

Probing the Critical Dipole Moment To Support Excited Dipole-**Bound States in Valence-Bound Anions**

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S Supporting Information

ABSTRACT: We report photodetachment spectroscopy and high-resolution photoelectron imaging of *para*-halogen substituted phenoxide anions, p-XC₆H₄O⁻ (X = F, Cl, Br, I). The dipole moments of the p-XC₆H₄O neutral radicals increase from 2.56 to 3.19 D for X = F to I, providing a series of similar molecules to allow the examination of charge-dipole interactions by minimizing molecule-dependent effects. Excited DBSs $([XC_6H_4O]^{*-})$ are observed for the four anions with binding energies of 8, 11, 24, and 53 cm⁻¹, respectively, for X = F to I, below their respective detachment thresholds. The binding energies exhibit a linear correlation with the dipole moments of the neutral radicals, extrapolating to a critical dipole moment of 2.5 D for zero binding energy. Because of the small binding energy of the excited DBS of $[FC_6H_4O]^{*-}$, rotational autodetachment is observed to compete with vibrational autodetachment in the resonant photoelectron spectra, resulting in electrons with near zero kinetic energies.

Teutral molecules possessing large enough dipole moments can weakly bind an excess electron by the charge-dipole interaction to form dipole-bound anions (DBAs).¹⁻⁴ Fermi and Teller first reported a critical dipole moment of 1.625 D for electron binding for a fixed dipole in 1947 when investigating the capture of negative mesotrons.⁵ Subsequently, numerous theoretical investigations arrived at a similar value of the minimum dipole moment for a finite dipole to bind an electron.⁶ When real molecular systems were considered, effects such as molecular rotation, moment of inertia, and dipole length needed to be taken into account, and a larger critical dipole moment of 2.0 D was obtained.^{7,8} Ground-state DBAs have been produced via Rydberg electron transfer (RET)⁹⁻¹³ or low-energy electron attachments.¹⁴⁻¹⁶ The binding energies of a variety of ground-state DBAs were measured by RET, suggesting empirically a minimum dipole moment of 2.5 D for a polar molecule to bind an electron.^{1,10-12} However, ab initio calculations have shown that the electron binding energies of DBAs also depend on electron correlations and are generally molecule-dependent.^{3,4,17,18} The question is then, does it even make sense to talk about a critical dipole moment for electron binding in real molecular systems because of the diverse range of molecules that can form DBAs?

A valence-bound anion (VBA), XY⁻, with a dipolar neutral core (XY) can support an electronically excited DBS ([XY]*-) below the detachment threshold, which was first observed as resonances in the photodetachment spectrum of the enolate anion of acetophenone with a dipolar neutral core that has a dipole moment of 3 D.¹⁹ Because of the very small binding energies, vibrational or even rotational excitations in the electronically excited DBS [XY]*- would be above the electron detachment threshold. Subsequent vibrational or

rotational autodetachment gives rise to the resonances observed in the photodetachment spectrum. A series of anions with similar neutral-core dipole moments were subsequently observed to support electronically excited DBSs just below the detachment thresholds.²⁰⁻²⁵ Recently, electronically excited DBSs have been observed for a number of cryogenically cooled VBAs produced using electrospray ionization (ESI) from solution samples.²⁶⁻³³ The excited DBSs have been probed by both photodetachment spectroscopy and high-resolution photoelectron imaging, resulting in the development of resonant photoelectron spectroscopy (rPES) via vibrational autodetachment.34 Excited DBSs from several diatomic and triatomic anions have also been investigated recently.^{35–39} All the VBAs studied thus far possess sufficiently large dipole moments in their neutral cores ranging from 3.0 to 6.4 D. The electronic structure of ground state DBAs is usually quite different from that of the excited DBSs. For ground state DBAs, the neutral cores are closed-shell molecules with a dipole-bound electron, whereas the neutral cores of the excited DBSs are usually radical species with an unpaired electron. It would be interesting to ask if there is a critical dipole moment for electron binding for electronically excited DBSs. Is this critical value different from that of the ground state DBAs? However, because of the large structural differences of the anions studied up to now, it is difficult to directly correlate the DBS binding energies with the dipole moments to derive a critical value. Therefore, it is crucial to look for molecular anions with similar geometries and sizes but varying dipole moments, which would allow the charge-dipole interactions

80

(cm⁻¹)

DBS Binding Energy (00 00 00 00

2.81 D

3.5

3.0

μ (Debye)

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to be evaluated while minimizing the molecule-dependent properties.

