Effect of Internal Energy on the Repulsive Coulomb Barrier of Polyanions

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The nature of the repulsive Coulomb barrier (RCB) in isolated molecular polyanions is studied by means of the photodetachment dynamics of the S_1 excited state of the fluorescein dianion which is bound solely by the RCB. Photoelectron spectra reveal a feature at constant electron kinetic energy, regardless of the excitation energy. This is explained using an adiabatic tunnelling picture for electron loss through successive RCBs correlating to vibrationally excited states. This physical picture is supported by time-resolved photoelectron spectra, showing that the tunnelling lifetime is also invariant with excitation energy.

Isolated molecular polyanions have attracted significant interest because of their electronic structure.[1–5] An inherent degree of instability arises from the repulsion between the negatively charged sites on the molecular skeleton. As a result, many polyanions common in the condensed phase, such as SO_4^{2-}, have not been observed in the gas-phase.[6] Yet, the same interactions can also lead to a dramatic increase in electronic stability. A potential barrier is present due to the balance between the short-range attraction and long-range electron-anion repulsion, which can prevent an excess electron from escaping.[7–10] This repulsive Coulomb barrier (RCB) can lead to exotic observations such as polyanions with negative electron binding energies.[11, 12] The RCB height can be related to the distance between localised charge sites, effectively providing an intra-molecular ruler.[8] Photoelectron (PE) spectroscopy coupled with electrospray ionisation (ESI) provides a route to understanding molecular polyanions, as the PE emission is sensitive to the RCB.[3] At low electron kinetic energy (eKE) there is an energetic cut-off below which the PE can only be emitted by tunnelling through the RCB.[5, 7, 10, 13] Above the RCB, the PE trajectory is guided by the anisotropic RCB.[14, 15] Despite the many important consequences of the RCB, there have been no detailed studies on the dependence of the RCB on internal energy of the polyanion and its effect on the tunnelling process.

For a given electronic state, there is not simply a single RCB. Instead, every ro-vibrational level will in principle have an RCB associated with it. An important question is how the RCBs vary with internal energy and how the electron emission is affected by this high density of RCBs. In this letter, we report on the adiabatic tunnelling of an electronically excited state of a molecular polyanion that is bound solely by an RCB. Using a combination of PE spectroscopy and time-resolved PE spectroscopy,[16, 17] we show that there exists an RCB for every vibrational state and that electron loss via tunnelling through the RCB conserves the vibrational energy. Our results provide detailed insight into the nature of the RCB and the dynamics of electron loss from polyanions.

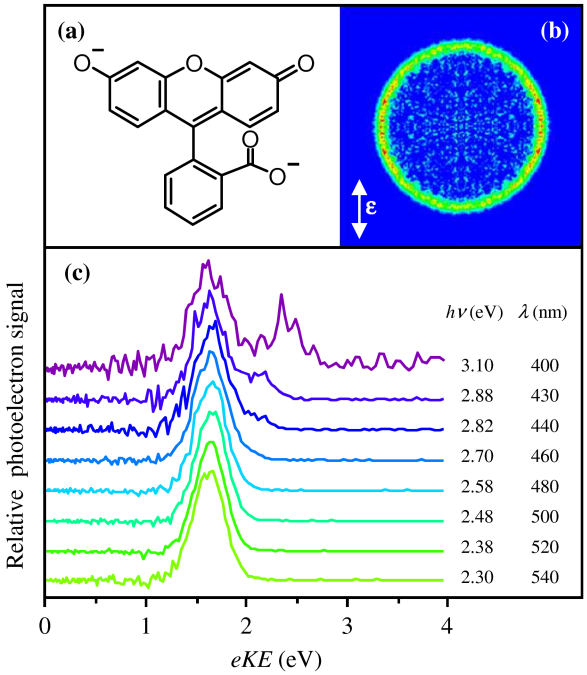

FIG. 1. (color online). Photoelectron (PE) spectra of the doubly-deprotonated fluorescein dianion, with its chemical structure shown in (a). (b) Deconvoluted PE image taken at 2.48 eV (500 nm) and (c) resultant PE spectra taken over a 0.8 eV energy range.

