RESEARCH ARTICLE | MAY 08 2024

Observation of bound valence excited electronic states of deprotonated 2-hydroxytriphenylene using photoelectron, photodetachment, and resonant two-photon detachment spectroscopy of cryogenically cooled anions \bigcirc

Jisoo Kang ⁽); Edward I. Brewer ⁽); Yue-Rou Zhang; Dao-Fu Yuan ^I ⁽); G. Stephen Kocheril ⁽); Lai-Sheng Wang ^I ⁽)

Check for updates

J. Chem. Phys. 160, 184301 (2024) https://doi.org/10.1063/5.0209948







Observation of bound valence excited electronic states of deprotonated 2-hydroxytriphenylene using photoelectron, photodetachment, and resonant two-photon detachment spectroscopy of cryogenically cooled anions



Jisoo Kang,¹ D Edward I. Brewer,¹ D Yue-Rou Zhang,¹ Dao-Fu Yuan,^{2,a)} D G. Stephen Kocheril,¹ A and Lai-Sheng Wang^{1,a)}

AFFILIATIONS

¹ Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

²Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

^{a)}Authors to whom correspondence should be addressed: ydfu@ustc.edu.cn and lai-sheng_wang@borwn.edu

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are common atmospheric pollutants, and they are also ubiquitous in the interstellar medium. Here, we report the study of a complex O-containing PAH anion, the deprotonated 2-hydroxytriphenylene (2-OtPh⁻), using high-resolution photoelectron imaging and photodetachment spectroscopy of cryogenically cooled anions. Vibrationally resolved photoelectron spectra yield the electron affinity of the 2-OtPh radical as 2.629(1) eV and several vibrational frequencies for its ground electronic state. Photodetachment spectroscopy reveals bound valence excited electronic states for the 2-OtPh⁻ anion, with unprecedentedly rich vibronic features. Evidence is presented for a low-lying triplet state (T_1) and two singlet states (S_1 and S_2) below the detachment threshold. Single-color resonant two-photon photoelectron spectroscopy uncovers rich photophysics for the 2-OtPh⁻ anion, including vibrational relaxation in S_1 , internal conversion to the ground state of 2-OtPh⁻, intersystem crossing from S_2 to T_1 , and a long-lived autodetaching shape resonance about 1.3 eV above the detachment threshold. The rich electronic structure and photophysics afforded by the current study suggest that 2-OtPh⁻ would be an interesting system for pump–probe experiments to unravel the dynamics of the excited states of this complex PAH anion.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0209948

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are known to be ubiquitous in the interstellar medium.^{1,2} They have attracted increasing attention due to their importance in environmental chemistry, combustion chemistry, and astrochemistry. PAHs have been reported to exist in the interstellar medium in both deprotonated and protonated forms.^{3–5} Not only are these compounds abundant and capable of adopting different forms, but their absorption features in the visible to infrared (IR) wavelengths also suggest

that PAHs may be viable candidates as carriers for the diffuse interstellar bands (DIBs).^{6–8} In particular, PAH anions are believed to serve as one of the predominant sources of free electrons in the interstellar medium, which can further lead to the formation of even larger PAH molecules via reactions from smaller deprotonated PAH radicals.^{9,10} Moreover, PAH anions have been previously reported to play significant roles in the formation of dense molecular clouds,^{11–13} adding weight to their astronomical relevance and increasing their prospects for being possible carriers of DIBs.

The first anion identified in the interstellar medium was C₆H⁻.¹⁴ Shortly after, a number of H- and N-containing carbon cluster anions were detected,¹⁵⁻¹⁸ leading to the perception that anions may be prevalent in the interstellar medium.¹⁹ Due to the reactive and transient nature of anions, the formation mechanisms of such species in the interstellar medium are not well understood.^{20,21} Dipole-bound states (DBSs) have been speculated to be one possible mechanism acting as a doorway to form stable valence bound anions.²²⁻²⁴ DBSs are non-valence electronic states that can be supported in an anion if the neutral core possesses a sufficient dipole moment. The theoretical critical dipole moment for electron binding was predicted to be 1.625 D,²⁵ while empirically this value has been determined to be 2.5 D^{26-28} if molecular polarizability does not play a significant role.²⁹ A number of PAHs with large dipole moments have been observed by rotational spectroscopy in the interstellar medium.³⁰⁻³⁴ Interestingly, all of these species could potentially support DBSs as anions due to their large dipole moments. Therefore, probing the energetics of polar PAH anions at high resolution may provide useful astronomical insights and assist in identifying their potential astrophysical sources.

Photoelectron spectroscopy (PES) is one of the most powerful experimental techniques to probe the electronic and vibronic structures of negative ions.³⁵ In particular, high resolution photoelectron imaging (PEI) of cryogenically cooled anions has enabled the determination of electron affinities (EAs) and vibrational frequencies of the corresponding neutral states with unprecedented resolution.^{36,37} Several PAH anions have been studied by PES, in particular by high resolution PEI of cryogenically cooled anions.^{48–53} We have developed a state-of-the-art PEI system coupled with an electrospray ionization (ESI) source and a cryogenically cooled 3D Paul trap³⁶ and have focused on using DBSs and resonant PES to obtain spectroscopic information about aromatic systems. We have investigated a number of PAH systems with variable complexity.^{59–63} In the study on the 1-pyronolate anion ($C_{16}H_9O^-$), we not only observed vibrational Feshbach resonances from a DBS but also a strong above-threshold valence excited state (shape resonance).⁶¹ In our recent study on the polarization-assisted DBS in the carbazolide anion (C12H8N⁻), we observed multiple shape resonances and even the relaxation process from the highly excited shape resonances.⁶³ Clearly, the high-resolution PEI and PDS afforded by our state-of-the-art instrumentation provide a great opportunity to investigate the energetics of DBS-supporting PAH anions, which can pave the way for investigations of their roles both in atmospheric chemistry and astronomical environments.