The phenoxide anion $(C_6H_5O^-)$, produced by ESI and cryogenically cooled, was among the first anions for which we have observed an electronically excited DBS.^{26,32} The binding energy of the DBS was measured to be 97 cm⁻¹, and the neutral phenoxy core (C_6H_5O) has a dipole moment of 4.06 D. By substituting the H atom in the *para*-position of phenoxy with a halogen atom (X), we have found that the dipole moments of neutral *para*-XC₆H₄O (X = F, Cl, Br, I) can be tuned systematically, as shown in Table 1. Hence, the halogen

Table 1. Dipole Moments, DBS Binding Energies, and Electron Affinities (EAs) of p-XC₆H₄O (X = F, Cl, Br, I and H)^{*a*}

			EA^{c}	
	dipole moment (D) ^b	DBS binding energy (cm ⁻¹) ^c	(eV)	(cm^{-1})
p-FC ₆ H ₄ O	2.56	8 (5)	2.2950 (6)	18510 (5)
p-ClC ₆ H ₄ O	2.81	11 (6)	2.4917 (8)	20097 (6)
p-BrC ₆ H ₄ O	2.96	24 (6)	2.5480 (7)	20551 (6)
p-IC ₆ H ₄ O	3.19	53 (5)	2.6094 (7)	21046 (5)
$C_6H_5O^d$	4.06	97 (5)	2.2532 (4)	18173 (3)

^{*a*}The EAs are measured from the photoelectron spectra of the p-XC₆H₄O⁻ anions. ^{*b*}The dipole moments are calculated at the B3LYP/ 6-311++G(d,p) level of theory. ^{*c*}The number in parentheses represents the uncertainty in the last digit. ^{*d*}Ref 26.

substituted phenoxides, p-XC₆H₄O⁻ (X = F, Cl, Br, I), provide an ideal series of similar anions for the investigation of the critical dipole moment to support electronically excited DBSs in VBAs while keeping molecule-dependent properties to a minimum (Tables S1 and S2).

The p-XC₆H₄O⁻ (X = F, Cl, Br, I) anions were produced using ESI from sample solutions of p-XC₆H₄OH dissolved in mixed solvents of CH₃OH/H₂O at pH \approx 10. More experimental details are given in the Supporting Information. Briefly, the experiment was carried out on our third-generation ESI-PES apparatus,⁴⁰ equipped with a cryogenically cooled Paul trap⁴¹ and a high-resolution PE imaging system.⁴² Figure S1 displays the nonresonant PE spectra of p-XC₆H₄O⁻ (X = F, Cl, Br, I), which show similar spectral patterns to that of phenoxide,^{26,32,43} each with a strong vibrational progression in the ν_{11} mode. The EAs of the p-XC₆H₄O radicals are measured more accurately by tuning the detachment laser close to the 0– 0 transition, as given in Table 1. The halogen substitution increases the EA relative to C₆H₅O, increasing from X = F to I.

