# Photodetachment spectroscopy and resonant photoelectron imaging of cryogenically cooled 1-pyrenolate

Cite as: J. Chem. Phys. **154**, 094308 (2021); https://doi.org/10.1063/5.0043932 Submitted: 12 January 2021 . Accepted: 15 February 2021 . Published Online: 04 March 2021

🔟 Chen-Hui Qian, 🔟 Yue-Rou Zhang, 🔟 Dao-Fu Yuan, and 🔟 Lai-Sheng Wang



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The Journal of Chemical Physics 154, 074303 (2021); https://doi.org/10.1063/5.0038560

Photodetachment spectroscopy and resonant photoelectron imaging of the 2-naphthoxide anion via dipole-bound excited states

The Journal of Chemical Physics 152, 214307 (2020); https://doi.org/10.1063/5.0011234

Ultrafast excited state dynamics of provitamin D<sub>3</sub> and analogs in solution and in lipid bilayers

The Journal of Chemical Physics 154, 094309 (2021); https://doi.org/10.1063/5.0041375





J. Chem. Phys. **154**, 094308 (2021); https://doi.org/10.1063/5.0043932 © 2021 Author(s).

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# Photodetachment spectroscopy and resonant photoelectron imaging of cryogenically cooled 1-pyrenolate

Cite as: J. Chem. Phys. 154, 094308 (2021); doi: 10.1063/5.0043932 Submitted: 12 January 2021 • Accepted: 15 February 2021 • Published Online: 4 March 2021

Chen-Hui Qian, 🔟 Yue-Rou Zhang, 🔟 Dao-Fu Yuan, ២ and Lai-Sheng Wang<sup>a)</sup> 问

#### AFFILIATIONS

Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

<sup>a)</sup>Author to whom correspondence should be addressed: Lai-Sheng\_Wang@brown.edu

#### ABSTRACT

We report an investigation of the 1-pyrenolate anion ( $PyO^{-}$ ) and the 1-pyrenoxy radical (PyO) using photodetachment spectroscopy and resonant photoelectron imaging of cryogenically cooled anions. The electron affinity of PyO is measured to be 2.4772(4) eV ( $19\,980 \pm 3 \text{ cm}^{-1}$ ) from high-resolution photoelectron spectroscopy. Photodetachment spectroscopy reveals a dipole-bound state (DBS) for  $PyO^{-}$  280 cm<sup>-1</sup> below the detachment threshold as well as a broad and intense valence excited state (shape resonance) 1077 cm<sup>-1</sup> above the detachment threshold. The shape resonance with an excitation energy of 21 055 cm<sup>-1</sup> is due to excitation of an electron from the highest occupied molecular orbital of  $PyO^{-}$  to its lowest unoccupied molecular orbital in the continuum. Twenty-nine vibrational levels of the DBS are observed, including 27 above-threshold vibrational levels (vibrational Feshbach resonances). Twenty-seven resonant photoelectron spectra are obtained by tuning the detachment laser to the vibrational Feshbach resonances, resulting in highly non-Franck–Condon photoelectron spectra and rich vibrational information. In total, the frequencies of 21 vibrational modes are obtained for the PyO radical by the combination of the photodetachment and resonant photoelectron spectroscopy, including 13 out-of-plane bending modes.

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#### I. INTRODUCTION

The 1-hydroxypyrene (PyOH) molecule is one of the alcohol derivatives of pyrene, a common polycyclic aromatic hydrocarbon (PAH), and it is known to be a major metabolite of pyrene upon exposure to PAHs by humans.<sup>1</sup> Due to the constant presence and relatively high concentration of pyrene in all PAHs that humans are usually exposed to, the urinary PyOH concentration is a widely used biomarker to estimate the total PAH exposure.<sup>2–4</sup> Thus, PyOH has attracted wide interest from chemists, biologists, and physiologists, and a variety of sensors have been developed for its quick detection.<sup>5–7</sup> Because of their interesting electronic and photophysical properties, pyrene and its derivatives have also been extensively studied as a class of materials for organic electronics.<sup>8,9</sup> Furthermore, PyOH, PyO<sup>–</sup> [see the inset in Fig. 1(a) for a structure model] and the PyO radical are also of astronomical interest. It has been shown that these species can be formed under vacuum ultraviolet

irradiation of PAH–ice mixtures known to exist in both interstellar and circumstellar environments, indicating the possible existence of these species in the interstellar medium.<sup>10,11</sup>

The photophysics of PyOH is interesting. Even though PyOH is known to be a weak acid with a  $pK_a$  of 8.93, its excited state is a much stronger acid with a  $pK_a$  of 4.5.<sup>12</sup> The pyrenoxy (PyO) radical is also important and it is prevalent in many thermochemical and photochemical processes involving PyOH and PAHs.<sup>10–13</sup> The PyO radical, along with other aromatic-oxy radicals, may also be involved in soot formation during hydrocarbon combustion.<sup>14</sup> However, there is little known about the energetics and spectroscopy of the PyO radical. We have developed a high-resolution photoelectron imaging apparatus coupled with an electrospray ionization (ESI) source and a cryogenically cooled ion trap,<sup>15</sup> which has allowed photodetachment spectroscopy (PDS) and resonant photoelectron spectroscopy (rPES) to be conducted on cold anions from solution samples.<sup>16</sup> We have demonstrated that the combination of PDS and rPES is a



**FIG. 1**. Photoelectron spectra of  $PyO^-$  at (a) 496.20 nm (2.4987 eV), (b) 484.70 nm (2.5580 eV), and (c) 479.20 nm (2.5873 eV). The resolved vibrational peaks are marked by uppercase letters. A Franck–Condon simulation at the B3LYP/6-311++G\*\* level of theory is shown in (c) (blue bars). The double arrow below the photoelectron images indicates the laser polarization direction. The inset in (a) shows the molecular structure of  $PyO^-$ .

