Experimental Observation of the Resonant Doorways to Anion Chemistry: Dynamic Role of Dipole-Bound Feshbach Resonances in Dissociative Electron Attachment

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ABSTRACT: Anion chemical dynamics of autodetachment and fragmentation mediated by the dipole-bound state (DBS) have been thoroughly investigated in a state-specific way by employing the picosecond time-resolved or the nanosecond frequency-resolved spectroscopy combined with the cryogenically cooled ion trap and velocity-map imaging techniques. For the ortho-, meta-, or para-iodophenoxide anion (\(\text{o-}, \text{m-}, \text{or} \ \text{p-IPhO}^-\)), the C–I bond rupture occurs via the nonadiabatic transition from the DBS to the nearby valence-bound states (VBS) of the anion where the vibronic coupling into the \(S_1 (\pi\sigma^*)\) state (repulsive along the C–I bond extension coordinate) should be largely responsible. Dynamic details are governed by the isomer-specific nature of the potential energy surfaces in the vicinity of the DBS–VBS curve crossings, as manifested in the huge different chemical reactivity of \(\text{o-}, \text{m-}, \text{or} \ \text{p-IPhO}^-\). It is confirmed here that the C–I bond dissociation is mediated by DBS resonances, providing the foremost evidence that the metastable DBS plays the critical role as the doorway into the anion chemistry especially of the dissociative electron attachment (DEA). The fragmentation channel is dominant when it is mediated by the DBS resonances located below the electron-affinity (EA) threshold, whereas it is kinetically adjusted by the competitive autodetachment when the DBS resonances above EA convey the electron to the valence orbitals. The product yield of the C–I bond cleavage is strongly mode-dependent as the rate of the concomitant autodetachment is much influenced by the characteristics of the individual vibrational modes, paving a new way of the reaction control of the anion chemistry.

INTRODUCTION

Since it was first conceived by Fermi and Teller in 1947, 1 the dipole-bound state (DBS) of the anion has been both extensively and intensively investigated for many recent decades in terms of its structure and dynamic role as its study becomes increasingly important for understanding the physics and chemistry of anions in many aspects. 2–6 The lower limit of the dipole moment for the DBS formation had been initially predicted to be 1.627 D, although it seems to be now widely regarded (as a rule of thumb) that the excess electron could be attached to the neutral core when its dipole moment exceeds ~2.5 D. 7,8 It should be emphasized though that the nature of the binding force between the excess electron and neutral core seems to be not straightforward as much as the literal meaning of the DBS may imply. Namely, the interaction potential is rather complex as all the possible monopole–multipole (such as dipole or quadrupole) interactions as well as the correlation effect should contribute corroboratively to the binding dynamics of the excess electron to the neutral core though the extents of their contributions should vary depending on the particular chemical systems under various circumstances. 9,10 In this regard, it may be fair to state that the DBS belongs to the category of the nonvalence bound state (NBS) in a sense that its excess electron does not occupy any empty valence orbital whereas the more stable anion of which the excess electron resides in the valence orbital could be called the valence bound state (VBS).

DBS has been ubiquitously found in a variety of chemical or biological systems, ranging from the simplest diatomic molecules 11 to the biological systems 12–15 or molecular complexes. 16–20 Recent spectroscopic studies have suggested that the DBS could be a primary candidate for the carrier of the diffuse interstellar species and/or the interstellar PAH anions, giving the enormous astrochemical implication. 21–23 As the size of the dipole-bound orbital is almost identical to the de Broglie wavelength of the incoming electron, the electron attachment to neutral in the frame of DBS is extremely efficient. 24,25 In this aspect, it should be noted that the DBS has also long been conceived as the major doorway in the dissociative electron attachment (DEA) process where the slow electron is captured to be followed by the immediate