Herein, we report an investigation of the deprotonated 2-hydroxytriphenylene anion ($C_{18}H_{11}O^-$, 2-OtPh⁻), the most complicated PAH anion that we have studied thus far. By utilizing our third-generation ESI-PES apparatus,³⁶ which is coupled with a cryogenically cooled 3D Paul trap and a high-resolution PEI system, we are able to determine an accurate EA for the 2-OtPh radical and a number of vibrational frequencies. Our initial aim was to use high-resolution PEI and the expected DBS to obtain detailed spectroscopic information about the 2-OtPh radical. However, we quickly found that PES at different photon energies was complicated by resonances and autodetachment due to the existence of above-threshold valence excited states in a broad photon energy range. PDS revealed unprecedented bound (below-threshold) low-lying valence electronic states, along with an extraordinary number

of vibronic features, while the putative DBS transitions were completely masked due to their weak oscillator strengths. Evidence is observed for a bound, spin-forbidden triplet state (T₁) and two bound singlet states (S₁ and S₂). Resonant two-photon detachment (R2PD) PES has uncovered rich photophysics for the bound valence excited states of the 2-Ot-Ph⁻ anion, including vibrational relaxation in S₁, internal conversion to the ground state of the anion (S₀), thermionic emission, intersystem crossing from S₂ to T₁, and a longlived autodetaching shape resonance that is 1.3 eV above the neutral ground state. The current article presents the rich electronic structure and photophysical information about the 2-OtPh⁻ anion, which will be valuable for future pump–probe experiments to examine the photophysics and dynamics of complex PAH anions.

II. EXPERIMENTAL METHODS

A. Photoelectron imaging

Photodetachment (PD) and photoelectron (PE) spectra were obtained using our third-generation ESI-PES apparatus, which has been described in detail previously.³⁶ Briefly, the apparatus is composed of an ESI source,⁶⁴ a cryogenically cooled Paul trap,⁶⁵ and a high-resolution PEI system.⁶⁶ The 2-OtPh⁻ anion was formed by electrospray of a 1 mM solution of 2-hydroxytriphenylene (Aaron Chemicals, 95%) dissolved in a mixed solvent of CH₃OH/H₂O (9/1 volume ratio), which was spiked with a few drops of NaOH solution to promote deprotonation. A series of quadruple and octupole ion guides were used to direct the 2-OtPh⁻ anions from the ESI source into the 3D Paul trap, which was maintained at a temperature of 4.6 K by connecting to the cold head of a closed-cycle helium refrigerator. The 2-OtPh⁻ anions were trapped for ~0.1 s and were thermally cooled through collisions with a mixture of He/H₂ (~1 mTorr, 4/1 in volume) background gas. The anions were pulsed out of the Paul trap at a rate of 10 Hz into the extraction zone of a time-of-flight mass spectrometer. The 2-OtPh⁻ anions were selected by a mass gate before being photodetached in the interaction zone of a multi-lens velocity map imaging (VMI) system using either a tunable dye laser, or the third (354.7 nm, 3.496 eV) or fourth (266.0 nm, 4.661 eV) harmonic of an Nd:YAG laser. The resulting photoelectrons were accelerated out of the detachment zone and detected by a pair of 75 mm diameter microchannel plates coupled to a phosphorus screen and a CCD camera. The photoelectron images were analyzed using the pBasex⁶⁷ and BASEX⁶⁸ programs and calibrated using the Au⁻ atomic anion at various photon energies. In particular, the calibration was performed using 266.0, 354.7, 480.00, 490.00, 500.00, 510.00, 520.00, 525.00, 530.00, 531.00, 533.00, and 535.00 nm for imaging extraction voltages of -300 and -1000 V. However, our calibration was not as robust for the very fast electrons detected at the edge of the imaging detector. A -1000 V imaging extraction voltage was used for the 266.0 nm spectrum, whereas -400 V was used for the 354.7 nm spectrum. For all R2PD PE spectra presented in the current work, an imaging extraction voltage of -1050 V had to be used to capture the fast electrons due to the R2PD processes. The resolution of the apparatus was 3.8 cm⁻¹ for photoelectrons with 55 cm⁻¹ kinetic energy (KE) and about 1.5% (Δ KE/KE) for photoelectrons with KE higher than 1 eV.66

B. Photoelectron angular distributions

PEI also yields information about photoelectron angular distributions. The photoelectron angular distribution depends on the molecular orbital (MO) from which the electron is detached, and it can be described by⁶⁹

$$I(\theta) = \frac{\sigma_T}{4\pi} \cdot (1 + \beta P_2(\cos{(\theta)})), \qquad (1)$$

where $I(\theta)$ denotes the differential detachment cross section by a linearly polarized light for randomly oriented molecules, σ_T denotes the total detachment cross section, $P_2(\cos(\theta))$ is the second-order Legendre polynomial, and θ is the angle between the polarization direction of the laser and the outgoing photoelectron. β is the anisotropy parameter, $\beta = 0$ corresponds to an isotropic *s*-outgoing wave, $\beta = 2$ corresponds to a *p*-outgoing wave where the maximum intensity occurs along the polarization direction of the laser, and $\beta = -1$ corresponds to a *s* + *d* outgoing wave, where the maximum intensity occurs perpendicular to the polarization direction of the laser.

