). The electrons were generated by a thermocathode and accelerated through a grid anode mounted in front of the cathode. An axial magnetic field provided by external coils guided the electrons through the interaction region and into a positively biased Faraday cup to provide a direct current measurement. The interaction length, i.e., the electron-

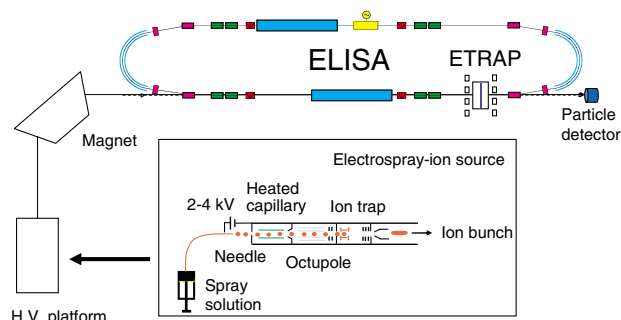
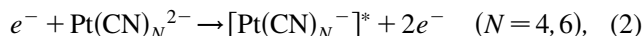


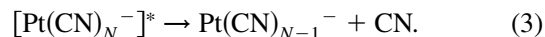
FIG. 2 (color online). The electrostatic ion-storage ring ELISA equipped with an electrospray-ion source. The combined electron-beam electron trap ETRAP and the detector for neutral products are also shown.

beam diameter, was 1.5 cm. The electron beam was chopped on and off at a frequency of 20 Hz in order to separate the signal of electron-dianion interactions from the background generated by collisions with rest gas in the ring (pressure $\sim 3 \times 10^{-11}$ mbar). The neutral particles resulting from electron-ion interactions were counted by a microchannel plate detector located about 1 m after the interaction region. The collisionally induced background, which is proportional to the ion current, was used for normalization. Relative cross sections for production of neutral products (including neutral fragment molecules or atoms) were hence obtained as a function of the collision energy after correcting the energies for the space-charge effect. The procedure for energy calibration is described in more detail elsewhere [19].

Based on knowledge of single and double electron loss from monoanions [20] and the relatively high electron-binding energy of the present systems, we expect that single-electron detachment is the dominant channel:



where the asterisk indicates that the monoanion may be unstable (for example, highly vibrationally excited). As discussed above, we detect only neutral fragments in the present experiment and ascribe the detected neutral fragments as being a result of a subsequent dissociation:



Significant CN loss from $\text{Pt}(\text{CN})_N^-$ formed after collisional electron detachment of $\text{Pt}(\text{CN})_N^{2-}$ was indeed observed previously [17]. Note that the final formal Pt oxidation state in the remaining monoanion is identical to that of the initial dianion (+II for $N=4$ and +IV for $N=6$, the usual oxidation states of platinum).

The cross sections for production of neutral particles from $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ are shown as a function of the electron energy in Fig. 3. Two contributions are observed for the $\text{Pt}(\text{CN})_4^{2-}$ dianion. The dominant part has an energy threshold of 17.2 ± 0.5 eV and is ascribed to a nonresonant electron-detachment process accompanied by dissociation. The data fit very well the function for

electron detachment from atomic and molecular anions, $\sigma_0 \times (1 - E_{\text{th}}/E)$, where σ_0 is a constant and E_{th} is the classical threshold. Evidently there is another contribution with a threshold at about 12 eV increasing moderately with electron energy. This contribution is well described by a Gaussian function with a maximum at 17.0 ± 0.5 eV, and it is ascribed to the resonant formation of a short-lived trianion, $\text{Pt}(\text{CN})_4^{3-}$. It is noted that the total contribution may reasonably well be fitted by combinations from two threshold functions for electron detachment [$\sigma_0 \times (1 - E_{\text{th}}/E)$]. However, this situation is rejected since the low-threshold contribution should be associated with the biggest cross section [7] which is obviously not the case.

Next we turn to the results for $\text{Pt}(\text{CN})_6^{2-}$, which are also displayed in Fig. 3. Again the data at high energies can be described by the $\sigma_0 \times (1 - E_{\text{th}}/E)$ cross-section formula from the classical model. The onset of the non-resonant contribution is here found to be 18.7 ± 0.5 eV which is slightly higher than the one for $\text{Pt}(\text{CN})_4^{2-}$. Like for $\text{Pt}(\text{CN})_4^{2-}$, detachment occurs at lower energies, and clear resonances are observed on the nonresonant detach-

ment contribution, which we ascribe to the formation of short-lived trianions, $\text{Pt}(\text{CN})_6^{3-}$. The resonances were fitted with Gaussian functions yielding resonance energies of 15.3, 18.1, and 20.1 eV, corresponding to three different states of the trianion. The contributions of the two first resonances are comparable but significantly smaller than the high-energy resonance, which is closer to the top of the energy barrier. Apart from the energy positions, the resonances differ also by their widths. This difference is due to either different autodetachment lifetimes or Franck-Condon vibrational broadening. We note that the resonance closest to the top of the barrier is the broadest as is expected when the lifetime is determined by tunneling.

