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Letter

Observation of Core-Excited Dipole-Bound States

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ABSTRACT: Polar molecules can bind an electron in a diffuse orbital due to the chargedipole interaction. Electronic excited states of polar molecules can also bind an electron to form core-excited dipole-bound states (DBSs), analogous to core-excited Rydberg states. However, core-excited DBSs have not been observed because of the complicated electronic structure of molecular systems. Here, we report the observation of a core-excited DBS in the pyrazolide anion as a result of the favorable electronic structure of the neutral pyrazolyl core, which has a low-lying excited state (\tilde{A}^2B_1) only 266 cm⁻¹ above its ground state (\tilde{X}^2A_2). The binding energy of the DBS associated with the ground state is measured to be 221 cm⁻¹, while that of the core-excited DBS is 276 cm⁻¹, which is still a bound state relative to the detachment threshold. Vibrational Feshbach resonances are observed for both DBSs, and their autodetachment behaviors are studied by resonant photoelectron imaging.



D ydberg series exist as electronically excited states for Rineutral atoms and molecules and converge on ionic states. Because of the strong, long-range, and tunable interactions, Rydberg atoms offer an ideal platform for quantum simulation experiments and are good candidates to study many-body phenomena.¹⁻³ Alkaline-earth Rydberg atoms have received increasing attention,^{4,5} because the second valence electron offers the possibility of engineering long-lived doubly excited states via long-range interactions between the weakly bound Rydberg electron and the valence electron in the ionic core, providing an additional degree of freedom to probe and manipulate Rydberg atoms. In addition to quantum simulation, core-excited Rydberg states have been proposed to play an important role in the understanding of autoionizing Rydberg series and the development of multichannel spectroscopy and plasma science.^{6,7}

Analogous to Rydberg states in neutral molecules, molecular anions with polar neutral cores ($\mu > \sim 2.5$ D) can support highly diffuse dipole-bound states (DBSs) just below the detachment threshold due to the long-range charge-dipole attraction $(\sim -1/r^2)$. Since first considered by Fermi and Teller,⁸ DBS has attracted persistent experimental and theoretical attention.⁹⁻²⁴ DBSs play significant roles in electron scattering of polar molecules, DNA damage by lowenergy electrons, and anion formation in the interstellar medium under astronomical environments.^{25–28} Very recently, π -type DBSs with angular nodes in the wave functions were observed in cryogenically cooled anions.²⁹⁻³¹ In analogy with the core-excited Rydberg states, core-excited DBSs should also exist. However, the dipole bound electron is generally considered as a quasi-free electron and supposed to be uncoupled with the electrons of the neutral core,³² thus making it extremely challenging to observe core-excited DBSs spectroscopically. While core-excited nonvalence bound states have been implicated previously,³³ recently, Li et al. studied the dissociative electron attachment (DEA) of three peptide molecules and attributed some of the DEA features to coreexcited dipole-supported resonances.³⁴ However, this interpretation has been challenged,³⁵ and the DEA features have been shown recently to be due to Feshbach resonances,³⁶ in which the incoming electron excites a valence electron to the same orbital that the incoming electron resides. Thus, the question is can core-excited DBSs exist. What would be their spectroscopic signatures?

In principle, every electronic state of a neutral molecule with a sufficiently large dipole moment can support a DBS. However, typical molecules can have complex electronic states, making it difficult to disentangle core-excited DBSs among the complicated molecular vibronic structures. An ideal system would be a neutral molecule with an excited state that is close to the ground state such that its DBS may be below the neutral ground state to allow unambiguous spectroscopic identification and characterization. The highly polar pyrazolyl radical ($C_3H_3N_{22}$ see Figure 1) may fulfill this requirement. It is a five-membered heterocyclic compound with two nitrogen atoms directly bonded to each other in the ring. The electronic structures of pyrazolyl and the electron detachment energies of the corresponding pyrazolide anion have been studied extensively.^{37–40} The pyrazolyl neutral radical (\tilde{X}^2A_2) is

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Figure 1. (a) The near-threshold photoelectron image and spectrum at 416.75 nm (2.9750 eV) and (b) nonresonant photoelectron images and spectrum at 400.25 nm (3.0977 eV) of the pyrazolide anion.