C. Computational methods

Geometry optimization and electronic structure calculations for the 2-OtPh⁻ anion were done at the B3LYP/6-311++g(d,p) level of theory. Vibrational frequencies for the ground state of 2-OtPh⁻ and its neutral, as well as those for the first excited electronic state (S₁) of the anion, were computed at the same level of theory. Vertical excitation energies and vertical detachment energies (VDEs) of 2-OtPh⁻ were calculated using time-dependent density functional theory (TD-DFT). The Gaussian 09 package was used to perform all the electronic structure calculations.⁷⁰ Franck–Condon (FC) factors were calculated using the FC-Lab2 program.⁷¹

III. RESULTS

A. Photoelectron imaging and spectroscopy of 2-OtPh⁻

The PE images and spectra of 2-OtPh⁻ are displayed in Fig. 1 at three detachment photon energies. The 3.496 eV spectrum [Fig. 1(a)] shows an intense ground state transition (band X) with unresolved vibrational structures. The onset of band X yields an estimate of the adiabatic detachment energy (ADE) of ~2.63 eV, which corresponds to the EA of the 2-OtPh radical. A strong signal (S_0) is observed at the threshold, which has the signature of thermionic emissions from the ground electronic state of the anion (S_0) due to resonant absorption of the detachment photon by the anion followed by internal conversion to S_0 .^{72–74} The weak signals between X and S₀ are likely due to autodetachment, consistent with the fact that the 3.496 eV photon is in resonance with an above-threshold excited state of the 2-OtPh⁻ anion. The 3.959 eV spectrum [Fig. 1(b)] shows a similar Franck-Condon (FC) profile for band X and a similar threshold feature (S_0) , indicating that the 3.959 eV photon is also in resonance with an above-threshold anion excited state. In addition, a broad band denoted as X_a is observed around 3.5 eV, which will be shown to be due to autodetachment. Two sharp peaks (separated by $\sim 1200 \text{ cm}^{-1}$) are observed, which come from vibrational levels of the first excited state (A) of the neutral 2-OtPh radical. The 4.661 eV spectrum [Fig. 1(c)] is complicated with a number of new features.



FIG. 1. Photoelectron images and spectra of 2-OtPh⁻ at (a) 3.496 eV (28 197 cm⁻¹), (b) 3.959 eV (31 931 cm⁻¹), and (c) 4.661 eV (37 593 cm⁻¹). The double arrow below the images denotes the polarization direction of the detachment laser. The structure of 2-OtPh⁻ is shown in the inset of (a).

The broad feature labeled S_a and the additional features on the high binding energy side of band X are evident of autodetachment. The new band B will be shown to be the second excited state of neutral 2-OtPh, and the threshold feature is likely a mixture of another excited state C and signals due to thermionic emission. The PE spectra in Fig. 1 suggest that the 2-OtPh⁻ anion has rich above-threshold electronic excited states in the photon energy range between 3.496 and 4.661 eV, resulting in autodetachment and thermionic emission in each of the three spectra. The binding energies of the four direct detachment transitions (X, A–C), their shifts relative to the ground state transition X, and their β parameters are summarized in Table I, where they are compared with theoretical calculations.

TABLE I. Measured binding energies (BE), excitation energies (Δ E), and their β values for the four PES bands observed for 2-OtPh⁻, compared with the computed excitation energies. All energies are in eV.

	BE	ΔE (exp.)	$\Delta E \text{ (theo.)}^{a}$	β
X	2.629 ^b	0	$0(^{2}A'')$	-0.13
А	3.67 ^c	1.04	$1.15(^{2}A')$	-0.22
В	4.3	1.7	$1.69(^{2}A'')$	0.05
С	4.6	2.0	2.17 (² A'')	0.05

^aCalculated using TD-DFT at the B3LYP level of theory. The electronic states are given in the parentheses.

 $^{\rm b}$ From the high resolution spectrum in Fig. 2. Uncertainty: ± 0.001 eV.

^cUncertainty: ± 0.01 eV.

