A Photoelectron Imaging and Quantum Chemistry Study of Phenolate, Difluorophenolate and Dimethoxyphenolate Anions

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Abstract

Phenolates and their substituted analogues are important molecular motifs in many biological molecules, including the family of fluorescent proteins based on green fluorescent protein. We have used a combination of anion photoelectron velocity-map imaging measurements and quantum chemistry calculations to probe the electronic structure of the phenolate anion and difluoro- and dimethoxy-substituted analogues. We report vertical detachment energies (VDEs) and quantify the photoelectron angular distributions. The VDEs for phenolate (2.26 ± 0.03 eV, 3.22 ± 0.02 eV) are in agreement with high-resolution measurements, whereas the values for the substituted analogues (2.61 ± 0.03 eV for difluorophenolate; ~ 2.35 eV for dimethoxyphenolate) are new measurements. We also report adiabatic excitation energies (AEEs) of anion resonances and discuss their contributions to the overall photoelectron angular distributions. The AEE of the lowest lying resonance in phenolate (~ 3.36 eV) is consistent with previous measurements, whereas the value for the next resonance (~ 3.7 eV) is a new measurement. The AEEs of the resonances in the substituted analogues (~ 3.74 eV for difluorophenolate; ~ 3.4 eV and 3.74 eV for dimethoxyphenolate) are new measurements.

Graphical TOC Entry

Introduction

Phenol is a prototypical heteroatom-containing aromatic molecule and is a common molecular motif in many biomolecules, including green fluorescent protein (GFP) which has revolutionised the life sciences by enabling a wide range of applications such as fluorescence imaging and biosensing. The characteristic intense fluorescence of GFP (quantum yield $\Phi \sim 0.8$) occurs from the deprotonated *p*-hydroxybenzylidene-2,3-dimethylimidazolinone chromophore (*p*HBDI⁻, Fig. 1, R=H) that is anchored, covalently and *via* a hydrogen-bonded network, to the protein that is wrapped around it in a β -barrel structure.¹⁻⁵ Although the isolated deprotonated chromophore is barely fluorescent in the gas-phase or solution, at biological temperatures,⁶⁻⁸ some difluoro- and dimethoxy-substituted analogues (Fig. 1, R=F and R=OMe, respectively) have been shown to become fluorescent when bound to specific ribonucleic acid (RNA) sequences.^{9,10} It has been proposed that the electronic structure of the deprotonated GFP chromophore anion is governed by the phenolate molecular unit,^{11,12} so our understanding of the electronic structure of the difluoro- and dimethoxy-substituted analogues will benefit from a detailed understanding of the electronic structure of the difluoro- and dimethoxy-substituted phenolate building blocks.

Figure 1: Structure of the deprotonated GFP chromophore anion (R=H) and difluoro- (R=F) and dimethoxy- (R=OMe) substituted analogues, with the phenolate anion and substituted analogues shown in black.

Experimentally, a direct way of probing the electronic structure of molecules is to use photoelectron spectroscopy. The electron kinetic energy (eKE) distribution of photoelectrons allows us to determine the electron binding energy (eBE) of the molecular orbital from which the electron is detached, with respect to the electronic state of the neutral radical that is

left behind. The photoelectron angular distribution (PAD) provides information about the electronic character of the molecular orbital from which the electron is detached. For a one-photon detachment process, the PAD can be expressed as

$$I(\theta) \propto 1 + \beta_2 P_2(\cos \theta), \quad (1)$$

where $I(\theta)$ is the probability of photoelectron emission at a particular angle θ , defined as the angle between the laser polarisation and the velocity vector of the photoelectron, $P_2(\cos \theta)$ is the 2nd order Legendre Polynomial and β_2 is the asymmetry parameter.¹³ The two limiting values of β_2 are +2 and -1, corresponding to photoelectron emission predominantly parallel ($\cos^2 \theta$ distribution) and perpendicular ($\sin^2 \theta$ distribution) to the laser polarisation, respectively. In the absence of resonances in the continuum, a negative β_2 can generally be attributed to photodetachment from an orbital with p or π character and a positive β_2 can be attributed to photoionisation from an orbital with s or σ character.

