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Dissociation of dicarboxylate and disulfonate dianions

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Collision-induced dissociation (CID), along with infrared multiple photon dissociation/detachment (IRMPD) techniques, is utilized to study a series of doubly substituted aromatic dianions containing sulfonate and carboxylate functionalities (1,2- and 1,3-benzenedisulfonate, 1,5-naphthalenedisulfonate, 2,6-naphthalenedisulfonate, 4-sulfobenzoate, 2,6-naphthalenedicarboxylate, and terephthalate dianions). The molecules were chosen because of the electronegativity of the CO₂ and SO₃ moieties along with their varied spatial separation in order to investigate the effect of the repulsive Coulomb barrier (RCB) on the dianions' respective dissociation pathways. Density functional theory calculations of the structures, electron detachment and dissociation energies, as well as vibrational frequencies are performed. Calculated infrared active vibrational frequencies are largely in agreement with the IRMPD spectra which provide support for interpretations based upon computed energies. Calculated and experimental results show that fragmentation dominates over electron detachment as the lowest energy dissociation pathway for these systems and the nature of this dissociation is dictated by properties of the substituent group. CID and IRMPD of dianions with two sulfonate groups (SO₃⁻) resulted in a single dissociation channel leading to observation of SO₃⁻ and its anion conjugate pair, whereas the carboxylate (CO₂⁻) containing dianions dissociated via loss of one or both CO₂ molecules and an electron. The SO₃⁻ collisional dissociation exhibited a clear energetic threshold toward ionic fragmentation with an isomeric dependence that is in reasonable agreement with a simple electrostatic model of the RCB, as well as with published reports on electron photodetachment. The loss of one or both CO₂ units and an electron from CID of the carboxylate dianions appeared with no threshold (dissociation occurs with no collision gas), implying these dianions to be metastable toward the dissociation pathway. However, calculations show these ions to be energetically stable toward dissociation as well as electron detachment. More importantly, in the case of the 2,6-naphthalenedicarboxylate dianion, experiments performed at the FELIX Fourier-transform ion cyclotron resonance facility and the ELISA electrostatic storage ring, where ions are collisionally cooled prior to analysis, showed this ion to be stable ($\tau > 1.5$ s). We conclude that the carboxylate (CO₂⁻) containing dianions formed in the present CID experiment are electronically stable but vibrationally metastable due to internal energy imparted in the harsh electrospray conditions. The delocalized nature of the excess electrons associated with the carboxylate containing dianions may lead to circumvention of the RCB by dissociating via neutral fragmentation followed by (or accompanied by) electron detachment. © 2010 American Institute of Physics.

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I. INTRODUCTION

Recently, the stability of gas-phase multiply charged anions (MCAs) toward dissociation and electron detachment (ED) has attracted wide interest. The stability of MCAs is due in part to the so-called "repulsive Coulomb barrier" (RCB), which has been compared with that experienced by α -particles in heavy atomic nuclei. The RCB is primarily the result of a long-range Coulomb repulsion and the short-range polarizability attraction between an electron or charged

fragment and a negative ion. The RCB adds stability to bound MCAs and can render unbound MCAs metastable and long lived. Thus, the RCB plays a crucial role in determining the lowest energy dissociation pathway for MCAs (i.e., ED, ionic or neutral fragmentation). In this study, dissociation of a series of dianions is examined employing collision-induced dissociation (CID) as well as infrared multiple photon dissociation/detachment (IRMPD) with the goal of furthering our understanding of the RCB.

A number of studies have established the existence of the RCB;¹⁻⁵ however Wang and co-workers⁶ provided the first experimental estimate of the magnitude of the Coulomb

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barrier from studies of photodetachment photoelectron spectroscopy of the phthalocyanine tetrasulfonate tetra-anion. Wang and co-workers⁶⁻⁹ further employed photodetachment photoelectron spectroscopy for a number of MCAs, which has significantly contributed to the understanding of the stability of MCAs toward ED and the role of the RCB. Of particular importance was this group's investigation of the dependency of the binding energy of the excess electrons to the equilibrium charge separation for a group of linear dicarboxylate dianions, $^-\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^-$ ($n=3-10$). They found that for increasing n , the electron binding (EB) energy increases due to the decreasing Coulombic repulsion between the two excess charges. It was demonstrated that the EB energy and charge separation fit a linear functional form, i.e., $\text{EB (eV)} = 3.21(4) - 16.7(3)/r_n$, where r_n (in Å) is the average distance between the oxygen atoms on which the excess electrons are broadly localized. The EB energy becomes negative for a critical value of $n=2$ corresponding to a charge separation of 5.3 Å. This distance is in close agreement with the critical charge separation value necessary for stable dianions estimated by Maas and Nibbering¹⁰ of ~ 5 Å. Furthermore, Wang's group demonstrated an inverse relation between the magnitude of the RCB and the distance between the two excess charges as $\text{RCB (eV)} = 0.00(5) + 16.8(3)/r_n$. This relationship closely follows the Coulomb law relationship of $e^2/4\pi\epsilon_0 r$ [$14.4 \text{ (eV Å)} / r(\text{Å})$ for vacuum where $\epsilon_0=1$]. The empirical relationship extrapolated by Wang *et al.* has a slightly higher coefficient of 16.8, which they attribute to the inherent difficulty in equating a point charge to a "charge distribution." In the linear dicarboxylate dianions studied, calculations show the charges are actually spread over the CO_2 moieties as opposed to only the outlying oxygen atoms.