In order to measure a more accurate EA for the 2-OtPh radical, we took a high-resolution PE spectrum for band X near the threshold at a photon energy of 2.7362 eV using the dye laser, as presented in Fig. 2(a). Surprisingly, weak and almost continuous signals were observed in the low binding energy range down to ~0.3 eV binding energy. Two bands can be tentatively identified: band X' with fine features at the lowest binding energy side and another broader feature (X") around 1.4 eV. These features must come from two-photon detachment processes involving resonant excitation to an above-threshold excited state of the 2-OtPh⁻ anion followed by fast relaxation to a long-lived bound excited electronic state, which is then detached by a second photon. The 0.3 eV binding energy of band X' indicates an anion excited state at an excitation energy of ~2.33 eV (using the EA of ~2.63 eV). This state is likely the lowest singlet excited state (S1) of the 2-OtPh⁻ anion (see Fig. 8 later). The 0-0 transition of band X is observed at the high binding energy side, yielding an accurate EA of 2.629 eV for the 2-OtPh radical. The threshold part in Fig. 2(a) is similar to that observed in the spectra in Fig. 1, suggesting thermionic emission or direct detachment from the rovibrational levels from S₀ of the anion by a second photon. To observe more vibrational features for the X band, we measured a PE spectrum at a slightly higher photon energy of 2.7994 eV [Fig. 2(b)]. Surprisingly, this photon energy appeared to be in resonance with an anion excited state that couples strongly to S₀. Due to the overwhelming thermionic emission signals from S₀, even the 0–0 transition was obscured in the 2.7994 eV spectrum. To cover the full FC range of the X band, we also took a PE spectrum at 2.9536 eV, as shown in Fig. 2(c), which resolved several vibrational peaks (a-f). The binding energies and assignments of these vibrational features are given in Table S1. Apparently,



FIG. 2. Photoelectron images and spectra of 2-OtPh⁻ at (a) 2.7362 eV (22 069 cm⁻¹), (b) 2.7994 eV (22 579 cm⁻¹), and (c) 2.9536 eV (23 822 cm⁻¹). The inset in (c) shows band X on a finer scale with the resolved vibrational features labeled. The double arrow below the images denotes the laser polarization direction.

the 2.9536 eV photon is also in resonance with an above-threshold electronic excited state of 2-OtPh⁻, as evidenced by the two-photon signals in the low binding energy range and the thermionic emission signals at threshold (S₀). The PE spectra in Figs. 1 and 2 suggest a complicated manifold of both bound and above-threshold valence excited electronic states for the 2-OtPh⁻ anion, which are entangled with the direct photodetachment processes. In principle, these electronic states can be directly probed by PDS.

B. Photodetachment spectroscopy

To search for the anticipated DBS and to probe the excited electronic states of 2-OtPh⁻, as hinted in Figs. 1 and 2, we conducted PDS, as shown in Fig. 3, in the spectral range from $17\,500 \text{ cm}^{-1}$ (2.1697 eV) to 22 000 cm⁻¹ (2.7277 eV). An extremely rich and complicated PD spectrum is observed in this spectral range, with exceptionally dense vibronic levels resolved below the threshold and nearly continuous vibronic transitions around and above the threshold. The spectrum cannot be due to the putative DBS on the basis of the strong two-photon signals and the large binding energies (relative to the detachment threshold). Instead, they should be due to valence electronic excited states of 2-OtPh⁻ via single-color R2PD. The strong valence transitions, in fact, would completely mask any transitions due to the putative DBS, which is expected to be much weaker.^{61,63} The strong valence transitions also smear out the threshold behavior, where no step is observed at the onset of the detachment threshold. The strongest and lowest vibronic peak in Fig. 3 at an excitation energy of 18816 cm⁻¹ (2.3329 eV), which is 0.296 eV below the detachment threshold, corresponds to the excited state that gives rise to band X' in Fig. 2 mentioned above. The measured binding energy of ~0.3 eV for band X' is similar to the more accurate 0.296 eV binding energy measured from the PD spectrum. Thus, the strongest peak should be the origin of S₁ for 2-OtPh⁻. Surprisingly, broad and weak R2PD signals are also observed below S1, which are likely due to transitions to the triplet excited state (T_1) of 2-OtPh⁻ (see Fig. 8 later). Such transitions are spin-forbidden, but they can be observed as a result of spin-orbit couplings.⁷⁵ No sharp vibronic peaks are resolved in the weak transitions to the T₁ state. The onset of T₁ is estimated to be around 18 309 cm⁻¹, yielding a singlet-triplet (S₁-T₁) splitting of 507 cm^{-1} . On the basis of the increasing spectral complexity, there may be more than one bound excited singlet state. The PD spectrum in Fig. 3 is divided approximately into four regions for the sake of discussion: (1) 18309-18816 cm⁻¹, corresponding possibly to the triplet state; (2) 18 816 to ~19 985 cm⁻¹, corresponding to S₁; (3) 19985-21204 cm⁻¹ (detachment threshold), which corresponds possibly to S₂; and (4) the above-threshold region. Region (4) could potentially contain transitions to above-threshold DBS levels, which would be totally overwhelmed by the intense valence transitions, as mentioned above. The PD spectrum is expected to extend to much higher excitation energies on the basis of the PE spectra in Figs. 1 and 2. We stopped at $22\,004$ cm⁻¹ because no fine vibronic features could be resolved at higher excitation energies.

The resolved vibronic features up to 20 500 cm⁻¹ covering region (1) and part of region (2) are shown in more detail with peak labels in Fig. 4. They are compared with the computed FC factors for the S₀ to S₁ transition of 2-OtPh⁻ in Fig. S1. The peak positions and



FIG. 3. Photodetachment spectrum of 2-OtPh⁻ in the spectral range of 17 500 cm⁻¹ (2.1697 eV) and 22 000 cm⁻¹ (2.7277 eV). The detachment threshold at 21 204 cm⁻¹ (2.629 eV) measured from the PE spectrum in Fig. 2 is indicated by the downward arrow. The upper axis gives the shift relative to the strong peak 0 at 18 816 cm⁻¹ (i.e., the 0–0 transition to S₁). Four spectral regions are marked as region (1) to region (4).



