Dipole-bound excited states and resonant photoelectron imaging of phenoxide and thiophenoxide anions (3)

Cite as: J. Chem. Phys. **149**, 164301 (2018); https://doi.org/10.1063/1.5049715 Submitted: 24 July 2018 . Accepted: 04 October 2018 . Published Online: 22 October 2018

Guo-Zhu Zhu ២, Chen-Hui Qian, and Lai-Sheng Wang ២

COLLECTIONS

EP This paper was selected as an Editor's Pick



ARTICLES YOU MAY BE INTERESTED IN

Probing the structures and bonding of auropolyynes, $Au-(C\equiv C)_n - Au^-$ (n = 1-3), using highresolution photoelectron imaging The Journal of Chemical Physics 149, 144307 (2018); https://doi.org/10.1063/1.5040336

Slow photoelectron velocity-map imaging of cold C_7^- and C_9^- The Journal of Chemical Physics **149**, 174306 (2018); https://doi.org/10.1063/1.5054792

Dynamics of electron attachment and photodissociation in iodide-uracil-water clusters via time-resolved photoelectron imaging

The Journal of Chemical Physics 149, 084301 (2018); https://doi.org/10.1063/1.5040673



ADVANCED LIGHT CURE ADHESIVES

READ NOW

Take a closer look at what these environmentally friendly adhesive systems can do

J. Chem. Phys. **149**, 164301 (2018); https://doi.org/10.1063/1.5049715 © 2018 Author(s).

PHYSICS TODAY WHITEPAPERS



Dipole-bound excited states and resonant photoelectron imaging of phenoxide and thiophenoxide anions

Guo-Zhu Zhu, Chen-Hui Qian, and Lai-Sheng Wang^{a)} Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

(Received 24 July 2018; accepted 4 October 2018; published online 22 October 2018)

We report photodetachment and resonant photoelectron-imaging studies of cryogenically cooled phenoxide ($C_6H_5O^-$) and thiophenoxide ($C_6H_5S^-$) anions. In a previous study [H. T. Liu *et al.* Angew. Chem., Int. Ed. 52, 8976 (2013)], a dipole-bound excited state was observed for $C_6H_5O^-$ at 97 cm⁻¹ below the detachment threshold. Eight resonant photoelectron spectra were obtained via excitations to eight vibrational levels of the dipole-bound state (DBS) followed by autodetachment. Here we present a complete photodetachment spectrum of $C_6H_5O^-$ covering a spectral range 2600 cm⁻¹ above the detachment threshold and revealing nine additional vibrational resonances of the DBS. We also report the first observation of a dipole-bound excited state for $C_6H_5S^-$, 39 cm⁻¹ below its detachment threshold of 18 982 cm⁻¹. Photodetachment spectroscopy covering a spectral range 1500 cm⁻¹ above the threshold reveals twelve vibrational resonances for the DBS of $C_6H_5S^-$. By tuning the detachment laser to the vibrational resonances in the DBS of $C_6H_5O^-$ and $C_6H_5S^-$, we obtain highly non-Franck-Condon resonant photoelectron spectra, as a result of mode-selectivity and the $\Delta v = -1$ propensity rule for vibrational autodetachment. Five new fundamental vibrational frequencies are obtained for the ground state of the $C_6H_5O(X^2B_1)$ radical. Intramolecular inelastic scattering is observed in some of the resonant photoelectron spectra, leading to the excitation of the Franck-Condon-inactive lowest-frequency bending mode (v_{20}) of C₆H₅O. The first excited state of C₆H₅O (A^2B_2) is observed to be 0.953 eV above the ground state. Twelve resonant photoelectron spectra are obtained for $C_6H_5S^-$, allowing the measurements of seven fundamental vibrational frequencies of the C_6H_5S radical, whereas the non-resonant photoelectron spectrum exhibits only a single Franck-Condon active mode. The current study again demonstrates that the combination of photodetachment spectroscopy and resonant photoelectron spectroscopy is a powerful technique to obtain vibrational information about polar radical species. Published by AIP Publishing. https://doi.org/10.1063/1.5049715

I. INTRODUCTION

Due to the important role as the chromophore in aromatic amino acid tyrosine, which acts as the key catalyst in biological enzymes like photosystem II and the water oxidizing enzyme,¹ the photochemistry of phenol has received considerable attention.²⁻⁴ Extensive studies on the photodissociation of phenol, i.e., fission of the O-H bond to form the H atom and the phenoxy radical (C_6H_5O), have shown the significance of the nonradiative decay pathway via the optically dark ${}^{1}\pi\sigma^{*}$ state for protection from photochemical damage following UV absorptions.^{2,5–12} The photodissociation of thiophenol, the sulfur analog of phenol, has also been widely investigated, revealing a similar ${}^{1}\pi\sigma^{*}$ -mediated pathway yielding the thiophenoxy radical $(C_6H_5S\cdot)$.^{13–17} As photodissociation products, C₆H₅O and C₆H₅S are also of great interest in many systems. For example, C₆H₅O is a crucial transient intermediate in the combustion and atmospheric chemistry of small aromatic molecules.¹⁸⁻²¹ As a part of the phenolic compounds, like vitamin E and resveratrol, C₆H₅O is also involved in the antioxidant and radical scavenging processes.²² Moreover,

both C_6H_5O and C_6H_5S have been considered as the potential candidate molecules for the diffuse interstellar bands (DIBs) in astrophysics.^{23,24}

The electronic and vibrational properties of C₆H₅O and C₆H₅S have been extensively investigated both experimentally and theoretically.²⁵⁻⁴² The electron affinities (EAs) of the C₆H₅O and C₆H₅S radicals were first estimated by photodetachment spectroscopy of the corresponding anions C₆H₅O⁻ and C₆H₅S⁻.²⁵ An improved value for C₆H₅O was later measured by anion photoelectron spectroscopy (PES),²⁶ which also yielded the excited state of C_6H_5O . Later, high-resolution PE spectra of C₆H₅O⁻ and C₆H₅S⁻ were obtained by slow electron velocity-map imaging (SEVI), which accurately determined the EAs of C₆H₅O and C₆H₅S to be 2.2538(8) eV and 2.3542(6) eV, respectively.²⁷ The electronically excited state of C_6H_5O was studied²⁸⁻³¹ and the lowest electronic transition $(X^2B_2 \leftarrow A^2B_1)$ was determined to be 0.9523(1) eV by cavity ringdown spectroscopy.³¹ The lowest excited state of C_6H_5S was also calculated³² and experimentally measured to be 0.3719(9) eV above the ground state.²⁷ In addition, the ground-state vibrational frequencies of C₆H₅O and C₆H₅S have been computed in several theoretical studies^{32–36} and examined by various spectroscopies, $^{26,27,37-41}$ such as anion PES, 26,27 resonance

a)Email: Lai-Sheng_Wang@brown.edu

Raman spectroscopy,^{37–39} IR spectroscopy,⁴⁰ and laserinduced fluorescence.⁴¹ Recently, we measured the vibrational frequencies of C_6H_5O by high-resolution resonant PE imaging of cold $C_6H_5O^-$ from vibrational autodetachment via dipole-bound states (DBSs).⁴²

Anions with dipolar neutral cores ($\mu > 2.5$ D) can support DBSs near the electron detachment thresholds, ^{43–45} which were first observed as resonances in the photodetachment spectra of enolate anions.^{46–48} DBS has been suggested to be the "doorway" for the formation of valence-bound anions⁴⁹⁻⁵¹ and also proposed as the carriers of the DIBs.⁵²⁻⁵⁴ Rotational autodetachment via DBS has been studied by highresolution photodetachment spectroscopy^{47,48,55} and Rydberg electron transfer time-of-flight experiment.⁵⁶ Recently, resonant PES from autodetachment via vibrational levels of DBS was reported for $C_6H_5O^-$ for the first time using cryogenically cooled anions.⁴² The ground vibrational level of the DBS of $C_6H_5O^-$ was found to be 97 cm⁻¹ below the detachment threshold. Mode-specific autodetachment from eight vibrational levels of the DBS was observed, yielding highly non-Franck-Condon resonant PE spectra due to the $\Delta v = -1$ vibrational propensity rule.^{57,58} Subsequently, we have investigated a number of anions with dipole-bound excited states using the cryogenic cooling approach^{59–67} and demonstrated that resonant PES via vibrational autodetachment from DBS can yield more abundant vibrational information, especially for low-frequency and Franck-Condon-inactive vibrational modes, as well as conformationselective information.^{63,64}

In the current study, we report the complete photodetachment spectra of C₆H₅O⁻ and C₆H₅S⁻ and resonant PE imaging. A DBS is observed for the first time for $C_6H_5S^-$, 39 cm⁻¹ below its detachment threshold. In addition to the eight DBS vibrational resonances reported previously,⁴² nine new resonances are observed for $C_6H_5O^-$, whereas twelve vibrational resonances are observed for C₆H₅S⁻. By setting the detachment laser wavelengths to the DBS resonances for $C_6H_5O^-$ and C₆H₅S⁻, we obtain resonant PE images and spectra, which are highly non-Franck-Condon due to mode-selectivity⁴² and the $\Delta v = -1$ vibrational propensity rule.^{57,58} In total, five new fundamental vibrational frequencies are obtained for C₆H₅O and seven for C₆H₅S. Interestingly, intramolecular inelastic rescattering is observed in some resonant PE spectra of $C_6H_5O^-$, allowing the excitation of the Franck-Condon-inactive lowestfrequency bending mode v₂₀ of C₆H₅O to be observed. It is further shown that the photodetachment spectra for both $C_6H_5O^-$ and $C_6H_5S^-$ are in perfect agreement with the nonresonant PE spectra, vividly demonstrating the similar geometries between the neutral radicals and the dipole-bound anions, i.e., the weakly dipole-bound electron has little effect on the structure of the neutral core. Hence, the combination of photodetachment spectroscopy and resonant PES can be used to yield vibrational information for neutral polar radicals, rivaling IR spectroscopy.