Experiments examining the stability of MCAs toward ionic fragmentation (IF) are still in their infancy. In this context, the Kappes¹¹ group has examined the stability of IrBr_6^{2-} toward fragmentation employing a photodissociation spectroscopy technique. In these experiments photodissociation of IrBr_6^{2-} into Br^- , IrBr_4^- , and IrBr_5^- was studied. They provided the first estimate of the magnitude of the RCB toward IF to be about 2.2 ± 0.2 eV for this molecule. Boxford and Dessent¹² also investigated the relative stability toward ED and IF for a series of MCAs, demonstrating that for some metal complex dianions, such as IrCl_6^{2-} , IrBr_6^{2-} , and PtBr_6^{2-} , the energetic thresholds toward IF are lower than those for ED. Boxford *et al.*¹³ also concluded that for the $\text{Pd}(\text{CN})_4^{2-}$ dianion IF is the lowest energy decay pathway. The propensity for a MCA to dissociate via IF or ED is a complicated problem involving geometric and electronic properties of the molecule, yet any decay pathway is heavily influenced by the effects of the RCB.

The precise role of the RCB in MCAs is determined primarily by the extent to which the excess electrons are delocalized over the molecule. A limited number of studies have examined the effects of molecular and electronic structure on the stability of a MCA toward ED. Skurski *et al.*¹⁴ experimentally and theoretically examined the electronic stability of two small dicarboxylate dianions having similar molecular size, geometry, and atomic composition: $[\text{O}_2\text{C}-\text{C} \equiv \text{C}-\text{CO}_2]^{2-}$ and $[\text{O}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CO}_2]^{2-}$ or (AD^{2-}) and (SD^{2-}) , respectively].

Employing electrospray ionization (ESI) mass spectrometry, photodetachment spectroscopy, and *ab initio* calculations, they found that SD dianions were very difficult to produce whereas large signals of AD dianions were observed, even though the chemical structure suggested that both MCAs have the same charge separations. Furthermore, their calculations showed that SD dianions are unstable toward ED [negative adiabatic electron affinity (AEA)] whereas AD dianions are stable with 0.418 eV adiabatic and 0.69 eV vertical EB energies. Their calculations also suggested that for AD dianions, the two excess charges are delocalized on the $\text{C} \equiv \text{C}$ π -type orbitals while for SD dianions, charges are heavily localized on the CO_2^- groups. Their results further indicated that even though the charge delocalization on AD dianions increases the Coulombic repulsion (as the charges are closer together), the D_{2d} structure of the AD dianions allows interaction between carboxylate groups and the $\text{C} \equiv \text{C}$ π -type orbitals, therefore increasing the stability of the AD dianions.

In 2003, Schwerdtfeger *et al.*¹⁵ performed a comprehensive theoretical study regarding the stability of some dianions with similar atoms and structure, but slightly different electronic structure, i.e., $^-\text{O}-(\text{CH}_2)_n-\text{O}^-$, $^-\text{O}-(\text{HC}=\text{CH})_n-\text{O}^-$, and $^-\text{O}-(\text{C} \equiv \text{C})_n-\text{O}^-$, where n is the number of carbon-carbon pairs (i.e., $\text{C}-\text{C}$, $\text{C}=\text{C}$, or $\text{C} \equiv \text{C}$). Their density functional theory (DFT) calculations revealed that aliphatic dialkoxides, $^-\text{O}-(\text{CH}_2)_n-\text{O}^-$, are unstable toward ED up to a chain length of $n=22$ (charge separation of 30 Å), while for $^-\text{O}-(\text{HC}=\text{CH})_n-\text{O}^-$ and $^-\text{O}-(\text{C} \equiv \text{C})_n-\text{O}^-$, stable dianions exist for $n \geq 10$ and $n \geq 6$, respectively. In an effort to explain the necessary charge separation for these species to overcome the Coulombic repulsion of the excess electrons, Schwerdtfeger and co-workers plotted the highest occupied molecular orbitals for stable $^-\text{O}-(\text{C} \equiv \text{C})_6-\text{O}^-$ and $^-\text{O}-(\text{HC}=\text{CH})_{10}-\text{O}^-$, and compared them with the unstable $^-\text{O}-(\text{CH}_2)_{22}-\text{O}^-$ dianion. Their results showed that increased delocalization of the charges over the carbon-carbon chain would reduce the charge separation needed to stabilize the dianions with respect to ED.

The goal of the present study is to employ dianion-neutral collisions to investigate the stability of a group of dicarboxylate and disulfonate dianions (1,2- and 1,3-benzenedisulfonate, 1,5- and 2,6-naphthalenedisulfonate, 4-sulfobenzoate, 2,6-naphthalenedicarboxylate, and terephthalate dianions) with respect to ED and fragmentation. Infrared multiple photon absorption leading to dissociation and ED (IRMPD) is also employed for a representative subset of these species. The IRMPD spectroscopy allows for a test of the calculated properties of the dicarboxylate and disulfonate dianions and a direct measurement of the competition between ED and fragmentation processes. The stability of one of the dicarboxylate dianions (2,6-naphthalenedicarboxylate dianion) was examined at the electrostatic ion storage ring (ELISA) in Denmark. These two groups of dianions were chosen as a result of their varied electronic properties arising from the different substituent functionalities; the two excess charges are delocalized across the dicarboxylate dianions

whereas the excess charges are heavily localized on the SO₃ groups of the disulfonate dianions. Results are interpreted in terms of the influence of charge separation and delocalization on the RCB, and consequently the stability of MCAs toward fragmentation and ED.