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rupture of the specific chemical bond.\textsuperscript{26–28} DEA is ubiquitously found, ranging from chemistry of the small environmentally important oxide species to radiative damages of biological genetic species of DNA/RNA double/single helices.\textsuperscript{29–32} Although the DEA dynamics have been much investigated in some elegant experimental\textsuperscript{33–37} or theoretical studies,\textsuperscript{38–40} the rather direct experimental evidence for the role of the DBS in the DEA has been quite rare to date. It should be noted here that the present work represents the anion chemistry of the isolated (or lightly solvated) systems as the chemistry/physics of the electron dynamics in heavily solvated or bulk medium is expected to be quite different.\textsuperscript{41,42} The anionic DBS either loses the excess electron by the autodetachment process or undergoes the transformation into the more stable valence bound anion via the radiative and/or nonradiative transitions before it may be followed by the subsequent chemical reactions. Although the autodetachment dynamics of DBS has been quite intensively and extensively investigated in recent years,\textsuperscript{43,44} the structural dynamics involved in the anion formation at various electronic states and its associated chemistry/physics especially mediated by the quantum resonant states of the DBS (as the doorways) have been less explored.

Recent real-time pump–probe experimental studies on the state-specific dynamics of the cryogenically cooled anions such as phenoxide and some of its analogues have revealed that the dynamic range of the DBS is quite wide especially in terms of its mode-specific lifetime.\textsuperscript{45–47} For the phenoxide anion, for instance, the DBS prepared below the photodetachment threshold decays quite slowly with its lifetime longer than tens of nanoseconds whereas the vibrational autodetachment of DBS above the detachment threshold takes place quite rapidly with a typical lifetime of tens of picoseconds. This experimental fact suggests that the DBS may undergo the rather slow radiative or nonradiative transition to the ground or excited state of the anion when the total energy is below the electron detachment threshold. On the other hand, when the internal energy given to the DBS gets higher than the detachment threshold, the excess electron is liberated very rapidly by the strong coupling between the electronic and nuclear motions. Actually, it has been found that the Fermi’s golden rule for such a coupling is extremely useful in accounting for the mode-specific autodetachment rates of the phenoxide,\textsuperscript{48} although the intrinsic complicated nature of the binding dynamics of the DBS requires the more sophisticated theoretical models which are needed to be adapted for different chemical systems. The obvious question thereafter is related to the nature of the DBS relaxation process. Does it really play the role as a doorway in its transformation into the ground (or excited) state of the valence-bound anion? If so, what would be the overall mechanism of the DBS–VBS transition in terms of the thermodynamic and/or kinetic properties?

Herein, we have investigated the autodetachment and fragmentation dynamics of ortho-, meta-, and para-iodophenoxide (\(o\)-, \(m\)-, and \(p\)-IPhO\(^{−}\)) anions. Vibrational Feshbach resonances of the DBS have been found for all three cryogenically cooled anions, although their dynamics are found to be quite distinct in terms of the state-specific lifetimes and associated chemistries. Especially, the competitive dynamics among the autodetachment and nonadiabatic transitions have been thoroughly investigated in a state-specific way by employing the picosecond time-resolved or the nanosecond frequency-resolved spectroscopy combined with the cryogenically cooled ion trap and the velocity-map electron imaging techniques. Nonadiabatic couplings through the curve crossings of the potential energy surfaces of the DBS and those of the nearby anionic valence electronic states govern the anion formation dynamics at particular electronic state(s) and subsequent chemical reactions, reflecting the quantum-mechanical dynamic role of the DBS as the doorway into the anion chemistry. Quite interestingly, the C–I chemical bond rupture (giving the I\(^{−}\) fragment) occurs near the photodetachment threshold for all three anions with the strong mode specificity, giving the unprecedented insights into the coupling between nuclear and electronic motions along the passages connecting the DBS and VBS in terms of the electron-attachment/detachment physics and fragmentation chemistry. This report provides one of the foremost experimental evidence for the actual dynamic role of the DBS as the doorway to the anion physics and chemistry.