UV photoelectron spectroscopy studies of the phenolate anion have been reported by several groups.^{12,14-17} An accurate value for the S_0 - D_0 adiabatic detachment energy (ADE) has been determined using slow-electron velocity-map imaging (SEVI) (2.2532 ± 0.0004 eV)¹⁶ and the vibrational envelope of the S_0 - D_0 transition has been found to be dominated by a progression in the v_{11} ring stretching mode.¹⁴⁻¹⁷ Direct detachment to D_0 has been observed to generate photoelectrons with perpendicular PADs, as expected for photodetachment from an orbital with π character, and become increasingly anisotropic with increasing photoelectron kinetic energy above the S_0 - D_0 threshold. However, the measured PADs were found to become more isotropic with decreasing wavelength when $\lambda \leq 370$ nm which was attributed to the onset of the $S_0 \rightarrow S_1$ electronic transition at $\lambda \sim 370$ nm, and rationalised by assuming that autodetachment from the S_1 state generates photoelectrons with an isotropic or parallel angular distribution that effectively cancels out the perpendicular anisotropy of the direct detachment contribution to the photoelectron spectrum.¹²

Here, we report the results of a combined photoelectron imaging and computational chemistry study of the phenolate anion and 2,6-difluoro- and 2,6-dimethoxy- substituted phenolate anions. We report values for the vertical detachment energies and we determine the adiabatic excitation energies of the lowest lying bright electronically excited states of the deprotonated anions, which are resonances in the detachment continua.

Methods

Experimental

Photoelectron images were recorded using our electrospray ionisation (ESI) velocity map imaging (VMI) instrument that has been described in detail elsewhere.¹⁸ Briefly, we generated anions by ESI of 1 mM solutions of phenol (PhOH), 2,6-difluorophenol (DFPhOH) or 2,6-dimethoxyphenol (DMPhOH) in methanol, with a few drops of ammonia. The anions were mass-selected by a quadrupole and guided into a hexapole ion trap where they were thermalised with He gas. For photoelectron spectra with maximum energy resolution, photoelectron images were recorded for ~ 12000 laser shots with $\times 2$ centroiding. For accurate β_2 measurements, images were recorded for ~ 36000 laser shots with $\times 1$ centroiding. Background counts (from collisions with the detector and from ionisation of background gas by the laser) were also recorded and subtracted and the resulting images were inverted using the pBASEX method.¹⁹ The eKE of the electrons was calibrated using the photodetachment spectrum of I^- ions, from which it was determined that the eKE resolution was $\leq 5\%$.

Computational

Anion geometries were optimised using density functional theory²⁰ (DFT) with the B3LYP functional^{21,22} and the 6-311++G(3df,3pd) basis set²³ within the Gaussian09 program suite.²⁴ Vertical detachment energies (VDEs) were calculated using the equation-of-motion coupled-cluster method with single and double excitations for the calculation of ionisation potentials²⁵

(EOM-IP-CCSD) and the aug-cc-pVDZ basis set²⁶ within the Q-Chem program package.²⁷ Photoelectron spectra were calculated using ezSpectrum (version 3.0)²⁸ using CAM-B3LYP 6-311++G(3df,3pd) equilibrium geometries, harmonic frequencies and normal mode vectors and assuming an anion vibrational temperature of 300 K. β_2 parameters were calculated over the relevant eKE range using ezDyson;²⁹ the Dyson orbitals for the S_0 - D_0 transition were obtained from the EOM-IP-CCSD calculations.

Results and Discussion

The B3LYP/6-311++G(3df,3pd) structures of phenolate (PhO^-), 2,6-difluorophenolate (DFPhO^-) and the rotamers of 2,6-dimethoxyphenolate (DMPHO^-) are shown in Table 1, together with the EOM-IP-CCSD/aug-cc-pVDZ calculated vertical detachment energies (VDEs) and corresponding Dyson orbitals. Out of the four possible rotamers of DMPHO^- , the most stable are the *syn* (C_s symmetry) and *anti* (C_2 symmetry) rotamers; they are more stable than the other two rotamers because they have two hydrogen bonding interactions between the phenolate oxygen and the hydrogen atoms on the methyl groups, with each hydrogen bonding interaction stabilising the negative charge by ~ 0.15 eV. It is worth noting that the VDEs of these two rotamers of DMPHO^- are very similar.

Photoelectron Spectra

The 364 - 310 nm photoelectron spectra of PhO^- , DFPhO^- and DMPHO^- were recorded as a function of eKE and are plotted in Fig. 2 as a function of eBE ($\text{eBE} = h\nu - \text{eKE}$) and in Fig. 3 as a function of eKE. Experimental VDEs were estimated from maxima in the 364 nm and 354 nm spectra (S_0 - D_0) and peaks in the photoelectron spectra at higher eBEs (S_0 - D_1).