II. METHODS

A. CID experiments

CID studies were conducted with a Micromass Quattro II (triple quadrupole) mass spectrometer in conjunction with an ESI source. Details of this experiment and procedure have been discussed in a previous paper.¹⁶ The dianions studied were formed from 20 μg/ml solutions of 1,2-benzenedisulfonic acid dipotassium salt [C₆H₄(SO₃)₂K₂], 1,3-benzenedisulfonic acid disodium salt C₆H₄(SO₃)₂Na₂, 2,6-naphthalenedisulfonic acid disodium salt [C₁₀H₆(SO₃)₂Na₂], 1,5-naphthalenedisulfonic acid disodium salt hydrate C₁₀H₆(SO₃)₂Na₂·xH₂O, terephthalic acid disodium salt [C₆H₄(CO₂)₂Na₂], 2,6-naphthalenedicarboxylic acid dipotassium salt [C₁₀H₆(CO₂)₂K₂], and 4-sulfobenzoic acid potassium salt [C₆H₄(SO₃)₁(CO₂)₁KH] in 50/50 water and methanol mixture and were introduced to the ESI at a rate of 5 μl/min. Salt samples were purchased from Sigma-Aldrich (USA) and used with no further purification. The source block temperature and desolvation temperature were set to be 80 and 120 °C, respectively. The optimum cone voltage for extraction of the dianions studied was empirically found to be 20 V. The CID experiments were performed using a target gas of argon under approximate single collision conditions. The collision energies ranged from 0 to 60 eV in the laboratory frame. Further details of the apparatus and energy calibration have been described previously and remain unchanged.¹⁶

B. IRMPD experiments

IRMPD experiments were performed at the FELIX free-electron laser¹⁷ (FEL) facility at Rijnhuizen. The 4-sulfobenzoate, 2,6-naphthalenedicarboxylate, and 2,6-naphthalenedisulfonate dianions were generated with a Micromass “Z-spray” ESI source from 2 mM solutions of the respective salts made in a 50/50 water and methanol mixture. Ions were then isolated, stored, and irradiated in a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer described in detail elsewhere.¹⁸ The ions were irradiated for 3 s with FEL macropulses of approximately 50 mJ in energy at a rate of 5 Hz. The FEL has a resolution of approximately 0.5% of central wavelength in the range of 600–1800 cm⁻¹. Three mass spectra were averaged per spectral point, and the ratio of fragment ions to the total ion signal is plotted as a function of laser wavelength. In addition to the spectrum recorded by detection of fragments from IR-induced dissociation, an ED spectrum is also recorded. Addition of a low pressure (10⁻⁷ torr) background gas of an electron scavenger such as SF₆ into the ICR cell facilitates detection of detached electrons from metastable anions, as described in detail previously.¹⁹

C. Dianion lifetime measurements

The stability of the 2,6-naphthalenedicarboxylate dianion was studied at the electrostatic ion storage ring (ELISA) in Aarhus, Denmark. The ELISA machine has been described by Møller.²⁰ Numerous studies have shown lifetimes in the range from 10⁻⁵ to 1 s under essentially field free conditions (see, e.g., Panja *et al.*²¹). In this experimental setup dianions are produced with an ESI source and then transported to an ion trap filled with helium buffer gas for nearly 0.1 s for accumulation and rovibrational “cooling” to room temperature before they are injected into the storage ring. Metastable decay as well as collisions with residual background gas leads to the production of neutral fragments, which are counted by a microchannel plate detector.

D. Computations

Full geometry optimizations and harmonic frequency calculations of the dianions, radical monoanions, and dissociation fragment species were performed with Becke’s 3-parameter hybrid DFT method (B3LYP) using the 6-311++G** basis set. The radical species were calculated as doublet states with unrestricted methods, and the remainder calculated as closed-shell singlet states with restricted methods. All calculations were performed using the GAUSSIAN 03 program suite.²² All structures were determined to be at least at a local minimum on the potential energy surface by verification of real harmonic frequencies. To investigate the stability of the dianions toward ED, the second electron affinity of each species was computed as a difference in total energies between the dianion and the singly charged anion. These energies are corrected for unscaled zero-point energies. To explore the dissociation pathways of each dianion into two singly charged ions, i.e., AB²⁻ → A⁻ + B⁻, the energies of the primary observed dissociation ionic fragments were calculated. These fragmentation pathways are compared with the neutral dissociation pathways, i.e., AB²⁻ → A²⁻ + B, by calculation of the energies of the primary neutral loss products. For comparison to the CID experiments employed herein, the thermally corrected energies of each of the anions and the fragments were employed in determination of dissociation energies for various pathways considered. In addition to the B3LYP DFT method, the MPW1PW91 DFT method was also employed for computation of the 4-sulfobenzoate and 2,6-naphthalendisulfonate dianion vibrational frequencies and the dissociation and detachment energies.

