

pubs.acs.org/JPCL

Probing Dipole-Bound States Using Photodetachment Spectroscopy and Resonant Photoelectron Imaging of Cryogenically Cooled Anions

Yue-Rou Zhang, Dao-Fu Yuan,* and Lai-Sheng Wang*



ABSTRACT: Molecular anions with polar neutral cores can support highly diffuse dipolebound states below their detachment thresholds due to the long-range charge-dipole interaction. Such nonvalence states constitute a special class of excited electronic states for anions and were observed in early photodetachment experiments to measure the electron affinities of organic radicals. Recent experimental advances, in particular, the ability to create cold anions using a cryogenically cooled Paul trap, have allowed the investigation of dipolebound excited states at a new level. For the first time, the zero-point level of dipole-bound excited states can be observed via resonant two-photon detachment, and resonant photoelectron spectroscopy can be performed via the above-threshold vibrational levels (Feshbach resonances) of the dipole-bound states. This Perspective describes recent progress in the investigation of dipole-bound states in the authors' lab using an electrospray photoelectron spectroscopy apparatus equipped with a cryogenically cooled Paul trap and high-resolution photoelectron imaging.



hile anions do not possess Rydberg states, those with polar neutral cores of large enough dipole moments can support diffuse dipole-bound states (DBSs) below their detachment threshold, analogous to Rydberg states in neutral molecules. That a dipole can bind an electron was first mentioned in a paper on mesotrons in 1947 by Fermi and Teller, ¹ who predicted a minimum dipole moment of 0.639 ea_0 (1.625 D) for electron binding. This result was rediscovered many times subsequently, as discussed by Turner.² The minimum dipole moment for electron binding increases when non-Born-Oppenheimer effects, such as molecular rotation, moment of inertia, and dipole length, were considered.³⁻⁷ More sophisticated theoretical methods have been used to investigate the electron binding energies in dipole-bound anions of molecules and clusters and the electron-molecule interactions in DBS.^{8–19} The dipole-bound electron resides in a spatially extended orbital on the positive end of the dipole moment far outside the molecular valence region with relatively small binding energies in the range of 1-100 meV. DBSs play important roles in many physical and chemical processes, such as DNA damage by low-energy electrons^{20,21} or even as potential carriers of the diffuse interstellar bands.^{22–26}

Ground-state dipole-bound anions have been produced by Rydberg electron transfer and studied via field-detachment and photoelectron spectroscopy (PES).^{27–37} Anions usually do not possess bound excited states because of their relatively low electron binding energies. Stable valence-bound anions with polar neutral cores can have DBSs as a special class of excited states. These nonvalence excited electronic states were first observed experimentally in photodetachment spectroscopy (PDS) of organic anions aimed at measuring the electron affinities (EAs) of organic radicals and have been studied by high-resolution rotational autodetachment spectroscopy.^{38–46} Dipole-bound excited states have been considered as a mechanism for the formation of anions in the interstellar medium.^{47–49} Excited DBSs have been observed in solvated iodide clusters and have been used to produce dipole-bound anions of the solvent molecules after ejection of the neutral iodine atom.^{50,51} DBSs in many valence anions have been observed using PDS.^{52–61} The ultrafast dynamics of dipole-bound excited states, have been initial excitations to valence-bound excited states.

Earlier PDS experiments were done with anions at room temperature.^{38–46} Thus, the ground vibrational state (zeropoint level) of the DBS, which requires resonant two-photon detachment (R2PD), could not be observed; the thermal broadening often smeared out the electron detachment

 Received:
 July 18, 2023

 Accepted:
 August 8, 2023

 Published:
 August 11, 2023





Figure 1. Schematic view of the third-generation ESI-PES apparatus, consisting of a cryogenically controlled Paul trap and a high-resolution photoelectron imaging system. TP: turbomolecular pump. CP: cryopump. Reproduced from ref 67. Copyright 2015 AIP Publishing.



Figure 2. Schematic of (a) PDS, (b) rPES at above-threshold feshbach resonances, and (c) R2PD spectroscopy through the zero-point level of DBS (green 0'). BE = binding energy; AD = autodetachment.

threshold, making it challenging even to measure the EAs accurately. A major advance in the investigation of DBSs was made using our third-generation electrospray-ionization PES (ESI-PES) apparatus,⁶⁷ which features a cryogenically cooled 3D Paul trap⁶⁸ and a high-resolution photoelectron imaging system (Figure 1).⁶⁹ Anions are produced by the ESI source, which was used initially to produce multiply charged anions in the first-generation ESI-PES apparatus.⁷⁰⁻⁷² The cryogenically cooled 3D Paul trap was developed subsequently to produce cold anions from the ESI source for PES studies in the secondgeneration ESI-PES apparatus.⁶⁸ The elimination of vibrational hot bands significantly improved the spectral resolution and allowed temperature-dependent phenomena to be investigated.⁷³⁻⁷⁵ In the third-generation ESI-PES apparatus (Figure 1), high-resolution photoelectron imaging replaced the magnetic-bottle PES analyzer.⁶⁷ The multilens velocity-map imaging (VMI) system can achieve an electron energy resolution of 1.2 cm⁻¹ (full width at half-maximum) for near threshold electrons and approximately 1.5% ($\Delta KE/KE$) for electrons with KE above 1 eV.⁶⁹

With the third-generation PES-ESI apparatus, four types of experiments can be performed. First, conventional nonresonant PES at fixed photon energies can be performed at a high resolution. This is valuable to obtain accurate EAs for near threshold detachment,^{76–79} similar to cryo-SEVI developed by the Neumark group.^{80,81} Second, PDS can be conducted with a tunable laser, which is critical to search for DBS.⁸²⁻⁸⁶ As schematically shown in Figure 2a, the PDS features continuous signals (black curve) as a function of the detachment photon energy. Electron signals appear promptly at the detachment threshold, governed by the Wigner threshold law,⁸⁷ and a step may appear at each new detachment channel.⁸⁸ If a DBS exists, one or more weak below-threshold peaks may appear as a result of R2PD from the zero-point level or bound vibrational levels of the DBS. Sharp and strong above-threshold peaks will appear due to resonant excitation to higher vibrational levels of the DBS (a.k.a. vibrational Feshbach resonances) followed by vibrational autodetachment.³⁸⁻⁴¹ Cold anions are critical to allow the bound DBS levels to be observed with R2PD, as well as the

detachment threshold in PDS.^{82–86} Third, resonant PES can be performed at vibrational Feshbach resonances (Figure 2b).^{82,84–86,89} Due to the $\Delta v = -1$ autodetachment propensity rule,^{90,91} highly non-Franck–Condon photoelectron (PE) spectra are obtained, which provide critical information for the assignment of the Feshbach resonances, as well as new vibrational information often not available in nonresonant PES.^{92–94} Finally, one-color R2PD PES can be conducted via bound DBS levels, in which the first photon prepares the DBS and the second photon detaches the dipole-bound electron (Figure 2c). R2PD PES probes the nature of the dipole-bound electron and possible relaxation processes of the bound DBS levels within the detachment laser pule (~5 ns).^{95–97}

A dipole-bound excited state was observed, using the thirdgeneration ESI-PES apparatus, first for cryogenically cooled phenoxide (PhO⁻).^{82,86} Mode-specific and mode-selective vibrational autodetachment was found in resonant PES at the Feshbach resonances of the DBS, giving rise to highly non-Franck-Condon PE spectra. The dipole-bound electron was shown to have little effect on the structure of the neutral radical, so that the measured vibrational frequencies for the DBS in the PD spectrum were observed to be the same as those of the neutral radical measured in the PE spectrum, as shown schematically by the parallel potential energy surfaces in Figure 2 between the DBS and the neutral radical. Thus, the dipole-bound electron can be viewed as "electron tagging" to the neutral radical to allow its vibrational levels to be accessed using PDS. Even though the PDS is governed by the Franck-Condon principle in the same way as nonresonant PES, the high resolution and high sensitivity of PDS allow many more vibrational features to be observed. For example, while the PES of PhO⁻ displayed one vibrational progression in the u_{11} mode,^{98,99} PDS and rPES together yielded vibrational frequencies for nine vibrational modes of the phenoxy radical.⁸⁶ In the PDS of deprotonated uracil, 46 vibrational peaks were observed, leading to the measurement of vibrational frequencies for 21 modes out of a total of 27 for the uracil radical in combination with resonant PES.^{83,89} No other experimental technique can yield such abundant vibrational information for a neutral radical species. Because different molecular conformers have different dipole moments, conformer-specific rPES has been demonstrated via DBS.^{100–102} The combination of PDS and rPES of cryogenically cooled anions has been shown to be a powerful approach to obtain vibrational information on neutral molecular species in the gas phase.⁹²

Several groups have used cryogenically cooled ion trap technologies to conduct PDS and PES of cold anions.^{80,81,103-113} In particular, the autodetachment dynamics and lifetimes from Fechbach resonances of DBSs have been studied using pump-probe experiments of cryogenically cooled anions recently, revealing mode-dependent autodetachment lifetimes.^{114–116} In this Perspective, we discuss recent progress in the Wang lab to probe DBSs of cryogenically cooled anions using a state-of-the-art ESI-PES apparatus. Many interesting findings have been made, primarily on anions of polar cyclic aromatic compounds or polycyclic aromatic compounds (PAHs) with one or more heteroatoms. The topics covered in this Perspective include (1) the critical dipole moments to form dipole-bound excited states, (2) rotational autodetachment for very weakly bound DBSs, (3) R2PD and adiabatic detachment processes via DBSs, (4) relaxation processes from bound DBS levels to valence-bound states

observed via R2PD, (5) observation of polarization effects by the dipole-bound electron on the valence electrons of the neutral core, (6) using PDS and rPES to unravel complicated vibronic levels due to strong nonadiabatic interactions, and (7) the observation of π -type DBSs.

