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On the intrinsic stability of the isolated dichromate dianion: Collision activated dissociation of a multiply charged anion *via* electron detachment

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ABSTRACT

Low-energy collision-induced dissociation in a quadrupole ion-trap (resonance excitation) has been used to investigate the intrinsic stability of the dichromate dianion, $Cr_2O_7^{2-}$. Upon isolation of $Cr_2O_7^{2-}$ in the ion-trap and subsequent resonant excitation, the lowest energy activated decay pathway corresponds to electron detachment with concomitant production of the $Cr_2O_7^{-}$ monoanion. This behaviour is distinctive since all of the previously studied small dianionic transition metal ions (*e.g.*, $Pt(CN)_4^{2-}$) decay preferentially *via* ionic fragmentation with production of a pair of monoanions upon resonance excitation. Since electron detachment decay can occur *via* electron tunnelling through the coulomb barrier, the behaviour of $Cr_2O_7^{2-}$ indicates that the barrier for decay *via* electron detachment occurs at either a lower energy than the barrier for ionic fragmentation, or at a broadly similar energy. A series of density functional theory calculations were performed to compare the potential energy surfaces for decay of $Cr_2O_7^{2-}$. The calculations indicate that the barrier for electron detachment lies below that for ionic fragmentation in $Cr_2O_7^{2-}$, consistent with the experimental observations. The distinctive behaviour of the dichromate dianion can be fully understood with reference to the computed potential energy surfaces and attributed to the strong covalent bonding that exists within this molecular anion.

1. Introduction

Gas-phase multiply charged anions (MCAs) represent a class of high-energy molecular ions that are prone to decay by either ionic fragmentation or electron detachment [1–4], with the potential energy surfaces for decay *via* both of these channels being dominated by the presence of novel repulsive coulomb barriers (RCBs). These features are of crucial importance in determining the intrinsic stability of a multiply charged ion since they can confer metastability on a system even when it is exothermic with respect to fragmentation [5–7].

Over the last 10 years, a number of important studies have been conducted to characterize the RCB surfaces of prototypical MCAs [4,8–10]. In our group, an innovative approach has been developed using resonance excitation (low-energy collision-induced dissociation) of MCAs within a quadrupole ion-trap to evaluate whether the barrier height for decay is lower for the electron detachment or ionic fragmentation channel of a given MCA [11]. Fig. 1 displays a schematic diagram of the potential energy surfaces for decay of an AB_2^{2-} dianion with the barrier height for ionic fragmentation being labelled RCB_{if} (inner), and the corresponding barrier for electron detachment labelled as RCB_{ed} (inner). For the range of systems studied to date, RCB_{if} (inner) was always observed to lie below RCB_{ed} (inner) [1,11–13], leading us to conclude that ionic fragmentation will represent the preferred lowest energy decay pathway for transition metal complex dianions that can dissociate to form a pair of stable monoanions [11].

We have recently embarked on a study of inorganic multiply charged systems that contain multiple metal atoms (*e.g.*, $Re_2Cl_8^{2-}$), to investigate the utility of resonance excitation as a technique for identifying metal–metal bonding within inorganic cluster ions. During this work, we investigated the dichromate dianion, $Cr_2O_7^{2-}$, a well-known polyoxometalate anion that is stable in aqueous solution and crystalline compounds [14,15]. Intriguingly, the dichromate dianion was observed to decay with electron loss upon resonance excitation, behaviour that contrasts with that of the other MCAs we have investigated [1]. In this paper, the results of the resonance excitation experiments and *ab initio* calculations for $Cr_2O_7^{2-}$ are presented to probe the intrinsic stability of $Cr_2O_7^{2-}$ and investigate why this dianion displays atypical low-energy fragmentation behaviour. The mononuclear chromate oxoanions and dichromate species have been studied previously by Wang and co-workers using photodetachment spectroscopy [16–18], with the positively charged mononuclear analogues having been investigated by Schwarz and co-workers [19].