III. RESULTS

A. CID experiments

The mass spectra of the dianions prior to collision were optimized toward obtaining the most intense signal of doubly charged anions (cone voltage=20 V). For the optimized conditions, the mass spectra of the dicarboxylate and disulfonate samples do not show singly charged ions of the doubly deprotonated species from the electrospray since they are not expected to exist in the solution. However, the singly charged species corresponding to the protonated dianions were observed. For the 2,6-naphthalendisulfonate dianions

FIG. 1. Mass spectra of secondary ions produced by collisions of the (a) 1,2-benzenedisulfonate, (b) 1,3-benzenedisulfonate, (c) 1,5-naphthalenedisulfonate, and (d) 2,6-naphthalenedisulfonate parent dianions with a static argon background at a laboratory collision energy of 60 eV.

there was no singly deprotonated monoanion observed at the optimized cone voltage; however, as the cone voltage was varied the singly deprotonated monoanion was observed as well.

The postcollisional mass spectra of dianions colliding with argon gas at 60 eV translational energy in the laboratory reference frame are shown in Figs. 1 and 2. The CID of the disulfonate dianions displays a single dissociation pathway, leading to the SO_3^- anion and its conjugate ion for all of the disulfonate dianions studied [Figs. 1(a)–1(d)]. The dicarboxylate dianions showed fragmentation resulting in singly charged anions without one or both CO_2 groups [Figs. 2(a) and 2(b)]. Long-lived CO_2^- ions were not observed from fragmentation of these dianions within the experimental time frame, which is estimated to be in the order of milliseconds. However, the CO_2^- anion is known to be metastable with respect to autodetachment with a lifetime varying between 20 and 90 μs depending upon the internal rovibrational energy present in the CO_2^- ion.²³ The CID of the dianion containing *both* SO_3 and CO_2 showed the most complicated fragmentation pattern. The SO_3^- anion is formed along with its conjugate ion. The loss of $\text{CO}_2 + e$ is again observed without the occurrence of detectable CO_2^- signal. As with the dicarboxylate dianions, unsubstituted singly charged aromatic anions are left after loss of both the SO_3 and CO_2 groups [Fig. 2(c)]; however anions of the carbon ring structure corresponding to the case where both SO_3 groups are fragmented are not observed in the collisional dissociation of the disulfonate dianions. Autodetachment or collisional ED of any of the dianions studied was not observed up to colli-

sion energies of 60 eV (laboratory frame). This is not surprising since the singly charged anions of these species are expected to be unstable.

The energy dependence of the relative cross section for collisional dissociation toward the formation of each of these ionic fragments was investigated. The relative cross section was taken as the ratio of the fragment signal to the remaining parent, which at near threshold conditions is directly proportional to the actual cross section. Furthermore, treatment in this manner allowed variations in signal intensity from experiment to experiment to be taken into account. These ratios were then plotted with respect to collision energy in the center-of-mass (COM) reference frame to probe the energy thresholds for fragmentation. The fragmentation of the SO_3^- anion from the disulfonate dianions showed a clear threshold [Figs. 3(a)–3(d)]. The values of these dissociation thresholds, as determined by a linear extrapolation of the near threshold behavior, range from 2.3 to 3.5 eV and are summarized in Table I.

The loss of a CO_2 unit and an electron from the carboxyl containing dianions appeared with no clear threshold [Figs. 4(a)–4(c)]. The CID of the single-ringed dicarboxylate dianion displayed a significant loss of a single CO_2 molecule and electron, as well as loss of both CO_2 groups (along with the loss of an electron) at the lowest collisional energies. The dianion containing two rings (naphthalenedicarboxylate dianion) showed a small, but measurable, signal for both fragmentation pathways at the lowest collision energies (and at zero pressure). Both the single (benzene) and double (naphthalene) ringed dicarboxylate dianions exhibited a peak

FIG. 2. Mass spectra of secondary ions produced by collisions of the (a) terephthalate, (b) 2,6-naphthalenedicarboxylate, and (c) 4-sulfobenzoate parent dianions with a static argon background at a laboratory collision energy of 60 eV.

in the signal corresponding to the loss of a single CO_2 and an electron as the signal for loss of both CO_2 groups and an electron began to rapidly increase, and at higher energies become the dominant fragmentation pathway observed. The dianion containing both CO_2 and SO_3 showed results in concurrence with the other dianions. The signal corresponding to loss of a CO_2 and electron again appears at the lowest collision energies, and in this case, remains relatively unchanged over the energies studied implying again the apparent metastability of this dianion to dissociation as a result of internal energy. The loss of SO_3^- appears with a clear threshold, as does the loss of both SO_3^- and CO_2 [Fig. 4(c)].

In the case of the carboxylate-containing dianions there is signal at “zero” collision energy implying that these ions are metastable. However, these dianions are expected to be stable in their ground state. This would imply that ions produced in the electrospray source that are subsequently accelerated into the mass spectrometer contain a significant amount of rovibrational energy. In order to examine this hypothesis, the terephthalate and 2,6-naphthalenedicarboxylate dianion were chosen for study at the ELISA ion storage ring, as described above, where ions are formed by electrospray and allowed to rovibrationally relax under thermal collisions with helium gas before analysis. Figure 5 shows the observed decay of the 2,6-naphthalenedicarboxylate dianion signal over a time interval from 0 to ~ 14 s. The nominal mean lifetime is taken to be 1.5 s. This corresponds to an estimated time for “leakage” and background collisional dissociation ion losses from the ion storage ring. Such a long lifetime is interpreted to imply an essentially stable ion. It is

concluded that this dianion with thermal energy is essentially stable and that the ions formed in the ESI source are rovibrationally “hot” due to the electrospray and ion inlet conditions. The terephthalate dianion was not observed in the ELISA experiment. One could conclude that this ion is truly metastable or that it is vibrationally hot and does not live long enough to arrive at the cooling cell. It is also possible the comparatively lower aqueous and gas-phase acidity of the singly deprotonated terephthalic acid monoanion simply results in less of the dianions being produced from the electrospray process.

