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Role of Polarization Interactions in the Formation of Dipole-Bound States

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ABSTRACT: Even though there is a critical dipole moment required to support a dipole-bound state (DBS), how molecular polarizability may influence the formation of DBSs is not well understood. Pyrrolide, indolide, and carbazolide provide an ideal set of anions to systematically examine the role of polarization interactions in the formation of DBSs. Here, we report an investigation of carbazolide using cryogenic photodetachment spectroscopy and high-resolution photoelectron spectroscopy (PES). A polarization-assisted DBS is observed at 20 cm⁻¹ below the detachment threshold for carbazolide, even though the carbazolyl neutral core has a dipole moment (2.2 D) smaller



than the empirical critical value (2.5 D) to support a dipole-bound state. Photodetachment spectroscopy reveals nine vibrational Feshbach resonances of the DBS, as well as three intense and broad shape resonances. The electron affinity of carbazolyl is measured accurately to be 2.5653 ± 0.0004 eV ($20,691 \pm 3$ cm⁻¹). The combination of photodetachment spectroscopy and resonant PES allows fundamental frequencies for 14 vibrational modes of carbazolyl to be measured. The three shape resonances are due to above-threshold excitation to the three low-lying electronic states (S_1 – S_3) of carbazolide. Resonant PES of the shape resonances is dominated by autodetachment processes. Ultrafast relaxation from the S_2 and S_3 states to S_1 is observed, resulting in constant kinetic energy features in the resonant PES. The current study provides decisive information about the role that polarization plays in the formation of DBSs, as well as rich spectroscopic information about the carbazolide anion and the carbazolyl radical.

1. INTRODUCTION

Although anions do not possess Rydberg states, polar anions may support highly diffuse dipole-bound states (DBSs) just below the electron detachment threshold, analogous to Rydberg states, if the neutral cores of the anions have a sufficiently large dipole moment.¹⁻¹¹ DBSs play critical roles in many molecular processes, such as DNA damages by low-energy electrons^{12,13} or as doorways for the formation of valence-bound anions.^{14,15} There have been extensive studies about the critical dipole moment that can support a DBS. Early theoretical studies on stationary dipoles predicted a critical dipole moment of 1.625 D,^{1,2} whereas a value of 2 D was obtained if non-Born-Oppenheimer effects were included.¹⁶⁻²⁰ Experimentally, the minimum dipole moment to form a DBS was empirically observed to be 2.5 D.9,21-24 However, molecules are complex many-body systems and ab initio calculations have shown that polarization and electron correlation effects can play significant roles in the electron binding in DBSs.^{4,11,25,26} Indeed, in a very recent study, we observed a DBS in the indolide anion (Scheme 1) as a result of its large polarizability, even though the dipole moment of the neutral indolyl radical is subcritical (2.4 D).²⁷ On the other hand, no DBS was observed for the smaller pyrrolide anion (Scheme 1) because of the subcritical dipole moment of the pyrrolyl radical (2.2 D).²⁸ An interesting question is if the

Scheme 1. Structures of Pyrrolide, Indolide, and Carbozolide along with the Dipole Moments of the Corresponding Neutral Radicals



carbazolide anion would possess a DBS, despite the fact that the carbazolyl radical has a similar dipole moment to pyrrolyl (Scheme 1) because carbazolyl is much more polarizable. The pyrrolide, indolide, and carbazolide anions, therefore, provide an ideal set of molecular systems to examine systematically the role that molecular polarizability plays in the formation of DBSs.

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Carbazole, present in coal tars, is an important nitrogencontaining heterocyclic aromatic compound.²⁹ Its derivatives have found wide applications in the development of biomedical and optoelectronic materials.^{30–33} Especially, derivatives of carbazole have been considered to be important candidates as liquid organic hydrogen carriers because they can be fully hydrogenated catalytically under relative mild conditions with high hydrogen storage capacities.^{34–36} The spectroscopy and photophysical properties of the carbazole molecule have been investigated extensively both in the condensed phase and in the gas phase.^{37–44} However, relatively little is known about the carbazolyl radical or the carbazolide anion ($C_{12}H_8N^-$, Scheme 1). To the best of our knowledge, there have been no previous reports on the spectroscopy of carbazolide and carbazolyl in the gas phase.

In the current work, we report a photodetachment spectroscopy (PDS) and high-resolution photoelectron (PE) imaging study of cryogenically cooled carbazolide, using our state-of-the-art electrospray ionization photoelectron spectroscopy (ESI-PES) apparatus.45 The electron affinity (EA) of carbazolyl is measured to be 2.5653 ± 0.0004 eV (20,691 ± 3 cm⁻¹) from the high-resolution PES. A polarization-assisted DBS is observed in carbazolide at 20 cm⁻¹ below the detachment threshold from the PDS, which also reveals nine DBS vibrational Feshbach resonances. Three shape resonances are also observed in the PDS at higher excitation energies, due to above-threshold valence excited electronic states of carbazolide. Resonant PES is conducted at the nine Feshbach resonances, yielding rich vibrational information for the carbazolyl radical. The combination of PDS and resonant PES allows the fundamental frequencies of 14 vibrational modes of carbazolyl to be measured. Resonant two-photon detachment (R2PD) via the bound zero-point level of the DBS reveals relaxation from the DBS to the ground state of carbazolide, allowing fundamental frequencies of three vibrational modes of the anion to be measured. The observed shape resonances are due to excitation to the three low-lying electronic states (S1, S2, and S3) of carbazolide. Resonant PE spectra of the three shape resonances are dominated by autodetachment features. Excitations to the S2 and S3 states are found to undergo ultrafast relaxation to the S1 state, yielding constant kinetic energy features in the resonant PES. The current study provides not only decisive information about the important role of polarization in the formation of DBSs but also rich spectroscopic information about the carbazolide anion and the carbazolyl radical.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. Experimental Details. The experiment was carried out using an ESI-PES apparatus, equipped with an ESI ion source,⁴⁶ high-resolution photoelectron imaging,⁴⁷ and a cryogenically cooled 3D Paul trap operated at 4.6 K.⁴⁸ Details of the apparatus and the experimental procedure can be found elsewhere.^{45,49} Briefly, the carbazolide anion was produced by ESI of a solution prepared by dissolving carbazole in the mixed solvent of MeOH/H₂O (9:1 volume ratio) and spiked by NaOH to promote deprotonation. Anions from the ESI source were guided into a cryogenically cooled 3D Paul trap by a series of quadrupole and octupole ion guides. The ion trap was cooled to about 4.6 K by a two-stage closed-cycle helium refrigerator. Anions were accumulated in the ion trap and thermally cooled via collisions with a background gas consisting of ~1 mTorr He/H₂ (4/1 in volume).⁴⁸ After being accumulated and cooled for 0.1 s, the anions were pulsed out at a 10 Hz repetition rate into the extraction zone of a time-of-flight mass spectrometer. The anions were selected by a mass