powerful approach to obtain energetic and spectroscopic information for polar molecules or radicals, which can support dipole-bound states (DBSs) in the underlying anions.  $^{16-22}$ 

In this article, we report a PDS and rPES study on PyO<sup>-</sup> and PyO, which has a large dipole moment to support a DBS. The electron affinity (EA) of the PyO radical is measured to be 2.4772(4) eV (19980  $\pm$  3 cm<sup>-1</sup>). PDS revealed a DBS for PyO<sup>-</sup> 280 cm<sup>-1</sup> below the detachment threshold and 29 vibrational levels of the DBS. The PDS also revealed a strong shape resonance at 1077 cm<sup>-1</sup> above the detachment threshold due to valence excitation from the highest occupied molecular orbital (HOMO) of PyO<sup>-</sup> to its lowest unoccupied molecular orbital (LUMO) in the continuum with an excitation energy of 21 055 cm<sup>-1</sup> (475 nm). Both resonant two-photon PES for the bound vibrational levels of the DBS and single-photon rPES via the above-threshold vibrational levels were performed. The combination of rPES and PDS yielded a total of 21 fundamental vibrational frequencies for the PyO radical, including 13 out-of-plane bending modes.

#### **II. EXPERIMENTAL METHODS**

The experiments were conducted using our third generation ESI-PES apparatus,<sup>15</sup> which consists of an ESI source,<sup>23</sup> a cryogenically cooled Paul trap,<sup>24</sup> and a high-resolution photoelectron imaging system.<sup>25</sup> The PyO<sup>-</sup> anions were produced by electrospray of a 1 mM PyOH solution in a mixed methanol/water solvent

prepared by adding a small amount of NaOH to enhance deprotonation. The PyO<sup>-</sup> anions produced from the ESI source were guided into a cryogenically controlled Paul trap operated at 4.6 K and were cooled by collisions with a mixed  $He/H_2$  (4/1 volume ratio) buffer gas for 0.1 s before being pulsed into the extraction zone of a time-of-flight mass spectrometer at a 10 Hz repetition rate. The PyO<sup>-</sup> anions were selected by a mass gate and allowed to enter the interaction zone of the velocity-map imaging system. The anions were detached by a dye laser, and the nascent photoelectrons were focused by the imaging lens onto a set of 75-mm diameter microchannel plates coupled with a phosphor screen. The final projected photoelectron images were collected by a charge-coupled device camera. To construct photoelectron spectra from the obtained images, we performed inverse-Abel transformation using both the BASEX and pBASEX programs.<sup>26,27</sup> In this work, the presented spectra were constructed by BASEX and the inverted photoelectron images were based on pBASEX because it produced higher quality images. The kinetic energies of the photoelectrons were calibrated with the known spectra of Au<sup>-</sup> at different wavelengths. The kinetic energy (KE) resolution was 3.8 cm<sup>-1</sup> for 55 cm<sup>-1</sup> electrons and was about 1.5% ( $\Delta$ KE/KE) for electrons over 1 eV.<sup>25</sup>

We also calculated the harmonic frequencies and dipole moment of PyO at the B3LYP/6-311++ $G^{**}$  level of theory. Calculations on the excited states of PyO<sup>-</sup> were also performed at the same level of theory. All calculations were done using Gaussian 09.<sup>28</sup>

#### **III. RESULTS**

#### A. Non-resonant photoelectron spectroscopy of PyO<sup>-</sup>

Figure 1 presents the non-resonant PE spectra of PyO<sup>-</sup> at three different wavelengths. Figure 1(a) taken near the detachment threshold yields a high-resolution 0–0 transition with a full width at half maximum (FWHM) of 12 cm<sup>-1</sup> and an EA of 2.4770 eV with an uncertainty of  $\pm 0.0006$  eV for the PyO radical. However, as will be shown later, one of the resonant PE spectra yields an even more accurate EA of 2.4772 eV with an uncertainty of  $\pm 0.0004$  eV or 19 980(3) cm<sup>-1</sup>. Figures 1(b) and 1(c) display multiple vibrational peaks (labeled with uppercase letters), corresponding to Franck–Condon-active vibrational modes from the ground state of the PyO<sup>-</sup> anion to that of the PyO neutral. Because of its large size, the PE spectra of PyO<sup>-</sup> are more complicated, relative to those of phenoxide and naphthoxide reported previously,<sup>21,22,29-31</sup> which each show a dominant Franck–Condon progression.

Our Franck–Condon simulation revealed that the 0–0 transition has the largest Franck–Condon factor, as shown in Fig. 1(c). However, we observed several intense peaks (D, F, and K) at binding energies where the calculated Franck–Condon factors are low or negligible. This could be due to either vibronic coupling<sup>32–34</sup> or autodetachment. As will be shown below, the photon energies used for the spectra in Figs. 1(b) and 1(c) are in the spectral range where both DBS resonances and a shape resonance are observed. Even though we chose the photon energies to avoid any DBS vibrational resonances, these photon energies were on the low energy side of the shape resonance and could still excite the shape-resonance state to induce autodetachment, leading to non-Franck–Condon behaviors. Figure S1 shows a PE spectrum taken at 3.2834 eV, far away from the shape resonance. Indeed, this spectrum is in much better agreement with the Franck–Condon simulation, even though the resolution of this spectrum is much poorer. The higher photon energy spectrum in Fig. S1 also gives hints of an excited state of PyO at higher binding energies above 3.1 eV. This is likely due to detachment from an O2p-based orbital. A similar excited state was observed in the PE spectra of phenoxide and naphthoxide at higher excitation energies.<sup>21,29-31</sup> The binding energies and assignments of the vibrational peaks resolved in Fig. 1 are given in Table I, along with other spectral features observed from rPES to be discussed below.