\section*{RESULTS AND DISCUSSION}

Nonresonant photoelectron spectra of the cryogenically cooled anions of \(o\)-, \(m\)-, and \(p\)-IPhO\(^{−}\) give the precise electron affinities (EAs) and structural changes upon the photodetachment, from their lowest electron binding energies and the Franck–Condon active vibrational modes, respectively (see Figure S1). Overall, the in-plane stretching mode along the C–O bond axis (\(v_{18}\) or \(v_{11}\)) is found to be highly activated, reflecting the structural changes of the iodophenoxide anions upon the instantaneous photodetachment process. The EA of each anion has been refined by the extrapolation method from a series of photoelectron spectra obtained at many different photon energies (Figure S2), giving the EA value of 21,656 ± 13, 21,778 ± 24, or 20,051 ± 15 cm\(^{-1}\) for \(o\)-IPhO\(^{−}\), \(m\)-IPhO\(^{−}\), or \(p\)-IPhO\(^{−}\), respectively. The EA of \(p\)-IPhO\(^{−}\) is in good agreement with the previous one of 21 046 cm\(^{-1}\) reported from the Wang group.\textsuperscript{49} Notably, EA of \(m\)-IPhO\(^{−}\) is larger than that of \(o\)-IPhO\(^{−}\) or \(p\)-IPhO\(^{−}\). This could be attributed to the destabilization of the latter anions (\(o\)-IPhO\(^{−}\) and \(p\)-IPhO\(^{−}\)) by the \(\pi\)-orbital donation to the benzyl ring of specific resonance forms. The larger EA value of \(o\)-IPhO\(^{−}\) compared to that of \(p\)-IPhO\(^{−}\) could be due to the relatively stronger inductive effect of the electronegative iodine atom in the former than that in the latter. These trends had been repetitively found in other different halogen-substituted benzyl\textsuperscript{50} or methyl-substituted phenoxyl anions.\textsuperscript{49,50}

Now, the photodetachment spectra of \(o\)-, \(m\)-, and \(p\)-IPhO\(^{−}\) taken by monitoring the total photoelectron yield as a function of the excitation (pump) photon energy using the nanosecond laser pulse (\(\Delta E \sim 3.5\) cm\(^{-1}\), \(\Delta t \sim 42\) ns) give rise to metastable vibrational Feshbach resonance states of DBS as sharp peaks in addition to the broad background signal arising from the direct electron detachment, Figure 1. Obviously, a number of vibrational Feshbach resonances are well pronounced in \(o\)- and \(p\)-IPhO\(^{−}\) whereas the identification of those seems to be less straightforward in \(m\)-IPhO\(^{−}\) (vide infra). The photodetachment spectrum of \(o\)-IPhO\(^{−}\) shows the DBS resonances strongly enhanced especially at the fundamental and overtone of the in-plane ring stretching (\(v_{19}\)) mode at the internal energy (\(E_{\text{int}}\)) of \(\sim 332\) and \(\sim 1070\) cm\(^{-1}\), respectively, indicating that the geometry of DBS remains unaltered from that of the neutral radical as expected. The zero-point level (ZPL) is clearly identified as a peak located just below the EA threshold, giving the electron binding energy (eBE) of \(\sim 231\).
cm$^{-1}$ for the DBS of o-IPhO$^-$. The photodetachment spectrum of p-IPhO$^-$. The photodetachment spectrum of o-IPhO$^-$ also gives the distinct vibrational Feshbach resonances above the featureless direct background signal although those are relatively less pronounced compared to the case of o-IPhO$^-$. The DBS resonances of the $\nu_{11}$ ($E_{\text{ad}} \sim 245$ cm$^{-1}$) and $\nu_{10}$ ($E_{\text{ad}} \sim 580$ cm$^{-1}$) modes as well as their overtone or combination bands are clearly identified for p-IPhO$^-$. It is a bit surprising that the DBS bands are nearly absent in the photodetachment spectrum of m-IPhO$^-$ despite that the dipole moment of its neutral radical is large enough (3.30 D) to hold an excess electron. The stepwise increases at the threshold and 530 cm$^{-1}$ above EA should be ascribed to the cumulative openings of the direct detachment channels according to the Franck-Condon factor. The ZPL just below the EA threshold is barely identified to give the eBE of $\sim 97$ cm$^{-1}$ for the DBS of m-IPhO$^-$ (vide infra). The photodetachment spectra have also been obtained by using the picosecond laser pulse ($\Delta E \sim 20$ cm$^{-1}$), giving the slightly less distinct spectral features though the overall features remain unchanged for all three anions (Figure S3). Photoelectron spectra taken at the vibrational Feshbach resonances reveal the clear-cut autodetachment feature of $\Delta \nu = -1$ (obeying the propensity rule) for o-IPhO$^-$.  