Previous photoelectron spectra of PhO^- have shown that the most intense feature is the vibrational origin transition, i.e. the adiabatic detachment energy (ADE) and VDE are approximately equal.¹⁴ There is a peak in the 364 - 346 nm spectra at 2.26 ± 0.03 eV

Table 1: B3LYP/6-311++G(3df,3pd) Optimised Structures, EOM-IP-CCSD/aug-cc-pVDZ Calculated VDEs (D_0 and D_1) and Corresponding Dyson Orbitals for PhO^- , DFPhO^- and DMPHO^- .

Anion	Structure	E_{rel}/eV	D_0/eV	D_0 hole	D_1/eV	D_1 hole
PhO^-			2.06		3.25
DFPhO^-			2.50		3.92
DMPHO^- (<i>syn</i>)		0.00	2.20		3.50
DMPHO^- (<i>anti</i>)		0.01	2.19		3.49
DMPHO^- (1 H-Bond)		0.14	1.95		3.40
DMPHO^- (no H-Bonds)		0.30	1.70		3.30

Figure 2: Photoelectron spectra of PhO^- (left), DFPhO^- (middle) and DMPhO^- (right) plotted as a function of eBE. Experimentally determined VDEs to the D_0 and D_1 states of the corresponding neutral radicals are marked with solid blue lines.

eBE (solid blue line), which is consistent with high-resolution measurements of the $\text{S}_0\text{-D}_0$ ADE (2.253 ± 0.006 eV,¹⁴ 2.2538 ± 0.0008 eV¹⁵ and 2.2532 ± 0.0004 eV¹⁶). There is another feature at 3.22 ± 0.02 eV eBE, which is consistent with previous measurements of the $\text{S}_0\text{-D}_1$ threshold (3.31 ± 0.05 ¹⁴ and 3.2 eV¹²). These are in good agreement with the EOM-IP-CCSD/aug-cc-pVDZ calculated VDEs listed in Table 1 (2.06 eV and 3.25 eV).

As the wavelength decreases in the range 364 - 318 nm (3.41 - 3.90 eV), the spectra broaden and the vibrational structure appears to shift with wavelength. From the eKE distribution, it can be seen that this is due to the presence of an additional feature in the 354 - 330 nm photoelectron spectra at constant eKE ~ 1.1 eV (dashed red line in Fig. 3; Fig. S2 in the Supplementary Information). As a result of the propensity for conserving vibrational energy during autodetachment, indirect photodetachment following photoexcitation of an excited state S_n with excess vibrational energy, $E_v = h\nu - E(\text{S}_n)$, where $E(\text{S}_n)$ is the adiabatic excitation energy (AEE) of S_n , will result in the emission of

photoelectrons with $\text{eKE} \sim h\nu - E(\text{D}_0) - E_v$, where $E(\text{D}_0)$ is the ADE. This last expression can be rewritten as, $\text{eKE} \sim E(\text{S}_n) - E(\text{D}_0)$; i.e. the photoelectrons are emitted with eKE corresponding to the $\text{S}_n\text{--D}_0$ energy difference (see Fig. 4). Thus, the additional feature at 1.1 eV eKE can be attributed to detachment from a resonance with an onset around 3.36 eV (~ 369 nm). Broadening of photoelectron spectra following photoexcitation of resonances in the continuum has been observed in similar sized molecular anions by many other groups^{14,30,31} including our own.^{11,32–42} This resonance in PhO^- has been observed before^{12,14} and assigned to indirect detachment from the $\text{S}_1(\pi\pi^*)$ state of PhO^- . The $\text{S}_0\text{--S}_1(\pi\pi^*)$ transition corresponds to promotion of an electron from the HOMO shown in Table 1 to the first antibonding orbital on the phenyl ring system (the LUMO of PhO^-) and therefore has shape resonance character with respect to the D_0 continuum.¹² In the 330 nm spectrum plotted as a function of eBE (Fig. 2), the vibrational structure of the direct detachment feature has disappeared and the maximum of the lowest eBE peak appears to have shifted to higher eBE. As the wavelength is decreased, the broadening of the direct detachment feature shifts to higher eBE and, by 310 nm, some of the vibrational structure is recovered. In the 330 - 310 nm photoelectron spectra plotted as a function of eKE, it can be seen that there is another region with an additional feature at constant $\text{eKE} \sim 1.45$ eV (dashed red line in Fig. 3; Fig. S2 in the Supplementary Information), which manifests itself as a shoulder on the high eKE edge of the 330 nm photoelectron spectrum. We assign this to indirect detachment from the second excited bright state (S_2) and deduce an approximate value for its adiabatic excitation energy, $\text{AEE} \sim 3.7$ eV (~ 335 nm).