B. Computational results

The zero Kelvin zero-point energy-corrected computed EB energies for all of the dianions studied show a positive EB energy predicting that they are adiabatically stable with respect to ED. In addition, all of the dianions are calculated to be stable with respect to dissociation according to the adiabatic dissociation energy except for the 1,2-benzenedisulfonate dianion. Dissociation is calculated to be higher in energy than direct ED for all the dianions. The calculated dissociation energies of the sulfonate dianions shown in Table I and the energies of the dissociation and detachment pathways of the carboxylate dianions are summarized in Table II. The lowest energy pathway for the disulfonate dianions is SO_3^- loss. The lowest energy pathway for the carboxylates corresponds to CO_2^- loss, and for the 4-sulfobenzoate dianion the CO_2^- loss is lower in energy than the SO_3^- loss pathway. The loss of a neutral CO_2 or SO_3

FIG. 3. Collisional energy dependence for the formation of SO_3^- and its conjugate pair from CID of (a) 1,2-benzenedisulfonate, (b) 1,3-benzenedisulfonate, (c) 1,5-naphthalenedisulfonate, and (d) 2,6-naphthalenedisulfonate parent dianions in the COM frame.

group is higher in energy than the loss of the corresponding anionic group for all dianions studied, demonstrating the importance of the multiple sulfonate and carboxylate groups in stabilizing the dianions.

Calculations regarding the thermodynamic stability of the dianions with respect to dissociation and detachment do not include the effect of the Coulomb barrier, and thus are only indicative of the underlying adiabatic energy of the processes. However, in this sense, the thermodynamic values provide a foundation for discussion of the Coulomb barrier. In order to determine the magnitude of the RCB for these systems, an estimate of the dissociation energy of the dianion

into two singly charged ions is required. Energies needed to dissociate the dianions into two singly charged ions were determined from calculations of the thermally corrected energy difference between the optimized dianions and singly charged ion fragmentations. Calculated dissociation energies were combined with the experimental threshold measurements to determine a value for the magnitude of the RCB toward IF. These results are summarized for the sulfonate dianions in Table I.

The calculations used for the estimation of the dissociation and detachment energies are also useful for interpretation of the vibrational spectrum obtained from the IRMPD

TABLE I. Thresholds to SO_3^- dissociation in the CID experiment, calculated SO_3^- dissociation energies, and Coulomb barriers (RCB) for 1,2-disulfonate, 1,3-disulfonate, 2,6-naphthalenedisulfonate, and 1,5-naphthalenedisulfonate dianions are presented. The dissociation energies are computed using DFT. The magnitudes of the RCBs are determined as the difference between the measured thresholds to dissociation and the calculated dissociation energies. All values are in eV.

	Threshold to dissociation	Calculated dissociation energy	RCB
1,2 benzenedisulfonate dianion	2.3	-0.4	2.7
1,3-benzenedisulfonate dianion	3.0	0.7	2.3
1,5 naphthalenedisulfonate dianion	3.0	0.9	2.1
2,6 naphthalenedisulfonate dianion	3.4	1.3	2.1

FIG. 4. Collisional energy dependence for various dissociation pathways observed for (a) terephthalate, (b) 2,6-naphthalenedicarboxylate, and (c) 4-sulfobenzoate parent dianions in the COM frame.

experiments (*vide infra*). To investigate the variation in the calculated harmonic vibrational frequencies with DFT method, an alternative functional with the same basis set is employed. The dissociation and detachment energy calculations done for the 4-sulfobenzoate and 2,6-naphthalenedisulfonate dianions with the B3LYP method were repeated with the MPW1PW91 DFT method, which

produces less than a 10% difference in all of the calculated energies of the sulfonate dianions.

C. IRMPD experiments

On-resonance irradiation of the 2,6-naphthalenedicarboxylate dianion led primarily to production of the radical $C_{10}H_6CO_2^-$ anion, involving loss of CO_2 plus an electron. As was observed in the low-energy CID experiments, a smaller amount of product due to loss of two CO_2 groups and one electron was also produced. Upon multiple photon IR absorption, the loss of only CO_2 (to produce $C_{10}H_6CO_2^{2-}$) or loss of only an electron (to produce $O_2CC_{10}H_6CO_2^-$) was not observed. The detached electron was observed indirectly by employing a recently refined technique¹⁹ using the SF_6 electron scavenger in the ICR cell, which attaches to form SF_6^- . An ensemble of ions is detected after 3 s of irradiation, so it is not possible to determine if the SF_6^- signal is due to electrons produced by direct ED or delayed autodetachment of metastable CO_2^- . As shown in Fig. 6, the SF_6^- signal as a proxy for the free ED channel

FIG. 5. Lifetime measurements of 2,6-naphthalenedicarboxylate dianion measured employing the electrostatic ion storage ring (ELISA) (Ref. 24).

TABLE II. Calculated EB energies and dissociation energies of the carboxylate dianions using DFT (B3LYP) with the 6-311++G** basis set. The first column indicates the positive second AEAs of the dianions. The second and third columns represent the final energies of the possible decarboxylation channels. The fourth is the adjustment for the electronic instability of CO_2^- . The last column indicates the electronic instability of the dianions after loss of CO_2 . All values are in eV.