The Critical Dipole Moment to Support DBS. Fermi and Teller first suggested that a stationary dipole with a dipole moment larger than 1.625 D can bind an electron.¹ However, for real molecular systems, the critical dipole moment for electron binding was predicted to be ~ 2 D, if non-Born– Oppenheimer effects were considered.³⁻⁷ Polarization and correlation effects have also been shown to be important in calculating the binding energies of the dipole-bound electron.⁸⁻¹⁹ The minimum dipole moment to form a dipole-bound anion was determined experimentally to be 2.5 D for a wide variety of molecules using the Rydberg electron transfer technique.²⁸⁻³² Molecules with a dipole moment of less than 2.5 D have not been observed to form dipole-bound anions. To examine the minimal dipole moment to allow dipole-bound excited states, we investigated a series of parasubstituted halogen phenoxide anions, para-X-PhO⁻ (X = F, Cl, Br, I),¹¹⁷ as summarized in Table 1. The neutral cores of these anions have different dipole moments; their similar structure and size minimize molecule-dependent effects.

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

	Dipole moment (D)	DBS binding energy (cm ⁻¹)	EA (eV)	EA (cm^{-1})
p-F-PhO	2.56	8(5)	2.2950(6)	18,510(5)
p-Cl-PhO	2.81	11(6)	2.4917(8)	20,097(6)
p-Br-PhO	2.96	24(6)	2.5480(7)	20,551(6)
p-I-PhO	3.19	53(5)	2.6094(7)	21,046(5)
PhO	4.06	97(5)	2.2532(4)	18,173(3)
^a Reproduced Society.	l from ref	117. Copyright	2019 American	Chemical

PDS was used to search for the DBS of *p*-X-PhO⁻, as shown in Figure 3. In each PD spectrum, the arrow refers to the anion detachment threshold, i.e., the EA of the corresponding neutral radical (Table 1). A weak peak below the threshold (labeled 0) was observed in each case, suggesting the existence of a DBS. Peak 0 represents the bound zero-point level of the DBS, and its separation from the detachment threshold defines the binding energy of the DBS, as given in Table 1. The dipole moment of p-F-PhO (2.56 D) is near the empirical critical value, corresponding to a DBS binding energy of only 8 cm^{-1} , which could be measured using only a high-resolution laser scan. The above-threshold peaks (labeled 1-8) represent transitions to vibrational levels of the DBS (a.k.a. vibrational Feshbach resonances). The data in Figure 3 illustrate the critical importance of cryogenically cooling the anions. The zero-point level and the detachment threshold of the DBS would be smeared out if the anions were not properly cooled.

Figure 4 plots the measured DBS binding energies versus the dipole moment of the neutral *p*-X-PhO radical. A linear relationship between BE and μ is obtained for this set of similar species, BE = 63.4 μ – 159.0, extrapolating to a minimal dipole moment of 2.5 D at zero binding energy. This value is exactly the same as that obtained by Rydberg electron transfer experiments for the formation of ground-state dipole-bound anions of neutral molecules.^{28–32} We note that the previous



Figure 3. PDS of (a) p-F-PhO⁻, (b) p-Cl-PhO⁻, (c) p-Br-PhO⁻, and (d) p-I-PhO⁻ at a laser scan rate of 0.1 nm/step. The inset in panel a displays a high-resolution scan at 0.005 nm/step near the threshold region of p-F-PhO⁻. Reproduced from ref 117. Copyright 2019 American Chemical Society.



Figure 4. DBS binding energies of p-X-PhO⁻ as a function of the dipole moments of p-X-PhO. Reproduced from ref 117. Copyright 2019 American Chemical Society.

studies on DBAs contained a wide variety of different molecules with a broad range of dipole moments, but no DBA was observed for molecules with a dipole moment <2.5 D. That a similar critical dipole moment is obtained for such a diverse range of molecules, either for ground-state DBS or DBS as an excited electronic state, suggests that the charge–dipole interaction (i.e., the $-1/r^2$ potential) is dominant.

We have studied two other *para*-substituted phenoxide, *p*-ethynyl-PhO⁻ and very recently *p*-ethyl-PhO⁻.^{96,97} A DBS was observed for *p*-ethynyl-PhO⁻ with a BE of 76 \pm 5 cm⁻¹ and for *p*-ethyl-PhO⁻ with a BE of 145 \pm 3 cm⁻¹, where the dipole moment for *p*-ethynyl-PhO was 3.8 and 4.85 D for *p*-ethyl-PhO. The binding energies of the DBS in both anions fall onto the linear curve in Figure 4, again confirming the 2.5 D empirical minimal dipole moment for the formation of DBS. It should be pointed out that in a recent study on indolide we found a DBS with a very small binding energy of 6 cm⁻¹, despite the fact that the indolyl radical has a dipole moment of only 2.4 D.¹¹⁸ The barely bound DBS in indolide is found to be assisted by polarization, i.e., a polarization-assisted DBS.

Very recently, a DBS is observed in carbazolide with a binding energy of 20 cm⁻¹ due to the large polarizability of the carbazolyl radical,¹¹⁹ even though its dipole moment is only 2.2 D. On the other hand, no DBS was observed for the less polarizable pyrrolide anion,¹²⁰ even though the corresponding neutral pyrrolyl radical has a similar dipole moment of 2.2 D. These results highlight the critcal roles that polarization plays in the DBS for large molecules with high polarizabilities.

Rotational Autodetachment. In the rPES of p-F-PhO⁻, near 0 eV (i.e., threshold) electron signals were observed at each Feshbach resonance. Three resonant PE images and spectra at peaks 1, 3, and 8 in Figure 3a are given in Figure 5. As indicated by the red dashed arrows in Figure 5d, the threshold signals came from rotational autodetachment from the vibrational levels of DBS to the corresponding neutral vibrational levels. The extremely small binding energy of the DBS in *p*-F-PhO⁻ could be overcome by rotational excitation of the anion, which was projected onto each DBS vibrational level. Rotational autodetachment was observed previously in high-resolution PDS.⁴²⁻⁴⁶ In the case of p-F-PhO⁻, rotational autodetachment competed with vibrational autodetachment in all of the resonant PE spectra via the Feshbach resonances, as shown in Figure 5d. All the vibrational autodetachment processes follow the $\Delta v = -1$ propensity rule.^{90,91} That both rotational and vibrational autodetachments were observed at the same time suggested that their time scales are similar. In the recent study of indolide, we observed similar rotational autodetachment because of the low binding energy (6 cm^{-1}) of its DBS.¹¹⁸

R2PD and Adiabatic Detachment Processes. Two photons are required to observe the bound DBS levels. R2PD PE spectra of bound DBS levels provide insights into the nature of the DBS orbital and relaxation processes of the DBS. Because the dipole-bound electron has such a weak interaction with the neutral core, no geometry change occurs from the DBS to the neutral final state. Thus, strict adiabatic

pubs.acs.org/JPCL



Figure 5. RPES images and spectra of p-F-PhO⁻ at the three wavelengths corresponding to the Feshbach resonances (a) 1, (b) 3, and (c) 8 in Figure 3a. (d) Schematic energy level diagram for both the vibrational and rotational autodetachment from the DBS vibrational levels of p-F-PhO⁻ to the p-F-PhO neutral levels. Reproduced from ref 117. Copyright 2019 American Chemical Society.



Figure 6. (a) PD spectrum of R-TFAE⁻. (b) The R2PD PE spectra at the seven bound DBS levels (the peak numbers are indicated). ES = excited states. (c) Schematic energy level diagram showing R2PD processes at the seven bound DSB levels (0–6). IC = internal conversion; ISC = intersystem crossing. Reproduced from ref 121. Copyright 2022 Royal Society of Chemistry.

detachment behavior is expected for the R2PD process, which was always observed for the zero-point level of any DBS and recently observed for several bound vibrational levels in the DBS of the (R)-(-)-1-(9-anthryl)-2,2,2-trifluoroethanolate anion (R-TFAE⁻, insert of Figure 6a).¹²¹ Figure 6a shows the PDS for R-TFAE⁻, revealing seven intense bound

pubs.acs.org/JPCL



Figure 7. (a) PDS of bPh⁻. The inset shows the dipole-bound orbital of bPh⁻. (b) R2PD PE spectra of bPh⁻ at wavelengths corresponding to the bound DBS vibrational levels 0 and 4 (bottom) and Feshbach resonances 14, 16, and 19 (top). The dashed line indicates the constant binding energy of peak X at all detachment wavelengths. (c) Expanded spectra in the binding energy range of 2.34–2.40 eV, showing the one-photon resonant PE spectra for the three Feshbach resonances. (d) Direct sequential R2PD processes responsible for peak X in panel b. (e) Indirect R2PD processes showing the intersystem crossing (ISC) responsible for peaks Y and Z in panel b. Reproduced from ref 95. Copyright 2019 American Chemical Society.

vibrational levels (peaks 0-6) including the zero-point level (peak 0) due to one-color R2PD.

These bound DBS vibrational levels were assigned with the help of the computed vibrational frequencies of neutral R-TFAE and Franck-Condon simulations. The seven R2PD photoelectron spectra in Figure 6b display similar features. The peak labeled as "DBS" is due to sequential R2PD via the DBS, giving rise to low binding energy (high KE) electrons. Features "S₀" and "ES" are due to indirect two-photon detachment, in which relaxation takes place from the bound DBS levels after the first photon absorption, but before electron detachment by the second photon within the 5 ns laser pulse. "S₀" designates detachment from the rovibrational levels of the ground electronic state of the anion, following internal conversion of the electronic energy in the DBS to internal energies of the ground electronic state of R-TFAE⁻. The broad feature "ES", observed between 0.2 and 1 eV, was due to detachment from the valence excited state of the anion as a result of intersystem crossing from the DBS. The relaxation and detachment processes in the indirect R2PD are schematically shown in Figure 6c.