For DFPhO^- , there is a peak in all the spectra plotted as a function of eBE (Fig. 2) around 2.61 ± 0.03 eV, which we assign to the $\text{S}_0\text{--D}_0$ origin; this is close to the EOM-IP-CCSD/aug-cc-pVDZ calculated VDE listed in Table 1 (2.50 eV) which, together with the profiles of the longer wavelength spectra, suggests that $\text{VDE} \approx \text{ADE}$, similar to PhO^- . The blue-shift in this transition relative to that in PhO^- can be rationalised in terms of the negative charge on the anion being stabilised by the electron withdrawing fluorine atoms. Also

Figure 3: Photoelectron spectra of PhO^- (left), DFPhO^- (middle) and DMPHO^- (right) plotted as a function of eKE . Regions with increased intensity at constant eKE corresponding to experimental AEEs (see text) are marked with dashed red lines.

similar to PhO^- , the photoelectron spectrum is broadened as the wavelength is decreased in the range 330 - 310 nm. This broadening can be attributed to an additional feature at constant $eKE \sim 1.13$ eV (dashed red line in Fig. 3; Fig. S3 in the Supplementary Information), which we attribute to a resonance in the continuum with AEE ~ 3.74 eV (~ 332 nm). As the electronic excited states of DFPhO^- can be expected to be blue-shifted with respect to those of PhO^- , this excited state is likely to correspond to a HOMO-LUMO transition in DFPhO^- .

For DMPHO^- , there is a peak in all the spectra plotted as a function of eBE (Fig. 2) around 2.35 eV (blue line). This is close to the EOM-IP-CCSD/aug-cc-pVDZ calculated VDEs listed in Table 1 for the *syn* and *anti* rotamers (2.20 eV and 2.19 eV) but significantly higher than those of the two higher energy rotamers (1.95 eV and 1.70 eV). This suggests that our anion beam is dominated by the two lowest energy rotamers, for which $E_{\text{rel}} < k_{\text{B}}T_{300\text{K}} \sim 0.03$ eV. We suspect that the very small blue-shift in this transition relative to that for

Figure 4: Schematic energy level diagram illustrating direct and indirect electron detachment processes observed in PhO^- . Thin horizontal black lines represent the vibrational levels of the electronic states of the anion and the blue shaded area represents the electron detachment continuum. Vertical blue arrows represent the eKE of direct and indirect electron detachment processes and the thin horizontal blue lines represent the vibrational energy left in the neutral radical following electron detachment (determined by the propensity for conservation of vibrational energy). The horizontal black arrow represents internal conversion (IC). (a) Direct photodetachment from S_0 to the D_0 continuum gives electrons with eKE, $\epsilon_1 \sim h\nu - \text{VDE}$; in this particular example, $\text{VDE} = \text{ADE}$. (b) Indirect photodetachment following photoexcitation of S_2 with excess vibrational energy, $E_v = h\nu - E(S_2)$ gives electrons with eKE, $\epsilon_2 \sim E(S_2) - E(D_0)$. Indirect photodetachment following photoexcitation of S_2 and subsequent IC to S_1 gives electrons with eKE, $\epsilon_3 \sim E(S_1) - E(D_0)$.