Experiments are performed on the doubly-deprotonated fluorescein dianion, $[\text{fl}-2\text{H}]^{2-}$, the structure of which is shown Fig. 1(a). In solution, $[\text{fl}-2\text{H}]^{2-}$ has a bright $S_1 \leftarrow S_0$ transition around 2.5 eV (500 nm) that decays predominantly by fluorescence, with a quantum yield of 0.92.[18] Recently, McQueen *et al.* showed that isolated $[\text{fl}-2\text{H}]^{2-}$ does not fluoresce.[19] Instead, excitation of the S_1 state leads to loss of an electron. This was used to determine the intrinsic absorption spectrum by monitoring the yield of $[\text{fl}-2\text{H}]^{-}$. Although it is not surprising that an electron is lost following $S_1 \leftarrow S_0$ excitation in $[\text{fl}-2\text{H}]^{2-}$, it is unclear if the S_1 state is completely unbound with respect to electron loss or if it is bound by a RCB. Here, we show that the S_1 state is bound by the RCB and utilise it as a probe to explore dependence of the RCB on internal energy.

The experiments were performed using our recently developed femtosecond PE imaging spectrometer.[20] Mass-selected $[\text{fl}-2\text{H}]^{2-}$ is generated from a 1mM solution of fluorescein in methanol (pH ∼ 11 through the addition of NaOH) in an ESI source that is coupled to a time-of-flight mass-spectrometer. Following mass-selection, the $[\text{fl}-2\text{H}]^{2-}$ ion packet is perpendicularly intersected with radiation from a tuneable nanosecond (ns) laser or by pump and probe pulses from a femtosecond (fs) laser system. The nanosecond pulses are generated by a Nd:YAG pumped optical parametric (OP) oscillator producing ∼5 mJ pulse^{-1} across the visible. Femtosecond pulses are generated from a commercial Ti:Sapphire amplified laser system. Pump pulses around 500 nm are generated using an OP amplifier and by mixing the signal output with residual 800 nm in a beta-barium borate (BBO) crystal. A portion of the fundamental 800 nm is used as probe pulses and the two are delayed relative to each other using a motorised delay stage. The temporal resolution is ∼140 fs based on a cross correlation in a thin BBO crystal. The interaction point between ions and laser is at the centre of a PE spectrometer. The emitted PE cloud is guided in the direction mutually perpendicular to the laser and ion beam onto a position sensitive detector, using a velocity-map imaging arrangement.[21] The point at which a PE strikes the detector is monitored using a CCD and the resultant PE images are analysed using the polar onion peeling method.[22] This provides PE spectra and PE angular distributions. Spectra have been calibrated to the known spectrum of I^- and the spectrometer has a spectral resolution of $\frac{\Delta E}{E} = 5\%$.

Fig. 1(b) shows a deconvoluted PE image taken at 2.48 eV (500 nm) with a ns laser. It reveals a single, slightly anisotropic feature ($\beta_2 = -0.2 \pm 0.1$). The PE spectra of $[\text{fl}-2\text{H}]^{2-}$ taken with a ns laser at various excitation wavelengths between 2.30 eV (540 nm) and 2.88 eV (430 nm) are shown in Fig. 1(c). Also shown is a PE spectrum taken at 3.10 eV (400 nm) with the fs laser. Note that there is no difference between PE spectra at a given excitation energy taken with the fs or ns laser.

The most striking aspect of the data in Fig. 1(c) is that a feature with $eKE = 1.64$ eV is seen in all the PE spectra. Ordinarily in PE spectroscopy, the electron binding energy (eBE) is defined as $eBE = h\nu - eKE$. Despite increasing the photon energy by ∼0.8 eV from 540 nm to 400 nm, there is no concomitant increase in eKE. This suggests that the eBE is increasing with increasing photon energy, which is unphysical. At photon energies above 2.60 eV (480 nm), an additional feature can be identified in the PE spectrum. At 2.70 eV (460 nm), this appears as a small shoulder to the main feature, and extends to higher eKE as the photon energy is increased. It also gains intensity relative to the PE feature at 1.64 eV. Fitting the PE spectra with a Gaussian for each feature reveals that the higher eKE feature shifts by an amount equal to the increase in photon energy. Hence, this feature behaves as expected in PE spectroscopy and its eBE is constant.