gate and photodetached in the interaction zone of the imaging lens by a tunable dye laser or the fourth harmonic of a Nd:YAG laser (266 nm). The detachment laser was operated at a repetition rate of 20 Hz to allow shot-by-shot background subtraction. Photoelectrons were projected onto a pair of 75 mm diameter microchannel plates coupled to a phosphor screen. Photoelectron images were captured by a charge-coupled device camera and were inverse-Abel-transformed using pBasex and BASEX.^{50,51} The photoelectron images were calibrated using the Au⁻ atomic anion at different photon energies. The kinetic energy (KE) resolution was 3.8 cm^{-1} for electrons with 55 cm⁻¹ KE and ~1.5% (Δ KE/KE) for KE above 1 eV.⁴⁷ Photoelectron spectra were taken near the detachment threshold to allow accurate measurement of the EA of the carbazolyl radical, and at higher photon energies to provide well-resolved PE spectra to be compared with Franck-Condon (FC) simulations. PDS was conducted by scanning the laser wavelength across the detachment threshold at a step size of 0.1 nm and monitoring the total electron yield. A finer scanning step of 0.01 nm was used to determine the excitation energies more accurately for the observed resonant peaks. Resonant PE spectra were taken at the peak positions observed in the PD spectrum.

2.2. Theoretical Calculations. Geometry optimization and frequency calculations for the ground state of carbazolyl and carbazolide were performed using density functional theory (DFT) at the B3LYP/6-311 ++ g(d,p) level of theory. All of the calculated vibrational frequencies (Tables S1 and S2) were scaled by a factor of 0.98 for comparison with the experimental measurements. The FC factors from the anion ground state to vibrational levels of the neutral were calculated using FC-LAB2⁵² with the optimized geometries and computed vibrational frequencies (scaled by a factor of 0.98). The vertical excitation energies (VEEs) to the excited electronic states of carbazolyl were obtained using time-dependent DFT (TD-DFT) at the B3LYP/def2TZVPP level of theory. The VEEs for the excited states of the carbazolide anion were obtained using ab initio calculations performed at the EOMCCSD/aug-cc-PVTZ level of theory. The anion geometry was pre-optimized at the MP2/aug-cc-PVTZ level of theory. All of the DFT and TD-DFT calculations were performed using the Gaussian 09 package.53

3. RESULTS

3.1. 266 nm Photoelectron Spectrum and the Electronic Structure of Carbazolide. The carbazolide anion has not been studied by PES previously; its PE spectrum and detachment threshold are not known. To obtain a global view of the electronic structure of carbazolide, we first measured its PE spectrum at a relatively high photon energy of 266 nm (4.661 eV), as shown in Figure 1. Three broad detachment bands are observed. The low binding energy features between 2.5 and 3 eV (\tilde{X}) correspond to the detachment transition from the ground state of carbazolide to that of the carbazolyl radical. The two weaker detachment bands at ~3.5 eV (\tilde{A}) and ~4.4 eV (\tilde{B}) represent detachment



Figure 1. Photoelectron image and spectrum of carbazolide at 266.0 nm (4.661 eV). The inset shows the structure of carbazolide. The double arrow below the image represents the polarization direction of the detachment laser.

transitions to the first two excited states of carbazolyl. The valence molecular orbitals (MOs) that give rise to the three detachment bands are shown in Figure S1. We also computed the VEEs for the two excited states of carbazolyl, compared with the experimental data in Table S3, where the anisotropic parameter (β) for each detachment band is also given. The computed VEEs for the \tilde{A} and \tilde{B} bands from TD-DFT are in reasonable agreement with the experimental data (Table S3). Both bands are weak and featureless, suggesting strong nonadiabatic vibronic couplings.^{27,28,54} All three valence MOs are π orbitals, which should produce s + d partial waves for the outgoing electrons. The angular distributions of the three detachment bands are relatively isotropic with small β values, consistent with the nature of the MOs.

3.2. High-Resolution Photoelectron Spectra of Carbazolide at Low Photon Energies. To better resolve the vibrational features for the carbazolyl ground state (\tilde{X}) , we tuned the detachment laser to lower photon energies and obtained high-resolution photoelectron images and spectra of carbazolide, as presented in Figure 2. The spectrum shown in



Figure 2. Photoelectron images and spectra of carbazolide at (a) 2.5666 eV (20,701 cm⁻¹) and (b) 2.8139 eV (22,696 cm⁻¹). The blue curve in (b) shows the FC simulation based on the anion and neutral geometries calculated at the B3LYP/6-311 ++ g(d,p) level of theory. Six FC-active features are marked with capital letters A to F. The double arrow below the images indicates the direction of the laser polarization.

Figure 2a is taken at 2.5666 eV (20,701 cm^{-1}) near the detachment threshold, yielding a high-resolution 0_0^0 transition with a full width at half-maximum (FWHM) of 0.0004 eV. This transition defines an accurate EA for the carbazolyl radical as 2.5653 ± 0.0004 eV (20,691 ± 3 cm⁻¹). The spectrum displayed in Figure 2b at 2.8139 eV (22,696 cm⁻¹) represents the detachment transition from the ground state of carbazolide to a broader FC region of the carbazolyl ground electronic state, resolving numerous weak vibrational features (A-F). The high-resolution spectrum is in good agreement with the FC simulation, as shown in Figure 2b. The 0_0^{0} peak displays a clear s + d angular distribution with a β value of -0.29, consistent with the π HOMO of carbazolide (Figure S1). Many of the vibrational features are better resolved in the resonant PES (vide infra). The BEs of all of the observed PES features are given in Table S4, along with the spectral

assignments and comparison with the calculated frequencies. There is not much FC activity, probably because there is relatively little geometry change between the ground states of carbazolide and carbazolyl. The most FC-active mode is the ν_{20} mode (Table S4), which gives rise to a short vibrational progression including peaks A (ν_{20}^{-1}) and B (ν_{20}^{-2}). The ν_{20} mode is an in-plane scissor mode of the two phenyl rings (Figure S2), which is the lowest totally symmetric mode of carbazolyl (Table S1).