#### B. Photodetachment spectroscopy of PyO<sup>-</sup>

Our calculation showed that the PyO radical has a dipole moment of 5.25 D, suggesting that the PyO<sup>-</sup> anion should have a DBS as an electronically excited state below the detachment threshold.<sup>35-38</sup> To search for the DBS, we performed PDS by monitoring the total electron yield as a function of wavelength across the detachment threshold,<sup>39-46</sup> as shown in Fig. 2 in the energy range from 19 600 cm<sup>-1</sup> to 21 400 cm<sup>-1</sup>. The arrow at 19 980 cm<sup>-1</sup> indicates the detachment threshold measured from the PES data. The spectrum

TABLE I. The observed vibrational peaks, their shifts relative to the 0–0 transition, and their assignments for the non-resonant and resonant photoelectron spectra of PyO<sup>-</sup>. The theoretical frequencies used for comparison were calculated at the B3LYP/6-311++G\*\* level of theory.

Observed peak	Binding energy (eV)	Binding energy (cm <sup>-1</sup> )	Shift ( $cm^{-1}$ )	Assignment	Theoretical frequency (cm $^{-1}$ )
000	2.4772(4)	19980(3)	0	Neutral ground state	
a	2.4871(6)	20 060(5)	80	$50^{1}$	86
b	2.4896(8)	20 080(6)	100	$51^{1}$	107
c	2.4996(8)	20161(6)	181	$52^{1}$	189
А	2.5013(6)	20174(5)	194	53 <sup>1</sup>	204
В	2.5080(8)	20 228(6)	248	$54^{1}$	257
d	2.5099(7)	20 244(6)	264	$50^{1}52^{1}$	275
e	2.5117(7)	20 258(6)	278	$1^{1}$	280
С	2.5130(9)	20 269(7)	289	55 <sup>1</sup>	303
f	2.5224(8)	20 345(6)	365	52 <sup>2</sup>	378
g	2.5242(8)	20 359(6)	379	$2^{1}$	386
D	2.5278(7)	20 388(6)	408	56 <sup>1</sup>	418
h	2.5332(12)	20 432(10)	452	$4^1$	458
Е	2.5368(10)	20 461(8)	481	$5^{1}/57^{1}$	488/484
i	2.5407(9)	20 492(7)	512	$58^{1}$	506
F	2.5426(7)	20 507(6)	527	$6^1$	525
j	2.5459(8)	20 534(6)	554	59 <sup>1</sup>	539
G	2.5481(8)	20 552(6)	572	$7^1$	565
k	2.5520(10)	20 583(8)	603	$8^1$	610
Н	2.5552(9)	20 609(7)	629	$60^1$	627
1	2.5589(9)	20639(7)	659	$4'^{1}53'^{1}$	662
Ι	2.5610(12)	20 656(10)	676	$9^{1}$	684
m	2.5633(10)	20674(8)	694	$1^{1}56^{1}$	698
n	2.5664(9)	20 699(7)	719	54 <sup>′1</sup> 57 <sup>′1</sup>	741
J	2.5701(12)	20729(10)	749	63 <sup>1</sup>	747
Κ	2.5755(12)	20773(10)	793	$2^{1}56^{1}$	804
L	2.5792(14)	20 803(11)	823	56 <sup>2</sup>	836
М	2.5831(12)	20 834(10)	854	$4^{1}56^{1}$	876
Ν	2.5882(8)	20 875(6)	895	$5^{1}56^{1}/56^{1}57^{1}$	906/902
0	2.5918(8)	20 904(6)	924	$56^{1}58^{1}$	924
Р	2.5947(9)	20 928(7)	948	6 <sup>1</sup> 56 <sup>1</sup>	943
Q	2.5976(9)	20 951(7)	971	$4^{1}6^{1}$	983
R	2.6026(12)	20 991(10)	1011	8 <sup>1</sup> 56 <sup>1</sup>	1028
S	2.6053(12)	21 013(10)	1033	6 <sup>2</sup>	1050
T	2.6117(9)	21 065(7)	1085	$6^{1}7^{1}/5^{1}8^{1}/57^{1}8^{1}$	1090/1098/1094



FIG. 2. Photodetachment spectrum of PyO<sup>-</sup> from 19 600 cm<sup>-1</sup> to 21 400 cm<sup>-1</sup>. The arrow at 19 980 cm<sup>-1</sup> indicates the detachment threshold. The blue and black curves are expanded by 5 and 100 times, respectively. A total of 30 vibrational peaks are marked from 0 to 29, and the labels from 30 to 35 are for reference only.

displayed in Fig. 2 was taken with a scanning step of 0.1 nm and finer scans with 0.01 nm/step were done for all the observed peaks (labeled from 0 to 29) to determine the excitation energies more accurately.

We observed three very weak vibrational peaks labeled as 0, 1, and 2 below the detachment threshold. Peak 0 at an excitation energy of 19700 cm<sup>-1</sup> should correspond to the ground vibrational state of the anticipated DBS for PyO<sup>-</sup> because no other transitions were observed at lower photon energies. Using the measured EA  $(19980 \text{ cm}^{-1})$  of PyO, we found that the binding energy of the DBS is 280  $\text{cm}^{-1}$ , which is significantly larger than the 202  $\text{cm}^{-1}$ value for the binding energy of the DBS in 2-naphthoxide,<sup>22,46</sup> even though the dipole moment of the 2-naphthoxy radical (4.9 D) is only slightly lower than that of PyO. This observation again indicates the importance of polarization and correlation effects in the electron binding in non-valence states.<sup>36,37,47-50</sup> Peaks 1 and 2, which are 183 cm<sup>-1</sup> and 197 cm<sup>-1</sup> above peak 0, respectively, should correspond to bound vibrational levels of the DBS. They can be assigned to the fundamental excitations of the bending modes  $v_{52}'$  and  $v_{53}'$  of the DBS, respectively, according to the computed vibrational frequencies of neutral PyO (Table S1 and Table II). As shown previously,<sup>16-22</sup> we could use the computed vibrational frequencies for PyO to aid the assignments of the vibrational levels of the DBS because the dipole-bound electron has very little effect on the PyO neutral radical core [note that we use the prime (') to designate the vibrational modes or levels of the DBS]. The relative intensities of the three below-threshold vibrational peaks were very weak because they were observed due to two-photon processes, i.e., resonant two-photon detachment (R2PD).