II. EXPERIMENTAL METHODS

The experiment was performed on our third-generation electrospray-photoelectron spectroscopy apparatus,⁶⁸

consisting of a cryogenically cooled 3D Paul trap⁶⁹ and a high-resolution PE imaging system.⁷⁰ The $C_6H_5O^-$ and C₆H₅S⁻ anions were produced by deprotonation of phenol and thiophenol, respectively, via electrospray ionization (ESI) of ~1 mM solutions in a mixed solvent of CH₃OH/H₂O (9/1 in volume) at pH \sim 10. Anions generated in the ESI source were guided into a cryogenically cooled Paul trap operated at 4.5 K. After being accumulated for 0.1 s and thermally cooled via collisions with 1 mTorr He/H2 (4/1 in volume) background gas,⁶⁹ the anions were pulsed out at a 10 Hz repetition rate into the extraction zone of a time-of-flight mass spectrometer. The C₆H₅O⁻ and C₆H₅S⁻ anions of interest were selected by a mass gate and photodetached in the interaction zone of the imaging lens by the third harmonic of a Nd:YAG laser (354.7 nm) or a tunable dye laser. Photoelectrons were focused by the imaging lens⁷⁰ and projected onto a pair of 75-mm diameter micro-channel plates coupled to a phosphor screen, which were finally captured by a charge-coupled device camera. The images were inverse-Abel transformed and reconstructed using the BASEX and pBasex programs,^{71,72} which were found to give similar results. The presented PE spectra are based on BASEX, whereas the presented PE images are based on pBasex because it gives higher quality images. The PE spectra were calibrated with the known spectra of Au⁻ at different photon energies. The kinetic energy (KE) resolution achieved was 3.8 cm⁻¹ for electrons with 55 cm⁻¹ KE and about 1.5% (Δ KE/KE) for KE above 1 eV.^{68,70}

III. RESULTS

A. Non-resonant PE spectra of C₆H₅O⁻

Figure 1 shows the non-resonant PE spectra of $C_6H_5O^-$ at 480.60 nm and 354.7 nm. At 480.60 nm, the first intense peak 0_0^0 represents the 0-0 transition from the anion to the neutral $(X^2B_1 \leftarrow X^1A_1)$, giving an accurate EA of 18 173 cm⁻¹.^{27,42} Peaks A–D define a single vibrational progression of mode v_{11} ,



FIG. 1. Non-resonant photoelectron spectra of $\rm C_6H_5O^-$ at 480.60 nm and 354.7 nm.

as also observed previously.^{27,42} At the higher photon energy of 354.7 nm, transitions to the neutral excited state (A^2B_2) are also observed. The origin transition represented by peak F is measured to be 3.2056 ± 0.0020 eV, which lies 0.9524(20) eV above the ground state, consistent with the value determined by cavity ringdown spectroscopy.³¹ Peaks G–J represent vibrational excitations of the excited state. The electron binding energies (BE) of all the observed peaks A–J for the ground and excited states of C₆H₅O, their shifts from the origin of each state, and assignments are summarized in Table I, where other vibrational features from the resonant PES are also given (*vide infra*).

B. Photodetachment spectrum of C₆H₅O⁻

The photodetachment spectrum of C₆H₅O⁻ was measured by monitoring the total electron yield while scanning the dye laser wavelength at 0.1 nm/step across the detachment threshold, as presented in Fig. 2. A smaller step size of 0.01 nm/step was used in separate scans near each observed resonance to determine a more accurate peak position. In the previous study,⁴² photodetachment spectra were only measured for the v_{11} progression without continuously scanning the dye laser. The blue arrow in Fig. 2 denotes the detachment threshold at 18 173 cm⁻¹. Below the threshold, the weak peak labeled as 0 represents the ground vibrational level of the DBS of C₆H₅O⁻, which is due to resonant twophoton detachment.⁴² The binding energy of the DBS, defined as the energy difference between the neutral ground state and the ground state of the DBS, was determined to be $97 \pm 5 \text{ cm}^{-1}$ previously.⁴² Above the threshold, the continuous baseline indicates the cross section of the non-resonant detachment signal. The seventeen peaks, labeled as 1-17, represent optical excitations to the vibrational levels of the DBS of C₆H₅O⁻, followed by autodetachment. The peak numbers in red were reported previously.⁴² The peaks labeled in black numbers are newly observed because of the continuous scan of the detachment wavelength and the broader spectral range covered in the current study (up to $\sim 2600 \text{ cm}^{-1}$ above the threshold). The vibrational progression of mode v_{11}' up



TABLE I. Summary of the observed vibrational peaks from the PE spectra of C₆H₅O⁻. Their binding energies (BE), shifts from the 0-0 transitions of the \tilde{X}^2B_1 and \tilde{A}^2B_2 states, and assignments are given. The calculated frequencies at the B3LYP/6-311++G(d,p) level of theory are also given for the fundamental vibrational modes (see Table S1 for all modes).

Peak ^a	BE (eV) ^b	Shift (cm ⁻¹)	Assignment	Theoretical frequencies (cm ⁻¹)
0 0 ⁰	2.2532(4)	0	$\tilde{X}^2 B_1$	
Å	2.3175(6)	519	11 ¹	531
в	2.3815(6)	1035	11^{2}	
С	2.4460(6)	1555	11 ³	
D	2.5097(6)	2069	11^{4}	
E	2.5740(20)	2587	11 ⁵	
а	2.2750(10)	176	20^{1}	184
b	2.2984(10)	365	14^{1}	375
с	2.3116(10)	471	19 ¹	474
d	2.3315(6)	632	18^{1}	642
e	2.3511(6)	790	10^{1}	804
f	2.3737(6)	972	9 ¹	983
g	2.3956(6)	1149	$11^{1}18^{1}$	
h	2.4044(6)	1220	$11^{2}20^{1}$	
i	2.4152(6)	1307	$10^{1}11^{1}$	
j	2.4298(10)	1425	$10^{1}18^{1}$	
k	2.4374(6)	1486	$9^{1}11^{1}$	
l	2.4602(6)	1670	$11^{2}18^{1}$	
т	2.4680(6)	1733	$11^{3}20^{1}$	
n	2.4928(6)	1933	$10^{1}11^{1}18^{1}$	
0	2.5008(6)	1997	$9^{1}11^{2}$	
F	3.2056(20)	0	$\tilde{A}^2 \mathbf{B}_2$	
G	3.2699(20)	519	11^{1}	524
Н	3.3328(20)	1026	11 ²	
I	3.3594(20)	1240	61	1319
J	3.4029(20)	1591	11 ³	

^aPeaks in bold were reported previously in Ref. 42. The peaks designated by lower case letters were observed in the resonant PE spectra.

^bNumbers in parentheses indicate the experimental uncertainties in the last digit.

to the fifth quantum (peak 17) is observed in the current spectrum.

The photon energies, shifts from the ground vibrational level of the DBS, and the assignments of the observed vibrational resonances are given in Table II. The assignments are

> FIG. 2. Photodetachment spectrum of C₆H₅O⁻ by measuring the total electron yield as a function of photon energy across the detachment threshold. The blue arrow at 18 173 cm⁻¹ marks the detachment threshold. The peak 0 below the threshold represents the vibrational ground state of the dipole-bound excited of C₆H₅O⁻ and it is from resonant twophoton detachment, while peaks 1-17 are due to autodetachment from the DBS vibrational levels. The peaks labeled in red were reported previously,42 and the peaks in black are newly resolved. The assignments of peaks 1, 7, 11, 15, and 17 to the vibrational progression of mode v_{11}' are also given.

TABLE II. The observed peaks, wavelengths, photon energies, and shifts from the ground vibrational level and assignments of the photodetachment spectrum of $C_6H_5O^-$ in Fig. 2.