3.3. Photodetachment Spectroscopy of Carbazolide. To find if carbazolide possesses a DBS, we conducted PDS for carbazolide by scanning the laser wavelength across the detachment threshold and monitoring the total electron yield as a function of photon energy, as shown in Figure 3. The



Figure 3. Photodetachment spectrum of carbazolide from 20,500 cm⁻¹ (2.5417 eV) to 25,500 cm⁻¹ (3.1616 eV). The detachment threshold was marked by the blue arrow. A weak peak below the detachment threshold is observed corresponding to the zero-point level of the DBS and marked with 0. A total of 9 sharp peaks corresponding to the vibrational levels of the DBS were labeled as 1–9. The broad bands (R₁–R₃) are shape resonances.

existence of a DBS is evidenced by the weak transition below the detachment threshold (peak 0) and nine sharp peaks above threshold (peaks 1-9). The PDS exhibits a step at the detachment threshold of 20,691 cm⁻¹, consistent with the Wigner threshold law,⁵⁵ because the π HOMO of carbazolide (Figure S1) is expected to yield s + d partial waves for the outgoing photoelectrons. The continuous signals beyond the detachment threshold are due to nonresonant photodetachment processes. The below-threshold peak 0 at 20,671 cm⁻¹ (2.5629 eV) should correspond to the zero-point level of the DBS, observed due to R2PD processes. The separation between peak 0 and the detachment threshold defines a binding energy of 20 ± 3 cm⁻¹ for the DBS. The nine abovethreshold sharp peaks observed between 20,500 and 22,150 cm⁻¹ are due to excitations to the vibrational levels of the DBS, followed by vibrationally induced autodetachment. These above-threshold vibrational excitations are also known as vibrational Feshbach resonances.

In addition, three broad and giant resonant bands centered at 23,506 cm⁻¹ (2.9144 eV), 24,170 cm⁻¹ (2.9967 eV), and 249,17 cm⁻¹ (3.0893 eV) are also observed in the photodetachment spectrum at higher photon energies (Figure 3) and are labeled as R_1 , R_2 , and R_3 , respectively. These bands should be due to transitions to unbound valence excited states of carbazolide, which are also known as shape resonances. The large spectral width suggests that the transition is lifetimebroadened. Thus, there are no well-resolved vibronic structures in these bands. The laser wavelengths and photon energies of the nine Feshbach resonances and the three shape resonances are presented in Table S5.

4. DISCUSSION

4.1. Polarization-Assisted DBS in Carbazolide. The dipole moment of the carbazolyl radical is calculated to be 2.2 D, which is smaller than the empirically determined critical dipole moment of 2.5 D for supporting a DBS.^{9,21-24} In a recent study, the indolide anion was observed to possess a DBS with a 6 cm⁻¹ binding energy due to polarization interactions²⁷ because the indolyl radical has a subcritical dipole moment of 2.4 D. The carbazolyl radical has a calculated isotropic polarizability of 162.3 Bohr³, which is much larger than that of the indolyl radical (98.8 Bohr³). Thus, the DBS observed in carbazolide should be considered to be a new example of polarization-assisted DBS. The much larger polarizability of the carbazolyl radical is responsible for the larger DBS binding energy (20 cm^{-1}) relative to that in indolide (6 cm^{-1}) , even though the dipole moment of carbazolyl (2.2 D) is smaller than that of indolyl (2.4 D). It should be pointed out that no DBS was observed for pyrrolide $(C_4H_4N^{-})^{28}$ because of the small polarizability of the pyrrolyl radical (47.8 Bohr³), despite the fact that its dipole moment (2.2 D) is comparable to that of carbazolyl (Scheme 1). The addition of one and two benzene rings in indolyl and carbazolyl, respectively, in comparison with pyrrolyl, successively increases their polarizability and the DBS binding energy. These results provide systematic and quantitative experimental evidence for the important role that polarizability plays in the formation of DBS in large and highly polarizable molecules. It is interesting to note that nonvalence anionic states due to polarization/ correlation effects have been observed in water clusters and the para-toluquinone trimer.4,56-5

4.2. Resonant Two-Photon Detachment via the Zero-Point Level of the DBS. The zero-point level of the DBS (peak 0 in Figure 3) at 20,671 cm⁻¹ (2.5629 eV) is bound and long-lived, allowing us to conduct one-color R2PD PE imaging with our nanosecond dye laser. The R2PD PE image and spectrum are shown in Figure 4. Two types of PE spectral



Figure 4. R2PD image and spectrum taken at the zero-point level of the DBS at 20,671 cm⁻¹ (2.5629 eV), peak 0 in Figure 3. The inset shows an expanded view of the high BE features from 2.2 to 2.6 eV. The double arrow below the image indicates the laser polarization.

features are observed, indicating two different R2PD processes. The low BE feature (labeled "DBS") is observed by first exciting the anion to the zero-point level of the DBS. A second photon within the same laser pulse then detaches the dipolebound electron, producing a high KE photoelectron, i.e., the outermost ring in the PE image in Figure 4. The position of the "DBS" feature is consistent with the very small binding energy of the DBS measured more accurately from the PD spectrum in Figure 3 (20 cm⁻¹). The PE image of the "DBS" feature displays a *p*-wave distribution ($\beta = 0.9$), consistent with the expected σ -type DBS orbital. The "DBS" feature is very weak, due to relaxation processes that take place from the bound zero-point level within the detachment laser pulse (~5 ns), giving rise to the high BE features (labeled "S₀").