The peaks labeled from 3 to 29 are due to above-threshold vibrational levels of the DBS (also known as vibrational Feshbach resonances), and they are derived from single-photon processes as a result of vibrationally induced autodetachment. The assignments of the above-threshold vibrational levels of the DBS are assisted by the rPES to be discussed in Sec. III C along with the computed vibrational frequencies of PyO.

The most surprising observation in the PDS is the broad and giant resonant band centered around  $21\,055 \text{ cm}^{-1}$  in Fig. 2. This band is likely due to a transition to a valence excited state of PyO<sup>-</sup> in the continuum, i.e., a shape resonance. The large spectral width suggests that the transition is lifetime-broadened. Thus, there are no well-resolved vibronic structures in this band. The labels 30-35 merely indicate the positions where resonant PE spectra were taken, and it is unlikely that they correspond to any specific vibronic levels of the shape resonance.

The wavelengths, excitation energies, shifts relative to peak 0, and the assignments of all the labeled peaks in the photodetachment spectrum are summarized in Table II.

#### C. Resonant photoelectron spectra of PyO<sup>-</sup>

Resonant PE spectra can be obtained by measuring PE images at detachment photon energies corresponding to the vibrational peaks 0-29 and the shape resonance in the PDS of Fig. 2. Three types of resonant PE spectra were measured. First, R2PD PE spectra were obtained for the three bound vibrational levels (0-2) of the DBS, as shown in Fig. 3. Second, resonant PE spectra were obtained, in which one or more vibrational peaks were enhanced by tuning the detachment laser to the 27 vibrational Feshbach resonances of the DBS (peaks 3-29), as given in Figs. 4, 5, and S2. Finally, resonant PE spectra were measured by tuning the detachment laser to different positions of the shape resonance (30-35), as displayed in Fig. 6. Figure 4 presents the resonant PE spectra of the Feshbach resonances corresponding to the fundamental vibrational levels of the DBS, whereas Fig. 5 shows the resonant PE spectra involving autodetachment from combinational vibrational levels of the DBS. Additional resonant PE spectra corresponding to the vibrational Feshback resonances are documented in Fig. S2.

		Photon			Theoretical
Peak	Wavelength (nm)	energy (cm $^{-1}$ )	Shift ( $cm^{-1}$ )	Assignment	frequency (cm $^{-1}$ )
0	507.61	19700(5)	0	Ground state DBS	
1	502.94	19883(5)	183	52' <sup>1</sup>	189
2	502.60	19 897(5)	197	53' <sup>1</sup>	204
3	500.16	19 994(5)	294	55′ <sup>1</sup>	303
4	497.36	20 106(5)	406	56′ <sup>1</sup>	418
5	495.58	20 178(5)	478	2'151'1	493
6	495.20	20 194(5)	494	5' <sup>1</sup> /57' <sup>1</sup>	488/484
7	494.46	20 224(5)	524	6′ <sup>1</sup>	525
8	491.98	20 326(5)	626	60′ <sup>1</sup>	627
9	491.15	20 360(5)	660	4' <sup>1</sup> 53' <sup>1</sup>	662
10	490.58	20 384(5)	684	1′ <sup>1</sup> 56′ <sup>1</sup>	698
11	489.62	20 424(5)	724	5 <sup>'1</sup> 54 <sup>'1</sup> /54 <sup>'1</sup> 57 <sup>'1</sup>	745/741
12	488.96	20 452(5)	752	63′ <sup>1</sup>	747
13	488.15	20 486(5)	786	2 <sup>'1</sup> 56 <sup>'1</sup>	804
14	487.79	20 501(5)	801	$1'^{1}6'^{1}$	805
15	487.22	20 525(5)	825	56′ <sup>2</sup>	836
16	486.70	20 547(5)	847	66′ <sup>1</sup>	854
17	486.47	20 556(5)	856	4′ <sup>1</sup> 56′ <sup>1</sup>	876
18	485.79	20 585(5)	885	6 <sup>'1</sup> 52 <sup>'2</sup>	903
19	485.55	20 595(5)	895	56 <sup>′1</sup> 57 <sup>′1</sup> /5 <sup>′1</sup> 56 <sup>′1</sup>	902/906
20	485.34	20 604(5)	904	$2'^{1}6'^{1}/4'^{2}$	911/916
21	484.96	20 620(5)	920	56 <sup>′1</sup> 58′ <sup>1</sup>	924
22	484.43	20 643(5)	943	6 <sup>'1</sup> 56 <sup>'1</sup>	943
23	484.01	20 661(5)	961	56 <sup>′1</sup> 59′ <sup>1</sup>	957
24	483.68	20 675(5)	975	$4'^{1}6'^{1}$	983
25	482.83	20711(5)	1011	8 <sup>'1</sup> 56 <sup>'1</sup>	1028
26	482.18	20739(5)	1039	6' <sup>2</sup>	1050
27	481.21	20781(5)	1081	6 <sup>'1</sup> 7 <sup>'1</sup> /5 <sup>'1</sup> 8 <sup>'1</sup> /57 <sup>'1</sup> 8 <sup>'1</sup>	1090/1098/1094
28	480.09	20 829(5)	1129	6′ <sup>1</sup> 8′ <sup>1</sup>	1135
29	478.49	20 899(5)	1199	6′19′1	1209
30	476.69	20 978(5)	1278		
31	476.10	21 004(5)	1304	For the shape resonance	
32	475.21	21 043(5)	1343		
33	474.94	21 055(5)	1355		
34	474.73	21 065(5)	1365		
35	473.92	21 101(5)	1401		

**TABLE II.** Summary of the observed vibrational features of the dipole-bound state of PyO<sup>-</sup> (0–29 in Fig. 2). The corresponding wavelengths, photon energies, and shifts relative to peak 0 and assignments are given. The theoretical frequencies given for comparison were calculated at the B3LYP/6-311++G\*\* level of theory.