Peak ^a	Wavelength (nm)	Photon energy (cm ⁻¹) ^b	Shift (cm ⁻¹)	Assignment
0	553.22	18076(5)		Ground state
1	537.78	18 595(5)	519	11'1
2	534.53	18708(5)	632	18'1
3	529.93	18870(5)	794	10'1
4	527.00	18975(5)	899	16'1
5	524.86	19053(5)	977	9′ ¹
6	524.42	19069(5)	993	8′ ¹
7	523.22	19112(5)	1036	11'2
8	520.17	19224(5)	1148	11' ¹ 18' ¹
9	515.90	19384(5)	1308	10'111'1
10	511.05	19568(5)	1492	9' ¹ 11' ¹
11	509.36	19632(5)	1556	11' ³
12	506.50	19743(5)	1667	11' ² 18' ¹
13	502.47	19902(5)	1826	$10'^{1}11'^{2}$
14	498.04	20079(5)	2003	9' ¹ 11' ² /10' ¹ 11' ² 20' ¹
15	496.33	20148(5)	2072	$11'^{4}$
16	485.67	20 590(5)	2514	9' ¹ 11' ³ /10' ¹ 11' ³ 20' ¹
17	483.90	20665(5)	2589	11′ ⁵

^aPeaks in bold were reported previously in Ref. 42.

^bNumbers in parentheses indicate the experimental uncertainties in the last digit.

all based on the resonant PE spectra in Figs. 3 and 4 and the calculated vibrational frequencies presented in Table S1 of the supplementary material.

C. Resonant photoelectron spectra of $C_6H_5O^-$ via vibrational autodetachment

By tuning the detachment laser to the newly observed peaks in Fig. 2, we obtain nine resonant PE spectra of $C_6H_5O^-$, as shown in Figs. 3 and 4. Resonant PE spectra corresponding to the peaks numbered in red were reported before.⁴² As discussed previously,^{42,60,61,64–67} two detachment pathways contributed to the resonant PE spectra: the non-resonant detachment process represented by the continuous signals in Fig. 2 and the resonantly enhanced vibrational autodetachment





FIG. 4. Resonant photoelectron images and spectra of $C_6H_5O^-$ at three different wavelengths, corresponding to peaks **3**, **5**, and **6** in Fig. 2. The first peak 0_0^0 labeled in bold face is enhanced due to autodetachments from fundamental vibrational levels of the DBS. The peak *a* assigned to the out-of-plane bending mode v_{20} of C_6H_5O is observed to be due to the intramolecular inelastic rescattering effect.^{60,65,66} The double arrow below the images indicates the direction of the laser polarization.

via the DBS. Due to the mode selectivity^{42,60,61,64–67} and the $\Delta v = -1$ propensity rule^{57,58} in the autodetachment process, the resonantly enhanced spectra in Figs. 3 and 4 are highly non-Franck-Condon in comparison to the non-resonant PE spectra in Fig. 1: one or more vibrational peaks are enhanced in the resonant PE spectra. Figures 3(b), 3(c), and 3(e) contain autodetachment from combinational and overlapping vibrational levels of the DBS of C₆H₅O⁻, while Figs. 3(a), 3(d), 3(f), and 4 are due to autodetachment from a single vibrational level of the DBS. The assignments of the enhanced vibrational peaks are given in bold face in Figs. 3 and 4. All the additionally observed peaks (*a-o*), their binding energies, shifts relative to the 0₀⁰ transition, and the assignments are also given in Table I.

FIG. 3. Resonant photoelectron images and spectra of $C_6H_5O^-$ at six different wavelengths, corresponding to the six resonances (in parentheses) in Fig. 2. The autodetachment-enhanced peaks are labeled in bold face. The assigned vibrational levels of DBS are given. The double arrows below the images indicate the direction of the laser polarization.



D. Dipole-bound excited state and photodetachment spectrum of $C_6H_5S^-$

High-resolution PE spectra of $C_6H_5S^-$ using SEVI were reported previously and the EA of C_6H_5S was measured to be 18 988(5) cm⁻¹.²⁷ For the ground state transition, a single vibrational progression in the v₁₁ mode was observed with a frequency of 427 cm⁻¹ without observable Franck-Condon activities in any other vibrational modes. We measured additional non-resonant PE spectra at several different laser wavelengths (Fig. S1 of the supplementary material). These spectra agree with the previous SEVI spectra. The near threshold spectrum (Fig. S1a) has a peak width of 1.5 meV mainly due to rotational broadening, yielding an EA of 2.3535(6) eV (189 882 ± 5 cm⁻¹).

To search for the DBS, we measured the photodetachment spectrum of $C_6H_5S^-$ from below the detachment threshold up to $\sim 1500 \text{ cm}^{-1}$ above the threshold, as shown in Fig. 5. We indeed found a DBS for C₆H₅S⁻, as revealed by the resonant peaks on top of the continuous detachment signals (1–12). The blue arrow indicates the detachment threshold at 18 982 cm⁻¹. It is interesting to note that the non-resonant detachment cross section of C₆H₅S⁻ seems to be significantly higher than that of $C_6H_5O^-$ (Fig. 2). The black up-pointing arrows indicate the wavelengths used to take the non-resonant PE spectra in Fig. S1 of the supplementary material. The twelve peaks, labeled as 1-12, correspond to resonant excitations to vibrational levels of the DBS of C₆H₅S⁻ followed by autodetachment, while peaks α and β exhibit a strong threshold enhancement (see below).⁷³ The weak below-threshold peak **0** at an excitation energy of 18 943 cm^{-1} came from resonant two-photon detachment, as revealed by the PE image in the inset of Fig. 5. This peak is 39 cm⁻¹ below the detachment threshold, defining the binding energy of the DBS. This value is smaller than the 97 cm^{-1} binding energy of the DBS in C₆H₅O⁻, as expected from the smaller dipole moment of C_6H_5S (3.2 D, see Sec. IV B) than that of C_6H_5O (4.1 D). The outmost ring in the inset of Fig. 5 is the resonant twophoton detachment signal from the DBS ground state, and the *p*-wave character of the image is consistent with the *s*-like FIG. 5. Photodetachment spectrum of C₆H₅S⁻ by measuring the total electron yield as a function of photon energy across the detachment threshold. The blue arrow at 18 982 cm⁻¹ marks the detachment threshold. The four black arrows pointing at the baseline indicate the detachment photon energies used in the non-resonant spectra presented in Figs. S1a-S1d. The peak 0 below the threshold represents the vibrational ground state of the DBS of C₆H₅S⁻. It is due to resonant two-photon detachment, corresponding to the outmost ring in the inset. The double arrow below the inset image indicates the direction of the laser polarization. The assignments of peaks 3, 8, and 12 to the vibrational progression of mode v_{11}' are given.

orbital of the DBS, as also observed in $C_6H_5O^-$ and other anions. $^{42,61,63-66}$

The photon energies, shifts from the ground vibrational level of the DBS, and assignments of the vibrational resonances observed in Fig. 5 are given in Table III. The assignments are all based on the resonant PE spectra in Fig. 6 and the calculated vibrational frequencies presented in Table S1 (supplementary material).

E. Resonant photoelectron images and spectra of $C_6H_5S^-$

The resonant PE images and spectra of $C_6H_5S^-$ are presented in Fig. 6. Similar to $C_6H_5O^-$, the resonant spectra, comprising of non-resonant detachment signals and resonant autodetachment signals, are highly non-Franck-Condon compared with the non-resonant spectra in Fig. S1 due to the

TABLE III. The observed peaks, wavelengths, photon energies, and shifts from the ground vibrational level and assignments of the photodetachment spectrum of $C_6H_5S^-$ in Fig. 5.

Peak	Wavelength (nm)	Photon energy (cm ⁻¹) ^a	Shift (cm ⁻¹)	Assignment
0	527.90	18943(5)		Ground state
1	523.53	19101(5)	158	20' ¹
2	519.22	19260(5)	317	20' ²
3	516.33	19367(5)	424	$11'^{1}$
4	515.68	19392(5)	449	19′ ¹
5	509.91	19611(5)	668	18′ ¹
6	508.51	19665(5)	722	10′ ¹
7	507.92	19688(5)	745	11'120'2
8	505.25	19792(5)	849	$11'^{2}$
9	500.91	19964(5)	1021	8'1
10	499.10	20036(5)	1093	11'118'1
11	497.72	20092(5)	1149	10'111'1
12	494.64	20217(5)	1274	11' ³
α	503.55	19859(5)	916	Threshold enhancement
β	501.84	19927(5)	984	Threshold enhancement

^aNumbers in parentheses indicate the experimental uncertainties in the last digit.