The high BE features in the R2PD PE spectrum correspond to low KE electrons, seen as the bright central spot in the PE image in Figure 4. These signals are derived from the photodetachment of vibrationally excited carbazolide in its ground electronic state (S_0) populated by relaxation from the zero-point level of the DBS within the 5 ns detachment laser pulse. Such relaxation processes have been observed often in R2PD PE spectra from bound DBS levels.⁵⁹⁻⁶¹ Five distinct peaks (labeled as a_a to e_a , where the subscript a indicates anion) are resolved, as shown more clearly in the inset of Figure 4. These features can be readily assigned using the calculated vibrational frequencies of carbazolide (Table S2, Figure S3), as given in Table S6. These features allow the frequencies of three vibrational modes of the carbazolide anion in its ground state (S_0) to be determined. The measured frequencies are compared with the computed frequencies in Table S7.

4.3. Resonant PES via the Feshbach Resonances of the DBS. By tuning the detachment laser to the nine vibrational Feshbach resonances, we obtained nine resonant PE images and spectra, as shown in Figure 5. These spectra are derived from one-photon resonant excitation to specific vibrational levels of the DBS, followed by autodetachment as a result of coupling the vibrational energy to the dipole-bound electron. Because the dipole-bound electron has little effect on the neutral core, the vibrational autodetachment follows the $\Delta v = -1$ propensity rule in the harmonic approximation,^{62,63} resulting in mode selectivity in the autodetachment process.⁶⁴ For example, for the autodetachment from a vibrational level of $\nu_x''\nu_y'''$ of the DBS (the prime ' designates vibrational levels of the DBS), the final neutral state can be either $\nu_x^{n-1}\nu_y^m$ or $\nu_x^n \nu_y^{m-1}$, which will be strongly enhanced in the resonant PE spectra, though mode-dependent vibronic coupling is commonly observed.^{49,64} Hence, the Feshbach resonances can be assigned readily by comparing the resonant PE spectra with the nonresonant PE spectra. Furthermore, because the dipole-bound electron has little effect on the neutral core, the vibrational frequencies of the DBS have been observed to be the same as in the neutral within our experimental accuracy, 49,64,65 as clearly shown by the similarity between the PD spectrum and the PE spectrum of carbazolide presented in Figure S4. Therefore, the PD spectrum can be combined with the resonant PE spectra to yield much richer and more accurate vibrational information for the neutral carbazolyl radical.⁴⁹ This has been shown to be a powerful spectroscopic approach, made possible by our ability to create cold anions using a cryogenically cooled Paul trap.^{45,48}

4.4. Assignments of the Resonant PE Spectra and the Feshbach Resonances. Compared to the nonresonant PE spectrum shown in Figure 2b, the resonant PE spectra in Figure 5 are all highly non-Franck–Condon, where one or more vibrational peaks are enhanced (labeled in boldface) due to vibrational autodetachment from the DBS. Even though the nonresonant photodetachment process still occurs, the resonant excitation followed by autodetachment dominates the resonant PE spectra. Furthermore, many new vibrational

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Figure 5. Resonant photoelectron images and spectra of carbazolide at the nine Feshbach resonances. (a) 20,884 cm⁻¹ (2.5893 eV), (b) 21,101 cm⁻¹ (2.6162 eV), (c) 21,325 cm⁻¹ (2.6440 eV), (d) 21,381 cm⁻¹ (2.6509 eV), (e) 21,434 cm⁻¹ (2.6575 eV), (f) 21,542 cm⁻¹ (2.6709 eV), (g) 21,815 cm⁻¹ (2.7047 eV), (h) 22,047 cm⁻¹ (2.7335 eV), and (i) 22,082 cm⁻¹ (2.7378 eV). The wavelengths and the corresponding assignments to the DBS levels from Table S5 are also given. The double arrows below the images indicate the direction of the laser polarization.

peaks are observed in the resonant PE spectra, as labeled with the lowercase letters a to o, as a result of both the higher spectral resolution and the high sensitivity of resonant excitation.

Peak 1 in the PDS is the strongest Feshbach resonance, corresponding to the most FC-active $20'^1$ (Figures 3 and S4), which results in the enhanced 0-0 transition in the resonant PE spectrum (Figure 5a) following the $\Delta v = -1$ autodetachment propensity rule. A very weak peak a (38¹) is also observed in Figure 5a, suggesting that the intense peak 1 in the PDS may also contain a very weak excitation to the 38^{'2} DBS level, which is close to $20^{\prime 1}$ in energy. The ν_{38} mode is the lowest-frequency bending mode of carbazolyl (Figure S2) and the 38'² DBS level is symmetry-allowed. Peak 2 in the PD spectrum corresponds to excitation to the 20'² DBS level, resulting in the strongly enhanced A peak (20^1) in Figure 5b. A new weak peak c $(20^{1}38^{1})$ is also observed in Figure 5b, indicating that peak 2 in the PD spectrum also contains a weak contribution from the $20'^{1}38'^{2}$ DBS level. Peak 3 is the second strongest Feshbach resonance, which gives rise to a strong new peak h (28^2) , suggesting the excitation to the $28'^2 38'^1$ DBS level followed by the coupling of the $38'^1$ vibrational quantum to the

dipole-bound electron during autodetachment. The weak new peak d (28¹38¹) also comes from the same DBS level via coupling of one 28' quantum during autodetachment. The ν_{38}' mode clearly has much stronger coupling with the dipole-bound electron to yield the dominant final state h (28²). Such mode-dependent vibronic coupling is common in autodetachment from DBS, which was first observed in phenoxide⁶⁴ and has been probed directly by pump-probe experiments.⁶⁶ The enhanced peak B (20²) indicates that peak 3 also contains a small contribution of the 20'³ DBS level of the most FC-active mode. The observation of a new peak b (37¹) and g (20¹37¹) in Figure 5c suggests that the strong peak 3 also contains a weak excitation to the 20'¹29'¹37'¹ DBS level. The appearance of peak b violates the $\Delta v = -1$ propensity rule, which can happen due to anharmonicity⁶² and is often observed for low-frequency bending modes.^{49,67}

Figure 5d displays a strongly enhanced 0-0 transition due to excitation to the $34'^1$ DBS level. However, the strongly enhanced peak C (28^238^1) is a surprise because it cannot come from autodetachment of any DBS level. Peak C is near the detachment threshold, and its anomalous intensity is likely due to threshold enhancement. The appearances of the strong