FIG. 4. Details of the photodetachment spectrum of 2-OtPh⁻ in the spectral range from 18 750 cm⁻¹ (2.3247 eV) to 20 450 cm⁻¹ (2.5355 eV) with labels. See Table S2 for the photon energies of the labeled peaks and their possible assignments. The top axis indicates the shift relative to peak 0.

their possible assignments for the features in region (2) are given in Table S2, in comparison with the computed frequencies of S_1 .

C. R2PD photoelectron imaging and spectroscopy

To understand the nature of the electronic excitations that give rise to the PD spectrum, we took R2PD photoelectron images and spectra at all the resolved vibronic transitions. The signals were too weak to obtain meaningful R2PD PE spectra off the T₁ state in region (1). Representative R2PD PE images and spectra acquired for region (2) are shown in Fig. 5, and those for region (3) are shown in Fig. 6. The R2PD PE spectra taken at all the vibronic levels in region (2) are similar, each consisting of three spectral bands labeled as X_S, S_a, and S₀ (Fig. 5). These features represent different multi-photon detachment processes within the 5 ns laser pulse. Band X_S is due to the direct R2PD process, where the first photon excites the anion to a vibronic level of S₁ and the second photon detaches the electron from S₁. Vibrational structures are observed in band X_S with a spacing of ~1500 cm⁻¹. The broad FC region of band X_S provides further

evidence that the intermediate excited state is a valence-bound state rather than a DBS, which would yield a single vibrational peak in each R2PD PE spectrum because there is little structural change from the DBS to the neutral final state.^{54–58} It should also be pointed out that band X_S in Fig. 5 is similar to band X' in Fig. 2, suggesting that the second photon detaches the electron from the same S₁ excited state in both cases. We further note that the binding energies of band X_S in Figs. 5(b)–5(f) are identical to those in Fig. 5(a), even though higher vibronic levels of the S₁ state are accessed by the first photon for these spectra. This observation suggests that there is fast vibrational relaxation (relative to the 5 ns pulse width of the detachment laser) in S_1 , so that the second photon always detaches from the vibrational ground state of S_1 (see Fig. 8 later). The excitation energy of the v = 0 level of S₁ (peak 0 in Fig. 3) is 2.3329 eV $(18816 \text{ cm}^{-1}, \text{ Table S2})$, which is 0.296 eV (2387 cm^{-1}) below the detachment threshold of 2.629 eV. This value agrees well with the measured binding energy from band X_S around 0.3 eV.

Furthermore, the high binding energy signals designated as S_0 in Fig. 5 indicate that there is also fast internal conversion from S_1 to

27 May 2024 18:23:39



FIG. 5. Representative R2PD PE images and spectra taken in region (2) of the PD spectrum in Fig. 3. The peak numbers are from Fig. 4. (a) At peak 0, (2.3329 eV, 18816 cm⁻¹), (b) at peak 6, (2.3581 eV, 19019 cm⁻¹), (c) at peak 10, (2.3753 eV, 19158 cm⁻¹), (d) at peak 21 (2.4099 eV, 19437 cm⁻¹), (e) at peak 34 (2.4529 eV, 19784 cm⁻¹), and (f) at peak 45 (2.4744 eV, 19957 cm⁻¹). The double arrow below the images denotes the polarization direction of the laser. The three observed spectral features are labeled as X_S , S_a , and S_0 .



FIG. 6. Representative R2PD photoelectron images and spectra taken in region (3) of the PD spectrum in Fig. 3. (a) At peak 48 (2.4828 eV, 20 025 cm⁻¹), (b) at 61 (2.5161 eV, 20 294 cm⁻¹), (c) at peak 66 (2.5258 eV, 20 372 cm⁻¹), (d) at 2.5512 eV (20 577 cm⁻¹), (e) 2.6071 eV (21 028 cm⁻¹), and (f) 2.6230 eV (21 156 cm⁻¹). Note that the spectra in (d), (e), and (f) were taken at the higher photon energy side of region (3), where vibronic levels are too dense to be labeled. The double arrow below the images denotes the laser polarization direction. The three observed spectral features are labeled as X_T , S_a , and S_0 .

the rovibrational levels of the ground state of the anion (S_0) . These high binding energy signals represent detachment from the highly excited rovibrational levels of the anion at S₀ by the second photon. The tail near the detachment threshold in the S₀ signals has the signature of thermionic emissions, which could occur if the energies of more than one photon are converted to the internal energies of the 2-OtPh⁻ anion in its ground electronic state. This tail is also reminiscent of the threshold tail in Figs. 1 and 2, suggesting that indeed those photon energies are all in resonance with excited electronic states of 2-OtPh⁻. The band designated by S_a is similar in all the R2PD PE spectra (Fig. 5), but its binding energy appears to increase with increasing photon energies. It turns out that the electron kinetic energy of band S_a is constant at ~1.3 eV (Fig. S2). This observation suggests that band S_a is due to autodetachment from the same excited electronic state, which is 1.3 eV above the detachment threshold, i.e., a long-lived shape resonance. This long-lived excited state is 3.9 eV above the anion ground state (considering the detachment threshold of 2.629 eV) (see Fig. 9 later). This excited state must be populated due to relaxation from higher excited states reached by resonant two-photon absorption. In fact, the feature labeled as Sa in Fig. 1(c) and $\mathbf{\tilde{X}}''$ in Fig. 2(a) comes from autodetachment from the same long-lived shape resonance.