It was expected that the binding energy of the "DBS" peak in the R2PD PE spectra should become smaller as higher vibrational levels of the DBS are reached by the first photon. In contrast, the binding energies of the "DBS" peak in the seven R2PD spectra were observed to be the same within the experimental error bar, as shown by the dashed line in Figure 6b. This provides direct evidence for the adiabatic detachment process from the DBS by the second photon, during which the vibrational levels of the neutral core remain the same. The observation of the adiabatic detachment process is a direct confirmation that the dipole-bound electron does not affect the structure of the neutral core, resulting in parallel potential energy surfaces between the DBS and the neutral ground state. Hence, the vibrational levels do not change upon detachment of the diffuse dipole-bound electron by the second photon, as indicated in Figure 6c; that is, the vibrational energies in the DBS are carried to the neutral final states. The height of the shaded area in Figure 6c represents the constant binding energy of the "DBS" feature in the seven R2PD PE spectra. Thus, the dipole-bound electron can be viewed merely as a "tag" to the neutral core.

We should reiterate that R2PD PE spectra from valencebound excited states display completely different Franck– Condon profiles for different intermediate vibrational levels, as reported previously for AuS⁻.¹²²

Intersystem Crossing to Valence-Bound States. R2PD PE spectra can reveal relaxation processes from the bound DBS levels, including conversion from the DBS to valence-bound states (VBSs), as shown in Figure 6c for R-TFAE⁻. The transition from a DBS to a VBS was first observed in $CH_3NO_2^{-,30}$ while the relaxation dynamics from DBS to VBS has been investigated using time-resolved PES.^{62–66} The first observation of conversion from an excited DBS to VBS using R2PD PES came from the deprotonated 4,4'-biphenol anion (bPh⁻, inset of Figure 7a).⁹⁵ The bPh radical has a large dipole moment of 6.35 D, and the PDS of bPh⁻ (Figure 7a) reveals a DBS with a BE of 695 cm⁻¹ and 13 bound excited vibrational



Figure 8. (a) PD spectrum of PEP⁻. (b) R2PD PE image at peak 0 in panel a. (c) R2PD PE spectra at peaks 0–3 in panel a. (d) Schematics showing the electron configurations of the DBS in direct two-photon detachment (X) and the shakeup process (B). (e) Projection probabilities of the electric-field-polarized HOMO–1 (red +) and HOMO–2 (blue *) to the HOMO of neutral PEP as a function of the distance between the center of PEP and the dipole-bound electron approximated by a point charge in the calculation (inset 1). The mixing coefficients are plotted in the form $|c_1|^2/|c_0|^2$ (inset 2). Reproduced from ref 124. Copyright 2020 American Chemical Society.

levels (1–13), as well as six Feshbach resonances (14–19) in the scanned photon energy range. The R2PD PE spectra for the bound DBS level 0 and 4 and the resonant PE spectra for the Feshbach resonances 14, 16, and 19 are shown in Figure 7b. Very weak R2PD signals are also observed for the three Feshbach resonances. The single-photon resonant PE signals at the high binding energy side for the three Feshbach resonances are shown in Figure 7c, all displaying enhanced 0_0^0 transitions due to the $\Delta v = -1$ propensity rule. The R2PD PE spectra corresponding to the bound DBS levels 0 and 4 consist of low binding energy PE signals due to sequential two-photon detachment (X), as well as relaxation from DBS to VBSs (Y and Z). The corresponding R2PD processes are shown in Figure 7d,e, respectively.

The binding energy of peak X in the R2PD PE spectra is the same for all of the DBS levels, representing direct adiabatic detachment from the DBS by the second photon, as indicated in Figure 7d and also discussed above (Figure 6c). It was surprising that direct R2PD PE signals were also observed for the Feshbach resonances, albeit at much weaker intensity (Figure 7b for peaks 14, 16, and 19), along with the dominant single-photon resonant PE signals (Figure 7c). This observation suggested that the autodetachment lifetime of the Feshbach resonances in bPh⁻ was likely relatively long. It would be interesting to directly study the autodetachment dynamics in this system using pump–probe techniques, as have been done recently for several DBS systems.^{114–116}

The peaks Y and Z in Figure 7b were due to indirect R2PD processes as a result of relaxation from the DBS to VBSs. Our theoretical calculations revealed two triplet (T_1, T_2) and one singlet (S_1) excited states below the detachment threshold of bPh^{-.95} On the basis of the long lifetime of the intermediate states, they were assigned to the triplet states as a result of intersystem crossing from the DBS (Figure 7e). Recently,

similar conversion from DBS to VBS was observed in p-I-PhO⁻, in a pump-probe experiment, resulting in C–I bond cleavage.¹²³

Polarization Effects by the Diffuse Dipole-Bound Electron. Even though the dipole-bound electron has little influence on the geometry of the neutral core, electron correlation effects are known to be crucial for accurately calculating the DBS binding energies.^{8–19} The diffuse dipole-bound electron, typically about 10–100 Å outside the neutral core, creates an oriented electron field, which can polarize the valence electrons. During a study of phenylethynyl phenoxide (PEP⁻, inset of Figure 8a), we observed strong configuration mixing in the PEP core as a result of interactions with the dipole-bound electron.¹²⁴ The interactions can be characterized as the polarization of the valence electrons by the oriented electric field of the dipole-bound electron.

The PD spectrum of PEP⁻ (Figure 8a) revealed a DBS with a binding energy of 348 cm⁻¹ (peak 0), three bound vibrational levels (1-3), and six vibrational Feshbach resonances (4-9). The R2PD PE image at peak 0 is shown in Figure 8b, and the R2PD PE spectra for all four bound DBS levels (0-3) are given in Figure 8c. Multiple features were observed in the R2PD PE spectra. The lowest-binding-energy peak (labeled as X_{DBS}) was from direct R2PD. The distinct pwave angular distribution (Figure 8b) was in agreement with the expected σ DBS orbital. The signals labeled as GS and ES referred to photoelectrons derived from the ground state and the first valence excited state of PEP-, respectively, as a result of relaxation from DBS to VBSs. The observation of the sharp peak "B_{DBS}" at around 2.2 eV in the R2PD PE spectra was unexpected. Its angular distribution had a clear p-wave character, similar to that of the X_{DBS} peak. It turned out that the B_{DBS} peak corresponded to the second excited state of PEP and was attributed to a shakeup process, which involved the



Figure 9. (a) PE image and spectrum of triazolide at 336.15 nm. (b) Structure of triazolide and a schematic energy level diagram for the ground state of triazolide and the first four electronic states of the triazolyl radical. (c) PD spectrum of triazolide from 27,450 to 29,965 cm⁻¹. The comparison of the nonresonant PE spectrum (blue) at 336.15 nm with the PD spectrum (red) is shown in the inset. Selected resonant PE images and spectra of triazolide at (d) 351.45 nm (peak 5) and (e) 341.53 nm (peak 21). (f) Schematic energy level diagram for autodetachment from the DBS vibrational levels of triazolide to the related neutral final state, corresponding to peak 5 in panel d and 21 in panel e. Reproduced from ref 136. Copyright 2022 American Chemical Society.

detachment of the DBS electron and the concomitant excitation of an electron from HOMO-2 to HOMO (Figure 8d).

Shakeup processes are direct manifestation of electron correlations, for which PES is the most powerful experimental technique to investigate.¹²⁵ However, the shakeup peak in the R2PD PE spectra from the DBS of PEP⁻ was a surprising observation, because of the weak interactions between the DBS electron and the neutral core. In a previous study, we found that the DBS electron in C_2P^- was not even spin-coupled with the valence electrons of neutral C_2P .¹²⁶ Furthermore, the shakeup process seemed to occur only from HOMO-2 to the HOMO. It was surprising that shakeup was not observed from the HOMO-1 to the HOMO in the R2PD PE spectra (Figure 8c). We carried out theoretical calculations to investigate the mechanisms of the shakeup process in the DBS. We considered the first two energetically allowed valence excited states of neutral PEP, i.e., the promotion of a spin-down electron from HOMO-1 and HOMO-2 to the singly occupied HOMO. The experimental observation implied that the DBS electron affects the electrons in the HOMO-2, inducing a mixing between the HOMO and HOMO-2. We can write the wave function of the spin-down electron ($\phi_{HOMO-2L'}$) in the DBS as a linear combination of the HOMO and HOMO-2:

$$\phi_{\text{HOMO}-2\downarrow} = c_0 \phi_{\text{HOMO}-2\downarrow} + c_1 \phi_{\text{HOMO}\downarrow} \tag{1}$$

where c_0 and c_1 are the mixing coefficients. Basically, configuration mixing can be considered as a polarization effect

of the valence electrons by the DBS electron. The HOMO–2 is delocalized, and it is expected to be more polarizable by the DBS electron, causing the mixing of HOMO–2 with the HOMO (inset 2 in Figure 8e). The electric field from the DBS electron is oriented along the molecular *z* axis with the largest polarizability, α_{zz} (inset 1 of Figure 8e). On the other hand, the HOMO–1 is more localized and less polarizable by the DBS electron; thus, there is no mixing with HOMO, as borne out by the theoretical calculations (red curve in Figure 8e). Thus, dipole-bound anions provide a new means to study the electric field effect on the valence electronic structure of complex molecules.