The real-time dynamics of vibrational Feshbach resonances, taken from the pump–probe time-resolved photoelectron images (TR-PEI), provide the lifetimes of individual DBS vibrational states in a state-specific way. The picosecond excitation laser pulse (pump) populates the specific DBS resonant state, whereas the 791 nm picosecond laser pulse (probe) depopulates the initial state into the detachment continuum to give the high kinetic energy electron (Figure 2a). The photoelectron yield in the low or high kinetic energy region is then separately monitored as a function of the delay time between pump and probe pulses. The typical photoelectron transient monitoring the low kinetic energy exhibits the initial depletion at the zero time-delay followed by the immediate recovery at the rate of the autodetachment process. The high kinetic energy photoelectron transient, on the other hand, reflects the rather direct real-time decay of the DBS population. For o-IPhO$^-$, the low kinetic energy photoelectron transient of the most prominent 18$^{1}$ band (532 cm$^{-1}$) gives the autodetachment lifetime ($\tau$) of 12.3 ± 2.2 ps whereas that of the 15$^{1}$ band (989 cm$^{-1}$) gives $\tau \sim 4.0 \pm 0.9$ ps (Figure 2). Within the experimental uncertainties, these are quite consistent with the DLS lifetime of 10.1 ± 0.8 or 6.3 ± 0.7 ps obtained from the high kinetic energy transient of the 18$^{1}$ or 15$^{1}$ mode, respectively. Lifetimes of the DMS modes of p-IPhO$^-$ taken from the high-kinetic energy transients are found to be much shorter, giving $\tau \sim 3.4 \pm 1.2$ or 4.5 ± 1.3 ps for the 11$^{1}$ or 10$^{1}$ mode, respectively. For the 11$^{1}$ mode of p-IPhO$^-$, it is quite notable that the signal of the low kinetic energy photoelectron arising from the autodetachment is extremely weak, hampering obtaining of the corresponding transient with the decent signal-to-noise ratio (vide infra). It is also quite

Figure 1. (a) Sketch of the experiment for the photofragment or photodetachment spectrum of o-, m-, and p-IPhO$^-$.

[Image 68x439 to 538x740]
The DBS for autodetachment may not be the major relaxation pathway of this experimental finding strongly indicates that the vibrational band is depicted in insets. Each transient was fitted by the single exponential decay function convoluted with the instrumental cross-correlation function.

As the autodetachment is intrinsically blocked at ZPL, the short lifetime has been attributed to the fast internal conversion to the low-lying S_1 state (see the text). The normal mode of each vibrational band is depicted in insets. Each transient was fitted by the single exponential decay function convoluted with the instrumental cross-correlation function.

Figure 2. (a) Schematic diagram of the picosecond time-resolved photoelectron imaging (TR-PEI) obtained at vibrational Feshbach resonances (VFR) of the DBS. Picosecond pump laser pulse populates specific vibrational states of the DBS and then the temporally delayed probe laser pulse depopulates into the detachment continuum yielding the high kinetic energy electron (HKE). The temporal evolution of the electron originating from autodetachment is intrinsically blocked. The TR-PEI transient obtained at ZPL of the DBS gives the relatively long lifetime of 724 ± 2 ps, indicating that the fast internal conversion to the low-lying S_1 state (see the text). The normal mode of each vibrational band is depicted in insets. Each transient was fitted by the single exponential decay function convoluted with the instrumental cross-correlation function.

Figure 2 (b) (d) shows the transients of the 10^-1 and (e) 10^-2 modes of p-IPhO^-, the LKE transient is hardly discernible due to the very low autodetachment yield (see the text). The normal mode of each vibrational band is depicted in insets. Each transient was fitted by the single exponential decay function convoluted with the instrumental cross-correlation function.