All the resonant PE spectra are non-Franck–Condon, where one or more final vibrational peaks are enhanced or in many cases completely new vibrational peaks appear in comparison to the non-resonant PE spectra in Fig. 1. Therefore, the resonant PE spectra yielded considerably more vibrational information for the PyO radical than is possible in the non-resonant PES data. All the additional PE features and their assignments from the resonant PE spectra are also given in Table I. We use the lowercase letters (a, b, c, ...) to designate the new vibrational peaks observed in the resonant PE spectra due to autodetachment from the DBS.

#### IV. DISCUSSION

#### A. Resonant two-photon PE spectra

The ground vibrational level of the DBS and peaks 1 and 2 in Fig. 2 are bound states, and two photon processes are required for electron detachment. The three R2PD PE spectra shown in Fig. 3 are similar, each with two features: a low binding energy peak marked as "DBS" and a high binding energy cutoff marked as "Anion G.S." The low binding energy feature was produced by R2PD during which the first photon excited the anion from the anion ground state to



**FIG. 3.** Resonant two-photon PE images and spectra of PyO<sup>-</sup> via the bound vibrational levels of the DBS: (a) at 507.61 nm, (b) at 502.94 nm, and (c) at 502.60 nm. The high binding energy features marked as "Anion G.S." come from photodetachment from vibrationally excited states of PyO<sup>-</sup> in its ground state following relaxation from the DBS. The double arrow indicates the laser polarization direction.

the bound vibrational levels of the DBS. A second photon within the same laser pulse detached the dipole-bound electron, producing high kinetic energy photoelectrons (the outer ring in the PE images of Fig. 3). The PE images display a *p*-wave distribution, as expected from the s-like DBS orbital. The binding energies of the "DBS" features are consistent with the binding energy of the DBS measured more accurately from the PDS in Fig. 2, i.e.,  $280 \text{ cm}^{-1}$  (0.0347 eV). Figures 3(b) and 3(c) correspond to excitation to the  $52'^1$  and  $53'^1$ vibrational levels of the DBS, respectively, by the first photon. However, the binding energies of the "DBS" feature in Fig. 3 are the same within the limited experimental accuracy in the R2PD PE spectra. This observation is due to the fact that the detachment by the second photon is an adiabatic process during which the vibrational energies of the neutral core do not change, as we have shown previously. <sup>23</sup> This observation confirms that the dipole-bound electron has little effect on the structure of the neutral core. Thus, there is no geometry change from the DBS vibrational levels to the final neutral states, regardless of the initial vibrational levels from which the dipole-bound electron is detached.

The high-binding energy signals correspond to near-threshold photoelectrons, i.e., the bright central spot in the PE images. These signals were derived from photodetachment of vibrationally excited PyO<sup>-</sup> in its ground electronic state due to internal conversion from the DBS followed by intramolecular vibrational redistribution (IVR) processes within the same 5 ns detachment laser pulse. Such IVR processes from nonvalence-bound states have been observed previously, always yielding near threshold photoelectrons in R2PD.  $^{51-53}_{\mbox{ }}$ 

### B. Resonant PE spectra of **PyO**<sup>-</sup>: Autodetachment from fundamental vibrational levels of the DBS

Excitations to the above-threshold vibrational levels of the DBS can induce vibrational autodetachment in which the vibrational energy is coupled to the dipole-bound electron to induce electron detachment. It has been shown that the vibrational autodetachment from the DBS is not only mode-selective<sup>17</sup> but also obeys the  $\Delta v = -1$  propensity rule under the harmonic approximation.<sup>54,55</sup> In other words, only one quantum of vibrational energy could be coupled to the dipole-bound electron during the autodetachment process. Thus, resonant PE spectra consist of two processes: the non-resonant photodetachment process and the autodetachment-enhanced vibrational peak, producing highly non-Franck–Condon PE spectra. In cases of excitations to fundamental vibrational levels of the DBS, the resulting resonant PE spectra would display a strongly enhanced 0–0 transition, as shown in Fig. 4.

Figure 4(a) corresponds to the rPES taken at the wavelength of peak 3 in Fig. 2, which is slightly above the detachment threshold. This resonant PE spectrum has the highest resolution for the 0-0 transition with a FWHM of only 5.6  $\text{cm}^{-1}$ , yielding the most accurate measurement for the EA of PyO as 2.4772(4) eV (19980  $\pm$  3 cm<sup>-1</sup>). Peak 3 is 294 cm<sup>-1</sup> above peak 0, in good agreement with the computed frequency for the  $v_{55}$  mode (303 cm<sup>-1</sup>, Table II). Similarly, Fig. 4(b) is assigned to excitation to the  $56'^{1}$  level of the DBS (Table II). In addition to the strongly enhanced 0-0 transition, some weak features are also observed in Fig. 4(b). The peaks a and b correspond to excitations of the two lowest-frequency bending modes of PyO,  $v_{50}$  and  $v_{51}$  (Fig. S3), respectively, as shown in Table I. Such low frequency bending vibrations have been observed frequently in rPES via non-valence states previously.<sup>18-22</sup> They are likely due to inelastic scattering or vibronic coupling<sup>56</sup> and represent a unique feature of rPES because such low frequency bending vibrations are difficult to measure experimentally.<sup>16</sup> The features between the 0–0 peak and peak a were most likely due to transitions from residual vibrational hot bands. The vibrational temperature of anions under our cryogenic cooling conditions was estimated to be about 30 K-35 K, which should eliminate most hot bands. However, under resonant conditions, some low frequency hot bands may be observable. Figure 4(e), due to autodetachment from the  $60'^{1}$  level of the DBS, shows direct evidence of such hot bands, though they are difficult to be assigned. Figure 4(d), due to excitation to the  $6'^1$ level of the DBS, also displays weak features attributable to hot band transitions.