Anion Ground State

Figure 6. Schematic energy level diagram for autodetachment from the DBS vibrational Feshbach resonances of carbazolide to the related neutral final states, corresponding to the nine resonant PE spectra presented in Figure 5. The relaxation from the zero-point level of the DBS during R2PD experiment (Figure 4) is also shown schematically.

threshold peak k (17¹) in Figure 5e and peak F (9¹) in Figure 5i are probably due to similar threshold enhancement. In addition to the strong peak k, several enhanced peaks are observed in Figure 5e, indicating that peak 5 in the PD spectrum contains overlapping DBS levels, as given in Figure 5e and Table S5. The DBS levels that give rise to the weak peaks e (36¹) and j (34¹) are not explicitly assigned. They could come from complicated combinational DBS levels involving low-frequency vibrational modes. Complicated overlapping vibrational levels become more likely with increasing excitation energies for such a large molecular system.

The three enhanced peaks in Figure 5f are all due to excitation to the $20'^{1}28'^{2}38'^{1}$ DBS level (peak 6 in Figure 3). The enhancement of the intense peak C ($28^{2}38^{1}$) and the new peak l ($20^{1}28^{2}$) follows the $\Delta v = -1$ propensity rule, via coupling of the $20'^{1}$ and $38'^{1}$ vibrational quantum to the

dipole-bound electron, respectively, whereas the appearance of peak *a* (38¹) violates the propensity rule. The resonant PE spectrum at peak 7 (Figure 5g) reveals several enhanced final vibrational states, where peaks $f(20^{1}28^{1})$, **D** ($18^{1}20^{1}$), and m ($18^{1}28^{1}$) all come from autodetachment from the same $18'^{1}20'^{1}28'^{1}$ combinational DBS level, obeying the $\Delta v = -1$ propensity rule. The new peak n (52^{1}) comes from autodetachment from the same todetachment from an overlapping DBS level, $29'^{1}52'^{1}$, which exhibits a strong mode-dependent autodetachment because the 52' mode has negligible coupling with the dipole-bound electron to produce an enhanced 29^{1} final state. Peak *e* is not explicitly assigned here, similar to the peaks *e* and *j* in Figure 5e mentioned above.

The resonant PE spectrum in Figure 5h exhibits the most complicated vibrational features, suggesting peak 8 in the PD spectrum also contains several overlapping DBS levels. The appearances of peak f (20¹28¹), peak i (37²), and peak o



Figure 7. Photoelectron spectra taken at the shape resonances corresponds to peaks R_1 , R_2 , and R_3 in Figure 3: (a) 23,506 cm⁻¹ (2.9144 eV), (b) 24,170 cm⁻¹ (2.9967 eV), and (c) 24,917 cm⁻¹ (3.0893 eV). The spectra (d)–(f) are plotted according to the electron kinetic energies.

 $(20^128^237^1)$ are all due to excitation to the $20^{\prime\,1}28^{\prime\,2}37^{\prime\,2}$ combinational DBS level, where the autodetachment that gives rise to peaks f and i does not obey the propensity rule. The intense peak m (18¹28¹) indicates that the resonant peak 8 also contains major contributions from either the $18'^{1}19'^{1}28'^{1}$ or $18'^{1}27'^{1}28'^{1}$ DBS level. Modes ν_{19} and ν_{27} cannot be distinguished because they have similar calculated frequencies: 424 cm⁻¹ for ν_{19} and 425 cm⁻¹ for ν_{27} (Table S1). Peak B is due to the 20^2 final state. However, the enhanced peak B in Figure 5h should be due to either 19^1 or 27^1 from autodetachment from the 18'19'128'1 or 18'127'128'1 DBS level because 20^2 and $19^1/27^1$ have similar energies. The strong peak E (12^1) in Figure 5h suggests excitation to the $12'^{1}38'^{2}$ DBS level. Finally, the 0-0 transition in Figure 5h is also slightly enhanced relative to peak A, suggesting that the $9'^1$ DBS level is excited. Thus, peak 8 in the PD spectrum contains excitations to at least four overlapping vibrational levels of the DBS, consistent with its relatively high intensity. The resonant PE spectrum in Figure 5i displays two strongly enhanced peaks: $f(20^{1}28^{1})$ and $m(18^{1}28^{1})$, which are due to excitation to the 18'120'128'2 DBS level. The autodetachment processes that give rise to f and m both violate the $\Delta v = -1$ propensity rule, which happens more frequently for highly excited vibrational levels of the DBS or complicated combinational levels.

As shown in Figure 3, no distinct Feshbach resonances are observed beyond peak 9, consistent with the short FC progression in the high-resolution PE spectrum (Figures 2b and S4), due to the small geometry change between the ground state of carbazolide and that of the carbazolyl radical. The detailed assignments of the nine Feshbach resonances in the PD spectrum are given in Table S5, and the corresponding autodetachment processes are shown in Figure 6, where the relaxation from the bound zero-point level of the DBS to the ground electronic state (S_0) of carbazolide is also indicated. The populated S_0 vibrational levels, as detected from the R2PD PE spectrum (Figure 4), are also given in Figure 6. A total of

14 fundamental vibrational frequencies are measured for the carbazolyl radical from the combination of PDS and rPES, as summarized in Table S7 and compared with the computed frequencies.

4.5. Shape Resonances and Their Ultrafast Relaxation **Processes.** The strong and broad features $(R_1 - R_2)$ in the PD spectrum (Figure 3) should be due to excitation to abovethreshold valence excited states, which are temporary anion states, also known as shape resonances. Such temporary anion states are often observed in electron scattering off neutral molecules⁶⁸⁻⁷⁰ but have also been observed in photodetachment of anions.⁷¹⁻⁷⁵ We have observed a shape resonance in the PDS of cryogenically cooled 1-pyrenolate anions previously,⁷⁶ which is much broader and has much higher oscillator strength in comparison to the DBS, similar to the shape resonances shown in Figure 3 for carbazolide. Such temporary anion states are observed sometimes in PES, yielding non-FC PES features due to autodetachment.75-Time-resolved PE imaging has been used to probe the dynamics of such temporary anion states.⁸⁰⁻⁸² PDS, on the other hand, yields more precise energetic information and essentially represents the solvent-free electronic absorption spectroscopy for the underlying anions. The R₁ band centered at 23,506 cm⁻¹ is very likely the first excited electronic state of carbazolide (S_1) , while the weaker R_2 band centered at 24,710 cm^{-1} is probably the second excited electronic state (S₂). The R₃ band is very broad, which may contain multiple electronic states or vibronic transitions. The most intense part of R₃ is centered at 24,917 cm⁻¹. The excitation energies of these three bands are given in Table S5 along with the Feshbach resonances, where they are compared with theoretical calculations to be discussed later.