known to display a low-lying excited state (\hat{A}^2B_1) with an excitation energy of only $32 \pm 1 \text{ meV} (258 \pm 8 \text{ cm}^{-1})$ as measured by anion photoelectron spectroscopy (PES).³⁹ A schematic energy level for photodetachment from pyrazolide to the low-lying electronic states of pyrazolyl is shown in Figure S1. The pyrazolyl radical has a dipole moment of 3.8 D, and the \hat{A}^2B_1 excited state has a dipole moment of 4.6 D,⁴¹ which are both higher than the critical value to support a DBS.⁴² The very small energy separation between the \tilde{X}^2A_2 and \tilde{A}^2B_1 states provides an opportunity to observe a coreexcited DBS in the pyrazolide anion near the detachment threshold and possibly even as a bound state.

Here, we use PES, photodetachment spectroscopy (PDS), and resonant PES (rPES) of cryogenically cooled anions to search for the core-excited DBS in pyrazolide. Besides the expected conventional DBS, which is 221 cm⁻¹ below the detachment threshold of the neutral ground state (\tilde{X}^2A_2), a core-excited DBS for the \tilde{A}^2B_1 state is observed with a binding energy of 276 cm⁻¹. Thirteen Feshbach resonances are detected in the PDS and assigned to transitions from the anion ground state to the vibronic levels of the two DBSs. In addition to vibrational autodetachment, in which the vibrational energy of the neutral core in the DBS is coupled to the dipole-bound electron, the electronic energy of the coreexcited DBS is also observed to couple to the dipole-bound electron. More surprisingly, we have observed electronic excitation of pyrazolyl by the dipole-bound electron associated with the ground state, demonstrating strong correlations between the dipole-bound electron and the valence electrons.

The experiment was carried out using an electrospray PES apparatus⁴³ equipped with a cryogenically cooled 3D Paul trap⁴⁴ and a high-resolution photoelectron (PE) imaging system.⁴⁵ The pyrazolide anions were produced by electrospray of a 1 mM solution of pyrazole (Sigma-Aldrich, 98%) in a mixed solvent of CH₃OH/H₂O (9/1 in volume) at pH ~ 10. Anions generated in the electrospray ionization source were guided into a cryogenically cooled 3D Paul trap operated at 4.6K.^{43,44} After being accumulated for 0.1 s and thermally cooled via collision with 1 mTorr He/H₂ (4/1 in volume) background gas,⁴⁴ the anions were pulsed out at a 10 Hz repetition rate into the extraction zone of a time-of-flight mass spectrometer. The pyrazolide anions were selected by a mass gate and photodetached in the interaction zone of the imaging

lens by a tunable dye laser. Photoelectrons were projected onto a pair of 75 mm diameter microchannel plates coupled to a phosphor screen and captured by a charge-coupled-device camera. The photoelectron (PE) images were inverse-Abel transformed and reconstructed using the programs pBasex⁴⁶ and BASEX.⁴⁷ The PE spectra were calibrated with the known spectra of Au⁻ at different photon energies. The kinetic energy (KE) resolution was 3.8 cm⁻¹ for electrons with 55 cm⁻¹ KE and about 1.5% (Δ KE/KE) for KE above 1 eV in the current experiment.⁴⁴

The near-threshold and nonresonant PE spectra of pyrazolide were shown in Figure 1. Peaks a and b in Figure 1a define an accurate electron affinity (EA) (peak a) and the binding energy for the \tilde{A}^2B_1 state (peak b) of pyrazolyl to be $2.9361 \pm 0.0025 \text{ eV} (23,681 \pm 20 \text{ cm}^{-1}) \text{ and } 2.9691 \pm 0.0011$ eV (23,947 \pm 9 cm⁻¹), respectively. The energy separation between these two peaks is measured to be 0.0330 eV (266 cm⁻¹), slightly more accurate than that reported previously.³⁵ In the nonresonant PE spectrum taken at the higher photon energy (Figure 1b), six more peaks are observed (e-g, i-k), which are due to vibrational excitations of the \tilde{X}^2A_2 and \tilde{A}^2B_1 states. The relative intensity of peak b is observed to be significantly enhanced in the near threshold spectrum (Figure 1a). The binding energies and assignments of all the observed peaks are summarized in Table S1, where the shifts to peaks a and b, the anisotropy parameters (β) , and the theoretical vibrational frequencies are also given. The peaks are assigned according to the theoretical frequencies and nonadiabatic simulations.^{37,40} Even though the three low-lying states (Figure S1) are strongly coupled to each other, we are able to assign all the vibronic peaks, as a result of the high spectral resolution and the angular distributions (β values). Peaks f and k are assigned to the \tilde{X}^2A_2 state, corresponding to the detachment from the highest occupied molecular orbital (HOMO) of pyrazolide (Figure S2). Peaks e_i , g_i , i_j , and j are assigned to the \tilde{A}^2B_1 state, corresponding to detachment from the HOMO-1.