	P ⁻ AEA	$[\text{P}-\text{CO}_2]^{2-} + \text{CO}_2$	$[\text{P}-\text{CO}_2]^- + \text{CO}_2^-$	$[\text{P}-\text{CO}_2]^- + \text{CO}_2 + e^-$	$[\text{P}-\text{CO}_2]^-$ AEA
Terephthalate dianion	0.50	3.00	1.36	0.99	-1.92
2,6-naphthalenedicarboxylate	0.98	2.71	1.83	1.46	-1.17
4-sulfobenzoate	1.06	2.83	1.61	1.24	-1.50

does clearly correlate spectroscopically with the simultaneously observed monoanion fragment dissociation channel. As shown in the same figure, scaled B3LYP harmonic vibrational frequency calculations give a good match to the spectrum, reproducing well the positions of the antisymmetric and symmetric carboxylate stretching modes at approximately 1600 and 1300 cm^{-1} , respectively.

On-resonance irradiation of the 4-sulfobenzoate dianion led primarily to production of the radical $\text{C}_6\text{H}_4\text{SO}_3^-$ anion, involving loss of CO_2 plus an electron. Some SO_3^- production is observed at certain wavelengths, but this was determined to be due to sequential dissociation of the $\text{C}_6\text{H}_4\text{SO}_3^-$ anion fragment. Thus, as in the case of the dicarboxylate dianion, the primary fragmentation pathway observed from IRMPD involves CO_2 plus an electron loss. The spectrum acquired via the dissociation and detachment action spectroscopy methods is shown in Fig. 7. Scaled B3LYP harmonic vibrational frequency calculations give a good match to the carboxylate stretching portion of the spectrum but there is a severe underestimate of the frequencies of the vibrational modes involving symmetric and antisymmetric stretching of the sulfonate group, which are the three intense bands located between 1000 and 1250 cm^{-1} . In addition to an overall

underestimate of the frequencies of these bands, the splitting between them is also poorly modeled. The use of a different DFT method, MPW1PW91, drastically improves the relative positions of the sulfonate vibrations (as shown in Fig. 7, unscaled), but scaling the frequencies by a factor of 0.98 to produce an acceptable match to the carboxylate stretching modes still results in a severe underestimate of the sulfonate vibrational frequencies. Thus, while each DFT method has its advantages, neither is entirely satisfactory with regard to this ion. This discrepancy suggests some degree of caution is required in the assessment of the accuracy of the DFT dissociation and detachment energy calculations, but use of the MPW1PW91 functional with the same basis set produces equivalent results for dissociation and detachment energies. Therefore, the conclusions drawn from the B3LYP calculated energies are not expected to be compromised by the improvement from the MPW1PW91 functional, although it is clear that further computational investigation is required for correct modeling of the sulfonate vibrations.

To investigate the photofragmentation behavior of the disulfonate dianions, the IRMPD spectrum of the 2,6-naphthalenedisulfonate dianion was acquired as a represen-

FIG. 6. IRMPD spectrum of 2,6-naphthalenedicarboxylate dianion. The dissociation channel is the anion produced by CO_2 and electron loss from the parent, and the detachment channel is the SF_6^- anion that results from free electron attachment to background SF_6 . SF_6^- signal is coincident with the dissociation signal, representing the ED from a metastable fragment. The B3LYP calculated frequencies are scaled by 0.98 and convolved with a Gaussian line shape function of 30 cm^{-1} full width at half maximum (FWHM).

FIG. 7. IRMPD spectrum of 4-sulfobenzoate dianion. The dissociation channel is the anion produced by CO_2 and electron loss from the parent, and the detachment channel is the SF_6^- anion that results from free electron attachment to background SF_6 . SF_6^- signal is coincident with the dissociation signal, representing the ED from a metastable fragment. The calculated frequencies from two DFT methods are shown in the lower panel, B3LYP scaled by 0.98 (in gray), and the MPW1PW91 unscaled (in black), each convolved with a Gaussian line shape function of 30 cm^{-1} FWHM. The sulfonate vibrations are the bands between 1000 and 1250 cm^{-1} .

FIG. 8. IRMPD spectrum of 2,6-naphthalenedisulfonate dianion. The dissociation channel is comprised of all of photofragmentation products observed. The calculated frequencies from two DFT methods are shown in the lower panel, B3LYP unscaled (in gray), and the MPW1PW91 unscaled (in black), each convolved with a Gaussian line shape function of 20 cm^{-1} FWHM.

tative sample. On-resonance irradiation of the dianion resulted primarily in SO_3^- radical anion production, accompanied by the concomitant $\text{C}_{10}\text{H}_6\text{SO}_3^-$ radical anion fragment. There was no dianion fragment product observed from the on-resonance dissociation. The IRMPD spectrum of the 2,6-naphthalenedisulfonate dianion is shown in Fig. 8. As compared with the 4-sulfobenzoate IRMPD spectrum in Fig. 7, the features due to the carboxylate stretching modes are clearly absent and the sulfonate vibrational modes in the region between 1000 and 1250 cm^{-1} are consistent. The failure of the B3LYP DFT method to accurately model the sulfonate vibrational modes is again improved by the MPW1PW91 DFT method, as shown in the lower panel of Fig. 8.