We have taken resonant PE spectra at the excitation energies of R_1 , R_2 , and R_3 , as presented in Figure 7a-c. These spectra should be dominated by autodetachment from the excited electronic states of the carbazolide anion. Indeed, the observed vibrational features in the spectrum taken at R_1 (Figure 7a) are

quite different from those in the nonresonant spectrum shown in Figure 2b because the FC profile of the resonant spectrum should be determined by the geometry change from the excited electronic state to the neutral final state. The binding energies of the five prominent vibrational peaks in the resonant spectrum (labeled as $r_1 - r_5$ in Figure 7a) are given in Table S8, along with their tentative assignments using the computed vibrational frequencies of carbazolyl (Table S1). The spectra taken at R₂ and R₃ are very different, both showing the 0-0 transition similar to the nonresonant PE spectrum, with a very strong peak labeled as α followed by some vibrational fine features. These spectra should contain contributions from both the nonresonant photodetachment processes as represented by the 0-0 transition and the much stronger autodetachment processes represented by the strong α peak and the following vibrational features. Interestingly, if we plot the three spectra in electron kinetic energies (Figure 7d-f), we find that the autodetachment features in the resonant PE spectra at the R₂ and R₃ shape resonances are exactly the same as the resonant PE spectrum taken at R₁. In fact, this similarity is displayed more strikingly already in the PE images: the strongest peak in the three images has the same radius (same KE) and the same angular distribution. This observation suggests that all the autodetachment takes place from the same temporary anion state represented by R₁, even for the higher-photon-energy shape resonances. The R₁ feature is presumably the lowest excited electronic state (S_1) of carbazolide. The same autodetachment features shown in Figure 7 imply that the initial excitation to the excited electronic states above S₁ undergoes ultrafast relaxation to the S1 state first, followed by autodetachment from S₁ to the neutral carbazolyl ground state. We took several resonant PE spectra at different photon energies across the broad R₃ band and observed similar spectral features to those shown in Figure 7c.

To gain further insight into the nature of the shape resonances, we computed the VEEs for the low-lying singlet excited electronic states of carbazolide at the EOMCCSD/augcc-PVTZ level of theory using anion geometries optimized at the MP2/aug-cc-PVTZ level of theory, as summarized in Table S9. We found three low-lying singlet excited states, which are close in energy to the observed shape resonances R_1 to R_3 , compared in Table S5. The dominant characters of the three resonances are all due to excitations from the HOMO to different LUMOs (Table S9), confirming their shape resonance nature. The S_1 state $({}^1B_1)$ has a computed VEE of 3.06 eV, which should correspond to R_1 with an excitation energy of 2.914 eV. The S_2 state (¹A₂) with a computed VEE of 3.17 eV is assigned to R₂ at 2.997 eV. This state has no computed oscillator strength (Table S9), consistent with the relatively low intensity of R₂. The R₃ shape resonance is quite broad and is assigned to the S_3 state $\binom{1}{B_1}$ with a computed VEE of 3.31 eV. Our experimental observations in Figure 7 suggest that relaxation from the S_2 or S_3 state to the S_1 state is faster than autodetachment. Such ultrafast relaxation processes imply that there may be strong vibronic couplings between the S_2/S_3 states and the S_1 state via conical interactions, as observed in the shape resonances of the p-benzoquinone anion.⁸⁰ On the other hand, the S_1 state is long-lived, relative to autodetachment. The nature of these temporary anion states and the competition between relaxation and autodetachment in carbazolide are interesting to be further investigated theoretically and experimentally. Pump-probe experiments have been used to directly investigate the dynamics of shape

resonances and Feshbach resonances in anions.^{66,74,80–84} Carbazolide would be an excellent candidate for this type of experiment, in light of the current spectroscopic findings.

5. CONCLUSIONS

In conclusion, we have found a polarization-assisted dipolebound excited state in the carbazolide anion below its detachment threshold, despite the fact that the carbazolyl radical has a subcritical dipole moment. Photodetachment spectroscopy of cryogenically cooled carbazolide revealed a binding energy of 20 cm⁻¹ for the dipole-bound state and nine vibrational Feshbach resonances, as well as three shape resonances. High-resolution photoelectron imaging yielded an accurate electron affinity of 2.5653 ± 0.0004 eV (or 20,691 \pm 3 cm⁻¹) for the carbazolyl radical. Resonant photoelectron spectroscopy at the Feshbach resonances in combination with the photodetachment spectrum allowed the measurement of fundamental vibrational frequencies for 14 vibrational modes of the carbazolyl radical. The three shape resonances are assigned to the first three above-threshold singlet valence excited states of the carbazolide anion $(S_1 \text{ to } S_3)$. Ultrafast relaxation from the S₂ or S₃ shape resonances to the S₁ state was observed, followed by autodetachment from S₁. Along with pyrrolide and indolide, the current study on carbazolide allows a systematic understanding about the role of polarization in the stabilization of dipole-bound states. The current work also suggests that the carbazolide anion is an excellent system to investigate the ultrafast relaxation processes and the competition between nonadiabatic relaxation and autodetachment from highly excited shape resonances.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c04740.

Valence molecular orbitals of carbazolide; normal modes of vibration of carbazolyl and carbazolide; detailed calculated results; detailed binding energies and assignments of all of the resolved vibronic levels of carbazolyl and carbazolide; detailed photon energies and assignments of all of the observed Feshbach resonances and shape resonances; and observed vibrational modes for carbazolyl and carbazolide (PDF)

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Notes

The authors declare no competing financial interest.