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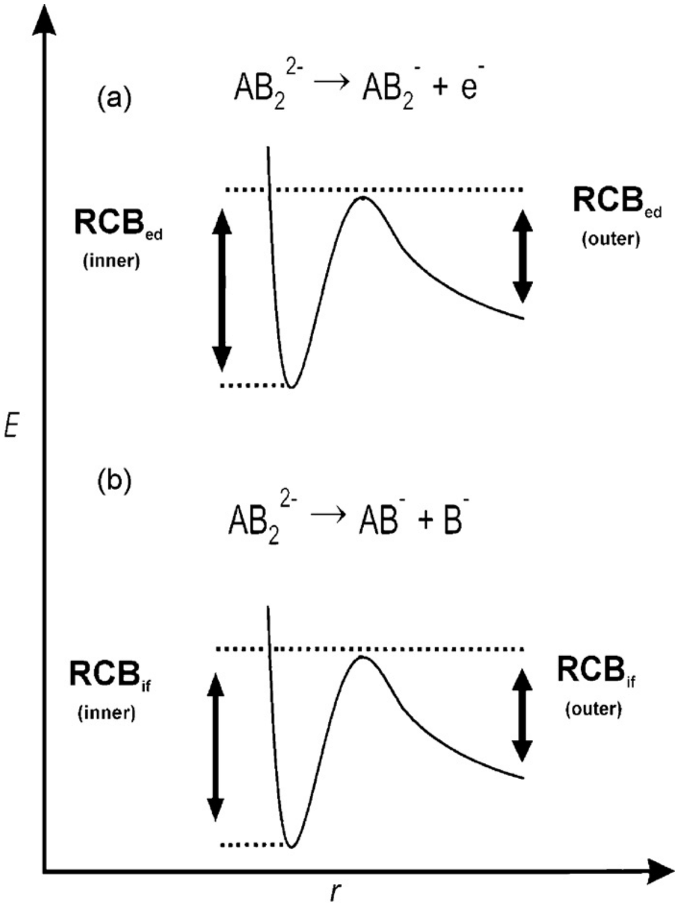

Fig. 1. Schematic potential energy curves for decay of an AB_2^{2-} dianion *via* (a) electron detachment and (b) ionic fragmentation into $AB^- + B^-$. The RCBs (inner) and (outer) for electron detachment (RCB_{ed}) and ionic fragmentation (RCB_{if}) are illustrated.

This is the first study we are aware of where a small molecular dianion has been observed to decay with electron detachment following low-energy activation in a quadrupole ion-trap. This observation is of interest since it suggests that the repulsive coulomb barrier for electron detachment lies below that for ionic fragmentation in this system. We emphasise that this result is atypical for small molecular dianions [1,11]. It should be noted, however, that there have been numerous previous studies relating to electron detachment of MCAs and that electron detachment is the most commonly studied decay pathway [3]. For example, Wang and co-workers have intensively used photodetachment spectroscopy to probe the properties of a very wide range of MCAs [4,20]. Kappes and co-workers have studied autodetachment of both fullerenes and small dianions such as $PtCl_4^{2-}$ in an FTICR mass spectrometer [21,22], with Herlert et al. observing delayed electron emission from gold cluster dianions [23]. Tuinman and Compton probed the electron detachment potential energy surfaces of dianions through charge-exchange collisions of fullerenes [10], while Nielsen and co-workers used electron scattering of *p*-benzoquinone to study autodetaching resonance states of dianions [24]. In addition, electron detachment has been recognized as a common decay channel in high-energy collisions of MCAs with noble gas atoms [25].

2. Experimental methods

The experiments were performed as described previously [1,11]. A Finnigan LCQ quadrupole ion-trap mass spectrometer run in negative-ion mode was used to perform the experiments. Sample solution concentrations were $\sim 1 \times 10^{-3}$ M (50:50 methanol/water), prior to electrospraying in pure methanol. The sodium salt complex was purchased from Aldrich (*e.g.*, $Na_2Cr_2O_7$) and used without further purification.