FIG. 6. Resonant photoelectron images and spectra of $C_6H_5S^-$ at twelve wavelengths, corresponding to peaks **1-12** (in parentheses) in Fig. 5. The autodetachment-enhanced peaks are labeled in bold face. And the assigned vibrational levels of DBS are also given. The double arrows below the images indicate the direction of the laser polarization.

mode selectivity and the $\Delta v = -1$ propensity rule. Except for the spectra in Figs. 6(g), 6(j), and 6(k), which involve autodetachment from combinational vibrational levels of the DBS, most of the resonant PE spectra are from vibrational



FIG. 7. The photoelectron images and spectra of $C_6H_5S^-$ at 503.55 nm and 501.84 nm, corresponding to the peaks α and β in Fig. 5. The enhanced peaks B (11²) and f (16¹) are due to threshold enhancement (supplementary material), rather than the autodetachment enhancement via DBS. The double arrow below the images indicates the directions of the laser polarization.

levels of single modes. The assignments of the enhanced vibrational peaks are given in bold face. As can be seen in Fig. 5, the non-resonant detachment cross sections of $C_6H_5S^-$ are

TABLE IV. Summary of the observed vibrational peaks from the photoelectron spectra of $C_6H_5S^-$. Their binding energies (BE), shifts from the 0-0 transition, and assignments are given. The theoretical frequencies of the fundamental vibrational modes of $C_6H_5S\bullet$ at the B3LYP/6-311++G(d,p) level of theory are also given (see Table S1 for a full list).

Peak	BE (eV) ^a	Shift (cm ⁻¹)	Assignment	Theoretical frequencies (cm ⁻¹)
000	2.3535(6)	0	Neutral ground state	
А	2.4058(6)	422	11^{1}	427
В	2.4587(6)	848	11 ²	
С	2.5109(6)	1269	11 ³	
a	2.3733(8)	160	20^{1}	161
b	2.3929(8)	318	20^{2}	
c	2.4274(10)	596	$11^{1}20^{1}$	
d	2.4362(10)	667	18^{1}	683
e	2.4435(10)	726	10^{1}	730
f	2.4678(6)	922	16 ¹	937

^aNumbers in parentheses indicate the experimental uncertainties in the last digit.

relatively high. Hence, some of the resonant enhancements in the resonant PE spectra of $C_6H_5S^-$ are not as dramatic as those in $C_6H_5O^-$. The resonant PE spectra corresponding to peaks α and β in Fig. 5 are displayed in Fig. 7 and there seems to be a strong threshold effect. All the observed peaks in the PE spectra, their binding energies, shifts from the 0_0^{0} transition, and assignments are summarized in Table IV.

IV. DISCUSSION

A. Non-resonant PE spectra of C₆H₅O⁻

The vibrational peaks shown in the non-resonant PE spectra in Fig. 1 are governed by the Franck-Condon principle, i.e., only symmetry-allowed modes with significant Franck-Condon activities can be observed. To assist the spectral assignments of the numerous non-Franck-Condon vibrational modes observed in the resonant PE spectra, we calculated the harmonic frequencies of the ground electronic state of C_6H_5O (X^2B_1) and C_6H_5S (X^2B_1) at the B3LYP/6-311++G(d,p) level of theory with the GAUSSIAN 09 package.⁷⁴ The frequencies of the excited state for C_6H_5O (A^2B_2) were calculated using the time-dependent density function theory at the same level. These computed frequencies are given in Table S1 of the supplementary material.

As reported previously,^{26,27,42} peaks A-E in Fig. 1 represent the vibrational progression of the most Franck-Condonactive mode v_{11} with a measured frequency of 519 cm⁻¹, which involves an in-plane ring stretching (Table S2). At 354.7 nm, peaks F-J at higher binding energies represent the excited state of $C_6H_5O(A^2B_2)$, which was observed in a previous low resolution PE spectrum at 1.06(5) eV above the ground state.²⁶ Peak F at 3.2056 eV is the 0_0^0 transition to the excited state, defining a more accurate excitation energy of 0.9524(20) eV above the ground state, in agreement with the value measured previously in the cavity ringdown experiment.³¹ Peaks F–H and J represent the vibrational progression of the ring-stretching v_{11} mode with a spacing of 519 cm⁻¹, the same as that of the ground state. Peak I is from a different vibrational mode with a frequency of 1240 cm^{-1} . Our calculation shows two A₁ modes v_6 (1319 cm⁻¹) and v_7 (1199 cm^{-1}) close to the 1240 cm⁻¹ experimental frequency. Previous high-level calculations reported scaled frequencies of $1201-1252 \text{ cm}^{-1}$ for v₆ and $1143-1154 \text{ cm}^{-1}$ for v₇.³⁰ Hence, we tentatively assign peak I to the fundamental mode v_6 of the excited state of C_6H_5O (A^2B_2). This mode involves the C-O stretching, as shown in Table S2 of the supplementary material.

B. Photodetachment spectra of $C_6H_5O^-$ and $C_6H_5S^-$

The vibrational resonances in $C_6H_5O^-$ were first observed serendipitously using our room temperature ion trap.⁶⁸ With the cryogenically controlled ion trap, we examined these resonances more carefully and observed the mode-selectivity in the first resonant PE spectra via vibrational autodetachment.⁴² Eight DBS resonances including the progression of mode v_{11}' up to the third quantum were probed then. The binding energy of the DBS was found to be 97 cm⁻¹, but the photodetachment spectrum was not continuously scanned. In the current work,

the full photodetachment spectrum of $C_6H_5O^-$ is obtained up to $\sim 2600 \text{ cm}^{-1}$ above the detachment threshold, as shown in Fig. 2. Apart from the previously reported DBS resonances labeled in red, nine more vibrational resonances are observed and labeled in black in the new photodetachment spectrum (Fig. 2). As shown previously, 59-67 all the resonances display the asymmetric Fano line shapes as expected,⁷⁵ due to the interference between the non-resonant direct detachment and the resonant autodetachment. The vibrational progression of mode v_{11}' is observed up to the fifth quantum in Fig. 2. We found previously that the vibrational frequencies of the v_{11}' mode in the DBS of $C_6H_5O^-$ were the same as those of the v_{11} mode in neutral C_6H_5O within our experimental accuracy (the ' was used to designate the DBS vibrational modes), consistent with the fact that the highly diffuse dipole-bound electron has no effect on the structure of the molecular core. This is further verified by the perfect match of the frequencies and relative intensities of almost all the vibrational peaks between the nonresonant PE spectrum and the photodetachment spectrum (Fig. S2 of the supplementary material).

We estimated the dipole moment of C_6H_5S to be 3.2 D at the B3LYP/6-311++G(d,p) level of theory. Hence, the $C_6H_5S^$ anion should also be able to support a DBS, which is indicated by the vibrational resonances in the photodetachment spectrum in Fig. 5. With a smaller dipole moment compared to that of C_6H_5O (4.1 D),⁴² the binding energy for the DBS of $C_6H_5S^$ is also expected to be smaller, as indicated by the peak 0 in Fig. 5, which is measured to be 39 cm⁻¹ below the detachment threshold. This peak represents the ground vibrational level of the DBS, which is confirmed by the resonant two-photon detachment image (inset of Fig. 5). This is further verified by the similarity of the non-resonant PE spectrum at 492.10 nm and the photodetachment spectrum of $C_6H_5S^-$, as shown in Fig. S3 of the supplementary material.

In addition, more vibrational peaks, which are absent in the non-resonant PE spectra, are observed in the photodetachment spectra (Figs. S2 and S3 of the supplementary material). The relative intensities of the v_{11} progression between the photodetachment spectra and the PE spectra obey the Franck-Condon principle for both systems. However, the resonant excitations to the DBS allow some vibrational levels with low or negligible Franck-Condon factors in the PE spectra to be observed in the photodetachment spectra. Therefore, richer and more accurate vibrational information for the C6H5O and C₆H₅S radicals can be obtained from the photodetachment spectra in Figs. 2 and 5, as well as the resonant PE spectra. The assignments of the observed vibrational resonances given in Tables II and III are all based on the resonant PE spectra presented in Figs. 3, 4, 6, and 7 along with the calculated vibrational frequencies given in Table S1. The schematic energy level diagrams showing autodetachment from the vibrational levels of the DBS to the neutral states are presented in Figs. 8 and 9 for $C_6H_5O^-$ and $C_6H_5S^-$, respectively.