Overall, the IRMPD results are in agreement with the CID results, and are also complementary. It was determined that on-resonance irradiation of the disulfonate dianions results primarily in dissociation by SO_3^- loss with no ED, in agreement with the CID studies. It is also corroborated that CO_2 plus electron loss is favored over loss of SO_3^- from the 4-sulfobenzoate dianions. Complementing the CID studies, the use of the SF_6 scavenger technique in the ICR cell reveals that the appearance of the monoanion fragments resulting from CO_2 plus electron loss from the carboxylate dianions does involve ED, resulting in coincident SF_6^- production. The good match between experimental and scaled DFT computed spectra imparts confidence to the DFT dissociation and detachment energy calculations and the interpretations regarding the effect of the Coulomb barrier on the dissociation dynamics.

IV. DISCUSSION

CID studies demonstrate that the carboxylate containing dianions produced for this study with CID are observed to be metastable toward fragmentation. However, the fact that dissociation is generally enhanced at higher collision energies

FIG. 9. Magnitude of the RCB toward IF and ED [Wang *et al.* (Ref. 7)] plotted vs the inverse of the average charge separation. The line shows the calculated value of $e^2/r = 14.4 \text{ (eV Å)} / r(\text{Å})$.

and the observation of long-lived dicarboxylate ions from the ELISA and FT-ICR experiments suggests that this is likely a result of excess internal rovibrational energy acquired from the electrospray conditions employed. Disulfonate dianions are observed to be stable toward ion fragmentation and clear energetic thresholds are seen in the dissociation cross sections. Interestingly, from CID the dianions resulting from 4-sulfobenzoic acid (containing both CO_2 and SO_3 groups) were observed to be stable toward SO_3^- loss and metastable toward loss of $\text{CO}_2 + e$. Thus a clear difference was observed in the facility of dissociation from sulfonate and carboxylate dianions, which is beyond what would be expected from the calculated adiabatic dissociation energies, as shown in Tables I and II. The IRMPD experiments further demonstrate that the carboxylate dissociation involves simultaneous or subsequent ED.

The clear thresholds observed and the increased localization of the excess electrons for the disulfonate dianions allow one to explore the relationship between the magnitude of the RCB toward IF and the nominal charge separation between the excess electrons. Calculations of the highest occupied molecular orbital for these dianions show that the excess electrons are heavily localized on the outlying oxygen atoms of the SO_3 groups, allowing for the excess charges to be treated as point charges “localized” on these outlying oxygens. Calculations of the dissociation energy are combined with the measured dissociation thresholds in order to obtain an estimate of the magnitude of the Coulomb barrier toward this dissociation ($\text{RCB} = \text{Threshold} - \text{Diss. Energy}$). Using an analysis similar to the approach adopted by Wang *et al.*⁷ in their study of ED for a series of linear dicarboxylate dianions, the magnitude of the RCB toward IF was plotted versus the inverse of the average distance between the outlying oxygens. Figure 9 shows these data as well as the results from the experiment of Wang *et al.*⁷ The results show a reasonable agreement with the previous findings for ED, that the magnitude of the Coulomb barrier is essentially e^2/r . For IF, there is likely to be some deviation from the classical treatment of the excess electrons as point charges, as the polarizability of the ionic fragments definitely plays some role. Unfortunately the large uncertainty inherent in this analysis, both from ascribing an energetic threshold from dissociation

FIG. 10. Secondary mass spectrum of anions formed from CID of the 1,11-undecanedicarboxylatedianion at a collision energy of 60 eV in the laboratory frame. The inset shows the relative cross section for the fragmentation of a mass corresponding to 44 amu which we ascribe to CO_2^- .

of vibrationally excited dianions produced from the electrospray source, as well as inclusion of computed dissociation energies for determination of the magnitude of the RCB, keeps one from determining with any certainty the exact nature of the RCB in this case. Furthermore, the reliance on calculations for determination of both charge separation as well as dissociation energies makes these inferred measurements of the magnitude of the RCB highly dependent on our calculation model.

For the carboxylate containing dianions, the fact that no CO_2^- ions were detected in the CID experiments raises an interesting question as to the lowest possible pathway for their respective dissociation. Due to the relatively long time scale of the CID experiments, it is difficult to determine with certainty whether the carboxylate containing dianions are simultaneously losing neutral CO_2 and an electron or autodeachment from an intact CO_2^- fragment ion is occurring. As mentioned before, the CO_2^- anion is metastable [adiabatic electron affinity = -0.6 ± 0.2 eV (Ref. 25)] and has a lifetime of ~ 60 μs ,²³ therefore the amount of CO_2^- present, if produced, would be practically unobservable in the experimentally available time window (on the order of microseconds for CID and seconds for the IRMPD experiments). However experiments on CID of the linear 1,11-undecanedicarboxylic dianion (Fig. 10) showed the formation of a product with a mass corresponding to CO_2^- with a clear above zero threshold. It is difficult to attribute this peak to other possible anions. We contend that this inconsistency can be attributed to

the significantly larger localization of the excess electrons on the CO_2 moieties for this nonaromatic dianion. Our calculations indicate that the aromatic carboxylate containing dianions studied are stable toward ionic dissociation as well as being adiabatically stable, i.e., having a positive EB energy (Table II). Although the loss of neutral CO_2 is computed to be higher in energy than loss of a CO_2^- ion for these dianions, the latter pathway is actually less likely due to the presumed influence of the Coulomb barrier (Fig. 11). As our

FIG. 11. Idealized potential energy surface encountered by the terephthalate dianion as it dissociates via barrierless CO_2 loss or RCB affected CO_2^- loss.

results for the disulfonate dianions imply, the RCB should provide added stability against the loss of CO_2^- (≥ 1 eV since the distance between the outlying oxygens would serve as an upper limit for the separation between excess charges) in addition to the calculated positive dissociation energy for this pathway. Therefore, relying on the computed results and the evidence of loss of a neutral CO_2 presented in other experiments,^{26,27} we propose that the observed decay of the aromatic dicarboxylate dianions occurs through neutral CO_2 loss followed by immediate autodetachment of an electron from the remaining dianion fragment.