The DBSs of p-XC₆H₄O⁻ are searched using photodetachment spectroscopy by monitoring the total electron yields while scanning the photon energy near the detachment thresholds. Figure 1 shows the photodetachment spectra of the four anions at a scanning rate of 0.10 nm/step. In each spectrum, the arrow indicates the detachment threshold of the anion, which is consistent with the EA of the neutral determined from the PE spectra (Table 1). Below the threshold, a weak peak, labeled as 0, represents the ground vibrational level of the electronically excited DBS of each anion, as a result of resonant two-photon detachment. The DBS binding energy is defined by the separation of peak 0 from the detachment threshold. This separation is the largest (53 cm^{-1}) for IC₆H₄O⁻, decreasing to 24 cm⁻¹ for BrC₆H₄O⁻ and 11 cm⁻¹ for $ClC_6H_4O^-$, consistent with the trend of the dipole moments of XC_6H_4O (Table 1). The dipole moment of FC₆H₄O is 2.56 D, and it is not clear if a DBS exists in FC₆H₄O⁻. No clear two-photon peak is observed below the threshold in the 0.10 nm/step photodetachment spectrum. A much finer scan at 0.005 nm/step is done for the near threshold region, as shown in the inset of Figure 1a. In the high resolution scan, a below-threshold peak is clearly observed, confirming the existence of a DBS in $FC_6H_4O^-$ with a binding energy of 8 ± 5 cm⁻¹. Above thresholds, the continuous signals represent the nonresonant photodetachment cross sections.



Figure 1. Photodetachment spectra of (a) p-FC₆H₄O⁻, (b) p-ClC₆H₄O⁻, (c) p-BrC₆H₄O⁻, and (d) p-IC₆H₄O⁻. The arrows show the position of the detachment thresholds. Peak 0 in each spectrum corresponds to the ground vibrational level of the electronically excited DBS of the respective anion, while other peaks are due to the excited vibrational levels of the DBS. The inset in (a) displays a high-resolution scan at 0.005 nm/step near the threshold region of p-FC₆H₄O⁻.

On top of the nonresonant signals, peaks labeled with numbers correspond to excited vibrational levels of the DBS (aka vibrational Feshbach resonances). The photon energies and assignments of the DBS vibrational resonances are given in Table S3.

Figure 2 displays the DBS binding energies (BEs) measured for $[XC_6H_4O]^{*-}$ including $[C_6H_5O]^{*-}$ as a function of the



Figure 2. DBS binding energies of the electronically excited DBSs of $[XC_6H_4O]^{*-}$ as a function of the dipole moments of the neutral XC_6H_4O cores. The binding energies (BEs) are found to be linearly dependent on the dipole moments for this set of molecules. The dashed line is a linear fit with a R^2 value of 0.96 and BE = $63.4\mu - 159.0$. The linear curve is extrapolated to a critical dipole moment of 2.5 D at zero binding energy.

dipole moments (μ) of the neutral XC₆H₄O cores. A linear dependence is observed, and a curve fitting gives rise to an equation: BE = 63.4 μ - 159.0, with a R^2 value of 0.96, extrapolating to a critical dipole moment of 2.5 D at zero

binding energy. This critical dipole moment is consistent with the empirical value of 2.5 D obtained for the binding energies of ground-state DBAs measured by the RET experiments previously.^{1,9–12} It should be pointed out that the previous studies on DBAs were for a variety of very different molecules with a wide range of μ and the BEs vs μ curves were generally nonlinear. The fact that a similar critical dipole moment is obtained for such a diverse range of molecules suggests that the dipolar binding of the extra electron (i.e., the $1/r^2$ potential) in these systems is dominant, while the molecule-dependent effects are minimal for polar molecular systems with $\mu > 2.5$ D. This critical dipole moment seems to hold true for both ground-state DBAs and excited DBSs of VBAs.

We also obtained resonant PE spectra by tuning the detachment laser to all the above-threshold resonances in Figure 1. The resonant spectra for $FC_6H_4O^-$ are shown in Figure 3, while those for $XC_6H_4O^-$ (X = Cl-I) are given in Figures S2–S4, respectively. The electron binding energies and assignments of the vibrational features observed in the PE spectra are given in Tables S4-S7 for X = F-I, respectively. As discussed previously, 2^{26-34} rPES contains both nonresonant detachment signals and resonant signals from vibrational autodetachment via the DBS. The vibrational autodetachment generally follows the $\Delta v = -1$ propensity rule^{44,45} because the extra electron in the DBS has little effect on the molecular structure of the neutral core. Thus, the vibrational levels in the photodetachment spectra can be readily assigned by examining the vibrational peaks that are enhanced in the resonant PE spectra. The resonant PE spectra for $XC_6H_4O^-$ (X = Cl–I) are