The more systematic approach has been made for the comparison of three different anions in terms of their behaviors at ZPLs located just below their EA thresholds where the autodetachment is intrinsically blocked. The TR-PEI transient obtained at ZPL of the p-IPhO^- DBS gives the relatively long lifetime of 724 ± 43 ps (Figure 3), suggesting that the internal conversion and/or intersystem crossing (ISC) into the low-lying anionic states should have been significantly slowed down compared to the case of p-IPhO^-.

The apparent absence of the DBS resonant features in the photodetachment spectrum of m-IPhO^- (Figure 1) thus could be readily rationalized by the fact that the autodetachment process of m-IPhO^- (which is totally responsible for the photoelectron signal originating from the DBS resonances)
should be diminished as the DBS relaxation pathway is overwhelmed by the much faster nonradiative transition to the short-lived anionic valence state(s).

In order to invoke the possible relaxation mechanism therein, the time-dependent density functional theory (TD-DFT) has been employed for calculating the low-lying valence electronic states of anions. As previously reported for $p$-IPhO$, the first electronically excited singlet state ($S_1$) is predicted to be closely located to the EA threshold for all three iodine-substituted phenoxide anions. For all of $o$, $m$, and $p$-IPhO$^-$, the $S_1 (\pi \sigma^*)$ is found to be repulsive in nature along the C–I bond extension coordinate leading to the ultrafast C–I bond rupture to give the I$^-$ fragment at the asymptotic limit; it should be noted that only the I$^-$ fragment channel (which is diabatically correlated to $S_1$) is thermodynamically plausible (see Supporting Information). The energetic location of the anionic $S_1$ state with respect to the neutral ground state ($D_0$) is quite different for the chemical species of three different substitution positions. Interestingly, the anionic $S_1$ state is predicted to be located below the EA threshold for $p$-IPhO$^-$ or $m$-IPhO$^-$, whereas that of $o$-IPhO$^-$ lies above the EA threshold (Figure 3). The vertical energy gap between $S_1$ and $D_0$ at the minimum energy structure of the ground anionic state is calculated to be $\sim 0.08$ or $\sim 0.21$ eV for $p$-IPhO$^-$ or $m$-IPhO$^-$, respectively, indicating that the corresponding DBSs are expected to be quite vulnerable to the rapid internal conversion processes into the low-lying repulsive $S_1$ states of VBSs. This strongly supports the experimental results that DBS lifetimes are exceptionally short (even at ZPL) for both $p$-IPhO$^-$ and $m$-IPhO$^-$, and they are little influenced by the mode character-
istics. It is quite notable that the $S_1$−$D_0$ gap of $m'$-IPhO$^-$ is predicted to be much larger than that of $p'$-IPhO$^-$, and this might be the reason for the earlier dominance of the DBS−VBS ($S_1$) transition in the ultrafast relaxation of the former compared to the case of the latter (vide infra).

The dominance of the ultrafast internal conversion should then be responsible for the featureless photodetachment spectrum of $m'$-IPhO$^-$ (Figure 1) as the competitive but relatively slower autodetachment channel is diminished even for the vibrational Feshbach resonances above the EA threshold. On the contrary, $S_1$ channel is diminished even for the vibrational Feshbach (Figure 1) as the competitive but relatively slower autodetachment process at the $10^3$ cm$^{-1}$ window, suggesting that the substantial structural change (at least along the C$_1$−I bond extension coordinate) is required for the nonadiabatic transition to be efficiently activated. This may explain why the DBS lifetime of $p'$-IPhO$^-$ at the ZPL is significantly longer than that of $m'$-IPhO$^-$ or $p'$-IPhO$^-$.