To search for the anticipated DBSs, we scanned the wavelength of the detachment laser and monitored the total electron yield (Figure 2). The arrows, $\tilde{X}EA$ at 23,681 cm⁻¹ and $^{\tilde{A}}EA$ at 23,947 cm⁻¹, represent the detachment thresholds of



Figure 2. Photodetachment spectrum of the pyrazolide anion. The axes on the top are used to indicate the shifts relative to peaks ${}^{\bar{X}}0$ (up) and ${}^{\bar{A}}0$ (below).

the X^2A_2 and the A^2B_1 states, respectively, measured from the PE spectra in Figure 1. The step-like features at the onsets of the two electronic states follow the Wigner threshold law,⁴⁸ because the HOMO and HOMO-1 are both π -type orbitals (Figure S2), resulting in (s+d)-wave photoelectrons. The above-threshold resonances (1-13) confirmed the existence of DBSs, and they should correspond to the vibrational levels of the DBSs (i.e., vibrational Feshbach resonances). The two weak peaks, labeled as ^x0 and ^A0, were observed below threshold at 23,460 cm⁻¹ (2.9087 eV) and 23,671 cm⁻¹ (2.9348 eV), respectively. Peak ^X0 represents the detachment transition to the ground vibrational level of a DBS, because there are no more transitions observed below this peak. The energy separation between $\tilde{X}0$ and $\tilde{A}0$ is 211 cm⁻¹, much smaller than the lowest vibrational frequency for pyrazolyl,^{37,40} i.e., peak ^A0 cannot be assigned to a vibrational level of the same DBS as peak ^x0. Therefore, peaks ^x0 and ^A0 must correspond to the zero-point levels of two different DBSs with the neutral core in the ground and the first excited states. Peak 1 at 23,829 cm⁻¹ is the most intense Feshbach resonance, and it should correspond to a vibrational level of the DBS associated with the $\tilde{X}^2 A_2$ state. The separation between peak 1 and the ^A0 peak is only 158 cm⁻¹, ruling out the ^A0 peak_as the zero-point level for the DBS of the \tilde{X}^2A_2 state. Thus, the ^X0 and ^A0 peaks should correspond to the zero-point levels of the DBSs associated with the \tilde{X}^2A_2 and $\tilde{A}_2^2B_1$ states, respectively. The shift of peak \tilde{x} 0 to the threshold \tilde{x} EA, 221 cm⁻¹, defines the binding energy of the DBS for the \tilde{X}^2A_2 state, and the shift of peak ^Ã0 to the threshold ^ÃEA, 276 cm⁻¹, defines the binding energy of a DBS for the excited state (A^2B_1) . The difference in the binding energies of the two DBSs is consistent with the slightly larger dipole moment of pyrazolyl in the A^2B_1 excited state.⁴¹ The increased baseline above the thresholds in Figure 2 is due to contributions from single-photon nonresonant detachment processes. The detachment cross section to the A^2B_1 final state is observed to be larger than that to the X^2A_2 state since the step at ^AEA is higher than the step at ^XEA, consistent with the relative intensities of peaks a and b in Figure 1. The 13 Feshbach resonances (1-13) are due to excitations to vibronic levels of the DBSs, followed by autodetachment. The excitation wavelengths and photon energies of all the observed vibronic peaks and their shifts relative to the zero-point levels of the two DBSs are summarized in Table S2, where their assignments and comparison with theoretical frequencies are also given.