Figure 3. Resonant photoelectron images and spectra of p-FC₆H₄O⁻ at the eight wavelengths corresponding to the above-threshold resonances in Figure 1a. The wavelengths, DBS vibrational levels, and the peak number are given. The enhanced peaks due to vibrational autodetachment are labeled in **bold** face. The cutoff at the high binding energy side (near threshold electrons) in each spectrum is due to rotational autodetachment. The double arrows below the images indicate the laser polarization.

relatively simple and can be readily assigned, as shown in Tables S5-S7, respectively, where the measured vibrational frequencies are compared with the calculated values (Table S8).

The resonant PE spectra of $FC_6H_4O^-$ are discussed here in more detail because of the unusual high binding energy cutoff (corresponding to near zero energy electrons) observed in each spectrum (Figure 3). These spectra are highly non-Franck-Condon with specific vibrational peaks being enhanced (labeled in **bold** face), due to autodetachment from the vibrational levels of the DBS following the $\Delta v = -1$ propensity rule. For example, in comparison to the relative intensities of peaks 0_0^0 and B (11^1) in the nonresonant spectrum of Figure S1a, peak 0_0^0 in the resonant spectrum of Figure 3d is enhanced. This enhancement is due to excitation to the fundamental DBS vibrational level $18^{\prime 1}$ followed by Δv = -1 autodetachment. In the resonant spectra of Figures 3f,h, peaks B (11^1) and E (11^2) are highly enhanced, respectively, due to the autodetachment from the combinational levels of $11^{\prime 1}18^{\prime 1}$ and $11^{\prime 2}18^{\prime 1}$, respectively: one quantum of the ν_{18}^{\prime} mode of the DBS is coupled to the DBS electron during autodetachment. It is interesting to note that the ν_{18} ' mode is favored to couple with the DBS electron; such mode-selectivity during vibrational autodetachment was first observed for $C_6H_5O^{-26}$ The photon energies used in Figures 3c,e,g involve excitations to overlapping and near-degenerate DBS vibrational levels, resulting in more complicated resonant PE spectra. In Figure 3e, the enhancement of peak B (11^1) is from autodetachment of the $11'^2$ DBS level, while peak b (11^120^1) and peak D $(11^{1}19^{1})$ are from autodetachment from the combinational level of 11'19'120'1. Similarly, in Figure 3g, the excitation to the 11'3 DBS level results in the enhancement of peak E (11²), while the excitation to the $11'^{2}19'^{1}20'^{1}$ combinational level gives the enhanced peaks c (11²20¹) and peak d (11^219^1) . The enhancement of peaks a (20^1) and A (19^1) in Figure 3c are due to autodetachment from the combinational level of $19'^{1}20'^{1}$, while the photon energy also matches the excitation to the DBS level 11^{'1}, resulting in the slightly enhanced peak 0_0^0 . All the autodetachment processes obey the $\Delta v = -1$ propensity rule, as schematically presented in Figure 4. The binding energies of all the observed vibrational peaks and their assignments are given in Table S4.

Besides the enhanced peaks due to the vibrational autodetachment, the resonant spectra in Figure 3 all display a strong cutoff in the high binding energy side corresponding to photoelectrons with near zero kinetic energies. No such threshold electron signals are observed in the nonresonant spectra of $FC_6H_4O^-$ (Figure S1) nor in the resonant PE spectra of $XC_6H_4O^-$ (X = Cl–I) (Figures S2–S4). The near zero energy electron signals are due to the extremely low binding energy of the DBS of $[FC_6H_4O]^{*-}$ (8 ± 5 cm⁻¹), as a result of rotational autodetachment from the DBS vibrational levels to the corresponding neutral vibrational levels, as schematically shown by the red dashed arrows in Figure 4. Such autodetachment processes would produce electrons with very low or near zero kinetic energies.