The R2PD PE spectra taken at region (3) are similar to those for region (2), as displayed in Fig. 6. region (3) should correspond to the second singlet excited state (S₂) of 2-OtPh⁻ (see Fig. 8 later). The thermionic emission signals labeled as S₀ in Fig. 6 indicate that internal conversions from S₂ to S₀ take place. The S_a band exhibits the same shift with photon energies with the same constant kinetic energy of ~1.3 eV, suggesting that it comes from autodetachment from the same long-lived shape resonance at 3.9 eV excitation energy above the anion ground state. The lowest binding energy band (labeled as X_T) is similar to X_S in Fig. 5 with similar vibrational structures, except that its binding energy exhibits a conspicuous shift to a higher binding energy by ~0.05 eV. This is a surprising observation. We expected that the binding energies of this band would be smaller because S2 is closer to the detachment threshold (see Fig. 8 later). The higher binding energy of band X_T suggests that the second photon detaches an electron from an even lower excited state of the anion than S_1 , i.e., the triplet state (T_1) . Thus, there must be a fast intersystem crossing from S₂ to T₁ upon the absorption of the first photon. There is also likely relaxation from S₂ to S₁ at the same time because the vibrational features in band X_T are broader in general, and they may contain contributions from detachment from S₁ simultaneously. The ~0.05 eV shift between X_T and X_S is consistent with the singlet-triplet (S_1-T_1) splitting of 507 cm⁻¹ measured from the PD spectrum in Fig. 3.

IV. DISCUSSION

A. The photoelectron spectroscopy of 2-OtPh⁻

The top four valence MOs of 2-OtPh⁻ are shown in Fig. S3. Band X in Fig. 1 corresponds to the detachment of an electron from the highest occupied molecular orbital (HOMO) of the anion to the ground state of the neutral. The HOMO is a π orbital involving part of the aromatic system and the O 2p_z orbital. The negative β value for the X band is consistent with the nature of the HOMO. We computed the FC factors for the ground state transition and compared



FIG. 7. Comparison of the calculated FC factors (vertical lines) for the ground state detachment transition of 2-OtPh⁻ with the PE spectrum at 2.9536 eV [Fig. 2(c)].

them with the vibrational structures resolved in the 2.9536 eV spectrum, as shown in Fig. 7. The most FC-active mode defined by peaks *a* and *b* is found to be the v_{53} mode, which can be viewed primarily as an O-rocking mode (Fig. S4) in agreement with the nature of the HOMO. The measured frequency of 353 cm⁻¹ for the v_{53} mode is in excellent agreement with the computed frequency of 359 cm⁻¹ (Table S1). Several modes with weak FC factors as well as several combination vibrational levels are also observed, as given in Table S1. The excited electronic states of the anion near the detachment threshold and the subsequent autodetachment and multi-photon processes interfered with our effort to obtain high resolution non-resonant PE spectra to resolve all the vibrational features in the ground state detachment transition, as exhibited in Figs. 2(a) and 2(b).

The anion resonances also interfered with the observations of the higher binding energy detachment transitions, as displayed in Figs. 1(b) and 1(c). Autodetachment resonances have been observed for clusters with large HOMO-LUMO gaps⁷⁶⁻⁷⁸ and have been increasingly observed in PES of complex PAH anions due to their ^{52,53} The 2-OtPh⁻ anion reprich low-lying electronic states.43 resents one of the most complicated PAH systems that we have investigated.⁵⁹⁻⁶³ It not only exhibits above-threshold autodetaching resonances, but also rich low-lying bound electronic transitions, as revealed in the PDS (Fig. 3) and discussed below. The second detachment channel of 2-OtPh- involves electron removal from the HOMO-1, which is mainly a localized O 2p orbital (Fig. S3). The computed excitation energy of 1.15 eV agrees well with the measured value of 1.04 eV for band A (Table I). The simple vibrational features observed for band A is consistent with the localized nature of the HOMO-1. The observed vibrational spacing for band A are \sim 1200 cm⁻¹, which is primarily due to the C–O stretching frequency in the first excited state of the 2-OtPh radical. The next two detachment channels come from electron removals from the HOMO-2 and HOMO-3 (Fig. S3), respectively. The computed excitation energies for these two detachment channels are in good agreement with the observed experimental values, as shown in Table I.

B. Photodetachment spectroscopy of 2-OtPh⁻

Due to their low electron detachment energies, anions can rarely support bound, excited electronic states.⁷⁹ The first anion observed with bound excited electronic states was $C_2^{-,80,81}$ which was studied extensively by the Lineberger group.^{82,83} Bound

27 May 2024 18:23:39

excited states have been observed for a number of carbon cluster anions, including C₆₀⁻, due to their high electron detachment energies,73,84-88 or for small open-shell molecular anions with lowlying electronic states.⁸⁹⁻⁹² Brauman and co-workers first observed bound electronic states of CN- or halogen-substituted aromatic anions,93 in which the electron-withdrawing CN or halogen substituents pull down the LUMO significantly while enhancing the electron detachment energies of the anions. As the PAH molecules increase in size, their electronic density of states increases, resulting in low-lying excited states. While shape resonances have been observed for a number of PAH anions, 43-45,47,52,53 bound valence excited states have not been reported. The large size and the O-atom in the 2-OtPh⁻ anion both increase its electronic density of states and its electron binding energy, giving rise to the bound excited states. The observation of the rich vibronic structures in the PDS of 2-OtPh⁻ is unprecedented, mainly owing to the cryogenic cooling of the anions that eliminate vibrational hot bands.