Using PDS and rPES to Unravel Strong Nonadiabatic Interactions. Nonadiabatic effects are due to the coupling of two or more adiabatic potential energy surfaces. Such breakdown of the Born–Oppenheimer approximation is common in complex molecular systems with close electronic states.^{127–129} Strong nonadiabatic effects were observed in the azolyl radicals (five-membered carbon–nitrogen heterocycles).^{130–133} Especially, strong vibronic coupling rendered the PES of 1,2,3-triazolide (Figure 9a) unassignable in an earlier study.¹³³ Electronic structure calculations indicated that the first four electronic sates of triazolyl ($^{2}B_{1}$, $^{2}A_{2}$, and $^{2}B_{2}$; Figure 9b) were close to each other in energy.¹³⁴ The complicated PE spectrum was due to the coupling of the four electronic states.¹³⁵

The nonresonant PE spectrum of 1,2,3-triazolide at 336.15 nm (Figure 9a) from our third-generation ESI-PES apparatus gives an accurate EA of 3.4463 ± 0.0004 eV for triazolyl, as



Figure 10. R2PD images and spectra of (a) $9AT^-$ and (b) PhO⁻ via the zero-point level of their respective DBS. The double arrows above the images represent the laser polarization direction. The calculated DBS wave functions of (c) $9AT^-$ and (d) PhO⁻. (e) Schematic diagram of the R2PD processes via DBS of the two anions from the anion ground state (G.S.). NAPT: nonadiabatic population transfer. The coordinate system is chosen such that the dipole moment is along the *z* axis. Reproduced from ref 137. Copyright 2020 American Physical Society.

well as 18 vibrational features labeled with A to R.¹³⁶ Nonresonant PE spectra can be fitted with Franck–Condon simulations, which was not possible for triazolyl, due to the strong nonadiabatic effects.¹³³ Since the PD spectrum of the DBS is known to mirror the nonresonant PE spectrum of the same anion,⁹² we are able to assign all the vibronic features in the PES using PDS. The PD spectrum of triazolide shown in Figure 9c resolved thirty-one DBS vibrational levels. The PD spectrum is compared with the 336.15 nm PE spectrum in the inset, where the 0_0^{0} transition in the PE spectrum is aligned with peak 0 of the PD spectrum. It can be clearly seen that the PD spectrum is similar to the PE spectrum. Every PE spectral feature has a corresponding transition in the PD spectrum. The similarity between the PD and PE spectra made it possible to assign the vibronic transitions in the PE spectra of triazolyl using the PD spectrum.¹³⁶

To assign the PD spectrum, we conducted rPES at the 31 Feshbach resonances. The resonant PE spectra at peaks 5 and 21 are selected as examples (Figure 9d,e). The spectrum taken at peak 5 (Figure 9d) produces the 15² final state and a significantly enhanced 15¹ peak. Based on the excitation energy and the calculated frequency, peak 5 was assigned readily to the $15'^3$ Feshbach resonance. The strong peak A (15^1) suggests that two quanta of the 15' mode are coupled with the DBS electron. Peak 5 is a relatively strong resonant peak in the PD spectrum, and it also contains an overlapping vibrational excitation of $7'^1$, resulting in an enhanced 0_0^0 transition, consistent with its more isotropic angular distribution. Since peak 5 in the PD spectrum aligned with peak D in the nonresonant PE spectrum, peak D could be assigned to $7^{1}/15^{3}$ of the triazolyl radical accordingly. Similarly, for the vibrational peaks at higher binding energies in the nonresonant PE spectrum, such as peak O, the rPES could also provide accurate information for their assignments. Peak O corresponds to peak 21 in the PD spectrum. In the resonant PE spectrum at peak 21 (Figure 9e), the three enhanced peaks B $(10^{2}15^{1})$, E (14^{1}) , and g $(9^{1}15^{2})$ indicate peak 21 is due to an overlapping DBS level of $9'^{1}10'^{2}15'^{1}$ and $10'^{2}14'^{1}15'^{1}$. The corresponding autodetachment processes involved are shown in Figure 9f. In total, we observed 28 vibronic levels for the ground state of triazolyl. These high densities of vibronic levels are assigned straightforwardly by comparing the PE spectrum with the PD spectrum. A total of 12 fundamental vibrational frequencies are measured for the triazolyl radical. This study shows again that combining PDS and rPES is not only an effective approach to obtain vibrational information but also is powerful to understand complex vibronic structures for polar radical species through DBSs.

II-Type Dipole-Bound States. The dipole-bound orbital is of σ -symmetry, similar to an *s* orbital, as evidenced by the *p*wave angular distribution in the R2PD PE image shown in Figure 8b. However, a π -type DBS is first observed in 9anthrolate (9AT⁻, see inset of Figure 10a), which is found to have a DBS with a binding energy of 191 cm⁻¹ (0.0237 eV).¹ The π -type DBS is revealed in the R2PD PE image at the zeropoint level of the DBS (Figure 10a). The angular distribution of the photoelectrons detached from the DBS exhibits a distinct (s+d)-wave character with a negative β value of -0.7. This observation is in stark contrast to the expected *p*-wave angular distribution, as observed for phenoxide (PhO⁻, Figure 10b). Our theoretical calculations indeed suggested the existence of both bound σ - and π -type DBSs for 9AT⁻, with the π -DBS being higher in energy than the σ -DBS by 9.3 meV (75 cm⁻¹). The σ and π DBS orbitals are shown in Figure 10c, compared with the σ DBS of PhO⁻ in Figure 9d. The π -DBS orbital of 9AT⁻ has one angular node and is seen mainly on both sides of 9AT (along the y axis), perpendicular to the dipole axis. According to the $C_{2\nu}$ symmetry of 9AT⁻, the transition from the anion with A_1 symmetry to the π -DBS with A_2 symmetry is dipole forbidden; only the transition to the σ -DBS (B_1 symmetry) is allowed. It is suggested that the large inplane polarizability of α_{yy} , as a result of the delocalized π electrons along the anthracene ring, preferentially stabilizes the in-plane π -DBS, lowering its energy close to or even below the σ -DBS.

This polarization stabilization cannot be fully captured by the time-dependent DFT calculations used to compute the DBS binding energies. Thus, a mechanism for the observation of the π -DBS is conceivable, where the first photon populated the σ -DBS that transfers quickly to the π -DBS before the second photon is absorbed, as schematically shown in Figure 10e (NAPT). The high polarizability of 9AT also significantly increases the binding energy of the DBS: the DBS of 9AT⁻ has a binding energy of 191 cm⁻¹, much higher than the 97 cm⁻¹ binding energy of PhO⁻, even though the dipole moment of 9AT (3.6 D) is smaller than the 4.0 D of PhO. A similar π -type DBS has been observed subsequently for the 9-phenanthrotate anion (a structural isomer of 9AT⁻)¹³⁸ and also in the diatomic anion KI⁻⁶⁰

Conclusions and Perspectives. In this Perspective, we discuss recent findings in our study of dipole-bound states using state-of-the-art electrospray-ionization photoelectron spectroscopy. The ability to create cold anions using cryogenic cooling and the high-resolution capability of photoelectron imaging have been proven to be critical experimental advances that have revolutionized our study of dipole-bound states. Resonant two-photon photoelectron spectroscopy has enabled investigation of the nature and relaxation processes of the bound vibrational levels of the dipole-bound states. Resonant photoelectron spectroscopy via the vibrational Feshbach resonances has been developed not only to assign the photodetachment spectra but also to obtain rich spectroscopic information on the neutral radical species. Even though the concept of dipole-bound states has been known for a long time, recent experimental advances have shown that there are many interesting questions to be addressed and new phenomena to be discovered. The critical dipole moment for the formation of a dipole-bound state was systematically investigated using a series of para-halogen substituted phenoxides (p-X-PhO⁻) to minimize molecule-dependent effects. A linear correlation between the dipole moments and the binding energies of the dipole-bound states was observed, extrapolating to a critical dipole moment of 2.5 D at a zero binding energy. The p-F-PhO radical has a dipole moment of only 2.56 D and a very small DBS binding energy of 8 cm^{-1} in p-F-PhO⁻, resulting in rotational autodetachment at each vibrational level of the DBS due to rotational broadening. Recently, a polarization-assisted DBS was observed at a subcritical dipole moment (2.4 D) in indolide with a very small DBS binding energy of 6 cm^{-1} , due to the large polarizability of the indolyl radical. A very recent study led to the discovery of a DBS in carbazolide with a binding energy of 20 cm⁻¹ despite the smaller dipole moment of the carbazolyl radical (2.2 D) as a result of its larger polarizability. In contrast, no DBS was observed for the pyrrolide anion, even though the pyrrolyl radical has a similar dipole moment (2.2 D), reinforcing the important role played by molecular polarizability in the formation of dipole-bound states in large and highly polarizable molecules. It should be pointed out that nonpolar large PAH molecules have been predicted to possess polarization/correlation-bound states.¹³⁹ Thus, it would be interesting to investigate the crossover from dipole-bound to polarization-bound states for large polar PAH molecules.

A number of new phenomena pertinent to the nature of the dipole-bound states have been uncovered. Because of its complicated molecular structure and numerous low-frequency modes, many bound vibrational levels were observed in the DBS of the chiral (R)-(-)-1-(9-anthryl)-2,2,2-trifluoroethanolate anion. A strict adiabatic detachment behavior was observed for the detachment of the dipole-bound electron from the seven bound vibrational levels, reaffirming the fact that the dipole-bound electron has little effect on the structure of the neutral core. The fact that structures of the neutral core

of the dipole-bound state and the neutral radical are similar has been observed by the similarity of photodetachment spectroscopy and nonresonant photoelectron spectroscopy. This fact allowed us to assign the complicated vibronic features of the 1,2,3-triazolide anion by using the vibrational information obtained from the photodetachment spectrum of its dipolebound state. Even though the dipole bound electron is found to have little effect on the structure of the neutral core, the dipole-bound electron was observed to influence the valence electrons in the dipole-bound state of the phenyl-ethynylphenoxide (PEP⁻) anion. Due to the elongated molecular structure of PEP⁻, the dipole-bound electron was observed to cast an oriented intramolecular electric field, which induced configuration mixing of the valence orbitals of the neutral core in the dipole-bound state. In addition to enhancing the binding energy of the dipole-bound electron, the anisotropic polarization in the 9-anthrolate (9AT⁻) anion was found to preferentially stabilize a π -type dipole-bound state, as clearly revealed in the photoelectron angular distribution. Though not discussed in the current Perspective, a core-excited dipolebound state was also observed in the pyrazolide anion.¹⁴⁰ The pyrazolyl radical is known to have two low-lying electronic states separated by only 266 cm⁻¹. A DBS was observed for each of these two electronic states. In principle, each electronic state of the neutral core should have its own DBS, if the dipole moment of the electronic state is high enough. However, in reality, the observation of such core-excited DBS would be very challenging; only in favorable cases can they be observed. The ability to create cold anions using cryogenic ion trap technology and the high-resolution capability of photoelectron imaging have allowed dipole-bound states to be investigated in great detail. They not only provide a new means to obtain unprecedented spectroscopic information on neutral radical species but have also yielded new information about the weakly dipole-bound electron.