C. Resonant PES of $C_6H_5O^-$ via vibrational autodetachment from the DBS

As shown previously,^{42,60–66} autodetachment from the vibrational levels of the DBS to final neutral states exhibits



FIG. 8. Schematic energy level diagram for autodetachment from the DBS vibrational levels of C6H5O⁻ to the neutral final states of C₆H₅O. The singlemode vibrational levels of the DBS are given on the left with arrows indicating the autodetachment. The combinational and overlapping vibrational levels of the DBS are given on the right. The vibrational progressions of mode v_{11} in the DBS and neutral states are highlighted in bold face. The detachment threshold $(18 \ 173 \ \text{cm}^{-1})$ and the DBS binding energy (97 cm⁻¹) of C₆H₅O⁻ are also given. The peaks and assignments in red were reported previously.⁴² The assignments of the final neutral states and the DBS levels are given in Tables I and II, respectively.

mode selectivity and obeys the $\Delta v = -1$ propensity rule under the harmonic approximation.^{57,58} For autodetachment involving vibrational levels of a single mode (v'_x) , the *n*th vibrational level of this mode $(\nu'_x{}^n)$ in the DBS autodetaches to the (n - 1)th level of the same mode in the neutral (v_x^{n-1}) , in which one quantum of vibrational energy is coupled to the dipole-bound electron. For autodetachment from a combinational vibrational level $(v'_x{}^m v'_y{}^n...)$ of the DBS, the final neutral level can be either $v_x{}^{m-1}v_y{}^n...$ or $v_x{}^m v_y{}^{n-1}...$ (mode selectivity), provided the vibrational frequencies are all larger than the binding energy of the DBS. Hence, relative peak intensities of these final neutral vibrational levels will be enhanced in comparison to those in non-resonant PE spectra, giving rise to highly non-Franck-Condon resonant PE spectra. It has also been shown that certain modes in the combinational levels have stronger couplings with the dipole-bound electron.42

Tuning the detachment laser to the seventeen resonances in Fig. 2 will result in seventeen resonant PE spectra for $C_6H_5O^-$. The resonant spectra obtained for peaks **1**, **2**, and **7**– **12** were reported previously.⁴² As can be seen in Fig. 2, these resonances are relatively strong, which was why they were found previously without systematic wavelength scans.^{42,68} The nine new resonant PE spectra presented in Figs. 3 and 4 are discussed in detail here.

Figure 3(a) at 527.00 nm is from the weak resonant peak 4 (Fig. 2). As shown previously,⁴² peaks d and e are due to the 18^1 and 10^1 final vibrational states, which have negligible Franck-Condon factors (Fig. 1), but they are very intense in Fig. 3(a) mainly due to threshold enhancement,⁷³ in particular, for peak e. The photon energy used in Fig. 3(a) agrees with the excitation to the $16'^1$ DBS level (Table II), which should show an enhancement of the 0_0^0 transition relative to peak A (11¹). However, this enhancement is not very obvious, probably due to the fact that peak A also displays some threshold enhancement. Figures 3(d) and 3(f) correspond to resonant excitations to $11'^4$ and $11'^5$ of the DBS, respectively, resulting in strong enhancement of 11³ (C) and 11⁴ (D), following the $\Delta v = -1$ propensity rule. However, peak A (11¹) is also significantly enhanced in Fig. 3(d), as well as peak B (11^2) in Fig. 3(f). These enhancements are surprising, indicating $\Delta v = -3$ for the autodetachment, i.e., coupling of three quanta of the v_{11}' mode to the dipole-bound electron to induce autodetachment. These deviations from the $\Delta v = -1$ propensity rule are due to anharmonic effects at higher vibrational levels, which have been observed previously.^{60,61,64,66} It is interesting to note that $\Delta v = -2$ does not seem to occur for this mode. This vibrational level dependence of the anharmonic effects is not well understood and deserves further theoretical attention.



FIG. 9. Schematic energy level diagram for autodetachment from the DBS vibrational levels of $C_6H_5S^-$ to the neutral final states of C_6H_5S . The single-mode vibrational levels of the DBS are given on the left with arrows indicating the autodetachment. The combinational vibrational levels of the DBS are given on the right. The vibrational progressions of mode v_{11} in the DBS and neutral states are highlighted in bold face. The detachment threshold (18 982 cm⁻¹) and the DBS binding energy (39 cm⁻¹) of $C_6H_5S^-$ are also given. The assignments of the DBS levels and the final neutral states are given in Tables III and IV, respectively.

In Fig. 3(b), peak A (11^1) is slightly enhanced and peak i (10¹11¹) is greatly enhanced, suggesting that the resonant peak 13 corresponds to a combinational DBS level of $10^{\prime 1}11^{\prime 2}$. However, it is surprising that the 11² final state, involving coupling of one quantum of the v_{10}' mode, is not enhanced, whereas the slight enhancement of the 11¹ final state would require the coupling of one quantum of the v_{11} ' mode and one quantum of the v_{10}' mode. We also observed previously that the v_{10}' mode does not seem to couple to the dipolebound electron in the resonant excitation to the 10'111'1 DBS level.⁴² In Fig. 3(c), the enhancements of three peaks, A (11^1) , $h(11^220^1)$, and $k(9^111^1)$, are due to autodetachment from two degenerate combinational DBS levels, 9'111'2 and $10'^{1}11'^{2}20'^{1}$. The same case is observed in Fig. 3(e), where the excitations to combinational vibrational levels of $9'^{1}11'^{3}$ and $10'^{1}11'^{3}20'^{1}$ give the enhancement of peak o (9¹11²) and peak m (11^{'3}20¹), respectively. Only one peak getting enhanced in each combinational level indicates the selectivity of vibrational mode in the vibronic coupling induced autodetachment, meaning that mode v_{11}' in $9'^1 11'^3$ and mode v_{10}' in $10^{\prime 1}11^{\prime 3}20^{\prime 1}$ are favored to couple with the dipole-bound electron, which cause the enhancement of peaks o and m, respectively.

In addition, numerous weak peaks *a*, *b*, *d*, *f*, *g*, *j*, *l*, and *n* are also observed in Fig. 3. The assignments of peaks *a*, *b*, and *j* are based on the comparison to the calculated frequencies in Table S1. Peak *a* will be discussed below. The weak peak *b* with a shift of 365 cm⁻¹ is assigned to the mode v_{14} (calculated frequency 375 cm⁻¹), which is an out-of-plane bending mode as shown in Table S2. Peak *j* shifted by 1425 cm⁻¹

from peak 0_0^0 is assigned to a combinational vibrational level of $10^1 18^1$ with the frequencies measured to be 790 cm⁻¹ for v_{10} and 632 cm⁻¹ for v_{18} .⁴² The other peaks were reported preiously.⁴² All the observed peaks, their binding energies, shifts, and the assignments are summarized in Table I. The observed vibrational resonances of the DBS and their autodetachment channels for C₆H₅O⁻ are given schematically in Fig. 8.

D. Intramolecular inelastic rescattering in autodetachment from DBS of $C_6H_5O^-$

Figure 4 shows three resonant PE spectra due to autodetachment from three fundamental vibrational levels, $10^{\prime 1}$, $9^{\prime 1}$, and $8'^1$, of the DBS of C₆H₅O⁻. The 0_0^0 peak in all spectra is enhanced, as expected from the $\Delta v = -1$ propensity rule. Interestingly, peak a is also observed in these spectra with significant intensities. With a shift of 176 cm^{-1} from the 0_0^0 peak, peak a is assigned to the lowest-frequency bending mode v_{20} of C₆H₅O (184 cm⁻¹ calculated frequency, Table S2), which is Franck-Condon-forbidden and absent in the non-resonant PE spectra.^{27,42} Excitation of this vibrational state in these resonant PE spectra is attributed to intramolecular inelastic rescattering, which has been observed previously and usually results in excitations of low-frequency and Franck-Condon-forbidden vibrational modes.^{60,65,66} The idea is that the outgoing autodetached electron from the DBS can interact with the neutral core to cause excitations of the low-frequency vibrations. The rescattering process is similar to electron energy loss spectroscopy,^{76,77} in which electrons with fixed kinetic energies cause vibrational excitations of surface adsorbates or gaseous molecules via electronic to vibrational energy transfers. In the current cases, autodetachment from vibrational levels $10'^1$ (794 cm⁻¹), $9'^1$ (977 cm^{-1}) , and $8'^1$ (993 cm^{-1}) results in outgoing photoelectrons with kinetic energies of 697 cm⁻¹, 880 cm⁻¹, and 896 cm⁻¹, respectively. Some of the outgoing electrons are rescattered inelastically by the neutral core and excite the v_{20} vibrational mode. In fact, the photoelectron kinetic energies in these three cases are all higher than the calculated frequencies of several other bending modes, i.e., v_{14} (375 cm⁻¹), $v_{30}~(446~cm^{-1}),~v_{19}~(474~cm^{-1}),~v_{29}~(597~cm^{-1}),$ and v_{18} (642 cm⁻¹). Some of these modes are indeed excited, such as peak d due to the v_{18} mode or peak b (v_{14}) and c (v_{19}) in Fig. 4(c) (Table I), but mode v_{20} exhibits the strongest rescattering effect.

Vibronic coupling or Herzberg-Teller coupling has been invoked previously to explain observations of Franck-Condoninactive vibrational modes or anomalous vibrational intensities in PES.^{78,79} While we cannot rule out the effects of vibronic coupling in the observation of the v_{20} mode, the strong intensity observed in the resonant PE spectra shown in Fig. 4 seems to be similar to the inelastic rescattering we observed previously,^{60,65,66} as well as that observed in electron-impact induced autodetachment⁸⁰ and that in rotationally resolved PE spectra of NH_3 .⁸¹ It appears that the relative intensity of the rescattering depends on the outgoing electron kinetic energies and the relative contribution of the autodetached electrons. For example, no significant v_{20} excitation was observed in any of the resonant PE spectra from autodetachment of the v_{11}' (519 cm⁻¹) levels of the DBS [Figs. 3(d) and 3(f) and in Ref. 42], resulting in an outgoing electron with a much smaller kinetic energy of 422 cm⁻¹. Autodetachment from the $16'^1$ (899 cm⁻¹) level would yield an outgoing electron with a kinetic energy similar to those from $10'^1$, $9'^1$, or $8'^1$. However, the autodetachment contribution to the 0_0^0 transition is very small [Fig. 3(a)], consistent with the very weak v_{20} excitation according to the rescattering model.