The more remarkable fragment-action spectrum could be found for the case of $p'$-IPhO$^-$. Here, the $\Gamma$ fragment yield is strongly enhanced for all DBS resonant bands regardless of their positions with respect to the EA threshold, Figure 1, indicating that the autodetachment (responsible for the resonant photoelectron signal in the photodetachment spectrum) and the DBS−VBS transition (responsible for the $\Gamma$ fragment yield) concomitantly occur quite competitively even when the former channel is fully opened as the latter process is also quite rapid for $p'$-IPhO$^-$. The relative yields of the DBS-resonant photoelectron and $\Gamma$ fragment should then be determined by the relative speeds of those two distinct processes, opening the new way of the reaction control for the anion chemistry possibly through the control of the quantum-mechanical nature of the DBS resonant doorway. The mode-specific competition dynamics is quite dramatic. For instance, the autodetachment signal of the $10^4$ mode is much stronger than that of the $11^{1'}$ mode in the photodetachment spectrum, whereas that of the latter ($11^{1'}$) is expected to be much stronger compared to that of the former ($10^4$) if it follows the Franck−Condon (FC) principle. On the contrary, the $\Gamma$ fragment yield at the $11^{1'}$ mode excitation is found to be much stronger than that observed at the $10^4$ mode excitation in the fragment action spectrum, Figure 1. This conforms with the FC simulation, and yet it is exactly opposite to the trend found in the photodetachment spectrum. This should be ascribed to the fact that the autodetachment rate of the $10^4$ mode is much faster than that of the $11^{1'}$ mode according to the Fermi's golden rule mainly due to the stronger IR intensity of the former (vide infra), giving the relatively larger autodetachment yield of $10^4$ compared to $11^{1'}$. That is, the autodetachment process at the $10^4$ mode excitation should prevail in competition with the DBS−VBS transition, while
it is completely the other way around for the $11^\text{11}$ mode excitation. Therefore, the photodetachment signal from the DBS of $p$-IPhO$^-$ is dynamically controlled! It should be emphasized that the DBS lifetime estimated from the photodetachment and DBS−VBS transition processes, and thus the autodetachment rate alone could not be solely extracted. Therefore, the relative yield of the autodetached photoelectron compared to the $\Gamma$ fragment yield, manifested in the respective photodetachment and fragment-action spectra, should reflect the mode-dependent competition dynamics between two major relaxation pathways.

The situation is somewhat different for the case of $m$-IPhO$^-$. The lifetime of the DBS is quite short ($\tau \approx 2$ ps) even at the ZPL (Figure 2), and thus the photodetachment yield originating from autodetachment is much diminished to give the featureless photodetachment spectrum. Instead, the resonant peak corresponding to the ZPL of DBS has been clearly observed in the $\Gamma$ fragment action spectrum, Figure 1. The bandwidth of the DBS band is quite broad, indicating that it might survive only briefly with a time constant of less than hundreds of femtoseconds. Although the additional spectral bands attributable to DBS resonances could be further identified, the broad structureless background signal is dominant in the whole $\Gamma$ fragment action spectrum. The overall shape of the $\Gamma$ fragment action spectrum in the wide excitation energy range does not follow that of the photodetachment spectrum (Figure S7), suggesting that there may exist a new channel responsible for the $\Gamma$ fragment regardless of the photodetachment cross section. The broad spectral feature in the $\Gamma$ action spectrum starts to appear much below the EA threshold, and this could be a consequence from the direct excitation to the repulsive $S_1 (\pi\sigma^*)$ state of the $m$-IPhO$^-$ anion especially since $S_1$ is predicted to be located much below $D_0$ in the vertical transition region (Figure 3). The direct anionic $S_1\rightarrow S_0$ excitation leading to the prompt C−I bond cleavage then competes with the direct photodetachment process, while the indirect fragmentation/autodetachment channel mediated by the DBS Feshbach resonances gets relatively less efficient for $m$-IPhO$^-$. The excited-state dynamics of the anion chemistry has been quite rarely investigated because the cross-section of the direct photodetachment is huge and increases quite rapidly with increasing the energy to overwhelm the whole excitation process. In this regard, the excited-state dynamics of the $m$-IPhO$^-$ anion found here is very unique and subject to the further investigation in the near future. It is noteworthy that the electron dynamics in the heavily solvated or bulk medium would be quite different from those in the isolated or light-solvated systems as predicted by many theoretical works.