At infinite distance between the electron and the centrosymmetric dianion, the two excess target electrons are localized symmetrically on the molecule. They move within an attractive potential from the polarizable molecule and a repulsive potential due to the mutual Coulomb repulsion. As the incoming electron approaches the dianion, this situation is perturbed, and the two target electrons are pushed closer to each other to reduce the Coulomb repulsion they feel from the intruder. As a first approximation, we assume that the mutual interaction between the target electrons merely shifts the energy levels of each target electron. In a single particle model each target electron is then regarded as being trapped by an attractive $1/r^4$ polarization potential modeled as $-E_{\text{det}}/[1 + (r/a)^4]$. We may evaluate the force from such a potential force, which at the maximum becomes [6,7]

$$F_{\text{max}}^{\text{Binding}} = 1.07E_{\text{det}}/a. \quad (4)$$

The distance of closest approach for an electron approaching an anion of charge Q is Q/E_0 , E_0 being the kinetic energy of the incoming electron. By equating the maximum binding force given above with the maximum force from the incoming electron, this yields the generalized threshold law [4]

$$E_{\text{th}} = 1.23(E_{\text{det}})^{3/4}\sqrt{Q}. \quad (5)$$

Thus, in the case of dianions, the threshold is shifted up by a factor $\sqrt{2}$ compared to monoanions [see Eqs. (1) and (5)]. To evaluate the effective binding force and thus obtain the threshold energy, we approximate E_{det} by the detachment energy of the monoanion, assuming that the effect of the other electrons primarily is a shift in energy with little influence on the binding force [Eq. (4)]. Wang *et al.* [21] found detachment energies for similar monoanion systems XY_4^- of the order 6 eV ($X = \text{Fe}, \text{Sc}; Y = \text{Br}$) and 6–7 eV ($X = \text{Fe}, \text{Sc}; Y = \text{Cl}$). Since CN has a larger electron affinity than both Br and Cl, one may expect an even higher vertical detachment energy for the two systems under investigation here. Based on the present experimental thresholds for detachment, E_{th} , we obtain from Eq. (5) detachment energies of 7.0 eV for

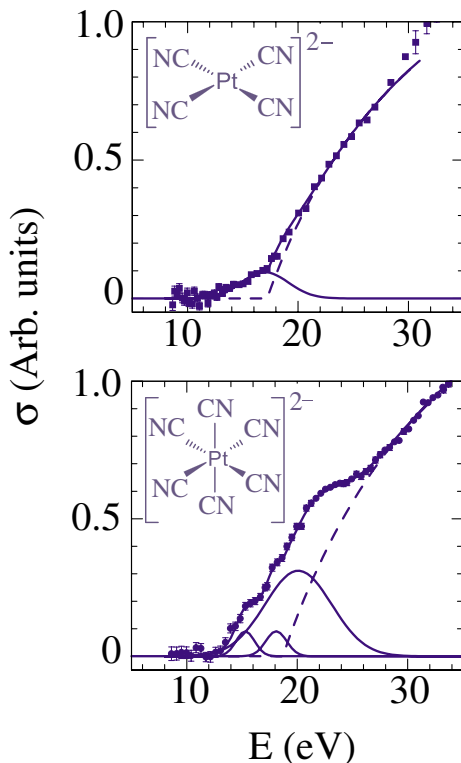


FIG. 3 (color online). The cross section for formation of neutrals as a function of electron energy [top figure $\text{Pt}(\text{CN})_4^{2-}$, bottom figure $\text{Pt}(\text{CN})_6^{2-}$]. The dashed lines are from the classical threshold law $\sigma_0 \times (1 - E_{\text{th}}/E)$ [yielding the thresholds of 17.2 and 18.7 eV for $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$, respectively] which together with Gaussian functions fit the data. The experimental energy resolution at these energies is estimated to be of the order 1–2 eV.

$\text{Pt}(\text{CN})_4^-$ and 7.9 eV for $\text{Pt}(\text{CN})_6^-$, which are in very good accordance with the estimates based on the known detachment energies for similar systems given above. Note that even though we use a single-electron model to estimate the classical detachment threshold, we do not neglect correlations. They are inherent in the model through the use of the detachment energies.

In conclusion, we have shown that $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ are essentially stable (on a time scale of several seconds), and have provided thresholds for neutral production in the interaction between free electrons and $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ dianions. These complexes constitute good models for highly symmetric dianions, planar and octahedral, respectively. Our data show evidence of trianion resonances for both $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ which occur when the incoming electron tunnels through the RCB and populates positive energy states. Through this investigation, we have shown that such multiply charged anion states may appear not only in collisions between electrons and monoanions but also in collisions with dianions, and their existence may change the cross section for neutralization by electron impact near threshold. The observed high thresholds may be explained by two effects: A strong repulsion in the incoming channel, which prevents the electron from getting close to the dianion, and a strong binding force acting on the target electrons.

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