PhO⁻ is the result of competing inductive and mesomeric effects of the OMe substituents. Unlike the photoelectron spectra of PhO⁻ and DFPhO⁻, those of DMPHO⁻ are completely unresolved; we attribute this to the measured photoelectron spectra having contributions from both the *syn* and *anti* rotamers. The rising edges of the photoelectron spectra are less steep than those of PhO⁻ and DFPhO⁻, which may be the result of the contributions of the two rotamers; however, upon photodetachment, the hydrogen bonds are broken and the methyl carbon atoms move into the plane of the molecule (Fig. S1 in the Supplementary Information), which could result in a shift in the maximum Franck-Condon overlap away from the origin of the S₀-D₀ transition. It is also possible that methyl rotations are activated upon photodetachment which may also result in additional spectral broadening. In the 330 nm - 310 nm spectra plotted as a function of eBE (Fig. 2), there is an additional peak around 3.50 eV (blue line), which we attribute to S₀-D₁ detachment. This value is in agreement with the EOM-IP-CCSD/aug-cc-pVDZ calculated VDEs listed in Table 1 for the *syn* and *anti* rotamers (3.50 eV and 3.49 eV). As the wavelength decreases in the range 364 - 310 nm, the feature attributed to S₀-D₀ detachment becomes broader towards higher eBE, which we again attribute to an indirect detachment process. There are two distinct regions in the spectra where there are additional features with constant eKE (dashed red lines in Fig. 3; Fig. S4 in the Supplementary Information). The first has a maximum eKE ~ 1.05 eV in the 364 nm - 346 nm spectra and can be attributed to a resonance with AEE ~ 3.4 eV (~ 365 nm). The second has a maximum eKE ~ 1.40 eV in the 330 nm - 310 nm spectra and can be attributed to a resonance with AEE ~ 3.75 eV (~ 331 nm). It seems most likely that these correspond to the first and second bright electronic transitions of the anions.

To assist with our interpretation of the vibrational resolution observed in the PhO⁻ and DFPhO⁻ spectra (Figs 2 and 3), we have calculated photoelectron spectra corresponding to direct photodetachment from the S₀ states of the anions to the D₀ states of the neutral radicals (Fig. 5). The vibrational spacings predicted by ezSpectrum agree very well with those

in the 364 nm (3.41 eV) experimental spectra at this wavelength and, for PhO^- , correspond to a progression in the v_{11} ring distortion mode of the PhO radical, as previously observed experimentally,^{14–16} and computationally.¹⁷ For DFPhO^- , the spectrum is dominated by the 0_0^0 transition and $v = 0 \rightarrow v = 1$ transitions of v_6 , v_{11} and v_{21} ring stretching modes (Fig 5). The discrepancy between the simulated spectrum of PhO^- and the 364 nm (3.41 eV) experimental spectrum can be attributed to indirect detachment from the lowest lying resonance. The AEE of the first bright resonance in PhO^- lies around 3.36 eV (369 nm), which is just below the photon energy and therefore has a significant impact on the spectrum. The AEE of the first bright resonance in DFPhO^- lies much higher in energy, around 3.74 eV (332 nm), so has less of an impact. Unfortunately, we were unable to calculate photoelectron spectra for *syn* or *anti* DMPHO^- even when using ezSpectrum with Duschinsky rotations. We suspect this is due to the geometry change upon photodetachment being rather complicated; it involves an out-of-plane flap of methyls for the *syn* conformer and an asymmetric wag of the methyls for the *anti* conformer.

Photoelectron Angular Distributions

ezDyson calculations of β_2 parameters have been shown to reproduce experimental trends for a range of molecular anions,^{12,41,43–46} and have been used to calculate the β_2 parameters that characterise direct $\text{S}_0\text{-D}_0$ detachment for PhO^- , DFPhO^- and *syn* and *anti* DMPHO^- ; they are plotted in Fig. 6. The anisotropy can be described qualitatively using partial waves of s and p character.⁴⁷ The orientation of the p partial waves with respect to the electric field vector of the light can be calculated by taking the direct products of the irreducible representation of the HOMO with those of the x, y, z axes in the molecular frame. For example, for PhO^- and DFPhO^- (C_{2v} point group), the HOMOs and z -axes have B_2 and A_1 symmetry, respectively, resulting in p partial waves being perpendicular to the electric field vector of the light ($\beta_2 < 0$), in broad agreement with the ezDyson calculations (Fig. 6). For *anti* DMPHO^- (C_2 point group), the HOMO and z -axis have B and A symmetry,

Figure 5: Top: calculated S_0 - D_0 stick spectra at 300 K (black) convoluted with instrument functions $\Delta E/E \sim 3.5\%$ (red) and experimental 364 nm (3.41 eV) photoelectron spectra (blue) for PhO^- (left) and DFPhO^- (right). The calculated photoelectron spectra have been plotted so that the calculated 0_0^0 peaks coincide with the experimental 0_0^0 peaks, which lies at 2.26 eV for PhO^- and 2.61 eV for DFPhO^- . Bottom: atomic displacement vectors of the ν_{11} mode of the PhO radical and the ν_6 , ν_{11} and ν_{21} modes of the DFPhO radical.

respectively, also resulting in p partial waves being perpendicular to the electric field vector of the light ($\beta_2 < 0$), and also in agreement with the ezDyson calculations (Fig. 6). For *syn* DMPHO[−] (C_s point group), the HOMO and principal axis have A' and A'' symmetry, respectively, resulting in p partial waves being parallel to the electric field vector of the light ($\beta_2 > 0$), in agreement with the ezDyson calculations (Fig. 6). Since both *syn* and *anti* DMPHO[−] rotamers are expected to be present in our anion beam, we might expect the experimentally measured PADs for DMPHO[−] to be reasonably isotropic, or at least only weakly anisotropic.