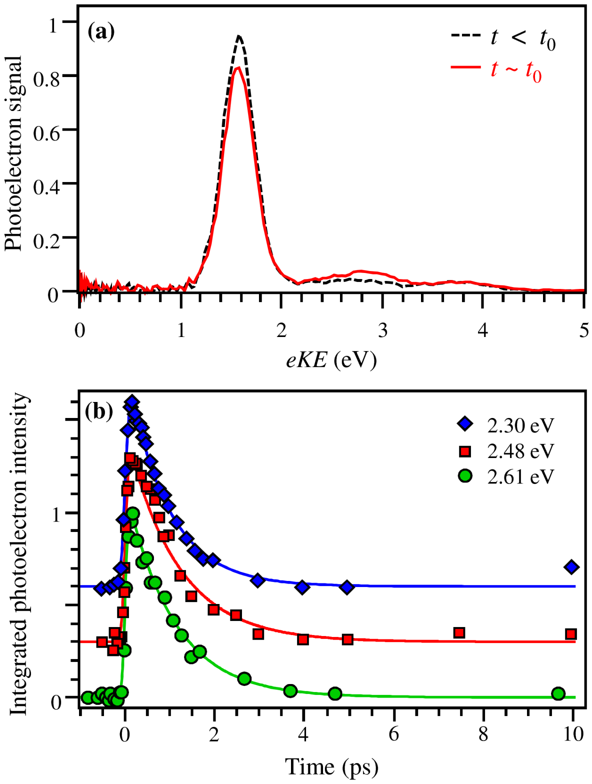

FIG. 2. (color online). Time-resolved photoelectron (PE) spectra following excitation to S_1. (a) representative PE spectra when pump and probe pulses are temporally overlapped and when pump arrives after probe. (b) Integrated PE signal of the S_1 feature at three different excitation energies, indicating an invariance of the lifetime with respect to excitation energy.

To gain further insight, we have also performed femtosecond time-resolved experiments in which the $S_1 \leftarrow S_0$ transition is excited and the ensuing S_1 dynamics probed using 1.55 eV (800 nm) light at variable delays. In Fig. 2(a), representative PE spectra are shown when the probe arrives before the pump ($t < t_0$) and when they are temporally overlapped ($t \sim t_0$). The $t < t_0$ PE spectrum is identical to a pump-only spectrum. The additional PE features at high eKE arise from multi-photon processes, as the laser pulses used in the time-resolved studies are focussed into the interaction region.[23] In the PE spectrum at $t \sim t_0$, a new PE feature can be identified around 2.9 eV. This corresponds to the removal of an electron from the S_1 state by the probe photon. With increasing delay, the pump-probe feature decays in intensity. In Fig. 2(b) the integrated PE counts are plotted as a function of time for three different excitation energies: 2.30 eV (538 nm), 2.48 eV (500 nm), and 2.61 eV (475 nm).

Each dataset is well reproduced using a single exponential decay with time-constants of $\tau = 0.9$, 1.1, and 1.1 ± 0.2 ps, respectively.

The time-resolved PE spectra clearly show that the PE feature at $eKE = 1.64$ eV is not due to direct photodetachment because, on the timescale of our experiment, this would be instantaneous. Instead, the S_1 state is bound by an RCB and the lifetime observed for the S_1 state corresponds to the tunnelling lifetime of the electron through the RCB.[24] The short lifetime indicates that the S_1 state is likely to be close to the top of the RCB. In order to explain the fact that the PE feature arising from tunnelling does not shift in eKE, we consider that the total energy must be conserved. The eKE of the PE can be expressed as: $eKE = h\nu - ABE - E_{\mathrm{int}}$, where ABE is the adiabatic binding energy (difference in energy between dianion and anion in their ground state geometries) and E_{int} is the internal energy of the anion. Accordingly, the observed invariance of eKE in Fig. 1(c) must be accompanied by a change in E_{int} as the photon energy is changed. In normal PE spectroscopy, photodetachment is a vertical transition and the E_{int} is determined by the Franck-Condon factors in going from the dianion to anion.[3] For $[\mathrm{fl}-2\mathrm{H}]^{2-}$ excited to the S_1 state, electron loss is not a vertical transition.