Low-energy collision-induced dissociation (CID) (or *resonance excitation*) was performed by applying an excitation AC voltage to the end caps of the trap to induce collisions of the isolated anions with the helium buffer gas ($\sim 1 \times 10^{-4}$ Torr). A Mathieu q_z parameter of 0.25 was used for resonance excitation and ions were subject to a 30-ms excitation time. The excitation voltage amplitude was varied between 0 and 2.5 V zero-to-peak resonant excitation potential. Measured minimum resonance excitation amplitudes for decomposition of polyatomic ions in the quadrupole ion-trap CID experiment have been shown to correlate with the literature critical dissociation energies; however, there is no straightforward conversion from the resonance excitation voltage to absolute dissociation energies [26,27]. (Note that this situation contrasts with other guided ion beam CID experiments [28].) CID energies in this work are therefore quoted as a percentage of the 2.5 V excitation voltage, in line with the standard, widely adopted practice [29,30]. Alternatively, energies could be quoted as the excitation voltage [31], but this provides exactly equivalent information.

Precursor ion excitation within the quadrupole ion-trap occurs through multiple low-energy collisions with the buffer gas at a frequency of $\sim 10^4$ s^{-1} [27,32]. Excitation is similar to thermal excitation in a hot, low pressure gas, so that when the high-energy tail of the ion energy envelope reaches the activation energy for the lowest energy decomposition pathway, decomposition begins to occur and fragment ions are observed. The fragment ions observed therefore characterize the ground-state potential energy surface, a significant advantage compared to higher-energy collision techniques which can simultaneously access numerous electronic states [1,28].

3. Computational methods

The equilibrium geometry, energies, and harmonic vibrational frequencies of the ions studied in this work were calculated with the B3LYP hybrid exchange and correlation functional. The LANL2DZ double-ζ basis set [33] was used for all of the calculations since this has been found to give reliable computational results for $Cr_2O_7^{2-}$ [34]. All of the calculations were carried out using GAUSSIAN 03, with the default convergence criteria applied to the geometry optimizations [35]. Partial charge distributions were calculated using the natural population analysis (NPA) method [36]. The potential energy surface for the lowest energy ionic fragmentation decay pathway was calculated by scanning the total energy as a function of the distance between the ionic fragments. The point charge model of Dreuw and Cederbaum was applied to model the potential energy surface for electron detachment [37,38].

4. Results and discussion

4.1. Resonance excitation of the $Cr_2O_7^{2-}$ dianion

Fig. 2a displays the negative-ion electrospray ionisation mass spectrum (ESI-MS) of $Cr_2O_7^{2-}$. CrO_4^-/$HCrO_4^-$ is the major peak in the spectrum, with the $Na^+ \cdot Cr_2O_7^{2-}$ and $Cr_2O_7^{2-}$ ions also appearing with significant intensity. To investigate the lowest energy decay pathway, the $Cr_2O_7^{2-}$ parent dianion was isolated in the quadrupole trap and activated using resonance excitation. At 0% collision energy (Fig. 2b), $Cr_2O_7^{2-}$ is observed to decay with production of a number of ionic fragments. Similar effects have