Figure 6: ezDyson calculated β_2 anisotropy parameters plotted as a function of eKE for PhO[−] (left), DFPhO[−] (middle) and DMPHO[−] (right). The shaded areas mark the eKE ranges of the experimental measurements reported in this paper (364 - 310 nm).

Experimental β_2 parameters obtained from photoelectron images recorded following 364 - 310 nm photodetachment of PhO[−] are plotted in Fig. 7. In the 364 nm spectrum, where the contribution from the S_1 resonance is weakest, the weighted average β_2 value is ~ -0.31 , which is in agreement with previous measurements and consistent with theoretical predictions.¹² This previous study found that ezDyson predicted a smaller β_2 parameter (a more isotropic angular distribution) than was observed experimentally for the direct detachment feature at wavelengths longer than 370 nm. At wavelengths shorter than 370 nm, the overlapping feature arising from autodetachment from the S_1 state led to a decrease in the β_2 parameter, leading to values which appear more in agreement with ezDyson predictions at

Figure 7: β_2 anisotropy parameters (blue line) and photoelectron intensity (black line) for PhO^- plotted as a function of eBE and eKE. The β_2 values are averaged over 3 data points and the error bars give the standard deviation. The horizontal blue line represents $\beta_2 = 0$. Experimental velocity-map images are also presented; the polarisation axis of the light lies in the vertical direction.

wavelengths just below 370 nm. Therefore, the experimental value of β_2 at 364 nm can be considered to result from overlapping direct and indirect detachment features. In the 346 nm and 330 nm spectra, where the contribution from the S_1 resonance is strongest, β_2 increases to near isotropic ($\beta_2 = 0$) in the region of the resonant feature. The ezDyson calculations predict that the β_2 parameter decreases monotonically from -0.2 to -0.3 for the $S_0 - D_0$ transition in the eKE range of this experiment. This suggests that the resonant feature gives rise to a parallel angular distribution which makes the image appear almost isotropic when it is overlapped with perpendicular contribution from direct detachment. Our observation is consistent with previous work where the experimental averaged value of β_2 at wavelengths < 370 nm was observed to deviate from the trend predicted by ezDyson, and it was concluded that this deviation was a result of the resonance with S_1 .¹² In the 330 nm spectrum, where the resonant autodetachment feature is clearly separated in eKE it can be seen that it indeed has a weakly parallel angular distribution ($\beta_2 > 0$). At 330 nm and 310 nm, the value of β_2 for the direct detachment peak is still not in agreement with the prediction of ezDyson, which gives a value of $\beta_2 \sim -0.3$ for direct detachment in this eKE range, even though the indirect detachment feature via S_1 is separated in eKE. This supports our assignment of an additional indirect detachment feature at 1.4 eV eKE in the 330 - 310 nm range (Fig. 3) corresponding to electron emission from the S_2 excited state.

Experimental β_2 parameters obtained from photoelectron images recorded following 364 - 310 nm photodetachment of DFPhO^- are plotted in Fig. 8. At 364 nm, where there is no contribution from resonant autodetachment, $\beta_2 \sim -0.35$ which is in excellent agreement with the prediction of ezDyson in this eKE range ($\beta_2 \sim -0.32$). In the range 346 nm to 310 nm, where the direct detachment feature is overlapped with the resonant autodetachment feature, the anisotropy of the images decreases with increasing photon energy. This is in part due to the variation of the PAD of the direct detachment feature with eKE, which is predicted by ezDyson to be more isotropic in this eKE range ($\beta_2 \sim -0.25$). However, at 310 nm the image is much more isotropic than the prediction ($\beta_2 \sim 0$), which indicates that the

Figure 8: β_2 anisotropy parameters (blue line) and photoelectron intensity (black line) for DFPhO^- plotted as a function of eBE and eKE. The β_2 values are averaged over 3 data points and the error bars give the standard deviation. The horizontal blue line represents $\beta_2 = 0$. Experimental velocity-map images are also presented; the polarisation axis of the light lies in the vertical direction.

contribution from indirect detachment from the resonance has a parallel distribution, similar to PhO^- .