In Figs. 4(f) and 4(g), the Franck–Condon-active transitions, D (56<sup>1</sup>) and F (6<sup>1</sup>) (see Table I), are significantly weaker than the 0–0 transition, in comparison with the non-resonant PE spectra presented in Fig. 1, providing direct evidence of autodetachment enhancement of the 0–0 transition following resonant excitations to the 63'<sup>1</sup> and 66'<sup>1</sup> fundamental vibrational levels of the DBS, respectively (Table II). The spectrum in Fig. 4(c) was taken at the detachment wavelength of peak 6, which is 494 cm<sup>-1</sup> above peak 0. Peak 6 could be assigned either to 5'<sup>1</sup> or to 57'<sup>1</sup> of the DBS because the computed frequencies for v<sub>5</sub> (488 cm<sup>-1</sup>) and v<sub>57</sub> (484 cm<sup>-1</sup>) are similar (Table S1). Both peaks *a* (50<sup>1</sup>) and A (52<sup>1</sup>) in Fig. 4(c) seem to



FIG. 4. Resonant PE images and spectra of PyO<sup>-</sup> corresponding to excitations to fundamental vibrational levels of the DBS: (a) at 500.16 nm, (b) at 497.36 nm, (c) at 495.20 nm, (d) at 494.46 nm, (e) at 491.98 nm, (f) at 488.96 nm, and (g) at 486.70 nm. The numbers in the parentheses are the peak labels from the PDS (Fig. 2). The wavelengths and assignments are also given. The double arrows below the images indicate the laser polarization direction.

be enhanced in comparison to the non-resonant PES, most likely due to intramolecular inelastic re-scattering (for peak *a*) and/or vibronic couplings.<sup>22,56</sup>

# C. Resonant PE spectra of **PyO**<sup>-</sup>: Autodetachment from overtones and combinational or overlapping vibrational levels of the DBS

Because of the presence of low frequency bending modes and increasing vibrational density of states, transitions to vibrational overtones and combinational or overlapping vibrational levels of the DBS are often observed in PDS. The rPES data resulting from autodetachment from these vibrational levels of the DBS are more complicated, as shown in Figs. 5 and S2, where multiple vibrational peaks of the PyO final state are enhanced. This is an important feature of rPES, which not only encodes information about the autodetaching vibrational levels of the DBS but also yields rich vibrational information for the final neutral state unavailable in non-resonant PES. As shown previously,<sup>17</sup> autodetachment from combinational vibrational levels of the DBS is mode-selective and obeys the  $\Delta v = -1$  propensity rule.<sup>54,55</sup> For autodetachment from a combinational vibrational level of  $v_x'^n v_y'^m \dots$ , for example, the final

neutral state can be either  $v_x{'n-1}v_y{'m}$ ... or  $v_x{'n}v_y{'m-1}$ ... if the frequencies of modes  $v_x{'}$  and  $v_y{'}$  are both larger than the binding energies of the DBS, resulting in enhancement of multiple vibrational peaks in the resonant PE spectra. Even though the vibrational modes and frequencies of the DBS and the neutral final states are the same, we usually use the prime (') to designate those of the DBS for clarity. Excitation of overlapping vibrational levels of the DBS can yield even more complicated resonant PE spectra. Nevertheless, the assignments can be usually done quite straightforwardly with the help of the calculated vibrational frequencies. Figure 5 shows the resonant PE spectra where Franck–Condon-inactive modes are involved, yielding new vibrational information that cannot be obtained from the non-resonant PES. Figure S2 displays the remaining 11 resonant PE spectra measured for PyO<sup>-</sup>, which will not be discussed in detail.

Figures 5(a) and 5(c) correspond to excitation to the  $1'^{1}56'^{1}$ and  $1'^{1}6'^{1}$  levels, resulting in a significantly enhanced  $1^{1}$  peak (*e*) as a result of the coupling of the 56'<sup>1</sup> or 6'<sup>1</sup> vibrational quantum to the dipole-bound electron, respectively. However, the expected 56<sup>1</sup> or  $6^{1}$  accompanying peaks are not observed prominently because the  $1'^{1}$  vibrational quantum is not sufficient to detach the dipole-bound electron. In fact, the  $1'^{1}$  vibrational quantum is 280 cm<sup>-1</sup> according



FIG. 5. Resonant PE images and spectra of PyO<sup>-</sup> corresponding to excitations to combinational vibrational levels of the DBS: (a) at 490.58 nm, (b) at 488.15 nm, (c) at 487.79 nm, (d) at 486.47 nm, (e) at 484.96 nm, (f) at 484.01 nm, (g) at 483.68 nm, (h) at 482.83 nm, and (i) at 481.21 nm. The numbers in the parentheses correspond to the peak numbers in Fig. 2. The wavelengths and the assignments are also given. The double arrows below the images indicate the laser polarization direction. The enhanced peaks are labeled in **boldface**. In (b), (d), (e), and (h), the zoomed-in spectra are plotted in black.

to the computed frequency for the  $v_1$  mode (Table S1), which is exactly equal to the binding energy of the DBS. Careful examination of Figs. 5(a) and 5(c) reveals a threshold peak in each case (more prominent in the PE images), which should be due to the 56<sup>1</sup> and 6<sup>1</sup> peaks, respectively. Additional non-Franck–Condon vibrational peaks, *a* (50<sup>1</sup>) in Fig. 5(a) and *b* (51<sup>1</sup>) in Fig. 5(c), corresponding to the two lowest-frequency modes (Table I), were observed due to the re-scattering effects or vibronic coupling with a low-lying excited state of PyO.