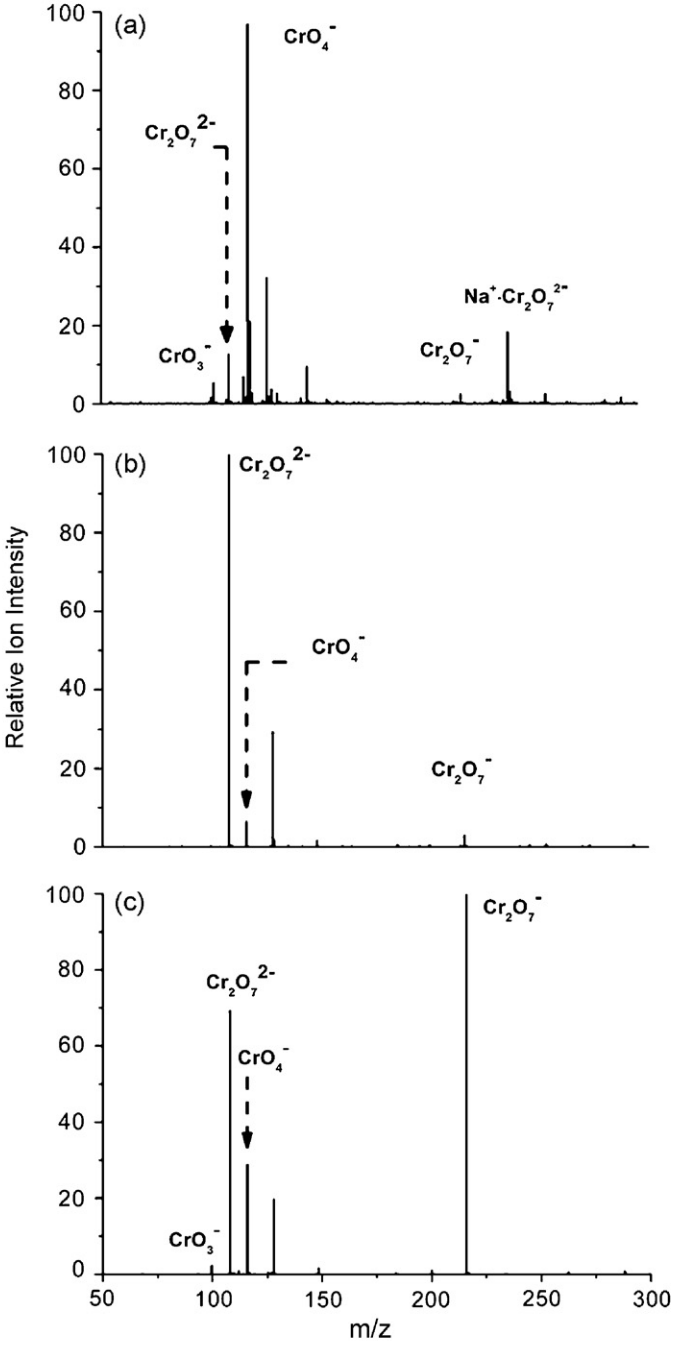

Fig. 2. (a) Negative-ion ESI-MS of the sodium salt of $Cr_2O_7{}^{2-}$ obtained by tuning on *m*/*z* 108 (*i.e.*, optimizing the ion optics to maximize the *m*/*z* 108 signal). (b) Isolation of $Cr_2O_7{}^{2-}$ in the quadrupole trap at 0% collision energy. (c) CID mass spectrum of $Cr_2O_7{}^{2-}$ at 9% collision energy illustrating fragmentation of $Cr_2O_7{}^{2-}$ primarily into $Cr_2O_7{}^{-}$. ($CrO_4{}^{-}$ and $CrO_3{}^{-}$ are also evident as product fragments; see text for a discussion.).

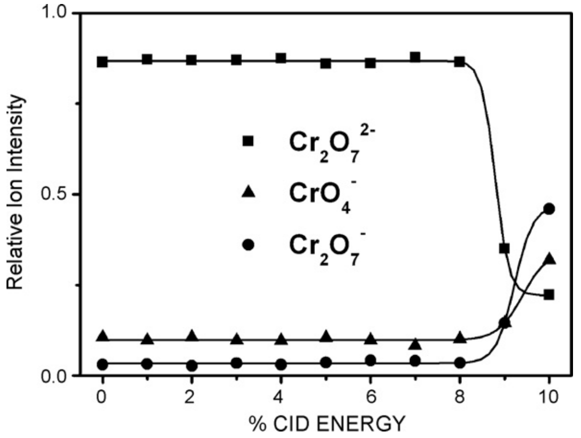

Fig. 3. Fragmentation curves for decay of the $Cr_2O_7{}^{2-}$ parent dianion, with production of the $CrO_4{}^{-}$ and $Cr_2O_7{}^{-}$ fragment ions. Typical experimental errors (obtained from repeat runs) were ±3%.

been observed in previous CID studies of multiply charged cluster ions [11,39], and were attributed to dissociation of metastable parent ions that are thermally or collisionally activated as they travel through the mass spectrometer. While such effects explain the appearance of the minor $CrO_4{}^{-}$ and $Cr_2O_7{}^{-}$ fragments, the $m/z = 128.5$ peak corresponds to a solvated cluster of dichromate, *i.e.*, $Cr_2O_7{}^{2-}\cdot CH_3CN$ which arises due to complexation of the dianion with residual solvent in the ion-trap [40]. Fig. 2c displays a typical fragment ion mass spectrum obtained after activated collision-induced dissociation (9% collision energy). $Cr_2O_7{}^{2-}$ can be seen to decay primarily with production of $Cr_2O_7{}^{-}$, *i.e.*, *via* electron detachment:

$$Cr_2O_7{}^{2-} \rightarrow Cr_2O_7{}^{-} + e^{-} \qquad (1a)$$

$CrO_4{}^{-}$ is also evident as a minor fragment, with $CrO_3{}^{-}$ also visible (ions with $m/z < 100$ are not strongly detected by the LCQ instrument), indicating that decay of $Cr_2O_7{}^{2-}$ is also occurring to a lesser extent *via* ionic fragmentation:

$$Cr_2O_7{}^{2-} \rightarrow CrO_4{}^{-} + CrO_3{}^{-} \qquad (1b)$$

(Note that Cr is not known to adopt a +VII oxidation state, so that the $CrO_4{}^{-}$ species is likely to have Cr in the +VI state, with one of the oxygens being peroxidic.)

Fig. 3 displays % fragmentation curves (*i.e.*, plots of fragment ion intensity *versus* collision energy) for decay of the $Cr_2O_7{}^{2-}$ parent dianion upon resonance excitation, with production of the $CrO_4{}^{-}$ and $Cr_2O_7{}^{-}$ product ions. The onset of fragmentation for $Cr_2O_7{}^{2-}$ occurs at ~8% CID energy, a value that is high compared to other transition metal complex dianions [1,11]. (For example, $IrCl_6{}^{2-}$ has a fragmentation onset around 4% CID energy [11].) The high fragmentation energy of $Cr_2O_7{}^{2-}$ indicates that the barrier to the lowest energy fragmentation pathway is relatively high in this system. While the fragmentation curve for production of $Cr_2O_7{}^{-}$ rises very sharply above 8% CID energy, the curve for production of $CrO_4{}^{-}$ has an onset of ~8.5% and increases more gradually above this energy [41]. This suggests that production of $Cr_2O_7{}^{-}$ is associated with decay of the $Cr_2O_7{}^{2-}$ parent dianion *via* the lowest energy dissociative surface, and that $Cr_2O_7{}^{2-}$ preferentially decays *via* electron detachment, *i.e.*, Eq. (1a). We note that it is possible that thermally excited (resonance excited) $Cr_2O_7{}^{2-}$ may be decaying *via* electron tunnelling through the coulomb barrier [4,9], so that from the experimental data it is not possible to unequivocally say that RCB_{ed} (inner) lies below RCB_{if} (inner) for this dianion. However, the data indicate that RCB_{if} (inner) certainly does not lie substantially below RCB_{ed} (inner). We return to the relative heights of RCB_{ed} (inner) and RCB_{if} (inner) in Section 4.2 where the barriers are calculated using *ab initio* methods.

To extend the current study, the $Cr_2O_7{}^{-}$ monoanion which was present in the parent ESI-MS of the sodium dichromate solution was also subjected to resonance excitation CID in the quadrupole ion-trap. Fig. 4a and b display the mass spectra associated with isolation of $Cr_2O_7{}^{-}$ in the ion-trap at 0% collision energy and excitation of $Cr_2O_7{}^{-}$ at 15% excitation energy, respectively. Upon resonance excitation, $Cr_2O_7{}^{-}$ can be seen to decay with production of $Cr_2O_6{}^{-}$,