Further supporting the loss of neutral CO_2 is the detection of the *p*-benzyne anion [C_6H_4 , $m=76$ amu, $\text{EA}=1.265 \pm 0.008$ eV (Ref. 24)] from dissociation of the terephthalic and 4-sulfobenzoate (containing both CO_2 and SO_3 groups) dianions as well as the double ring analog from the 2,6-naphthalenedicarboxylate dianion, yet no “ring” anions are formed from fragmentation of any disulfonate dianions. To further investigate this interesting feature, molecular orbital calculations of these dianions using the GAUSSIAN G03 suite of programs²² at the density functional level of theory with 6-311++G** basis set were employed. Orbital visualization of these dianions shows that the two excess electrons in the dicarboxylate dianions are distributed across the CO_2 and the benzyne ring while for the disulfonate dianions the two electrons reside primarily on the SO_3 moieties. For the 4-sulfobenzoate dianion the two electrons are found mostly on the CO_2 moiety as well as the benzyne ring. These orbital visualizations suggest the delocalization of the excess electrons in the carboxylate containing dianions allows the excess electron density to partially reside on the ring structure, allowing for the fragmentation of neutral CO_2 , uninhibited by the RCB. This neutral fragmentation pathway would be unavailable to the disulfonate anions, as well as the 1,11-undecanedicarboxylic dianion, due to the significant localization of their respective excess electrons on the likely neutral fragments. This hypothesis is supported experimentally by photoelectron spectroscopy of single ringed dicarboxylate dianions by Wang *et al.*²⁸ In this study, photoelectrons emanating from the carboxylate groups were observed as expected, and also observed were photoelectrons which they ascribed to originating from the ring structure. Thus, the delocalization of the electrons on the carboxylate containing dianions seems to play an important role in the dissociation of these molecules by neutral CO_2 fragmentation, essentially opening a path “around” the Coulomb barrier as the subsequent ED from the parent- CO_2 dianion fragment is from a less stable and highly delocalized molecular orbital.

As discussed above, the anions formed from ESI are vibrationally hot, with a significant population above the ground rovibrational state. Possible mechanisms leading to metastable dissociation deserve a comment. Dissociation via neutral CO_2 fragmentation is unencumbered by an additional barrier toward dissociation, thus no mechanism remains for imparting metastability. Molecules of sufficient internal energy would simply dissociate immediately upon creation. If the dianion dissociates via CO_2^- loss and its internal energy was greater than the necessary dissociation energy, it may be expected to tunnel through the RCB with some finite life-

time. However, since we are discussing a heavy fragment, as opposed to a light electron, we would not expect the tunneling dissociation rate to be large enough to account for the abundant metastable decay observed. We suggest that the delocalization of the excess electrons in this system may provide an answer. As the electron probability distribution is spread across the ring structure as well as the CO_2 moiety, the potential energy surface toward dissociation could be considered as a superposition of the barrierless dissociation via CO_2 neutral, corresponding to the electron probability on the ring, and the RCB affected dissociation via CO_2^- , obviously corresponding to the electron probability on the CO_2 group. We illustrate this possibly through calculations for the dissociation of the terephthalate dianion. Figure 11 shows an idealized potential energy surface encountered by the terephthalate dianion as it dissociates via barrierless CO_2 loss, or RCB affected CO_2^- loss. Thus a molecule with enough internal energy to dissociate via neutral CO_2 loss would seem metastable so long as the electron remained associated with the CO_2 group. Although the disulfonate dianions studied are likely to be vibrationally hot as well, the localized nature of the excess electrons does not allow for a dissociation/detachment pathway around the RCB, thus these vibrationally excited dianions would only be observed as an increased “tail” to the dissociation threshold, the extent of which is impossible to discern with any certainty from the present experiment.

V. CONCLUSION

CID, along with IRMPD techniques, is utilized to study a series of doubly substituted aromatic dianions containing multiple sulfonate and carboxylate functionalities toward understanding the effect of the RCB on the dissociation pathways of the respective dianions. The dianions containing two SO_3 groups dissociate via fragmentation into SO_3^- and its conjugate pair with clear thresholds allowing for determination of the magnitude of the RCB toward IF. It was found that the magnitude of the RCB is in reasonable agreement with that found for ED, found by Wang *et al.*⁷ to be $|\text{RCB}| \approx e^2/r$. This model is likely to fail for small charge separations as the polarizability of the resultant fragments plays a greater role, likely significantly affecting the dissociation of very small MCAs. The dissociation of the dicarboxylate dianions is believed to occur through loss of neutral CO_2 and an electron due to the delocalization of the excess electrons allowing for a dissociation pathway circumventing the RCB for these systems. Furthermore, this delocalization of the excess charges may allow for a superposition of potential surfaces encountered by the dianion during dissociation and detachment, possibly accounting for the observed metastable decay of vibrationally hot dianions, as observed in our CID experiments. The exact role of the RCB in determining the preferred dissociation pathway in a MCA, as well as the effects of charge delocalization on the potential surface, remains an important question, worthy of further theoretical and experimental investigation.

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