E. Resonant PES of C₆H₅S⁻

Similar to the resonant PE spectra of $C_6H_5O^-$, twelve resonant PE spectra are obtained for $C_6H_5S^-$ (Fig. 6) by tuning the detachment laser to the twelve resonances in Fig. 5. The non-resonant PE spectra of C₆H₅S⁻ are very simple, showing a progression of the v_{11} mode only (Fig. S1).²⁷ The resonant PE spectra of C₆H₅S⁻ are also quite simple, and some of the expected enhancements are not very prominent. Figures 6(a), 6(c), and 6(d), corresponding to resonances 1, 3, and 4 in Fig. 5, show only the single 0_0^0 peak, suggesting excitations to fundamental vibrational levels of $20'^1$, $11'^1$, and $19'^1$ of the DBS, respectively, following the $\Delta v = -1$ vibrational autodetachment propensity rule. Figures 6(e), 6(f), and 6(i) correspond to excitations to the $18'^1$, $10'^1$, and $8'^1$ DBS levels, respectively, according to the computed frequencies (Table S1). However, the enhancement of peak 0_0^0 relative to peak A in these resonant PE spectra is not so obvious, probably due to the fact that there may also be a slight near-threshold enhancement of peak A. In Figs. 6(b), 6(h), and 6(l), the peaks a (20¹), A (11¹), and B (11²) are greatly enhanced, respectively. These spectra correspond to excitations to the $20'^2$, 11^{'2}, and 11^{'3} DBS levels, respectively, following straightforwardly the $\Delta v = -1$ propensity rule. The peak *a* in Fig. 6(b) with a shift of 160 cm^{-1} from the 0_0^{0} peak is due to the lowestfrequency bending mode v₂₀ of C₆H₅S, which has a calculated frequency of 161 cm⁻¹ (Tables S1 and S2 of the supplementary material).

The remaining resonant PE spectra in Figs. 6(g), 6(j), and 6(k) all involve autodetachment from combinational vibrational levels of the DBS of $C_6H_5S^-$. The enhancement of peak A (11¹) in Fig. 6(j) and peak $e(10^1)$ in Fig. 6(k) is due to autodetachment from combinational levels of $11'^{1}18'^{1}$ and $10'^{1}11'^{1}$, respectively. Clearly, one vibrational mode is more favored to couple with the dipole-bound electron during autodetachment, i.e., mode v_{18}' in $11'^118'^1$ and mode v_{11}' in $10'^111'^1$, resulting in the significantly enhanced peak A (11^1) and peak e (10¹). Such mode-selectivity in the autodetachment processes involving combinational vibrational levels is observed previoully, $^{42,60,61,64-67}$ as well as above for C₆H₅O⁻. Finally, Fig. 6(g) shows three enhanced peaks, b (20²), A (11¹), and c (11¹20¹), implying autodetachment from a combinational level of $11'^{1}20'^{2}$. The autodetachment to peak b and c follows the $\Delta v = -1$ rule, but autodetachment to peak A (11¹) would involve $\Delta v = -2$ in the bending mode v_{20}' . A weak peak d is also observed in Fig. 6(g) with a shift of 667 cm⁻¹ from the 0_0^0 peak, consistent with the excitation of v₁₈ (computed frequency of 683 cm⁻¹, Table S1). Peak *d* is likely due to a threshold effect, which is in fact also observed near the threshold in Fig. 6(f).

All the observed vibrational resonances of the DBS and their autodetachment channels for $C_6H_5S^-$ are schematically shown in Fig. 9.

F. Near-threshold resonances of C₆H₅S⁻

Figure 7 shows the PE spectra of $C_6H_5S^-$ taken at the photon energies corresponding to the weak resonant peaks α and β in Fig. 5. Peak B in Fig. 7(a) is the 11² vibrational level of C₆H₅S. The photon energy of peak α is $916 \,\mathrm{cm}^{-1}$ above the ground state of the DBS, but $916 \,\mathrm{cm}^{-1}$ does not correspond to any combinational levels of $v_{11}'^2$. Hence, the enhanced 11^2 peak seems to be a near-threshold effect. Similarly, peak f in Fig. 7(b) also seems to be due to a nearthreshold enhancement. Peak f is at 922 cm⁻¹ relative to the 0_0^0 peak and corresponds to 16^1 (computed frequency of v₁₆ is 937 cm⁻¹, Table S1), which is not present in the non-resonant PE spectra (Fig. S1). The photon energy of peak β is 984 cm⁻¹ above the DBS ground state of $C_6H_5S^-$, but 984 cm⁻¹ does not correspond to any combination level of $v_{16}'^1$. According to the Wigner threshold law,⁷³ s-wave detachment channels from *p*-type orbitals should have significant intensities near the detachment threshold. As shown in Fig. S4 of the supplementary material, the HOMO of $C_6H_5S^-$ is a *p*-type delocalized π orbital. The detachment from the HOMO results in an s + d angular distribution,²⁷ as also shown in the current non-resonant PE spectra.

However, in the vicinity of the 11^1 detachment channel near 19 420 cm⁻¹ (Fig. 5), a step was observed, also consistent with the expected threshold behavior for *s*-wave detachment, rather than a peak as observed in the case of peak α for the 11^2 detachment channel. Hence, the α peak was most likely due to vibronic coupling.^{78,79} The v₁₆ mode is an out-of-plane bending mode (Table S2) and should be Franck-Condon-inactive. Hence, the strong enhancement of the 16^1 peak corresponding to peak β is also most likely due to vibronic coupling.

G. Photoelectron angular distributions

For one-photon detachment with linearly polarized light, the photoelectron angular distribution (PAD) depends on the symmetry of the orbital where the electron is detached and is governed by an anisotropy parameter β which varies between -1 and 2.^{82,83} The π type HOMOs of C₆H₅O⁻ and C₆H₅S⁻ (Fig. S4) are similar and are expected to give rise to PADs of s + d characters, in agreement with the observed β values of -0.6 to -0.3 in the non-resonant PE spectra.^{27,42} The resonant two-photon detachment from the ground vibrational level of a DBS always gives a distinct *p*-wave character, $\frac{42,61,63-66}{6}$ as presented in the inset of Fig. 5 for $C_6H_5S^-$, which indicates an s-type orbital for the DBS. However, autodetachment from the above-threshold resonances results in isotropic distributions.⁴² With contributions from both direct detachment and autodetachment via DBS, the enhanced peaks in the resonant PE spectra can have various PADs depending on the relative ratio of the two detachment channels. For example, the weakly enhanced peak 0_0^0 in Figs. 3(a) and 4 from autodetachment of resonances 3–6 in Fig. 2 has a β value of -0.5 to -0.2, close to the value from direct detachment. On the other hand,

TABLE V.	Summary	for a	all the	observed	fundamental	vibrational	frequencies	of	C_6H_5O	and	C_6H_5S	by
photodetac	hment and j	photo	electro	n spectroso	copy.							

	State	Mode ^a	Observed frequency (cm ⁻¹) ^b	Observed peaks ^c	B3LYP/6-311++G(d,p)	B3LYP/aug-cc-pVTZ (scaled by 0.9687) ^d
	$\tilde{X}^2 B_1$	ν ₂₀	176(8)	а	184	182
		v ₁₄	365(8)	b	375	369
		v_{19}	471(8)	с	474	466
		\mathbf{v}_{11}	519(6)/519(5)	A/1	531	515
		\mathbf{v}_{18}	632(6)/632(5)	d/2	642	635
C ₆ H ₅ O		\mathbf{v}_{10}	790(6)/794(5)	e/3	804	782
		v_{16}	899(5)	4	919	906
		v 9	977(5)	5	983	959
		ν_8	993(5)	6	1008	979
	$\tilde{A}^2 \mathbf{B}_2$	v_{11}	519(15)	G	524	501-508 ^e
		ν_6	1240(15)	Ι	1319	1201-1252 ^e
	$\tilde{X}^2 B_1$	v ₂₀	160(6)/158(5)	a/1	161	156
		v_{11}	422(6)/424(5)	A/3	427	414
		v_{19}	449(5)	4	463	450
C ₆ H ₅ S		v_{18}	667(8)/668(5)	d/5	683	667
		v_{10}	726(8)/722(5)	e/6	730	709
		v_{16}	922(5)	f	937	923
		ν_8	1021(5)	9	1038	1009

^aThe modes in bold were reported previously in Ref. 42.