AUTHOR INFORMATION

Corresponding Authors

- Dao-Fu Yuan Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States; Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China; orcid.org/0000-0001-8461-6889; Email: ydfu@ustc.edu.cn
- Lai-Sheng Wang Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States; orcid.org/0000-0003-1816-5738; Email: Lai-Sheng Wang@brown.edu

Author

Yue-Rou Zhang – Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.3c01994

Notes

The authors declare no competing financial interest.

Biographies

Yue-Rou Zhang received her B.S. degree from Tongji University in 2018 and her Ph.D. from Brown University in 2023 under the tutelage of Prof. Lai-Sheng Wang. Her Ph.D. thesis was focused on high-

resolution photoelectron imaging of cryogenically cooled anions. She is currently employed in the electronics industry.

Dao-Fu Yuan received his B.S. degree in 2013 and Ph.D. in 2018 from University of Science and Technology of China (USTC) under the joint tutelage of Profs. Xueming Yang and Xingan Wang. After a brief postdoctoral stay at USTC, he joined Brown University in 2019 as a postdoctoral fellow under the supervision of Prof. Lai-Sheng Wang. He is currently a research professor at Hefei National Research Center for Physical Sciences at the Microscale of USTC.

Lai-Sheng Wang received his B.S. degree in chemistry from Wuhan University in 1982 and his Ph.D. from the University of California at Berkeley in 1990 under the joint supervision of Profs. Yuan T. Lee and David A. Shirley. After conducting postdoctoral research in the Smalley lab at Rice University, he took up a joint position in 1993 between Pacific Northwest National Laboratory and Washington State University. He moved to Brown University in 2009 and is currently Jesse H. and Louisa D. Sharpe Metcalf Professor of Chemistry.

ACKNOWLEDGMENTS

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division under Grant DE-SC0018679.

REFERENCES

(1) Fermi, E.; Teller, E. The Capture of Negative Mesotrons in Matter. *Phys. Rev.* **1947**, *72*, 399–408.

(2) Turner, J. E. Minimum Dipole Moment Required to Bind an Electron - Molecular Theorists Rediscover Phenomenon Mentioned in Fermi-Teller Paper Twenty Years Earlier. *Am. J. Phys.* **1977**, *45*, 758–766.

(3) Garrett, W. R. Critical Binding of an Electron to a Non-Stationary Electron Dipole. *Chem. Phys. Lett.* **1970**, *5*, 393–397.

(4) Crawford, O. H. Negative Ions of Polar Molecules. *Mol. Phys.* 1971, 20, 585-591.

(5) Garrett, W. R. Thermally Stable Negative Ions of Polar Molecules. J. Chem. Phys. 1978, 69, 2621–2626.

(6) Garrett, W. R. Critical Binding and Electron Scattering by Symmetric-Top Polar Molecules. J. Chem. Phys. 2014, 141, 164318.

(7) Slimak, S.; Jordan, K. D. Binding of an Electron by a Finite Fixed Dipole. *J. Phys. Chem. Lett.* **2022**, *13*, 10331–10334.

(8) Simons, J.; Jordan, K. D. Ab Initio Electron Structure of Anions. *Chem. Rev.* **1987**, *87*, 535–555.

(9) Adamowicz, L. Dipole-Bound Anionic State of Nitromethane. Ab Initio Coupled Cluster Study with First-Order Correlation Orbitals. J. Chem. Phys. **1989**, *91*, 7787–7790.

(10) Gutowski, M.; Skurski, P.; Jordan, K. D.; Simons, J. Energies of Dipole-Bound Anionic States. Int. J. Quantum Chem. 1997, 64, 183–191.

(11) Gutowski, M.; Skurski, P. Dispersion Stabilization of Solvated Electron and Dipole-Bound Anions. J. Phys. Chem. B **1997**, 101, 9143–9146.

(12) Wang, F.; Jordan, K. D. A Drude-Model Approach to Dispersion Interactions in Dipole-Bound Anions. J. Chem. Phys. 2001, 114, 10717–10724.

(13) Jordan, K. D.; Wang, F. Theory of Dipole-Bound Anions. Annu. Rev. Phys. Chem. 2003, 54, 367–396.

(14) Sommerfeld, T. Intramolecular Electron Transfer from Dipole-Bound to Valence Orbitals: Uracil and 5-Chlorouracil. *J. Phys. Chem. A* **2004**, *108*, 9150–9154.

(15) Simons, J. Molecular Anions. J. Phys. Chem. A 2008, 112, 6401-6511.

(16) Zhang, Y.; Weber, P. M.; Jónsson, H. Self-Interaction Corrected Functional Calculations of a Dipole-Bound Molecular Anion. *J. Phys. Chem. Lett.* **2016**, *7*, 2068–2073.

(17) Jagau, T.-C.; Bravaya, K. B.; Krylov, A. I. Extending Quantum Chemistry of Bound States to Electronic Resonances. *Annu. Rev. Phys. Chem.* **201**7, *68*, 525–553.

(18) Hao, H.; Shee, J.; Upadhyay, S.; Ataca, C.; Jordan, K. D.; Rubenstein, B. M. Accurate Predictions of Electron Binding Energies of Dipole-Bound Anions via Quantum Monte Carlo Methods. *J. Phys. Chem. Lett.* **2018**, *9*, 6185–6190.

(19) Sommerfeld, T.; Davis, M. C. Excluded-Volume Descriptors for Dipole-Bound Anions: Amine N-Oxides as a Test Case. *J. Chem. Phys.* **2020**, *152*, 054102.

(20) Boudaiffa, B.; Cloutier, P.; Hunting, D.; Huels, M. A.; Sanche, L. Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons. *Science* **2000**, *287*, 1658–1660.

(21) Burrow, P. D.; Gallup, G. A.; Scheer, A. M.; et al. Vibrational Feshbach Resonances in Uracil and Thymine. *J. Chem. Phys.* 2006, 124, 124310.

(22) Sarre, P. J. The Diffuse Interstellar Bands: A Dipole-Bound State Hypothesis. *Mon. Not. R. Astrom. Soc.* **2000**, 313, L14–L16.

(23) Guthe, F.; Tulej, M.; Pachkov, M. V.; Maier, J. P. Photodetachment Spectrum of $I-C_3H_2^{-1}$: The role of Dipole-Bound States for Electron Attachment in Interstellar Clouds. *Astrophys. J.* **2001**, 555, 466–471.

(24) McCall, B. J.; Oka, T.; Thorburn, J.; Hobbs, L. M.; York, D. G. A. A Critical Examination of the $I-C_3H_2^-$ Spectrum and the Diffuse Interstellar Bands. *Astrophys. J.* **2002**, *567*, L145–L148.

(25) Fortenberry, R. C. Theoretical Electronic and Rovibrational Studies for Anions of Interest to the DIBs. *Proc. Int. Astron. Union* **2013**, *9*, 344–348.

(26) Laws, B. A.; Levey, Z. D.; Schmidt, T. W.; Gibson, S. T. Velocity Map Imaging Spectroscopy of the Dipole-Bound State of CH_2CN^- : Implications for the Diffuse Interstellar Bands. J. Am. Chem. Soc. **2021**, 143, 18684–18692.

(27) Stockdale, J. A.; Davis, F. J.; Compton, R. N.; Klots, R. N. Production of Negative Ions from CH₃X Molecules (CH₃NO₂, CH₃CN, CH₃1, CH₃Br) by Electron Impact and by Collisions with Atoms in Excited Rydberg States. *J. Chem. Phys.* **1974**, *60*, 4279–4285.

(28) Desfrancois, C.; Abdoulcarime, H.; Khelifa, N.; Schermann, J. P. From 1/r to $1/r^2$ Potentials: Electron Exchange between Rydberg Atoms and Polar-Molecules. *Phys. Rev. Lett.* **1994**, *73*, 2436–2439.

(29) Desfrancois, C.; Abdoul-Carime, H.; Schermann, J. P. Ground-

State Dipole-Bound Anions. Int. J. Mod. Phys. B 1996, 10, 1339–1395.
(30) Compton, R. N.; Carman, J. H. S.; Desfrancois, C.; Abdoul-Carime, H.; Schermann, J. P.; Hendricks, J. H.; Lyapustina, S. A.; Bowen, K. H. On the Binding of Electrons to Nitromethane: Dipole and Valence Bound Anions. J. Chem. Phys. 1996, 105, 3472–3478.

(31) Hammer, N. I.; Diri, K.; Jordan, K. D.; Desfrancois, C.; Compton, R. N. Dipole-Bound Anions of Carbonyl, Nitrile, and Sulfoxide Containing Molecules. *J. Chem. Phys.* **2003**, *119*, 3650– 3660.

(32) Hammer, N. I.; Hinde, R. J.; Compton, R. N.; Diri, K.; Jordan, K. D.; Radisic, D.; Stokes, S. T.; Bowen, K. H. Dipole-Bound Anions of Highly Polar Molecules: Ethylene Carbonate and Vinylene Carbonate. *J. Chem. Phys.* **2004**, *120*, 685–690.

(33) Ard, S. G.; Compton, R. N.; Garrett, W. R. Rotational Auto-Detachment of Dipole-Bound Anions. *Chem. Phys. Lett.* **2016**, 650, 154–158.

(34) Dunning, F. B.; Buathong, S. Collision of Rydberg Atoms with Neutral Targets. *Int. Rev. Phys. Chem.* **2018**, *37*, 287–328.