Figures 5(b), 5(d)–5(f), and 5(h) are all due to autodetachment from the combinational levels consisting of a Franck–Condoninactive mode with mode  $v_{56}'$ , i.e.,  $2'^{1}56'^{1}$ ,  $4'^{1}56'^{1}$ ,  $56'^{1}58'^{1}$ ,  $56'^{1}59'^{1}$ , and  $8'^{1}56'^{1}$ , respectively. Clearly, the 56<sup>1</sup> final vibrational state in each of these spectra is the dominating feature. The expected accompanying Franck–Condon-inactive final states,  $2^1$  (peak g),  $4^1$  (peak h),  $58^1$  (peak i),  $59^1$  (peak j), and  $8^1$  (peak k) due to coupling of the  $56'^1$  vibrational quantum to the DBS electron, are observed, although their relative intensities are much weaker than that of  $56^1$ . This observation suggests that the coupling of mode  $v_{56}'$  with the dipole-bound electron is weak. Such mode-dependent vibronic coupling in autodetachment was observed previously.<sup>17,21</sup> Recently, the mode-dependent autodetachment behavior has been directly investigated using a pump-probe experiment.<sup>59</sup> In Fig. 5(b), relatively strong non-Franck–Condon low frequency bending vibrations,  $50^1$  (peak a),  $52^1$  (peak c), and  $50^152^1$  (peak d), are also observed. The mode  $v_{56}$  (A'') is a bending mode (Fig. S3) and is the most

Franck–Condon-active mode in the PE spectra (Fig. 1), suggesting that the neutral PyO radical may not be strictly planar. In fact, among the 29 vibrational levels observed for the DBS, ten involve the  $v_{56}$ ' mode.

Figure 5(g) is quite simple and can be readily assigned to excitation to the  $4^{'1}6^{'1}$  combinational level of the DBS, resulting in the enhancement of the  $4^1$  (peak h) and  $6^1$  (peak F) final vibrational states. Figure 5(i) is more complicated with multiple vibrational peaks being enhanced, suggesting excitation to multiple neardegenerate vibrational levels of the DBS at peak 27 (481.21 nm). The enhancement of the  $6^1$  and  $7^1$  final states can be readily assigned to excitation to the  $6'^17'^1$  combinational level of the DBS. The enhanced peak **E** could be assigned to either  $5^1$  or  $57^1$  because the computed frequencies of the  $v_5$  (488 cm<sup>-1</sup>) and  $v_{57}$  (484 cm<sup>-1</sup>) modes are close to each other (Table S1). The observation of the  $8^1$ (peak k) suggests that the  $5'^{1}8'^{1}$  and/or  $57'^{1}8'^{1}$  combinational levels were also excited. As shown in Table II, the  $6'^{17'}$ ,  $5'^{18'}$ , and  $57'^{18'}$ combinational levels all have very similar energies (~1090 cm<sup>-1</sup>). As shown in Fig. 1, the  $v_6$  mode (peak F, Table I) is also a Franck-Condon-active mode. Indeed, ten of the observed vibrational levels in the PDS also involve the  $v_6$  mode (Table II). Many of the resonant PE spectra involving these levels can be found in Fig. S2.

## D. Autodetachment from the valence excited state of **PyO**<sup>-</sup>

Bound valence excited states in anions are rare and are known in carbon cluster anions because of their high electron binding

energies.<sup>60–63</sup> Above-threshold excited states (shape resonances) can exist as transient excited states, which are usually observed in electron-molecule scattering experiments.<sup>64-66</sup> Above-threshold excited states are often inferred indirectly in PES experiments when photon-energy-dependent non-Franck-Condon behaviors are observed.<sup>32,67–69</sup> Schiedt and Weinkauf directly observed a shape resonance in the photodetachment spectrum of the *p*-benzoquinone anion due to the transition of the extra electron occupying the LUMO of the neutral to the LUMO + 1 in the continuum.<sup>70</sup> They also measured resonant PE spectra at different detachment energies across the broad shape resonance, showing strong photon-energydependent non-Franck-Condon behaviors. Our observation of the intense and broad shape resonance around 21 055  $\rm cm^{-1}$  in the PDS of PyO<sup>-</sup> is interesting (Fig. 2).<sup>71</sup> To understand the nature of the shape resonance, we calculated the excited states of PyO<sup>-</sup>, as given in Table S2. We found that a singlet excited state in the continuum, corresponding to the HOMO-LUMO transition ( $\pi \rightarrow \pi^*$ ) at 2.6825 eV (21636 cm<sup>-1</sup>), has the largest oscillator strength, and it agrees well with our observed shape resonance at 21 055 cm<sup>-1</sup>. In an alkali solution of PyOH, a broad emission spectrum centered around 450 nm ( $22\,222\,\text{cm}^{-1}$ ) was attributed to PyO<sup>-</sup>,<sup>12</sup> consistent with the HOMO-LUMO transition in the gas phase.

We measured resonant PE images across the shape resonance at photon energies according to the labels in Fig. 2 (i.e., 30–35), as shown in Fig. 6. These spectra are dominated by autodetachment from the shape-resonance state due to its large absorption cross section relative to the non-resonant detachment process. Thus, the resonant PE spectra should reflect the Franck-Condon factors between the intermediate shape-resonance state and the



FIG. 6. Resonant photoelectron images and spectra taken across the shape resonance: (a) at 476.69 nm, (b) at 476.10 nm, (c) at 475.21 nm, (d) at 474.94 nm, (e) at 474.73 nm, and (f) at 473.92 nm. The photon energies correspond to the peak positions (given in the parentheses) labeled in Fig. 2. The double arrows below the images indicate the direction of the laser polarization.