^bNumbers in parentheses indicate the experimental uncertainties in the last digit.

^cPeaks in letter are observed in the PE spectra and peaks in numbers are observed in the photodetachment spectra.

^dThe calculated frequencies are from Ref. 27.

^eThe calculated frequencies for the C₆H₅O (\tilde{A}^2B_2) at various high level of theories are from Ref. 30.

peak 0_0^0 in Fig. 6(c), peak A (11¹) in Fig. 6(h), and peak B (11²) in Fig. 6(l), corresponding to strong resonances of **3**, **8**, and **12** in Fig. 5, respectively, possess a β value of ~0.15, almost isotropic, because of the large contribution from the autodetachment channel.

However, the images of the enhanced peaks i (10¹11¹), m (11³20¹), and o (9¹11²) in Fig. 3 for C₆H₅O⁻ show clear p-wave distributions with β values of 0.5–0.8. Similarly, the images of peaks a (20¹) and d (18¹) in Figs. 3(a) and 4 for C₆H₅O⁻ also exhibit distinct p-wave distributions. Similar PADs are observed for peaks a (20¹), c (11¹20¹), and d (18¹) with β values of 0.1–0.3 in Fig. 6 for C₆H₅S⁻. It turns out that these peaks all represent out-of-plane bending excitations of C₆H₅O and C₆H₅S (Table S2). It is understandable that the low-frequency bending modes play important roles in the PADs for electron ejections. Further studies of these PADs may gain interesting insights into the vibronic coupling leading to autodetachment from the DBS.

H. Fundamental vibrational information resolved for C_6H_5O and C_6H_5S

The resemblances between the non-resonant PE spectra and the photodetachment spectra (Figs. S2 and S3) suggest similar geometries of the neutral radicals and the dipolebound anions because the weakly dipole-bound electron has little effect on the structure of the neutral core. Since photodetachment spectroscopy has a higher spectral resolution, it could be a powerful tool to resolve vibrational information for the neutral radicals with large dipole moments.^{59–68} Furthermore, the vibrational features with negligible Franck-Condon factors can be resolved in resonant PE spectra via vibrational autodetachment from DBS. As summarized in Table V, the combination of photodetachment spectroscopy and resonant PE spectra yields five new fundamental vibrational modes for the ground state of the C₆H₅O radical and seven fundamental vibrational modes for the ground state of C₆H₅S. Two vibrational modes, v_{11} and v_6 , are also obtained for the excited state (A^2B_2) of C₆H₅O from the non-resonant spectrum at 354.7 nm (Fig. 1). The experimental frequencies for the ground states of the two radicals agree well with the theoretical frequencies calculated at both the B3LYP/6-311++G(d,p) level and the B3LYP/aug-cc-pVTZ (scaled by 0.9687 in Ref. 27) level of theory. It is interesting to note that the frequencies calculated by the B3LYP/6-311++G(d,p) level have not been scaled. The good agreement with the experimental values suggest the suitability of using B3LYP/6-311++G(d,p) to calculate vibrational frequencies, in particular, the low frequencies of small organic molecules.

V. CONCLUSIONS

In conclusion, we report an investigation of the photodetachment spectroscopy and resonant photoelectron imaging of cryogenically cooled $C_6H_5O^-$ and $C_6H_5S^-$ anions via vibrational levels of the dipole-bound states. Nine new DBS vibrational resonances are observed for $C_6H_5O^-$. The dipole-bound excited state is observed for the first time for $C_6H_5S^-$ with a binding energy of only 39 cm⁻¹. Twelve above-threshold vibrational resonances are observed for $C_6H_5S^-$. Resonant photoelectron images and spectra are obtained by tuning the detachment laser to the vibrational levels of the DBS. The observed vibrational features in both the photodetachment spectra and the resonant photoelectron spectra are assigned using the calculated frequencies and the $\Delta v = -1$ propensity rule for vibrational autodetachment from DBS. Five extra fundamental vibrational modes, including three low-frequency modes, are resolved for the ground state of $C_6H_5O(X^2B_1)$, and two fundamental vibrational modes are also resolved for its excited state (A^2B_2) . Intramolecular inelastic rescattering has been observed in the autodetachment process leading to the excitation of the lowest-frequency bending mode (v_{20}) of C₆H₅O. Seven fundamental vibrational modes, including several low-frequency modes, are resolved for the ground state of $C_6H_5S(X^2B_1)$, compared to the single v₁₁ vibrational progression observed in the non-resonant photoelectron spectra. The combination of photodetachment spectroscopy and resonant photoelectron imaging for cold anions is again shown to be a powerful method to obtain vibrational information of dipolar neutral radicals.

SUPPLEMENTARY MATERIAL

See supplementary material for the full sets of calculated vibrational frequencies for C_6H_5O and C_6H_5S , selected normal modes, non-resonant photoelectron spectra of $C_6H_5S^-$, comparisons of the photodetachment spectra and the non-resonant photoelectron spectra for $C_6H_5O^-$ and $C_6H_5S^-$, and the highest occupied molecular orbital pictures of $C_6H_5O^-$ and $C_6H_5S^-$.

ACKNOWLEDGMENTS

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

- ¹J. Stubbe and W. A. van der Donk, Chem. Rev. 98, 705–762 (1998).
- ²A. L. Sobolewski, W. Domcke, C. Dedonder-Lardeux, and C. Jouvet, Phys. Chem. Chem. Phys. **4**, 1093–1100 (2002).
- ³S. J. Harris, D. Murdock, Y. Y. Zhang, T. A. A. Oliver, M. P. Grubb, A. J. Orr-Ewing, G. M. Greetham, I. P. Clark, M. Towrie, S. E. Bradforth, and M. N. R. Ashfold, Phys. Chem. Chem. Phys. 15, 6567–6582 (2013).
- ⁴K. R. Yang, X. F. Xu, J. J. Zheng, and D. G. Truhlar, Chem. Sci. 5, 4661
- (2014).
- ⁵C. M. Tseng, Y. T. Lee, and C. K. Ni, J. Chem. Phys. **121**, 2459 (2004).
- ⁶M. G. D. Nix, A. L. Devine, B. Cronin, R. N. Dixon, and M. N. R. Ashfold, J. Chem. Phys. **125**, 133318 (2006).
- ⁷C. M. Tseng, Y. T. Lee, M. F. Lin, C. K. Ni, S. Y. Liu, Y. P. Lee, Z. F. Xu, and M. C. Lin, J. Phys. Chem. A **111**, 9463 (2007).
- ⁸A. Iqbal, L. J. Pegg, and V. G. Stavros, J. Phys. Chem. A **112**, 9531 (2008).
- ⁹R. N. Dixon, T. A. A. Oliver, and M. N. R. Ashfold, J. Chem. Phys. **134**, 194303 (2011).
- ¹⁰G. M. Roberts, A. S. Chatterley, J. D. Young, and V. G. Stavros, J. Phys. Chem. Lett. 3, 348 (2012).
- ¹¹X. F. Xu, J. J. Zheng, K. R. Yang, and D. G. Truhlar, J. Am. Chem. Soc. 136, 16378 (2014).
- ¹²C. J. Xie, J. Y. Ma, X. L. Zhu, D. R. Yarkony, D. Q. Xie, and H. Guo, J. Am. Chem. Soc. **138**, 7828 (2016).
- ¹³J. S. Lim, I. S. Lim, K. S. Lee, D. S. Ahn, Y. S. Lee, and S. K. Kim, Angew. Chem., Int. Ed. 45, 6290 (2006).
- ¹⁴I. S. Lim, J. S. Lim, Y. S. Lee, and S. K. Kim, J. Chem. Phys. **126**, 034306 (2007).