CONCLUSION

In summary, the long-time premise that the dipole-bound state plays the dynamic role of the doorway to the anion chemistry (of the isolated or light-solvated system) has been experimentally demonstrated here. The C−I chemical bond rupture of ortho-, meta-, or para-iodophenoxide anion (giving the $\Gamma$ fragment) is found to be mediated by the distinct DBS resonances and occurs competitively with the concomitant autodetachment process. For DBS resonant states above EA, the relative yields of the C−I fragmentation and the electron detachment channels are found to be kinetically controlled and thus strongly mode-specific to give the great promise for the new way of the anion reaction control by tuning the quantum-mechanical nature of the vibronic excitation. Dynamic behavior at the DBS resonances below EA unravels the mechanism of the DBS−VBS nonadiabatic transitions of three different isomers. For meta- or para-iodophenoxide, the efficient internal conversion from the metastable DBS into the valence-bound $S_1 (\pi\sigma^*)$ state (which is repulsive along the C−I bond elongation coordinate) should be responsible for the fast relaxation followed by the subsequent C−I bond fragmentation. The nonadiabatic transition of the ortho-iodophenoxide anion is however found to be nearly 2 orders of magnitude slower than that of meta- or para-iodophenoxide, explaining why the C−I bond fragmentation yield of ortho-iodophenoxide stands out only at the DBS resonance below the EA threshold. Curve crossings of the potential energy surfaces of DBS and the nearby anionic valence state(s) particularly along the dissociative C−I bond extension coordinate are found to be critical for the conveyance of the electron into or out of the valence orbital, whereas the more sophisticated theoretical calculations would be quite desirable.

METHODS

Details of the experimental setups were described elsewhere. Briefly, the 1 mM samples of $o$, $m$, or $p$-iodophenol (TCI Chemicals Inc.) were dissolved in the 9:1 methanol/water mixed solvent. Each anion was generated by the negative mode of the homemade electrospray ionization (ESI) source by applying the −3000 V emission voltage. Anions were entered into the vacuum chamber through a heated capillary at ~180 °C and desolvated by a dual-stage ion funnel (IF141, Masstech Inc.). Isolated anions were guided into the cryogenically cooled ($8$ K) Paul ion trap by passing through a series of hexapole, quadrupole, and octopole ion guides. After the trapping time of ~50 ms, the internally cooled anions were extracted into the velocity map photoelectron imaging electrodes to be intersected by the picosecond or nanosecond laser pulses. Photoproducts (electron or fragment) generated by the laser pulses were detected by chevron-type microchannel plates (MCPs) backed by a phosphor screen. The photoelectron images were recorded by a charge-coupled device (CCD) camera, whereas the photoelectron signals were recorded by a photomultiplier tube (PMT). Photoelectron images were reconstructed by the BASEX™ or polar onion peeling (POP) program. Picosecond laser pulses were generated from the Ti:sapphire regenerative amplifier (Legend Elite-P, Coherent) seeded by the femtosecond oscillator (Vitura-T-HP, Coherent). A half of fundamental output was frequency tuned by the optical parametric amplifier (TOPAS-800, Light Conversion) to be used as the pump laser pulse, while the other half was used for probing. The temporal delay between the pump and probe laser pulses was controlled by using a retroreflector (UBBR2.5-1UV) placed on a 220 mm long optical delay stage (DDS220, Thorlabs). A tunable nanosecond laser pulse was generated from a Nd:YAG laser system equipped with multiple harmonic generators (NT342, Ekspla). All calculations were performed by using the density functional theory (DFT) at the B3LYP/def2TZVP level in the Gaussian 09 package. The Franck–Condon principle is used to determine the energies and intensities of the vibronic bands.
Condon simulation of the $S_0$–$D_0$ transition was calculated using the ezSpectrum program\textsuperscript{2} based on the calculated harmonic frequencies of $S_0$ and $D_0$ at the optimized geometries.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c06334.

Details of the DBS vibrational peak assignments, resonant/nonresonant photoelectron spectra, and other supportive experimental/theoretical data (PDF)

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**Notes**

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