neutral ground state, whereas the non-resonant PE spectra reflect those between the anion ground state and the neutral final state. The photon energy dependence of the resonant PE spectra in Fig. 6 is due to the fact that different parts of the potential energy surface of the shape-resonance state are reached at different detachment photon energies. Furthermore, different DBS vibrational levels could also be excited at the energies of the shape resonance, contributing to the enhancements of certain vibrational peaks in the resonant PE spectra in Fig. 6. Therefore, it is difficult to assign these spectra since multiple processes might be present at the same time. Fortunately, because it is known that the dipole-bound electron has little effect on the geometry or vibrational levels of the neutral core, we could use the PDS data to help the assignments of the new vibrational structures observed in the resonant PE spectra. The binding energies of the newly observed vibrational peaks (M–T) are also given in Table I. We found that the vibrational energies corresponding to peaks M, N, O, P, Q, R, S, and T agree well with those of peaks 17, 19, 21, 22, 24, 25, 26, and 27 in the PDS, respectively, within the experimental



FIG. 7. Schematic energy level diagram showing the observed vibrational levels of neutral PyO and those of the DBS of PyO<sup>-</sup>, as well as the autodetachment processes from the DBS levels. The numbers in the parentheses correspond to those in Fig. 2.

accuracy. Not surprisingly, all these vibrational peaks correspond to combinational levels of the two most Franck–Condon-active modes,  $\nu_6$  and  $\nu_{56}$  (Table I).

## E. Energy level diagram for the DBS of **PyO**<sup>-</sup> and the neutral PyO radical

Figure 7 presents a schematic energy level diagram showing all the observed vibrational levels for the neutral PyO radical from both non-resonant and resonant PES and autodetachment from all the observed vibrational levels of the DBS and the shape resonance. Autodetachment from the vibrational levels of the DBS is modeselective and obeys the  $\Delta v = -1$  propensity rule, as indicated by the straight arrows. However, the autodetachment from the shaperesonance state is not selective and depends on the geometry change between the intermediate state and the final PyO neutral state. The resonant PE spectra not only help the assignments of the vibrational levels of the DBS observed in the PDS but also yield rich vibrational information for the PyO radical. In total, 35 vibrational peaks are observed from the combination of the non-resonant and resonant PES data (Table I and Fig. 7). Combining these vibrational information and that from the PDS, we are able to obtain 21 fundamental vibrational frequencies for the PyO radical, as given in Table III, including 8 in-plane modes and 13 out-of-plane bending modes. The atomic displacement vectors for these 21 normal modes are shown

**TABLE III.** The observed vibrational modes and their experimental frequencies for the PyO radical, in comparison with the calculated values.

Vibrational mode	Theoretical frequency $(cm^{-1})^a$	Experimental frequency $(cm^{-1})$	Observed peaks <sup>b</sup>
$\overline{\nu_{50}(A'')}$	86	80	а
$\nu_{51}(A'')$	107	100	b
$v_{52} (A'')$	189	181/183	c/1
v <sub>53</sub> (A")	204	194/197	A/2
$\nu_{54} (A'')$	257	248	В
v55 (A'')	303	289/290	C/3
v <sub>56</sub> (A'')	418	408/406	D/4
$\nu_{57} (A'')^{c}$	484	481/494	E/6
ν <sub>58</sub> (A")	506	512	i
ν <sub>59</sub> (A'')	539	554	j
$v_{60} (A'')$	627	629/626	H/8
v <sub>63</sub> (A'')	747	749/752	J/12
v <sub>66</sub> (A'')	854	847	16
$v_1$ (A')	280	278	e
$\nu_2$ (A')	386	379	g
$v_4 (A')$	458	452	ĥ
$\nu_5 (A')^c$	488	481/494	E/6
$\nu_6 (A')$	525	527/524	F/7
v7 (A')	565	572	G
$\nu_8 (A')$	610	603	k
v9 (A')	684	676	Ι

<sup>a</sup>The theoretical frequencies come from Table S1.

<sup>b</sup>Peak labels are from Tables I and II.

<sup>c</sup>These two modes could not be distinguished in this experiment.

in Fig. S3. Some vibrational frequencies are observed in both the PES and PDS data, and they are both given in Table III, in comparison with the computed frequencies. Within our experimental uncertainties, the vibrational frequencies from the PES or PDS are the same, though, in general, the data from the PDS should be more accurate.

#### V. CONCLUSION

In conclusion, we report a photodetachment and highresolution resonant photoelectron imaging study of the cryogenically cooled pyrenolate anion, PyO<sup>-</sup>. High-resolution resonant photoelectron spectra yielded an accurate electron affinity of 2.4772(4) eV (19980  $\pm$  3 cm<sup>-1</sup>) for the pyrenoxy radical. The photodetachment spectrum revealed a dipole-bound state for PyO<sup>-</sup> 280 cm<sup>-1</sup> below the detachment threshold and 29 vibrational levels. A much more intense valence excited state (shape resonance) was also observed at an excitation energy of 21 055 cm<sup>-1</sup> due to the excitation of an electron from the HOMO of PyO- to its LUMO in the continuum. Resonant two-photon photoelectron spectra were measured for the three below-threshold vibrational levels of the DBS, and 27 resonant photoelectron spectra were obtained at detachment photon energies corresponding to the above-threshold vibrational levels of the DBS. The resonant photoelectron spectra yielded much more vibrational information, as well as helping the assignments of the DBS vibrational levels. With both the photodetachment and resonant photoelectron spectroscopy, the frequencies of 21 vibrational modes for the PyO radical were measured, including 13 outof-plane bending modes. This study demonstrates again the rich spectroscopic information that can be obtained by using photodetachment and resonant photoelectron spectroscopy of cryogenically cooled anions for complex PAH radicals. The experimental vibrational information of the pyrenoxy radical can be used for calibrating theoretical methods and for the potential identification of PAHs in the interstellar medium.

#### SUPPLEMENTARY MATERIAL

See the supplementary material for a photoelectron spectrum of PyO<sup>-</sup> at 3.2834 eV, the full set of calculated vibrational frequencies of PyO and calculations for the valence excited states of PyO<sup>-</sup>, additional resonant photoelectron spectra that are not discussed in the main text, and the atomic displacements of the 21 observed normal modes of vibration.

#### ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Science, Geosciences, and Bioscience Division under Grant No. DE-SC0018679.

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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