Each vibrational level of product A^- will have an associated RCB leading to the formation of A^{2-}. The RCB can be viewed either from the perpective of the dianion (inner RCB) or from the perspective of an electron approaching the anion (outer RCB).[25] In Fig. 3(a), two scenarios are depicted for the overall shape of the RCB: (i) the height of the outer RCB is constant while the inner RCB increases with E_{int}, or (ii) the inner RCB is constant while the height of the outer RCB decreases with E_{int}. Wang *et al.* have presented arguments favouring the latter,[7] but if this is the case, then for photon energies that exceed the inner RCB height, direct detachment is the only open channel for electron loss. This is not observed because at *all* photon energies in Fig. 1(c), a PE feature due to tunnelling appears at $eKE = 1.64$ eV. Invoking a constant outer RCB height for every vibrational level allows the observed PE spectra to be fully understood.

With reference to Fig. 3(b), excitation to the lowest part of the S_1 band at 2.30 eV leads to tunnelling through an RCB correlating adiabatically to a low vibrational level of $[\mathrm{fl}-2\mathrm{H}]^-$. Note that, in principle, the RCB leading to the S_1 state is not the same as that leading to the S_0, as depicted.[26] They are identical at long-range, as both RCBs share the same final product state, $[\mathrm{fl}-2\mathrm{H}]^-$. Differences are only expected to arise at very short range and hence, we anticipate that the height of the S_1 outer RCB is similar to that of the S_0 outer RCB.

Increasing the photon energy beyond 2.30 eV accesses higher vibrational levels in the S_1 state. If E_{int} is conserved during tunnelling, then $[\mathrm{fl}-2\mathrm{H}]^-$ will be formed vibrationally excited, resulting in a constant eKE. Increasing the photon energy further will lead to a similar scenario until the excitation energy is sufficient to overcome the inner RCB between the S_0 state and the final product state, $[\mathrm{fl}-2\mathrm{H}]^-$. At this point a new electron loss channel opens up, as direct photodetachment into the continuum becomes possible. This occurs between 2.58 eV $< h\nu <$ 2.70 eV.

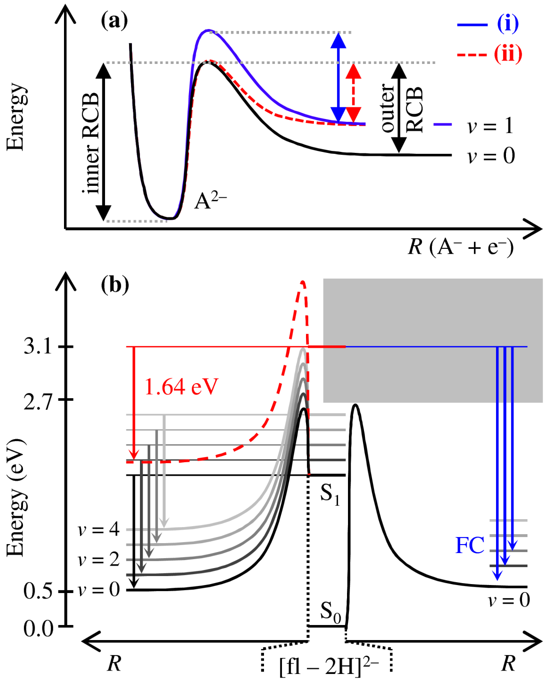

FIG. 3. (color online). Effect of internal energy on repulsive Coulomb barrier (RCB). (a) shows two scenarios in which the height of the outer RCB is (i) constant or (ii) changes with internal energy. The case for the fluorescein dianion is shown in (b), with the RCB correlating to the S_0 state (right) and to the S_1 state (left) are shown. With increasing internal energy in S_1, there is a progression of RCBs. Tunnelling through this leads to photoelectrons (PE) with constant kinetic energy (downward arrows). Once above the RCB for S_0, a direct detachment channel opens up leading to a PE spectrum determined by the Franck-Condon (FC) factors.