The assignments of the Feshbach resonances were assisted by rPES, as presented in Figure 3 and Figure S3. In general, two detachment processes contribute to the rPES: 1) nonresonant photodetachment represented by the enhanced baseline in the PDS and 2) resonantly enhanced autodetachment via vibrational levels of the DBSs. It should be noted that three additional peaks, c, d, and h, are observed in the rPES compared with the nonresonant spectra in Figure 1. On the basis of their binding energies and previous nonadiabatic simulations, 37,40 c and d are assigned to features derived from vibronic coupling with the second excited electronic state $\tilde{B}^2 B_{2}$, whereas h is assigned to the ν_7 mode of the X^2A_2 ground state. These additional peaks are very weak in the simulations or negligible in the nonresonant PES but are significantly enhanced in the rPES at certain detachment wavelengths, as shown in Figures S3a and S3b and Figure 3d.

Figure 3a shows the resonant PE spectrum at peak 1 in Figure 2, representing excitation to the X12'1 vibrational level



Figure 3. Resonant PE images and spectra of pyrazolide at (a) 419.66 nm (2.9544 eV), (b) 413.47 nm (2.9986 eV), (c) 407.16 nm (3.0451 eV), and (d) 405.92 nm (3.0544 eV). The enhanced peaks are labeled in boldface. The wavelengths and the assignments of the DBS vibrational levels are given, as well as the peak numbers from Figure 2 in the parentheses. The double arrow below the images indicates the laser polarization.

of the DBS for the \tilde{X}^2A_2 ground state. The prime denotes the vibrational mode of the DBS, while the superscript on the left indicates the origin of the DBS (either the \tilde{X}^2A_2 state or the core-excited $\tilde{A}^2 B_1$ state). Coupling of the vibrational energy to the dipole-bound electron induces autodetachment, resulting in the enhanced 0–0 transition (peak *a*) of the \tilde{X}^2A_2 state, according to the $\Delta v = -1$ propensity rule.^{49–52} The observation of the intense $\tilde{X}12'^1$ vibrational peak of the DBS was surprising, possibly a result of the strong vibronic coupling in the neutral core.^{37,40} The resonant PE spectrum in Figure 3b is assigned to the excitation of the $^{x}11^{71}$ level of the DBS. However, peak b (the zero-point level of A^2B_1) is also enhanced, in addition to the expected enhancement of the zero-point level of \tilde{X}^2A_2 (peak *a*). This observation means that the vibrational energy in $\frac{x}{11}$ is not only coupled to the dipole-bound electron but can also excite the neutral core to the \tilde{A}^2B_1 state, another manifestation of strong electron correlations between the dipole-bound electron and the valence electrons in the pyrazolyl core. Similar autodetachment behavior is also observed in other resonant PE spectra (Figures S3a, S3b, and S3f). The resonant PE spectrum shown in Figure 3c is due to excitation to the $^{A}9'^{3}$ vibrational level (8 in Figure 2) of the core-excited DBS. Coupling of one quantum of the ν_{9} mode to the dipole-bound electron leads to the

enhancement of peak $g({}^{\tilde{A}}9^2)$, following the $\Delta \nu = -1$ propensity rule. The peak $e({}^{\tilde{A}}9^1)$ also shows some enhancement in Figure 3c, indicating two quanta of the ν_9' mode are coupled to the dipole-bound electron. This violation of the $\Delta \nu = -1$ propensity rule could happen due to anharmonic effects.⁴⁹ A similar situation was also observed in Figures S3c and S3f.