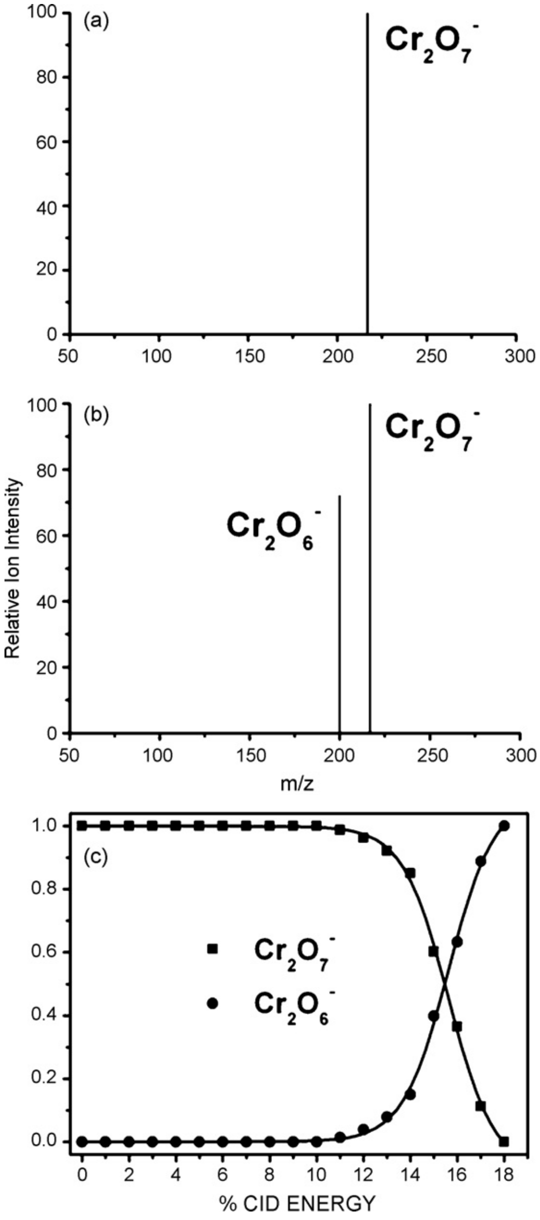

Fig. 4. (a) Isolation of $Cr_2O_7^-$ in the quadrupole trap at 0% collision energy. (b) CID mass spectrum of $Cr_2O_7^-$ at 15% collision energy illustrating fragmentation of $Cr_2O_7^-$ into $Cr_2O_6^-$. (c) % fragmentation curves for decay of the $Cr_2O_7^-$ parent monoanion, with production of the $Cr_2O_6^-$ fragment ion.

i.e., *via* loss of a neutral oxygen atom. Fig. 4c displays the % fragmentation curves for decay of the $Cr_2O_7^-$ parent monoanion upon resonance excitation, with production of the $Cr_2O_6^-$ product ion. The onset of fragmentation for $Cr_2O_7^-$ occurs at ~12% CID energy, a value that is somewhat higher than for $Cr_2O_7^{2-}$, indicating the higher intrinsic stability of the monoanion relative to the dianion.

The $Na^+{\cdot}Cr_2O_7^{2-}$ cation–dianion cluster ($m/z = 239$) was also isolated in the quadrupole ion-trap and subjected to resonance excitation. The ion was stable through the collisional energy range over which the bare $Cr_2O_7^{2-}$ dianion decayed (8–12% CID energy). This behaviour mirrors that of other cation–dianion complexes [42], and can be attributed to the Na^+ cation electrostatically stabilizing the dianion. Above 18% CID energy, the parent-ion intensity decays rapidly, but without the clear production of any product ion fragments, consistent with the dianion within the ion-pair complex decaying with loss of an electron, *i.e.*,

$$Na^+{\cdot}Cr_2O_7^{2-} \rightarrow Na^+{\cdot}Cr_2O_7^- + e^- \qquad (2)$$

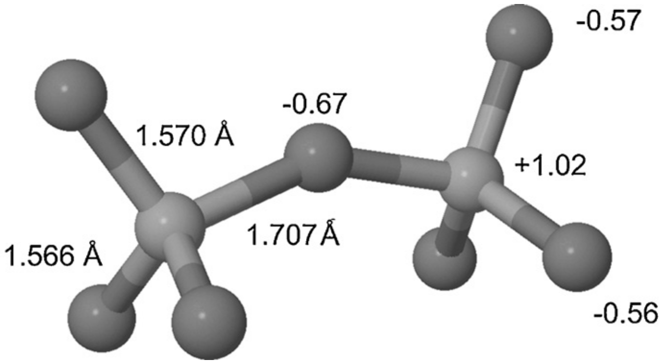

Fig. 5. The optimized C_{2v} symmetry structure of $Cr_2O_7^{2-}$ obtained at the B3LYP/LANL2DZ level, with bond lengths and NPA atomic charges.

This behaviour is again in line with that of other cation–dianion complexes, which decay with production of fragments associated with the decay of the uncomplexed dianion [42].

4.2. Stability of $Cr_2O_7^{2-}$ with respect to electron detachment and ionic fragmentation

To investigate the intrinsic stability of $Cr_2O_7^{2-}$, a series of *ab initio* calculations were performed to probe the potential energy surfaces for decay. Fig. 5 displays the optimized C_{2v} structure (B3LYP/LANL2DZ) of $Cr_2O_7^{2-}$, with the CrO_3 groups oriented in an eclipsed configuration across the central oxygen atom. This structure agrees well with the known structure of the dianion [34,43].