For photon energies above 2.70 eV, direct detachment is a vertical transition and the E_{int} of the product $[\mathrm{fl}-2\mathrm{H}]^-$ is determined by the Franck-Condon factors between dianion and anion, which are independent of excitation energy. The direct detachment feature provides a measure of the adiabatic binding energy, which we estimate to be $ABE = 0.5 \pm 0.1$ eV. Based on the onset of this feature and the ABE, the outer RCB height of the S_0 state can be estimated to be approximately 2.1 to 2.2 eV. Concomitant to direct detachment, 3.10 eV is still resonant with the $S_1 \leftarrow S_0$ transition, exciting high vibrational levels of the S_1 state. Even at a photon energy more than 0.4 eV in the continuum above the RCB for direct detachment from the $S_0(v = 0)$ state, the S_1 state preferentially tunnels adiabatically through the RCB corresponding to its internal energy. As this state is above a continuum, nonadiabatic autodetachment may be expected to compete, but this would appear as a broadening of the PE feature towards higher eKE. The PE spectrum at 3.10 eV shows no evidence for this. Hence, the emerging physical picture is one in which there is a dense progression of potential energy surfaces, each corresponding to a vibrational (and rotational) level of the anion. The effective height of the outer RCB is approximately constant.

Further evidence for the validity of this conceptual picture can be gained from time-resolved PE spectroscopy. If the outer RCB has the same height regardless of E_{int}, then the RCB experienced by the electron at a given excitation energy may be expected to have a similar shape. This is consistent with the observation that the lifetime for tunnelling does not vary significantly over a 0.3 eV window. The tunnelling lifetime should be very sensitive to changes in barrier height and width, as the tunnelling probability scales exponentially with these variables.

This physical picture of a series of vibrational potential energy surfaces also explains tandem mass-spectra of $[\mathrm{fl{-}2H}]^{2-}$.[19] Following $S_1 \leftarrow S_0$ photoexcitation, an electron is lost leading to $[\mathrm{fl{-}2H}]^{-}$. For thermal activation methods, such as off-resonance irradiation collisionally activated dissociation (SORI-CAD) or infra-red multiphoton dissociation (IRMPD), electron loss may be expected to be a facile mechanism as $ABE = 0.5$ eV. This is however not observed and instead dissociation with loss of the CO_2^- group is favoured.[19] As vibrational energy is imparted to $[\mathrm{fl{-}2H}]^{2-}$, the electron is prevented from escaping because the inner RCB is increasing with increasing E_{int}. Dissociation in favour of electron loss is a common feature of tandem mass-spectrometry using activation methods through collisions or photons.[27, 28]

To conclude, we have presented the first detailed study of the dependence of an RCB on internal energy. This is done by using an excited state bound solely by the RCB which is probed by PE spectroscopy in the frequency and time domain. A PE feature that arises from tunnelling of the excited state through the RCB is observed at $eKE = 1.64$ eV, regardless of the excitation energy used. This can be accounted for by invoking a physical picture in which every vibrational level has an RCB associated with it, and the height of the outer RCB is approximately constant for all vibrational levels. This is supported by time-resolved PE spectroscopy experiments, which reveal that the tunnelling lifetime is insensitive to excitation energy, suggesting that the barrier width and height are similar at all energies. This picture remains valid also above the lowest RCB and tunnelling can be seen in parallel to direct detachment into the continuum. Electron loss by tunnelling through the RCB is strongly adiabatic and can be viewed as a diagonal transition, exhibiting dramatically different behaviour to direct detachment. Our results highlight the complexity of the RCB in molecular polyanions and its consequences for interpreting PE spectra. Moreover, it provides a framework in which to understand tandem-mass spectrometry of polyanions.

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[1] M. K. Scheller, R. N. Compton, and L. S. Cederbaum, Science **270**, 1160 (1995).