1. Observation of $S_0 \rightarrow T_1$ transition

The weak R2PD signal below peak 0 in the PD spectrum (Fig. 3) is assigned to a direct transition to the triplet state (T_1) of 2-OtPh⁻ from S₀ by the first photon, followed by electron detachment from T_1 by the second photon. The $S_0 \rightarrow T_1$ transition is spin-forbidden and is rarely observed directly, whereas the T₁ \rightarrow S₀ transition, i.e., phosphorescence, is more commonly observed, where the T1 state is populated from intersystem crossing from spin-5,94 Direct $S_0 \rightarrow T_1$ transitions have allowed singlet excited states.7 been observed for molecules containing heavy atoms as a result of strong spin-orbit coupling.^{95,96} We have previously observed a direct transition from the ground state of AuS⁻ ($^{1}\Sigma^{+}$) to a bound and long-lived spin-forbidden triplet excited state $({}^{3}\Sigma^{+})$, which allowed interesting vibrationally selective R2PD PE spectra to be obtained.92 The intense ${}^{1}\Sigma^{+} \rightarrow {}^{3}\Sigma^{+}$ transition observed for AuS⁻ was due to the strong spin-orbit coupling effect. The observation of the $S_0 \rightarrow$ T₁ transition in the PDS of 2-OtPh⁻ testifies to the high sensitivity of the current experimental method due to the cryogenically cooled anions, so that there are no vibrational hot bands and the experiment is essentially noise-free. The onset of the triplet state is measured to be at an excitation energy of 18 309 cm⁻¹, which gives a singlet-triplet (S_1-T_1) splitting of 507 cm⁻¹ for the 2-OtPh⁻ anion. We performed preliminary TD-DFT calculations to understand the low-lying electronic states of 2-OtPh⁻, as shown in Table S3. Our TD-DFT calculations yielded a computed T₁ excitation energy of 2.0062 eV (16 181 cm⁻¹), which is significantly lower than our experimental measurement. The calculations also predict that T₂ is below S_1 as well, suggesting that region (1) in Fig. 3 might contain excitations to two triplet states. The direct $S_0 \rightarrow T_1$ transition is too weak to allow us to conduct R2PD PES in region (1). However, R2PD PE spectra from the T1 state are observed indirectly from excitation to S_2 [region (3)], which seems to have a strong intersystem crossing to T_1 (vide infra).

2. The $S_0 \rightarrow S_1$ transitions

The parent triphenylene molecule has D_{3h} symmetry with a degenerate HOMO (e''),⁹⁷ corresponding to HOMO-2 and HOMO-3 in 2-OtPh⁻ (Fig. S3). The $S_0 \rightarrow S_1$ transition in triphenylene is electric dipole forbidden, and only sparse vibronic levels were observed in previous spectroscopic studies of triphenylene.^{97–99} The

presence of the O atom reduces the symmetry of 2-OtPh⁻ to C_s and also alters its frontier orbitals. As shown in Fig. S3, the HOMO and HOMO-1 of 2-OtPh⁻ are O-based. The strong R2PD signals in the PDS (Fig. 3) suggest that the $S_0 \rightarrow S_1$ transitions should be dipoleallowed. The spectral region for the $S_0 \rightarrow S_1$ transition in 2-OtPh- is much more complicated, with rich vibronic features, in comparison to those of the parent triphenylene. We labeled individual vibronic peaks up to 20 414 cm⁻¹ (peak 69), as shown in Fig. 4 and Table S2. To help understand these rich vibronic features, we optimized the structures of S₀ and S₁ and computed their vibrational frequencies (Figs. S5 and S6). We also simulated the FC factors for the $S_0 \rightarrow S_1$ transition, as compared with the PD spectrum in Fig. S1. However, the computed FC factors are much simpler than the experimental R2PD spectrum, suggesting that there must be strong vibronic couplings between S1 and nearby electronic states. Thus, it is challenging to make any definitive assignments to the observed vibronic structures. We made tentative assignments using the computed harmonic frequencies for S₁, as shown in Table S2. It should be pointed out that the three minor peaks (α , γ , δ) around the 0–0 transition (peak 0 in Fig. 4) are due to hot bands of the anion, which happen to be in resonance with a vibrational level of S_1 and are, thus, resonantly enhanced, as shown in Table S2. Even though vibrational hot bands are negligible for anions from our cryogenically cooled ion trap, we have observed similar minor resonantly enhanced hot band transitions in previous studies related to dipole-bound excited states in cryogenically cooled anions for low frequency vibrational modes.¹⁰⁰