Fig. 6a displays the calculated potential energy curve for ionic fragmentation of $Cr_2O_7^{2-}$ into CrO_4^- and CrO_3^-, obtained as a function of the central Cr-O distance. (Only this channel is considered in this work since there is no evidence for ionic fragmentation of the dianion into $Cr_2O_6^-$ and O^-.) The surface displays the expected RCB (barrier height = 3.9 eV) which is characteristic of an MCA, and indicates that the system is stable with respect to ionic fragmentation since dissociation of the dianion into the ionic fragments is endothermic.

Calculations were also performed to investigate electron detachment decay of $Cr_2O_7^{2-}$, using the point charge model of Dreuw and Cederbaum [37]. Fig. 6b displays the 1D-cut along the electron detachment surface obtained for removal of the electron along the direction indicated, with the maximum value of $V(r)$ representing the RCB_{ed} (outer) height, *i.e.*, the barrier measured from the $Cr_2O_7^- + e^-$ asymptote. (The geometry of the dichromate ion is frozen across the electron detachment scan.) The point-charge method describes the short-range interaction rather poorly, so that the magnitude of RCB_{ed} (inner) is more reliably obtained as the sum of the RCB_{ed} (outer) of 2.61 eV and the calculated vertical detachment energy of 0.89 eV (VDE) [37,38]. Combining these values gives RCB_{ed} (inner) as 3.5 eV. We note that the $Cr_2O_7^{2-}$ VDE and RCB_{ed} (outer) values calculated in this work are in reasonable agreement with the experimental values of ~1.3 eV and ~2.3 eV, respectively, measured by Wang and co-workers using photodetachment photoelectron spectroscopy [18].

5. Further discussion

The calculations for $Cr_2O_7^{2-}$ presented in Section 4.2 indicate that the dianion is intrinsically stable with respect to dissociation *via* either electron detachment or ionic fragmentation. The calcu-

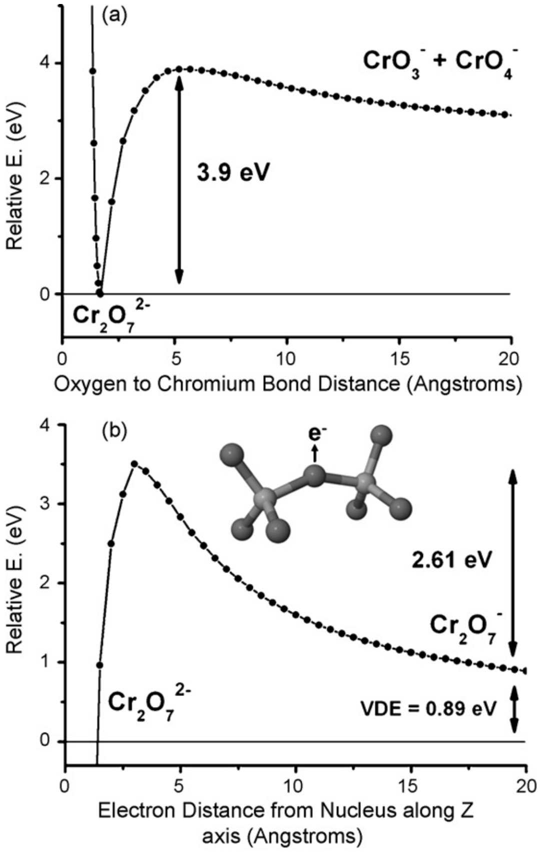

Fig. 6. (a) Calculated potential energy curve (B3LYP/LANL2DZ) for the ionic fragmentation of $Cr_2O_7^{2-} \rightarrow CrO_3^- + CrO_4^-$, obtained as a function of the oxygen-chromium bond distance. (b) One-dimensional cut through RCB_{ed} of $Cr_2O_7^{2-}$ calculated using the point-charge model (see text) at the B3LYP/LANL2DZ level. The direction of electron detachment is indicated.

lated values of 3.5 eV and 3.9 eV for RCB_{ed} (inner) and RCB_{if} (inner), respectively, indicate that the lowest energy decay pathway for $Cr_2O_7^{2-}$ should be *via* electron loss, with the barrier for decay *via* ionic fragmentation lying just higher in energy. This picture is in excellent agreement with the low-energy collision-induced dissociation results. We note that electron detachment decay is likely to be occurring *via* electron tunnelling through the RCB_{ed} before the barrier energy is reached.