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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) Desfrançois, C.; Abdoul-Carime, H.; Schermann, J. P. Ground-State Dipole-Bound Anions. *Int. J. Mod. Phys. B* 1996, *10*, 1339–1395.
(4) Jordan, K. D.; Wang, F. Theory of Dipole-Bound Anions. *Annu.*

Rev. Phys. Chem. 2003, 54, 367-396.
(5) Zimmerman, A. H.; Brauman, J. I. Resonances in Electron Photodetachment Cross Section. J. Chem. Phys. 1977, 66, 5823-5825.
(6) 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.

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

(8) 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.

(9) Compton, R. N.; Hammer, N. I. Multiple-Bound Molecular Anions. In *Advances in Gas Phase Ion Chemistry*, Elsevier Science, 2001; Vol. 5, pp 257–305.

(10) 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.

(11) Simons, J. Molecular Anions. J. Phys. Chem. A 2008, 112, 6401–6511.

(12) Boudaïffa, 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.

(13) Burrow, P. D.; Gallup, G. A.; Scheer, A. M.; et al. Vibrational Feshbach Resonances in Uracil and Thymine. *J. Chem. Phys.* 2006, *124*, No. 124310.

(14) Mikulski, P.; Klahn, T.; Krebs, P. Excess Electron Mobility in Low Density CH₃CN Gas: Short-Lived Dipole-Bound Electron Ground States as Precursors of Localized Electron States. *Phys. Rev.* A **1997**, 55, 369–377.

(15) 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.

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

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

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

(19) Garrett, W. R. Critical Binding and Electron Scattering by Symmetric-Top Polar Molecules. J. Chem. Phys. 2014, 141, No. 164318.

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

(21) Desfrançois, C.; Abdoul-Carime, 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.

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

(23) Smith, B. H.; Buonaugurio, A.; Chen, J.; Collins, E.; Bowen, K. H.; Compton, R. N.; Sommerfeld, T. Negative Ions of *p*-Nitroaniline: Photodetachment, Collisions, and *ab initio* Calculations. *J. Chem. Phys.* **2013**, *138*, No. 234304.

(24) 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.

(25) Gutowski, M.; Skurski, P.; Boldyrev, A. I.; Simons, J.; Jordan, K. D. Contribution of Electron Correlation to the Stability of Dipole-Bound Anionic States. *Phys. Rev. A* **1996**, *54*, 1906–1909.

(26) Sommerfeld, T.; Davis, M. C. Excluded-Volume Descriptors for Dipole-Bound Anions: Amine N-Oxides as a Test Case. J. Chem. Phys. **2020**, 152, No. 054102.

(27) 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.

(28) 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.

(29) Joule, J. A. Recent Advances in the Chemistry of 9H-Carbazoles. In Advances in Heterocyclic Chemistry, 1984; Vol. 35, pp 83–198.

(30) Schmidt, A. W.; Reddy, K. R.; Knolker, H. J. Occurrence, Biogenesis, and Synthesis of Biologically Active Carbazole Alkaloids. *Chem. Rev.* **2012**, *112*, 3193–3328.

(31) Yin, J. L.; Ma, Y. Y.; Li, G. H.; Peng, M.; Lin, W. Y. A Versatile Small-Molecule Fluorescence Scaffold: Carbazole Derivatives for Bioimaging. *Coord. Chem. Rev.* **2020**, *412*, No. 213257.

(32) Wex, B.; Kaafarani, B. R. Perspective on Carbazole-Based Organic Compounds as Emitters and Hosts in TADF Applications. J. Mater. Chem. C 2017, 5, 8622–8653.

(33) Sathiyan, G.; Sivakumar, E. K. T.; Ganesamoorthy, R.; Thangamuthu, R.; Sakthivel, P. Review of Carbazole Based Conjugated Molecules for Highly Efficient Organic Solar Cell Application. *Tetrahedron Lett.* **2016**, *57*, 243–252.

(34) Papp, C.; Wasserscheid, P.; Libuda, J.; Steinruck, H.-P. Liquid Organic Hydrogen Carriers: Surface Science Studies of Carbazole Derivatives. *Chem. Rec.* **2014**, *14*, 879–896.

(35) Zhou, L.; Sun, L.; Xu, L.; Wan, C.; An, Y.; Ye, M. Recent Development of Effective Catalysts for Hydrogen Storage Technology Using N-Ethylcarbazole. *Catalysts* **2020**, *10*, 648.

(36) Chen, X.; Li, G.; Gao, M.; Dong, Y.; Yang, M.; Cheng, H. Wet-Impregnated Bimetallic Pd-Ni Catalysts with Enhanced Activity for Dehydrogenation of Perhydro-N-Propylcarbazole. *Int. J. Hydrogen Energy* **2020**, *45*, 32168–32178.

(37) Bree, A.; Zwarich, R. Absorption Spectrum of Carbazole in a Fluorene Matrix. J. Chem. Phys. **1968**, 49, 3355–3358.

(38) Martin, M.; Breheret, E.; Tfibel, F.; Lacourbas, B. Two-Photon Stepwise Dissociation of Carbazole in Solution. *J. Phys. Chem. A* **1980**, *84*, 70–72.

(39) Purkayastha, P.; Bera, S. C.; Chattopadhyay, N. Ground and Excited State Proton Transfer of Some Carbazole Derivatives: A Linear Correlation between the Acidity Constant and Charge Density on the Deprotonation Centre. J. Mol. Liq. 2000, 88, 33–42.

(40) Knochenmuss, R.; Leutwyler, S. Selective Spectroscopy of Rigid and Fluxional Carbazole-Argon Clusters. J. Chem. Phys. **1990**, 92, 4686-4697.

(41) Auty, A. R.; Jones, A. C.; Phillips, D. Spectroscopy and Decay Dynamics of Jet-Cooled Carbazole and N-Ethylcarbazole and Their Homocyclic Analogs. *Chem. Phys.* **1986**, *103*, 163–182.

(42) Hiyoshi, R.; Hiura, H.; Sakamoto, Y.; Mizuno, M.; Sakai, M.; Takahashi, H. Time-Resolved Absorption and Time-Resolved Raman Spectroscopies of the Photochemistry of Carbazole and N-Ethylcarbazole. J. Mol. Struct. 2003, 661-662, 481–489.