As reported previously,^{27,28,46} the rotational temperature of the anions in our cryogenic trap is around 30–35 K, which can populate higher rotational levels within the ground vibrational state of the anions. The rotational broadening for the 0–0 transition in the PE spectrum of phenoxide was observed to be about 10 to 12 cm^{-1,26} We observe similar rotational broadening (~10 cm⁻¹) in the PE spectra and photodetach-



Figure 4. Schematic energy level diagram for both the vibrational and rotational autodetachment from the DBS vibrational levels of $FC_6H_4O^-$ to the FC_6H_4O neutral levels. The red lines above each DBS vibrational level represent rotational levels, and the dashed red arrows indicate rotational autodetachment to the corresponding vibrational level of neutral FC_6H_4O .

ment spectrum (Figure 1a) of $FC_6H_4O^-$. We have also observed rotational structures in the photodetachment spectra of several anions with similar rotational broadening, which allowed us to estimate the rotational temperatures in the first place.^{27,28,46} Hence, there must be significant rotational populations in the vibrationally cold $FC_6H_4O^-$ anion in the cryogenic ion trap. If the rotational energy is above $\sim 8 \text{ cm}^{-1}$, i.e., the binding energy of the DBS of $[FC_6H_4O]^{*-}$, this rotational energy will be carried to the DBS vibrational levels, inducing rotational autodetachment to the same vibrational levels in the neutral, as indicated by the dashed arrows in Figure 4. In other words, such rotational excited levels in the DBS vibrational states can be considered as rotational Feshbach resonances. The kinetic energies of the high binding energy features in Figure 3 range from 1.6 to 2.4 cm⁻¹, which are consistent with the ~ 10 cm⁻¹ rotational broadening estimated for FC₆H₄O⁻. Rotational autodetachment was observed previously in high resolution photodetachment spectroscopy of DBAs near their vibrational ground states.^{23-25,37} In the current case, except for the ground vibrational level of the DBS (Figure 3a), rotational autodetachment competes with vibrational autodetachment in all the resonant PE spectra via vibrationally excited states (Figures 3b-h). The fact that we observe both vibrational and rotational autodetachment simultaneously suggests that they have similar time scales.

In conclusion, we have observed electronically excited DBSs for a series of halogen-substituted phenoxide anions, $p \cdot XC_6H_4O^-$ (X = F, Cl, Br, I), in which the dipole moments of the neutral $p \cdot XC_6H_4O$ cores increase systematically from 2.56 D for X = F to 3.19 D for X = I. These anions provide ideal systems to evaluate the charge–dipole interactions on electron binding, while minimizing the molecule-dependent effects. The binding energies of the DBSs are observed to

exhibit a linear correlation with the dipole moments of the p-XC₆H₄O neutral cores, extrapolating to a critical dipole moment of 2.5 D for the existence of excited DBSs in VBAs. This critical dipole moment is identical to that estimated from ground-state DBAs. The extremely low binding energy of the excited DBS in FC₆H₄O⁻ makes it possible for rotational autodetachment in rPES along with vibrational autodetachment, producing photoelectrons with near zero kinetic energies.

ASSOCIATED CONTENT

S Supporting Information

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Experimental and theoretical methods; nonresonant and resonant photoelectron images and spectra of p- $\rm XC_6H_4O^-$ (X = F, Cl, Br, I); computed quadrupole moments, polarizabilities, and moments of inertia for p- $\rm XC_6H_4O$ (X = F, Cl, Br, I, H); summary of the resonant peaks in the photodetachment spectra; summary of the observed vibrational peaks in the resonant and non-resonant photoelectron spectra; calculated harmonic frequencies for the p- $\rm XC_6H_4O$ (X = F, Cl, Br, I) neutral radicals (PDF)

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Notes

The authors declare no competing financial interest.

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