The appearance of the extra peaks c in Figure S3a and d in Figure S3b suggests strong vibronic couplings in the neutral core because these two peaks could only be assigned to features due to couplings with the second excited state \tilde{B}^2B_2 of pyrazolyl, as shown in the nonadiabatic simulations.^{37,40⁻} In addition, the enhancement of peak k (x_{51}) in Figure S3i indicates both the vibrational and electronic energies of the core-excited DBS are coupled to the dipole-bound electron, as well as the ν_5 mode of the X^2A_2 state (Figure S4), another indication of the strong vibronic interactions between the first two electronic states of pyrazolyl. Combinational vibronic levels of the DBSs were also observed, as shown in the resonant PE spectra of Figure 3d and Figures S3c and S3f-S3i. Because of accidental degeneracies, such as 5^1 and the combination level 8^19^1 of the \tilde{A}^2B_1 state, some Feshbach resonances (4, 9, 10, and 11) in the PDS could be assigned to more than one vibrational level. The unexpected enhancement of peak $h(^{X}7^{1})$ in Figure 3d might be due to the coupling between different vibrational modes in the \tilde{X}^2A_2 state. A similar enhancement is also observed for peak $g(^{A}9^{2})$ in Figure 3d and peak j (^A8¹) in Figures S3h and S3i. Some near threshold peaks in the resonant spectra appear to be enhanced, probably due to the threshold effects, 48 such as peak f in Figure S3c and peak g in Figure S3e. The enhancement of peak g in Figure S3f may also be due to the overlap of the Feshbach resonances 9 and 8 (Figure 2). Assignments of the observed Feshbach resonances are summarized in Table S2. The autodetachment corresponding to Figure 3 is shown in Figure 4, and the complete autodetachment for all 13 Feshbach resonances is shown in Figure S4.

Tuning the detachment laser to the bound zero-point levels of the DBSs, ^X0 and ^A0 in Figure 2, we obtained R2PD images and spectra of pyrazolide via the ground vibrational states of the two DBSs, as shown in Figure S5. An intense peak at the high binding energy end is observed, labeled as peaks α and γ in Figures S5a and S5b, respectively, in addition to several weak vibrational peaks in Figure S5b. These signals are attributed to detachment from the excited vibrational levels of the anion ground state, populated due to relaxation from the DBSs, ⁵³ after absorption of the first photon. The peaks α and γ are assigned to the detachment transition from the 8_a^{1} vibrational level of pyrazolide (the subscript a is used to denote the vibrational level of the anion ground state) to the ${}^{\tilde{X}}11^1$ and ${}^{\tilde{A}}18^1$ levels of the neutral pyrazolyl, respectively, as summarized in Table S3 and Figure S4. We note that no sequential R2PD signals were detected, probably because of the relative short lifetimes of the DBSs, compared to the pulse width of the detachment laser (~ 5 ns). Thus, firm evidence is provided for the observation of a core-excited DBS in the pyrazolide anion. In general, there should be a manifold of DBSs associated with the electronic states of polar neutral molecules. However, such core-excited DBSs are challenging to be observed spectroscopically, because of the complex electronic structures of molecular systems in comparison to the core-excited Rydberg atoms.^{4,5}



Figure 4. Schematic energy level diagram for autodetachment from the vibrational levels of the ground state and core-excited DBSs of pyrazolide to the related neutral final states, corresponding to the four resonant PE spectra shown in Figure 3. Neutral states are labeled in black, and DBSs are labeled in blue. The EAs of the two electronic states of pyrazolyl and the binding energies of their DBSs are also given. For the \tilde{X}^2A_2 state, the observed vibrational modes ν_5 and ν_7 have a_1 symmetry; ν_{11} and ν_{12} have b_1 symmetry. For the \tilde{A}^2B_1 state, the ν_9 mode has a_2 symmetry and the ν_{11} mode has b_1 symmetry.

In conclusion, we report the first observation of a coreexcited DBS in the pyrazolide anion with the neutral core in the \tilde{A}^2B_1 electronically excited state, in addition to the DBS with the neutral core in the ground electronic state. The unique low-lying electronic excited state of pyrazolyl makes it ideal for observing the core-excited DBS. The binding energies of the DBS for the ground state and the core-excited DBS are measured to be 221 and 276 cm⁻¹, respectively. Thirteen Feshbach resonances are observed due to excitations to the vibronic levels of the two DBSs. The study of core-excited DBSs is important for understanding resonances in molecular anions and the electron capture mechanisms by polar neutral molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c00275.

Theoretical details, schematic energy diagram showing photodetachment from ground state of pyrazolide anion to first three electronic states of pyrazolyl radical as well as corresponding anion valence molecular orbitals, additional resonant photoelectron spectra, full schematic energy level diagram for autodetachment processes, resonant two-photon photoelectron spectra, and assignments of all observed peaks in nonresonant, resonant, and photodetachment spectra (PDF)

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Notes

The authors declare no competing financial interest.

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