[2] A. I. Boldyrev, M. Gutowski, and J. Simons, Acc. Chem. Res. **29**, 497 (1996).

[3] L. S. Wang and X. B. Wang, J. Phys. Chem. A **104**, 1978 (2000).

[4] A. Dreuw and L. S. Cederbaum, Chem. Rev. **102**, 181 (2002).

[5] X. B. Wang and L. S. Wang, *Annu. Rev. Phys. Chem.*, Annual Review of Physical Chemistry, **60**, 105 (2009).

[6] X. B. Wang, J. B. Nicholas, and L. S. Wang, J. Chem. Phys. **113**, 10837 (2000).

[7] X. B. Wang, C. F. Ding, and L. S. Wang, Phys. Rev. Lett. **81**, 3351 (1998).

[8] L. S. Wang, C. F. Ding, X. B. Wang, and J. B. Nicholas, Phys. Rev. Lett. **81**, 2667 (1998).

[9] O. T. Ehrler, J. M. Weber, F. Furche, and M. M. Kappes, Phys. Rev. Lett. **91**, 113006 (2003).

[10] K. Matheis, L. Joly, R. Antoine, F. Lepine, C. Bordas, O. T. Ehrler, A. R. Allouche, M. M. Kappes, and P. Dugourd, J. Am. Chem. Soc. **130**, 15903 (2008).

[11] X. B. Wang and L. S. Wang, Nature **400**, 245 (1999).

[12] J. M. Weber, I. N. Ioffe, K. M. Berndt, D. Loffler, J. Friedrich, O. T. Ehrler, A. S. Danell, J. H. Parks, and M. M. Kappes, J. Am. Chem. Soc. **126**, 8585 (2004).

[13] X. B. Wang, C. F. Ding, and L. S. Wang, Chem. Phys. Lett. **307**, 391 (1999).

[14] X. P. Xing, X. B. Wang, and L. S. Wang, Phys. Rev. Lett. **101** (2008).

[15] C. G. Ning, P. D. Dau, and L. S. Wang, Phys. Rev. Lett. **105** (2010).

[16] A. Stolow, A. E. Bragg, and D. M. Neumark, Chem. Rev. **104**, 1719 (2004).

[17] J. R. R. Verlet, Chem. Soc. Rev. **37**, 505 (2008).

[18] D. Magde, R. Wong, and P. G. Seybold, Photochem. Photobiol. **75**, 327 (2002).

[19] P. D. McQueen, S. Sagoo, H. Yao, and R. A. Jockusch, Angewandte Chemie-International Edition **49**, 9193 (2010).

[20] J. Lecointre, G. M. Roberts, D. A. Horke, and J. R. R. Verlet, J. Phys. Chem. A **114**, 11216 (2010).

[21] A. Eppink and D. H. Parker, Rev. Sci. Instrum. **68**, 3477 (1997).

[22] G. M. Roberts, J. L. Nixon, J. Lecointre, E. Wrede, and J. R. R. Verlet, Rev. Sci. Instrum. **80** (2009).

[23] The feature at 3.8 eV corresponds to 2-photon resonance enhanced photo-detachment leaving $[\mathrm{fl{-}2H}]^{-}$ in its D_0 ground state, while the feature at 2.7 eV corresponds to

a similar process but leading to an electronically excited state of [fl−2H]$^-$.

[24] O. T. Ehrler, J. P. Yang, A. B. Sugiharto, A. N. Unterreiner, and M. M. Kappes, J. Chem. Phys. **127** (2007).

[25] J. C. Marcum and J. M. Weber, J. Chem. Phys. **131**, 194309 (2009).

[26] A. Dreuw and L. S. Cederbaum, Phys. Rev. A **63**, 049904(E) (2001).

[27] H. J. Cooper, K. Hkansson, and A. G. Marshall, Mass Spectrom. Rev. **24**, 201 (2005).

[28] S. Ard, N. Mirsaleh-Kohan, J. D. Steill, J. Oomens, S. B. Nielsen, and R. N. Compton, J. Chem. Phys. **132** (2010).