Experimental β_2 parameters obtained from photoelectron images recorded following 364 - 310 nm photodetachment of DMPPhO^- are plotted in Fig. 9. The photoelectron images are almost, if not completely, isotropic at all wavelengths in this experiment. This is largely as expected as a result of the parallel and perpendicular angular distributions from direct detachment from the two rotamers cancelling each other out (Fig. 6). However, there is also expected to be some contribution from indirect detachment from the first bright resonance at all wavelengths in this experiment and there is a very small increase in β_2 as the indirect detachment feature becomes more intense at shorter wavelengths. This could indicate that, similar to PhO^- and DFPhO^- , indirect detachment from the first bright resonance in DMPPhO^- yields photoelectrons with an isotropic or parallel angular distribution ($\beta_2 \geq 0$).

Figure 9: β_2 anisotropy parameters (blue line) and photoelectron intensity (black line) for DMPHO⁻ plotted as a function of eBE and eKE. The β_2 values are averaged over 3 data points and the error bars give the standard deviation. The horizontal blue line represents $\beta_2 = 0$. Experimental velocity-map images are also presented; the polarisation axis of the light lies in the vertical direction.

Summary

Photoelectron spectra and PADs of PhO^- , DFPhO^- and DMPHO^- following photodetachment in the range 364 nm - 310 nm have been reported and interpreted with the assistance of quantum chemistry calculations. For PhO^- , the measured VDEs for D_0 (2.26 ± 0.03 eV) and D_1 (3.22 ± 0.02 eV) are in excellent agreement with previous work.^{12,14-17} Good agreement was also found between the experimentally determined onset of the $S_1(1\pi\pi^*)$ state (~ 369 nm) and previous photoelectron spectroscopy measurements;¹² however, the higher resolution of the photoelectron spectra presented here has allowed us to locate a second bright resonance with AEE ~ 335 nm. The experimentally determined average value of β_2 deviates from the trend predicted by ezDyson in the wavelength range where the direct detachment feature is overlapped in eKE with the resonant autodetachment feature, in agreement with the previous observations.¹² This allowed us to conclude that the resonant autodetachment processes give rise to photoelectrons with parallel or isotropic PADs, with $\beta_2 \geq 0$.

Photoelectron spectra of DFPhO^- and DMPHO^- showed that for DFPhO^- , the electron withdrawing substituents increased the VDE to the first detachment threshold to 2.61 ± 0.03 eV but for DMPHO^- , the VDE was only slightly blue shifted to ~ 2.35 eV which we attributed to the competing electron withdrawing and electron donating effects of the substituents. The photoelectron spectra of DMPHO^- were not vibrationally resolved due to overlapping contributions from the *syn* and *anti* rotamers. For DMPHO^- , features corresponding to resonant autodetachment were observed, with approximate values for the AEEs being ~ 365 nm and ~ 331 nm; these were assigned to indirect detachment from the lowest two resonances in DMPHO^- . For DFPhO^- , only one feature could be assigned to autodetachment from a resonance with AEE ~ 332 nm; this was attributed to the $S_1(1\pi\pi^*)$ state as it is expected to be blue shifted by the electron withdrawing groups. It was found that the observed β_2 parameters for DFPhO^- were in agreement with ezDyson in the range 364 nm - 346 nm, which predicted strongly negative β_2 parameters. ezDyson predicted opposite angular distributions for the two rotamers of DMPHO^- , which cancelled each other out to give a

near-isotropic angular distribution experimentally. A similar observation has been made for *gauche* and *anti* conformers of *para*-ethyl phenolate anions.⁴⁴ For both sets of substituents, resonant autodetachment is found to give rise to parallel or isotropic photoelectron angular distributions, resulting in the measured average β_2 parameters being more positive than the ezDyson predictions in the wavelength range of the resonances.

This work also shows more generally how anion photoelectron spectroscopy and angular distribution measurements, together with quantum chemistry calculations, allow us to improve our understanding of resonances in the detachment continua of molecular anions.

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Supporting Information Available

Structural comparisons; optimised geometries; difference photoelectron spectra; anion temperature.

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