- ¹⁵A. L. Devine, M. G. D. Nix, R. N. Dixon, and M. N. R. Ashfold, J. Phys. Chem. A **112**, 9563 (2008).
- ¹⁶T. S. Venkatesan, S. G. Ramesh, Z. Lan, and W. Domcke, J. Chem. Phys. 136, 174312 (2012).
- ¹⁷G.-S.-M. Lin, C. Xie, and D. Xie, J. Phys. Chem. A **121**, 8432–8439 (2017).
- ¹⁸R. A. Shandross, J. P. Longwell, and J. B. Howard, Symp. (Int.) Combust. 26, 711–719 (1996).
- ¹⁹J. Platz, O. J. Nielsen, T. J. Wallington, J. C. Ball, M. D. Hurley, A. M. Straccia, W. F. Schneider, and J. Sehested, J. Phys. Chem. A **102**, 7964 (1998).
- ²⁰H. Richter and J. B. Howard, Phys. Chem. Chem. Phys. **4**, 2038–2055 (2002).
- ²¹P. Hemberger, G. da Silva, A. J. Trevitt, T. Gerber, and A. Bodi, Phys. Chem. Chem. Phys. **17**, 30076 (2015).
- ²²T. Jahnert, M. D. Hager, and U. S. Schubert, J. Mater. Chem. A 2, 15234 (2014).
- ²³M. Araki, Y. Matsushita, and K. Tsukiyama, Astron. J. 150, 113 (2015).
- ²⁴M. Araki, K. Niwayama, and K. Tsukiyama, Astron. J. 148, 87 (2014).
- ²⁵J. H. Richardson, L. M. Stephenson, and J. I. Brauman, J. Am. Chem. Soc.
 97, 2967 (1975).
- ²⁶R. F. Gunion, M. K. Gilles, M. L. Polak, and W. C. Lineberger, Int. J. Mass Spectrom. Ion Processes **117**, 601 (1992).
- ²⁷J. B. Kim, T. I. Yacovitch, C. Hock, and D. M. Neumark, Phys. Chem. Chem. Phys. **13**, 17378 (2011).
- ²⁸J. Takahashi, T. Momose, and T. Shida, Bull. Chem. Soc. Jpn. **67**, 964 (1994).
- ²⁹J. G. Radziszewski, M. Gil, A. Gorski, J. Spanget-Larsen, J. Waluk, and B. J. Mróz, J. Chem. Phys. **115**, 9733 (2001).
- ³⁰C. W. Cheng, Y. P. Lee, and H. A. Witek, J. Phys. Chem. A **112**, 2648 (2008).
- ³¹C. W. Cheng, H. Witek, and Y. P. Lee, J. Chem. Phys. **129**, 154307 (2008).
- ³²C. W. Cheng, Y. P. Lee, and H. A. Witek, J. Phys. Chem. A **112**, 11998 (2008).
- ³³D. M. Chipman, R. F. Liu, X. F. Zhou, and P. Pulay, J. Chem. Phys. 100, 5023 (1994).
- ³⁴Y. Qin and R. A. Wheeler, J. Chem. Phys. **102**, 1689 (1995).
- ³⁵Y. Qin and R. A. Wheeler, J. Am. Chem. Soc. 117, 6083 (1995).
- ³⁶W. Xu and A. Gao, J. Phys. Chem. A **110**, 997–1004 (2006).
- ³⁷G. N. R. Tripathi and R. H. Schuler, J. Chem. Phys. 81, 113 (1984).
- ³⁸G. N. R. Tripathi, S. Qun, D. A. Armstrong, D. M. Chipman, and R. H. Schuler, J. Phys. Chem. **96**, 5344 (1992).
- ³⁹A. Mukherjee, M. L. McGlashen, and T. G. Spiro, J. Phys. Chem. **99**, 4912– 4917 (1995).
- ⁴⁰J. Spanget-Larsen, M. Gil, A. Gorski, D. M. Blake, J. Waluk, and J. G. Radziszewski, J. Am. Chem. Soc. **123**, 11253 (2001).
- ⁴¹K. Shibuya, M. Nemoto, A. Yanagibori, M. Fukushima, and K. Obi, Chem. Phys. **121**, 237 (1988).
- ⁴²H. T. Liu, C. G. Ning, D. L. Huang, P. D. Dau, and L. S. Wang, Angew. Chem., Int. Ed. **52**, 8976 (2013).
- ⁴³R. N. Compton and N. I. Hammer, in *Advances in Gas-Phase Ion Chemistry*, edited by N. Adams and I. Babcock (Elsevier Science, New York, 2001) Vol. 4, pp. 257–291.
- ⁴⁴K. D. Jordan and F. Wang, Annu. Rev. Phys. Chem. **54**, 367–396 (2003).
- ⁴⁵J. Simons, J. Phys. Chem. A **112**, 6401–6511 (2008).
- ⁴⁶A. H. Zimmerman and J. I. Brauman, J. Chem. Phys. 66, 5823–5825 (1977).
- ⁴⁷R. D. Mead, K. R. Lykke, W. C. Lineberger, J. Marks, and J. I. Brauman, J. Chem. Phys. **81**, 4883–4892 (1984).
- ⁴⁸K. R. Lykke, R. D. Mead, and W. C. Lineberger, Phys. Rev. Lett. **52**, 2221– 2224 (1984).
- ⁴⁹R. N. Compton, J. H. S. Carman, C. Desfrancois, H. Abdoul-Carime, J. P. Schermann, J. H. Hendricks, S. A. Lyapustina, and K. H. Bowen, J. Chem. Phys. **105**, 3472–3478 (1996).
- ⁵⁰J. H. Hendricks, S. A. Lyapustina, H. L. de Clercq, and K. H. Bowen, J. Chem. Phys. **108**, 8–11 (1998).
- ⁵¹T. Sommerfeld, Phys. Chem. Chem. Phys. 4, 2511–2516 (2002).
- ⁵²P. J. Sarre, Mon. Not. R. Astron. Soc. **313**, L14–L16 (2000).
- ⁵³F. Güthe, M. Tulej, M. V. Pachkov, and J. P. Maier, Astrophys. J. 555, 466–471 (2001).
- ⁵⁴R. C. Fortenberry, T. D. Crawford, and T. J. Lee, Astrophys. J. **762**, 121 (2013).
- ⁵⁵K. Yokoyama, G. W. Leach, J. B. Kim, and W. C. Lineberger, J. Chem. Phys. **105**, 10696–10705 (1996).
- ⁵⁶S. G. Ard, R. N. Compton, and W. R. Garrett, Chem. Phys. Lett. 650, 154– 158 (2016).
- ⁵⁷R. S. Berry, J. Chem. Phys. 45, 1228 (1966).
- ⁵⁸J. Simons, J. Am. Chem. Soc. **103**, 3971 (1981).

- ⁵⁹H. T. Liu, C. G. Ning, D. L. Huang, and L. S. Wang, Angew. Chem., Int. Ed. 53, 2464–2468 (2014).
- ⁶⁰D. L. Huang, H. T. Liu, C. G. Ning, P. D. Dau, and L. S. Wang, Chem. Phys. 482, 374–383 (2017).
- ⁶¹D. L. Huang, H. T. Liu, C. G. Ning, G. Z. Zhu, and L. S. Wang, Chem. Sci. 6, 3129 (2015).
- ⁶²D. L. Huang, G. Z. Zhu, and L. S. Wang, J. Chem. Phys. **142**, 091103 (2015).
- ⁶³D. L. Huang, H. T. Liu, C. G. Ning, and L. S. Wang, J. Phys. Chem. Lett. 6, 2153 (2015).
- ⁶⁴G. Z. Zhu, D. H. Huang, and L. S. Wang, J. Chem. Phys. **147**, 013910 (2017).
- ⁶⁵D. L. Huang, H. T. Liu, C. G. Ning, and L. S. Wang, J. Chem. Phys. **142**, 124309 (2015).
- ⁶⁶D. L. Huang, G. Z. Zhu, and L. S. Wang, J. Mol. Spectrosc. **332**, 86–93 (2017).
- ⁶⁷G. Z. Zhu, Y. Liu, and L. S. Wang, *Phys. Rev. Lett.* **119**, 023002 (2017).
- ⁶⁸L. S. Wang, J. Chem. Phys. **143**, 040901 (2015).
- ⁶⁹X. B. Wang and L. S. Wang, Rev. Sci. Instrum. **79**, 073108 (2008).
- ⁷⁰I. León, Z. Yang, H. T. Liu, and L. S. Wang, Rev. Sci. Instrum. 85, 083196 (2014).
- ⁷¹V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, Rev. Sci. Instrum. **73**, 2634 (2002).
- ⁷²G. A. Garcia, L. Nahon, and I. Powis, Rev. Sci. Instrum. **75**, 4989 (2004).
- ⁷³E. P. Wigner, Phys. Rev. **73**, 1002–1009 (1948).
- ⁷⁴M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson,

- J. Chem. Phys. 149, 164301 (2018)
- H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino,
- G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda,
- J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark,
- J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi,
- J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar,
- J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. J. Knox,
- B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
- R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, GAUSSIAN 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.
- ⁷⁵U. Fano, Phys. Rev. **124**, 1866 (1961).
- ⁷⁶H. Ibach, Surf. Sci. 299, 116–128 (1994).
- ⁷⁷R. F. Egerton, Rep. Prog. Phys. **72**, 016502 (2009).
- ⁷⁸J. B. Kim, M. L. Weichman, T. I. Yacovitch, C. Shih, and D. M. Neumark, J. Chem. Phys. **139**, 104301 (2013).
- ⁷⁹D. L. Huang, P. D. Dau, H. T. Liu, and L. S. Wang, J. Chem. Phys. 140, 224315 (2014).
- ⁸⁰K. Regeta and M. Allan, Phys. Rev. Lett. **110**, 203201 (2013).
- ⁸¹P. Hockett, M. Staniforth, K. L. Reid, and D. Townsend, Phys. Rev. Lett. 102, 253002 (2009).
- ⁸²K. L. Reid, Annu. Rev. Phys. Chem. 54, 397–424 (2003).
- ⁸³A. Sanov, Annu. Rev. Phys. Chem. **65**, 341–363 (2014).