(35) Ciborowski, S. M.; Liu, G.; Graham, J. D.; Buytendyk, A. M.; Bowen, K. H. Dipole-Bound Anions: Formed by Rydberg Electron Transfer (RET) and Studied by Velocity Map Imaging-Anion Photoelectron Spectroscopy (VMI-aPES). *Eur. Phys. J. D* **2018**, *72*, 139.

(36) Liu, G.; Ciborowski, S. M.; Pitts, C. R.; Graham, J. D.; Buytendyk, A. M.; Lectka, T.; Bowen, K. H. Observation of the Dipole- and Quadrupole-Bound Anions of 1,4-Dicyanocyclohexane. *Phys. Chem. Chem. Phys.* **2019**, *21*, 18310–18315. (37) Liu, G.; Ciborowski, S. M.; Graham, J. D.; Buytendyk, A. M.; Bowen, K. H. Photoelectron Spectroscopic study of Dipole-Bound and Valence-Bound Nitromethane Anions formed by Rydberg Electron Transfer. J. Chem. Phys. **2020**, 153, 044307.

(38) Zimmerman, A. H.; Brauman, J. I. Resonances in Electron Photodetachment Cross Section. J. Chem. Phys. 1977, 66, 5823-5825.
(39) Jackson, R. L.; Zimmerman, A. H.; Brauman, J. I. Resonant States at Threshold Observed in Electron Photodetachment Cross Sections of Polyatomic Negative Ions. J. Chem. Phys. 1979, 71, 2088-2094.

(40) Jackson, R. L.; Hiberty, P. C.; Brauman, J. I. Threshold Resonances in the Electron Photodetachment Spectrum of Acetaldehyde Enolate Anion. Evidence for a Low-Lying, Dipole-Supported State. J. Chem. Phys. **1981**, 74, 3705–3712.

(41) Marks, J.; Comita, P. B.; Brauman, J. I. Threshold Resonances in Electron Photodetachment Spectra. Structural Evidence for Dipole-Supported States. J. Am. Chem. Soc. **1985**, 107, 3718–3719.

(42) Lykke, K. R.; Mead, R. D.; Lineberger, W. C. Observation of Dipole-Bound States of Negative Ions. *Phys. Rev. Lett.* **1984**, *52*, 2221–2224.

(43) Mead, R. D.; Lykke, K. R.; Lineberger, W. C.; Marks, J.; Brauman, J. I. Spectroscopy and Dynamics of the Dipole-bound State of Acetaldehyde Enolate. *J. Chem. Phys.* **1984**, *81*, 4883–4892.

(44) Andersen, T.; Lykke, K. R.; Neumark, D. M.; Lineberger, W. C. Autodetachment Study of the Electronic Spectroscopy of FeO⁻. *J. Chem. Phys.* **1987**, *86*, 1858–1867.

(45) Mullin, A. S.; Murray, K. K.; Schulz, C. P.; Szaflarski, D. M.; Lineberger, W. C. Autodetachment Spectroscopy of Vibrationally Excited Acetaldehyde Enolate Anion, CH₂CHO⁻. *Chem. Phys.* **1992**, *166*, 207–213.

(46) Yokoyama, K.; Leach, G. W.; Kim, J. B.; Lineberger, W. C.; Boldyrev, A. I.; Gutowski, M. Autodetachment Spectroscopy and Dynamics of Vibrationally Excited Dipole-Bound States of H_2CCC^- . *J. Chem. Phys.* **1996**, *105*, 10706–10718.

(47) Pino, T.; Tulej, M.; Guthe, F.; Pachkov, M.; Maier, J. P. Photodetachment Spectroscopy of the $C_{2n}H^-$ (n = 2-4) Anions in the Vicinity of Their Electron Detachment Threshold. *J. Chem. Phys.* **2002**, *116*, 6126–6131.

(48) Fortenberry, R. C.; Crawford, T. D. Singlet Excited States of Silicon-Containing Anions Relevant to Interstellar Chemistry. J. Phys. Chem. A 2011, 115, 8119–8124.

(49) Fortenberry, R. C.; Crawford, T. D.; Lee, T. J. The Possible Interstellar Anion CH_2CN^- : Spectroscopic Constants, Vibrational Frequencies, and Other Considerations. *Astrophys. J.* **2013**, *762*, 121. (50) Dessent, C. E.; Bailey, C. G.; Johnson, M. A. Dipole-Bound Excited States of the I⁻CH₃CN and I⁻(CH₃CN)₂ Ion–Molecule Complexes: Evidence for Asymmetric Solvation. *J. Chem. Phys.* **1995**, *103*, 2006–2015.

(51) Dessent, C. E. H.; Kim, J.; Johnson, M. A. Photochemistry of Halide Ion–Molecule Clusters: Dipole-Bound Excited States and the Case for Asymmetric Solvation. *Acc. Chem. Res.* **1998**, *31*, 527–534.

(52) Lecomte, F.; Carles, S.; Desfrancois, C.; Johnson, M. A. Dipole Bound and Valence State Coupling in Argon-Solvated Nitromethane Anions. J. Chem. Phys. **2000**, 113, 10973–10977.

(53) Adams, C. L.; Schneider, H.; Ervin, K. M.; Weber, J. M. Low-Energy Photoelectron Imaging Spectroscopy of Nitromethane Anions: Electron Affinity, Vibrational Features, Anisotropies, and the Dipole-Bound State. J. Chem. Phys. **2009**, *130*, 074307.

(54) Jagau, T. C.; Dao, D. B.; Holtgrewe, N. S.; Krylov, A. I.; Mabbs, R. Same but Different: Dipole-Stabilized Shape Resonances in CuF⁻ and AgF⁻. *J. Phys. Chem. Lett.* **2015**, *6*, 2786–2793.

(55) Mascaritolo, K. J.; Gardner, A. M.; Heaven, M. C. Autodetachment Spectroscopy of the Aluminum Oxide Anion Dipole Bound State. J. Chem. Phys. **2015**, *143*, 114311.

(56) Lyle, J.; Wedig, O.; Gulania, S.; Krylov, A. I.; Mabbs, R. Channel Branching Ratios in CH_2CN^- Photodetachment: Rotational Structure and Vibrational Energy Redistribution in Autodetachment. *J. Chem. Phys.* **2017**, *147*, 234309.

(57) Dobulis, M. A.; Thompson, M. C.; Patros, K. M.; Sommerfeld, T.; Jarrold, C. C. Emerging Nonvalence Anion States of [Isoprene- $H\cdot$]· H_2O Accessed via Detachment of OH^- ·Isoprene. *J. Phys. Chem. A* **2020**, *124*, 2279–2287.

(58) Anstoter, C. S.; Verlet, J. R. R. Gas-Phase Synthesis and Characterization of the Methyl-2,2-Dicyanoacetate Anion Using Photoelectron Imaging and Dipole-Bound State Autodetachment. *J. Phys. Chem. Lett.* **2020**, *11*, 6456–6462.

(59) Anstoter, C. S.; Mensa-Bonsu, G.; Nag, P.; Rankovic, M.; Kumar T. P., R.; Boichenko, A. N.; Fedor, J.; Verlet, J. R. R. Mode-Specific Vibrational Autodetachment Following Excitation of Electronic Resonances by Electrons and Photons. *Phys. Rev. Lett.* **2020**, *124*, 203401.

(60) Lu, Y.; Tang, R.; Ning, C. Observation of an Excited Dipole-Bound State in a Diatomic Anion. J. Phys. Chem. Lett. **2021**, 12, 5897–5902.

(61) Rankovic, M.; Nag, P.; Anstoter, C. S.; Mensa-Bonsu, G.; Kumar T. P., R.; Verlet, J. R. R.; Fedor, J. Resonances in Nitrobenzene Probed by the Electron Attachment to Neutral and by the Photodetachment from Anion. J. Chem. Phys. **2022**, 157, 064302.

(62) Yandell, M. A.; King, S. B.; Neumark, N. M. Decay Dynamics of Nascent Acetonitrile and Nitro-Methane Dipole-Bound Anions Produced by Intracluster Charge-Transfer. *J. Chem. Phys.* **2014**, *140*, 184317.

(63) Li, W. L.; Kunin, A.; Matthews, E.; Yoshikawa, N.; Dessent, C. E. H.; Neumark, D. M. Photodis-sociation Dynamics of the Iodide-Uracil (I-U) Complex. *J. Chem. Phys.* **2016**, *145*, 044319.

(64) Kunin, A.; Neumark, D. M. Time-Resolved Radiation Chemistry: Femtosecond Photoelectron Spectroscopy of Electron Attachment and Photodissociation Dynamics in Iodide-Nucleobase Clusters. *Phys. Chem. Chem. Phys.* **2019**, *21*, 7239–7255.

(65) Bull, J. N.; West, C. W.; Verlet, J. R. R. Ultrafast Dynamics of Formation and Autodetachment of a Dipole-Bound State in an Open-Shell π -Stacked Dimer Anion. *Chem. Sci.* **2016**, *7*, 5352–5361.

(66) Verlet, J. R. R.; Anstoter, C. S.; Bull, J. N.; Rogers, J. P. Role of Nonvalence States in the Ultrafast Dynamics of Isolated Anions. *J. Phys. Chem. A* **2020**, *124*, 3507–3519.

(67) Wang, L. S. Electrospray Photoelectron Spectroscopy: From Multiply-Charged Anions to Ultracold Anions. J. Chem. Phys. 2015, 143, 040901.

(68) Wang, X. B.; Wang, L. S. Development of a Low-Temperature Photoelectron Spectroscopy Instrument Using an Electrospray Ion Source and a Cryogenically Controlled Ion Trap. *Rev. Sci. Instrum.* **2008**, 79, 073108.

(69) León, I.; Yang, Z.; Liu, H. T.; Wang, L. S. The Design and Construction of a High-Resolution Velocity-Map Imaging Apparatus for Photoelectron Spectroscopy Studies of Size-Selected Clusters. *Rev. Sci. Instrum.* **2014**, *85*, 083106.