(43) Nguyen, D. D.; Trunk, J.; Nakhimovsky, L.; Spanget-Larsen, J. Electronic Transitions of Fluorene, Dibenzofuran, Carbazole, and Dibenzothiophene: From the Onset of Absorption to the Ionization Threshold. *J. Mol. Spectrosc.* **2010**, *264*, 19–25.

(44) Sekine, M.; Sekiya, H.; Nakata, M. Infrared and Electronic Spectra of Radicals Produced from 2-Naphthol and Carbazole by UV-Induced Hydrogen-Atom Eliminations. *J. Phys. Chem. A* **2012**, *116*, 8980–8988.

(45) Wang, L. S. Perspective: Electrospray Photoelectron Spectroscopy: From Multiply-Charged Anions to Ultracold Anions. *J. Chem. Phys.* **2015**, *143*, No. 040901.

(46) 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.

(47) 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*, No. 083106.

(48) 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*, No. 073108.

(49) 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.

(50) Garcia, G. A.; Nahon, L.; Powis, I. Two-Dimensional Charged Particle Image Inversion Using a Polar Basis Function Expansion. *Rev. Sci. Instrum.* **2004**, *75*, 4989–4996.

(51) Dribinski, V.; Ossadtchi, A.; Mandelshtam, V. A.; Reisler, H. Reconstruction of Abel-Transformable Images: The Gaussian Basis-Set Expansion Abel Transform Method. *Rev. Sci. Instrum.* **2002**, *73*, 2634–2642.

(52) Pugliesi, I.; Müller-Dethlefs, K. The Use of Multidimensional Franck-Condon Simulations to Assess Model Chemistries: A Case Study on Phenol. J. Phys. Chem. A 2006, 110, 4657–4667.

(53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji. et al.*Gaussian 09*, Rev. D.01. Gaussian, Inc.: Wallingford, CT, 2016.

(54) 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.

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

(56) Sommerfeld, T.; Jordan, K. D. Electron Binding of $(H_2O)_n^-$ Clusters. J. Am. Chem. Soc. 2006, 128, 5828–5833.

(57) Verlet, J. R. R.; Bragg, A. E.; Kammrath, A.; Cheshnovsky, O.; Neumark, D. M. Observation of Large Water-Cluster Anions with Surface-Bound Excess Electrons. *Science* **2005**, 307, 93–96.

(58) Bull, J. N.; Verlet, J. R. R. Observation and Ultrafast Dynamics of a Nonvalence Correlation–Bound State of an Anion. *Sci. Adv.* **2017**, *3*, No. e1603106.

(59) 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.

(60) 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*, No. 124305.

(61) 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.

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

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

(64) 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.

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

(66) 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*, No. 093001.

(67) 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.

(68) Jordan, K. D.; Burrow, P. D. Temporary Anion States of Polyatomic Hydrocarbons. *Chem. Rev.* **1987**, *87*, 557–588.

(69) Tobita, S.; Meinke, M.; Illenberger, E.; Christophorou, L. G.; Baumgartel, H.; Leach, S. Polyatomic Aromatic Hydrocarbons: Negative Ion Formation Following Low Energy (0-15 eV) Electron Impact. *Chem. Phys.* **1992**, *161*, 501–508.

(70) Hotop, H.; Ruf, M.-W.; Allan, M.; Fabrikant, I. I. Resonances and Threshold Phenomena in Low-Energy Electron Collisions with Molecules and Clusters. *Advances In Atomic, Molecular, and Optical Physics*, 2003; *110*, 85–216.

(71) Schiedt, J.; Weinkauf, R. Resonant Photodetachment via Shape and Feshbach Resonances: *p*-Benzoquinone Anions as a Model System. *J. Chem. Phys.* **1999**, *110*, 304–314.

(72) Bailey, C. G.; Dessent, C. E. H.; Johnson, M. A.; Bowen, K. H. Vibronic Effect in the Photon Energy-Dependent Photoelectron Spectra of the CH_3CN^- Dipole-Bound Anion. J. Chem. Phys. **1996**, 104, 6976–6983.

(73) Adams, C. L.; Knurr, B. J.; Weber, J. M. Photoelectron Spectroscopy of 1-Nitropropane and 1-Nitrobutane Anions. *J. Chem. Phys.* **2012**, *136*, No. 064307.

(74) Stephansen, A. B.; King, S. B.; Yokoi, Y.; Minoshima, Y.; Li, W. L.; Kunin, A.; Takayanagi, T.; Neumark, D. M. Dynamics of Dipoleand Valence Bound Anions in Iodide Binary Complexes: A Time-Resolved Photoelectron Imaging and Quantum Mechanical Investigation. J. Chem. Phys. **2015**, 143, No. 104308.

(75) Jalehdoost, A.; von Issendorff, B. Photon Energy Dependence of the Photoelectron Spectra of the Anthracene Anion: On the Influence of Autodetaching States. *J. Chem. Phys.* **2023**, *158*, No. 194302.

(76) 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*, No. 094308.

(77) Wang, X. B.; Ding, C. F.; Wang, L. S. High Resolution Photoelectron Spectroscopy of C_{60} . J. Chem. Phys. **1999**, 110, 8217–8220.

(79) Li, J.; Li, X.; Zhai, H. J.; Wang, L. S. Au₂₀: A Tetrahedral Cluster. *Science* 2003, 299, 864–867.

(80) Horke, D. A.; Li, Q.; Blancafort, L.; Verlet, J. R. R. Ultrafast Above-Threshold Dynamics of the Radical Anion of a Prototypical Quinone Electron-Acceptor. *Nat. Chem.* **2013**, *5*, 711–717.

(81) Anstöter, C. S.; Bull, J. N.; Verlet, J. R. R. Ultrafast Dynamics of Temporary Anions Probed Through the Prism of Photodetachment. *Int. Rev. Phys. Chem.* **2016**, *35*, 509–538.

(82) Ashworth, E. K.; Anstor, C. S.; Verlet, J. R. R.; Bull, J. N. Autodetachment Dynamics of 2-Naphthoxide and Implications for Astrophysical Anion Abundance. *Phys. Chem. Chem. Phys.* **2021**, *23*, 5817–5823.

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

(84) 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.

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