The similar values for RCB_{ed} (inner) and RCB_{if} (inner) observed here are surprising, since in other inorganic ions we have studied (*e.g.*, $Pt(CN)_4^{2-}$ and $IrBr_6^{2-}$) RCB_{if} (inner) has typically been considerably smaller than RCB_{ed} (inner). The unusual behaviour of $Cr_2O_7^{2-}$ can be traced to its relatively high value of RCB_{if} (inner), 3.9eV, compared to values of ∼2 eV for MX_6^{2-} dianions, where M = Ir, Os, Re, Pt, and X = Cl, Br [11]. Since RCB_{if} (inner) is relatively high for $Cr_2O_7^{2-}$, it occurs in the same region as the barrier for electron detachment. We have previously proposed that RCB_{if} (inner) for an MX_6^{2-} dianion should be associated with the purely attractive binding energy of an X^- ion to the MX_5^- moiety, *i.e.*,

$$RCB_{if}\,(\text{inner}) = \Delta E(MX_5^- + X^-) \text{—intramolecular Coulomb repulsion} \tag{3a}$$

By analogy, the corresponding expression for the dichromate dianion will be:

$$RCB_{if}\,(\text{inner}) = \Delta E(CrO_4^- + CrO_3^-) \text{—intramolecular Coulomb repulsion} \tag{3b}$$

Comparing $Cr_2O_7^{2-}$ with an MX_6^{2-} dianion such as $IrBr_6^{2-}$, the intramolecular Coulomb repulsion should be broadly similar for both dianions, so that the high value of RCB_{if} (inner) for $Cr_2O_7^{2-}$ can be attributed to a comparatively stronger intramolecular bond. This is consistent with the known structural differences of $Cr_2O_7^{2-}$ and MX_6^{2-} type dianions, since $Cr_2O_7^{2-}$ is regarded as a covalent molecular ion composed of two corner-sharing tetrahedral chromate units [43], whereas MX_6^{2-} ions are more weakly associated complex anions. (We calculate the bond dissociation energy of $Cr_2O_7^{2-}$ into $CrO_4^- + CrO_3^-$ is 3.1 eV at the B3LYP/LANL2DZ level, whereas the corresponding calculated value for ionic fragmentation of $IrCl_6^{2-}$ is −0.20 eV [38].)

Finally, we note that the atypical fragmentation behaviour of $Cr_2O_7^{2-}$ can also be viewed as arising from the stoichiometry of the system. A metal halide dianion such as $PtCl_4^{2-}$ does not change its valence state upon ionic fragmentation, *i.e.*,

$$Pt(II)Cl_4^{2-} \rightarrow Pt(II)Cl_3^- + Cl^- \tag{4}$$

whereas ionic fragmentation of $Cr_2O_7^{2-}$ requires a single electron transfer process to produce a (peroxidic) Cr(VI) and a Cr(V):

$$(Cr(VI))_2O_7^{2-} \rightarrow Cr(VI)O_4^- + Cr(V)O_3^- \tag{5}$$

The thermochemical location of the ionic fragmentation exit channel is therefore considerably less favourable, as reflected by the *ab initio* calculations presented above.

6. Concluding remarks

$Cr_2O_7^{2-}$ displays atypical behaviour for an inorganic MCA since it preferentially decays with electron loss upon low-energy collision activated dissociation in a quadrupole ion-trap. This is the first such system we are aware of that decays *via* electron loss under these conditions, and therefore illustrates that the resonance excitation technique is suitable for identifying electron detachment as well as ionic fragmentation pathways. Finally, we note that the relatively high barrier for ionic fragmentation that is present for $Cr_2O_7^{2-}$ is indicative of the relatively strong covalent bonding within this anion. This is important since it illustrates the utility of low-energy CID studies within quadrupole ion-traps for probing structural features of inorganic cluster ions.

Acknowledgments

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