(70) Wang, L. S.; Ding, C. F.; Wang, X. B.; Barlow, S. E. Photodetachment Photoelectron Spectroscopy of Multiply Charged Anions Using Electrospray Ionization. *Rev. Sci. Instrum.* **1999**, *70*, 1957–1966.

(71) Wang, X. B.; Ding, C. F.; Wang, L. S. Photodetachment Spectroscopy of a Doubly Charged Anion: Direct Observation of the Repulsive Coulomb Barrier. *Phys. Rev. Lett.* **1998**, *81*, 3351–3354.

(72) Wang, X. B.; Wang, L. S. Observation of Negative Electron-Binding Energy in a Molecule. *Nature* **1999**, 400, 245–248.

(73) Wang, X. B.; Woo, H. K.; Wang, L. S. Vibrational Cooling in A Cold Ion Trap: Vibrationally Resolved Photoelectron Spectroscopy of Cold C_{60}^{--} Anions. J. Chem. Phys. **2005**, 123, 051106.

(74) Wang, X. B.; Woo, H. K.; Kiran, B.; Wang, L. S. Observation of Weak C-H. . .O Hydrogen-Bonding by Unactivated Alkanes. *Angew. Chem., Int. Ed.* **2005**, *44*, 4968–4972.

(75) Woo, H. K.; Wang, X. B.; Kiran, B.; Wang, L. S. Temperatures Dependent Photoelectron Spectroscopy of Methyl-Benzoate Anions: Observation of Steric Effect in *Ortho*-Methyl-Benzoate. *J. Phys. Chem. A* **2005**, *109*, 11395–11400.

(76) Dau, P. D.; Liu, H. T.; Huang, D. L.; Wang, L. S. Photoelectron Spectroscopy of Cold UF₅⁻. *J. Chem. Phys.* **2012**, *137*, 116101.

(77) Huang, D. L.; Dau, P. D.; Liu, H. T.; Wang, L. S. High-Resolution Photoelectron Imaging of Cold C_{60}^- Anions and Accurate Determination of the Electron Affinity of C_{60} . J. Chem. Phys. **2014**, 140, 224315.

(78) Zhu, G. Z.; Hashikawa, Y.; Liu, Y.; Zhang, Q. F.; Cheung, L. F.; Murata, Y.; Wang, L. S. High-Resolution Photoelectron Imaging of Cryogenically-Cooled $C_{59}N^{-1}$ and $(C_{59}N)_2^{2-}$ Azafullerene Anions. J. Phys. Chem. Lett. **2017**, 8, 6220–6225.

(79) Zhu, G. Z.; Liu, Y.; Hashikawa, Y.; Zhang, Q. F.; Murata, Y.; Wang, L. S. Probing the Interaction between the Encapsulated Water Molecule and the Fullerene Cages in $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$. *Chem. Sci.* **2018**, *9*, 5666–5671.

(80) Hock, C.; Kim, J. B.; Weichman, M. L.; Yacovitch, T. I.; Neumark, D. N. Slow Photoelectron Velocity-Map Imaging Spectroscopy of Cold Negative Ions. *J. Chem. Phys.* **2012**, *137*, 244201.

(81) Weichman, M. L.; Neumark, D. N. Slow Photoelectron Velocity-Map Imaging of Cryogenically Cooled Anions. Annu. Rev. Phys. Chem. 2018, 69, 101–124.

(82) Liu, H. T.; Ning, C. G.; Huang, D. L.; Dau, P. D.; Wang, L. S. Observation of Mode-Specific Vibrational Autodetachment from Dipole-Bound States of Cold Anions. *Angew. Chem., Int. Ed.* **2013**, *52*, 8976–8979.

(83) Liu, H. T.; Ning, C. G.; Huang, D. L.; Wang, L. S. Vibrational Spectroscopy of the Dehydrogenated Uracil Radical by Autodetachment of Dipole-Bound Excited State of Cold Anions. *Angew. Chem., Int. Ed.* **2014**, *53*, 2464–2468.

(84) Huang, D. L.; Liu, H. T.; Ning, C. G.; Wang, L. S. Vibrational State-Selective Autodetachment Photoelectron Spectroscopy from Dipole-Bound States of Cold 2-Hydroxyphenoxide: o-HO(C₆H₄)O⁻. *J. Chem. Phys.* **2015**, *142*, 124309.

(85) Huang, D. L.; Liu, H. T.; Ning, C. G.; Zhu, G. Z.; Wang, L. S. Probing the Vibrational Spectroscopy of the Deprotonated Thymine Radical by Photodetachment and State-Selective Autodetachment Photoelectron Spectroscopy via Dipole-Bound States. *Chem. Sci.* **2015**, *6*, 3129–3138.

(86) Zhu, G. Z.; Qian, C. H.; Wang, L. S. Dipole-Bound Excited State and Resonant Photoelectron Imaging of Phenoxide and Thiophenoxide Anions. J. Chem. Phys. **2018**, *149*, 164301.

(87) Wigner, E. P. On the Behavior of Cross Sections Near Thresholds. *Phys. Rev.* 1948, 73, 1002–1009.

(88) Schulz, P. A.; Mead, Roy D.; Jones, P. L.; Lineberger, W. C. OH⁻ and OD⁻ Threshold Photodetachment. *J. Chem. Phys.* **1982**, 77, 1153–1165.

(89) Huang, D. L.; Liu, H. T.; Ning, C. G.; Dau, P. D.; Wang, L. S. Resonant Photoelectron Imaging of Deprotonated Uracil Anion via Vibrational Levels of a Dipole-Bound Excited State. *Chem. Phys.* 2017, 482, 374–383.

(90) Berry, R. S. Ionization of Molecules at Low Energies. J. Chem. Phys. **1966**, 45, 1228–1245.

(91) Simons, J. Propensity Rules for Vibration-Induced Electron Detachment of Anions. J. Am. Chem. Soc. **1981**, 103, 3971–3976.

(92) Zhu, G. Z.; Wang, L. S. High-Resolution Photoelectron Imaging and Resonant Photoelectron Spectroscopy via Noncovalently Bound Excited States of Cryogenically Cooled Anions. *Chem. Sci.* **2019**, *10*, 9409–9423.

(93) Qian, C. H.; Zhu, G. Z.; Zhang, Y. R.; Wang, L. S. Photodetachment Spectroscopy and Resonant Photoelectron Imaging of the 2-Naphthoxide Anion via Dipole-Bound Excited States. *J. Chem. Phys.* **2020**, *152*, 214307.

(94) Qian, C. H.; Zhang, Y. R.; Yuan, D. F.; Wang, L. S. Photodetachment Spectroscopy and Resonant Photoelectron Imaging of Cryogenically Cooled 1-Pyrenolate. *J. Chem. Phys.* **2021**, *154*, 094308.

(95) Zhu, G. Z.; Cheung, L. F.; Liu, Y.; Qian, C. H.; Wang, L. S. Resonant Two-Photon Photoelectron Imaging and Intersystem Crossing from Excited Dipole-Bound States of Cold Anions. *J. Phys. Chem. Lett.* **2019**, *10*, 4339–4344.

(96) Zhang, Y. R.; Yuan, D. F.; Qian, C. H.; Wang, L. S. Observation of a Dipole-Bound Excited State in 4-Ethynylphenoxide and

Comparison with the Quadrupole-Bound Excited State in the Isoelectronic 4-Cyanophenoxide. *J. Chem. Phys.* **2021**, *155*, 124305. (97) Yuan, D. F.; Zhang, Y. R.; Qian, C. H.; Zhu, G. Z.; Wang, L. S.

Cryogenic Photodetachment Spectroscopy and High-Resolution Resonant Photoelectron Imaging of Cold *para*-Ethylphenolate Anions. *Precis. Chem.* **2023**, *1*, 161–174.

(98) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. Ultraviolet Photoelectron Spectroscopy of the Phenoxide, Benzyl and Phenoxide Anions with Ab Initio Calculations. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601–620.

(99) Kim, J. B.; Yacovitch, T. I.; Hock, C.; Neumark, D. M. Slow Photoelectron Velocity-Map Imaging Spectroscopy of the Phenoxide and Thiophenoxide Anions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 17378–17383.

(100) Huang, D. L.; Ning, C. G.; Liu, H. T.; Wang, L. S. Conformation-Selective Resonant Photoelectron Spectroscopy via Dipole-Bound States of Cold Anions. *J. Phys. Chem. Lett.* **2015**, *6*, 2153–2157.

(101) Zhu, G. Z.; Huang, D. H.; Wang, L. S. Conformation-Selective Resonant Photoelectron Imaging from Dipole-Bound States of Cold 3-Hydroxyphenoxide. *J. Chem. Phys.* **2017**, *147*, 013910.

(102) Zhu, G. Z.; Qian, C. H.; Wang, L. S. Tautomer-Specific Resonant Photoelectron Imaging of Deprotonated Cytosine Anions. *Angew. Chem., Int. Ed.* **2019**, *58*, 7856–7860.

(103) Bartels, C.; Hock, C.; Huwver, J.; Kuhmen, R.; Schwobel, J.; Issendoff, B. v. Probing the Anguler Momentum Character of the Valence Orbitals of Free Sodium Nanoclusters. *Science* **2009**, 323, 1323–1327.

(104) Johnson, C. J.; Shen, B. B.; Poad, B. L. J.; Continetti, R. E. Photoelectron-Photofragment Coincidence Spectroscopy in a Cryogenically Cooled Linear Electrostatic Ion Beam Trap. *Rev. Sci. Instrum.* **2011**, *82*, 105105.

(105) Best, T.; Otto, R.; Trippel, S.; Hlavenka, P.; Zastrow, A. V.; Eisenbach, S.; Jezouin, S.; Wester, R.; Vigren, E.; Hamberg, M.; Geppert, W. D. Absolute Photodetachment Cross-Section Measurements for Hydrocarbon Chain Anions. *Astrophys. J.* **2011**, 742, 63.

(106) Simpson, M.; Notzold, M.; Michaelsen, T.; Wild, R.; Gianturco, F. A.; Wester, R. Influence of a Supercritcal Electric Dipole Moment on the Photodetachment of C_3N^- . *Phys. Rev. Lett.* **2021**, *127*, 043001.

(107) Zagorec-Marks, W.; Foreman, M. M.; Verlet, J. R. R.; Weber, J. M. Cryogenic Ion Spectroscopy of the Green Fluorescent Protein Chromophore in Vacuo. J. Phys. Chem. Lett. **2019**, *10*, 7817–7822.

(108) Zagorec-Marks, W.; Dodson, L. G.; Weis, P.; Schneider, E. K.; Kappes, M. M.; Weber, J. M. J. Am. Chem. Soc. **2021**, 143, 17778– 17785.

(109) Kregel, S. J.; Thurston, G. K.; Garand, E. Photoelectron Spectroscopy of Anthracene and Fluoranthene Radical Anions. *J. Chem. Phys.* **2018**, *148*, 234306.

(110) Sagan, C. R.; Garand, E. Anion Resonances and Photoelectron Spectroscopy of the Tetracenyl Anion. *J. Phys. Chem. A* **2021**, *125*, 7014–7022.

(111) Noble, J. A.; Marceca, E.; Dedonder, C.; Jouvet, C. Influence of the N Atom and Its Position on Electron Photodetachment of Deprotonated Indole and Azaindole. *Phys. Chem. Chem. Phys.* **2020**, 22, 27290–27299.

(112) Marshall, M.; Zhu, Z.; Harris, R.; Collins, E.; Bowen, K. H. Photoelectron Spectroscopic Study of Ascorbate and Deprotonated Ascorbate Anions Using an Electrospray Ion Source and a Cryogenically Cooled Ion Trap. *J. Phys. Chem. A* **2021**, *125*, 7699–7701.

(113) Lu, Y.; Tang, R.; Fu, X.; Liu, H.; Ning, C. Dipole-Bound and Valence Excited States of AuF Anions via Resonant Photoelectron Spectroscopy. *J. Chem. Phys.* **2021**, *154*, 074303.

(114) Kang, D. H.; An, S.; Kim, S. K. Real-Time Autodetachment Dynamics of Vibrational Feshbach Resonances in a Dipole-Bound State. *Phys. Rev. Lett.* **2020**, *125*, 093001.

(115) Kang, D. H.; Kim, J.; Kim, S. K. Dynamic Role of the Correlation Effect Revealed in the Exceptionally Slow Autodetach-

ment Rates of the Vibrational Feshbach Resonances in the Dipole-Bound State. *Chem. Sci.* 2022, 13, 2714–2720.

(116) Kang, D. H.; Kim, J.; Eun, H. J.; Kim, S. K. State-Specific Chemical Dynamics of the Nonvalence Bound State of the Molecular Anions. *Acc. Chem. Res.* **2022**, *55*, 3032–3042.

(117) Qian, C. H.; Zhu, G. Z.; Wang, L. S. Probing the Critical Dipole Moment to Support Excited Dipole-Bound States in Valence-Bound Anions. *J. Phys. Chem. Lett.* **2019**, *10*, 6472–6477.

(118) Yuan, D. F.; Liu, Y.; Zhang, Y. R.; Wang, L. S. Observation of a Polarization-Assisted Dipole-Bound State. J. Am. Chem. Soc. 2023, 145, 5512–5522.

(119) Zhang, Y. R.; Yuan, D. F.; Qian, C. H.; Zhu, G. Z.; Wang, L. S. The Role of Polarization Interactions in the Formation of Dipole-Bound States. J. Am. Chem. Soc. **2023**, 145, 14952–14962.

(120) Zhang, Y. R.; Yuan, D. F.; Wang, L. S. Probing the Electronic Structure and Spectroscopy of Pyrrolyl and Imidazolyl Radicals Using High-Resolution Photoelectron Imaging of Cryogenically Cooled Anions. *Phys. Chem. Chem. Phys.* **2022**, *24*, 6505–6514.

(121) Yuan, D. F.; Zhang, Y. R.; Qian, C. H.; Wang, L. S. Resonant Two-Photon Photoelectron Imaging and Adiabatic Detachment Processes from Bound Vibrational Levels of Dipole-Bound States. *Phys. Chem. Chem. Phys.* **2022**, *24*, 1380–1389.

(122) Liu, H. T.; Huang, D. L.; Liu, Y.; Cheung, L. F.; Dau, P. D.; Ning, C. G.; Wang, L. S. Vibrational State-Selective Resonant Two-Photon Photoelectron Spectroscopy of AuS⁻ via a Spin-Forbidden Excited State. J. Phys. Chem. Lett. **2015**, *6*, 637–642.

(123) Kang, D. H.; Kim, J.; Kim, S. K. Recapture of the Nonvalence Excess Electron into the Excited Valence Orbital Leads to the Chemical Bond Cleavage in the Anion. *J. Phys. Chem. Lett.* **2021**, *12*, 6383–6388.

(124) Yuan, D. F.; Liu, Y.; Qian, C. H.; Kocheril, S.; Zhang, Y. R.; Rubenstein, B. M.; Wang, L. S. Polarization of Valence Orbitals by the Intramolecular Electric Field from a Diffuse Dipole-Bound Electron. *J. Phys. Chem. Lett.* **2020**, *11*, 7914–7919.

(125) Heimann, P. A.; Becker, U.; Kerkhoff, H. G.; Langer, B.; Szostak, D.; Wehlitz, R.; Lindle, D. W.; Ferrett, T. A.; Shirley, D. A. Helium and Neon Photoelectron Satellites at Threshold. *Phys. Rev. A: At., Mol., Opt. Phys.* **1986**, *34*, 3782–3791.

(126) Czekner, J.; Cheung, L. F.; Kocheril, G. S.; Wang, L. S. Probing the Coupling of a Dipole-Bound Electron with a Molecular Core. *Chem. Sci.* **2019**, *10*, 1386–1391.

(127) Domcke, W.; Yarkony, D. R.; Koppel, H., Eds. Conical Intersections: Theory, Computation and Experiment, Vol. 17; World Scientific: London, 2011.

(128) Domcke, W.; Yarkony, D. R. Role of Conical Intersections in Molecular Spectroscopy and Photoinduced Chemical Dynamics. *Annu. Rev. Phys. Chem.* **2012**, *63*, 325–352.

(129) Schuurman, M. S.; Stolow, A. Dynamics at Conical Intersections. *Annu. Rev. Phys. Chem.* **2018**, *69*, 427–450.

(130) Gianola, A. J.; Ichino, T.; Hoenigman, R. L.; Kato, S.; Bierbaum, V. M.; Lineberger, W. C. Thermochemistry and Electronic Structure of the Pyrrolyl Radical. *J. Phys. Chem. A* **2004**, *108*, 10326–10335.

(131) Gianola, A. J.; Ichino, T.; Hoenigman, R. L.; Kato, S.; Bierbaum, V. M.; Lineberger, W. C. Photoelectron Spectra and Ion Chemistry of Imidazolide. *J. Phys. Chem. A* 2005, *109*, 11504–11514. (132) Gianola, A. J.; Ichino, T.; Kato, S.; Bierbaum, V. M.; Lineberger, W. C. Thermochemical Studies of Pyrazolide. *J. Phys. Chem. A* 2006, *110*, 8457–8466.

(133) Ichino, T.; Andrews, D. H.; Rathbone, G. J.; Misaizu, F.; Calvi, R. M. D.; Wren, S. W.; Kato, S.; Bierbaum, V. M.; Lineberger, W. C. Ion Chemistry of 1*H*-1,2,3-Triazole. *J. Phys. Chem. B* **2008**, *112*, 545–557.

(134) Melin, J.; Mishra, M. K.; Ortiz, J. V. Electronic Structure Analysis and Electron Detachment Energies of Polynitrogen Pentagonal Aromatic Anions. *J. Phys. Chem. A* **2006**, *110*, 12231– 12235.

(135) Dillon, J.; Yarkony, D. R.; Schuurman, M. S. On the Simulation of Photoelectron Spectra Complicated by Conical

Intersections: Higher-Order Effects and Hot Bands in the Photoelectron Spectrum of Triazolide $(CH)_2N_3^-$. J. Chem. Phys. **2011**, 134, 184314.

(136) Zhang, Y. R.; Yuan, D. F.; Wang, L. S. Probing the Strong Nonadiabatic Interactions in the Triazoylyl Radical Using Photodetachment Spectroscopy and Resonant Photoelectron Imaging of Cryogenically Cooled Anions. J. Am. Chem. Soc. **2022**, 144, 16620– 16630.

(137) Yuan, D. F.; Liu, Y.; Qian, C. H.; Zhang, Y. R.; Rubenstein, B. M.; Wang, L. S. Observation of a π -Type Dipole-Bound State in Molecular Anions. *Phys. Rev. Lett.* **2020**, 125, 073003.

(138) Yuan, D. F.; Zhang, Y. R.; Qian, C. H.; Liu, Y.; Wang, L. S. Probing the Dipole-Bound State in the 9-Phenanthrolate Anion by Photodetachment Spectroscopy, Resonant Two-Photon Photoelectron Imaging, and Resonant Photoelectron Spectroscopy. *J. Phys. Chem. A* **2021**, *125*, 2967–2976.

(139) Voora, V. K.; Jordan, K. D. Nonvalence Correlation-Bound Anion States of Polycyclic Aromatic Hydrocarbons. *J. Phys. Chem. Lett.* **2015**, *6*, 3994–3997.

(140) Zhang, Y. R.; Yuan, D. F.; Wang, L. S. Observation of Core-Excited Dipole-Bound States. J. Phys. Chem. Lett. **2022**, 13, 2124– 2129.