3. The $S_0 \rightarrow S_2$ transitions

With increasing excitation energies, the PD spectrum becomes more complicated with a significantly higher density of vibronic features, especially above $\sim 20\,000 \text{ cm}^{-1}$ in region (3) (Fig. 3). The PD spectrum eventually becomes continuous around the detachment threshold. Our TD-DFT calculations suggested that there might be another bound singlet excited state (S_2) for 2-OtPh⁻. Due to the limited accuracy of the TD-DFT calculations, the question is if there is any spectral evidence for the appearance of S₂. As shown in Fig. 5 and discussed below, the R2PD PE spectral feature (Xs) in region (2) all exhibits the same electron binding energies, indicating fast vibrational relaxation in S_1 to the v = 0 level before the second photon detaches the electron from S₁. The adiabatic electron binding energy defined by band X_S was ~0.3 eV, consistent with the excitation energy of the 0-0 transition of S₁. However, we noticed that the X_T band in the R2PD PE spectra for region (3) (Fig. 6), although similar to the X_S band in the R2PD PE spectra from region (2), displays an apparent shift to higher binding energies. This shift occurs starting from the R2PD PE spectrum of peak 47, as shown in Fig. S7. This observation suggests that the second photon detaches the electron from a state that is lower in energy than the origin of S_1 , which must be T₁. Thus, we conclude that peak 47 is most likely the origin of S₂, which apparently has a strong intersystem crossing with T₁. In fact, the vibrational features in the X_T band in Fig. 6 all seem to be slightly broader than those in the X_S band in Fig. 5, suggesting that there is also relaxation from S_2 to S_1 , in addition to intersystem crossing with T₁, such that the X_T features also contain contributions from X_S. As will be discussed below, the shift between the binding energies of X_S and X_T is consistent with the singlet-triplet splitting measured from the PDS in Fig. 3. Peak 47 defines an excitation energy of 2.4793 eV (19997 cm⁻¹), compared with the computed

value of 2.6078 eV (Table S3). As shown in Table S3, the TD-DFT calculations slightly underestimated the excitation energy of S_1 but overestimated that of S_2 .

C. Single-color R2PD photoelectron spectroscopy

The ultrafast relaxation processes of anion excited states have been investigated using femtosecond pump-probe techniques.^{88,101-103} Our detachment laser pulse was ~5 ns. Thus, any relaxation processes of the anion excited states that take place within this time frame can be indirectly probed by the second photon within the same laser pulse via single-color R2PD PES. The complicated R2PD PE spectra shown in Figs. 5 and 6 suggest that a number of relaxation processes are at play upon the absorption of the first photon.

1. The X_s band and vibrational relaxation in S_1

We measured single-color R2PD PE spectra for all the observed vibronic peaks in region (2) of the PD spectrum (Fig. 3), i.e., peaks 0-46 in Fig. 4. All the spectra are similar, and representative spectra are shown in Fig. 5 for six vibronic levels of S₁. Figure 5(a) displays the spectrum at peak 0, where the first photon excites 2-OtPh⁻ to the v = 0 level of S₁, and the second photon detaches the electron from the zero-point level. The first peak of band X_S defines a binding energy of 0.328 eV. However, the binding energy of S₁ is measured accurately to be 0.296 eV using the excitation energy of the zero-point level (peak 0 in Fig. 4) of S_1 and the EA of 2-OtPh. The discrepancy arose from the fact that the high electron kinetic energies of band X_S could not be measured accurately in our PEI experiment because they fell on the edge of our VMI detector, where we did not have good calibration (see Sec. II A in experimental methods). Thus, a 0.028 eV systematic error in measuring the high energy electrons at the edge of the imaging detector for the two-photon detachment was conceivable. More importantly, we observe that the binding energies of band Xs are the same in all the R2PD PE spectra in S1, even though different vibrational levels of S1 are excited. This observation suggested that there must be fast vibrational relaxation in S₁, so that the second photon always detaches an electron from the zero-point level of S1, regardless of the initial vibrational levels excited by the first photon. The origin of band Xs is schematically shown in Fig. 8.



FIG. 8. Schematic energy level diagram showing the excitation and relaxation processes that give rise to bands X_S and X_T in the R2PD PE spectra of 2-OtPh⁻ in Figs. 5 and 6, respectively. The measured excitation energies for T₁, S₁, and S₂ for the anion and the electron affinity of the 2-OtPh radical are shown.

The S_a band in all the R2PD PE spectra will be discussed below. The strong signals (S_0) at the high binding energy end (low energy electrons) in each spectrum of Fig. 5 suggest internal conversion from S_1 to S_0 , so that highly excited vibrational levels are populated in S_0 , which could be then detached by the second photon. Another process that could produce low energy electrons is thermionic emission, which would be due to the internal conversion of at least two photons to S_0 . Thermionic emission is a well-known process in PES of anions when photoabsorption at a specific detachment photon energy and the subsequent internal conversion can compete with photodetachment.^{72–74} It should be pointed out that the threshold features due to thermionic emission are observed in all the PE spectra in Figs. 1 and 2, as well.

2. The X_T band and intersystem crossing from S_2 to T_1

At first glance, the R2PD PE spectra in Fig. 6 at higher excitation energies [region (3) in Fig. 3] are very similar to those shown in Fig. 5. However, close examination reveals that the binding energies of band X_T in Fig. 6 are slightly increased relative to band X_S in Fig. 5, indicating that the second photon detached an electron from a state even lower in energy than S₁. This state, then, must be T₁, suggesting that there is a strong intersystem crossing from the excited state reached by the first photon to T₁. Fig. S7 shows that the shift to higher binding energies for band X_T occurs at peak 47, which is likely the origin of a new excited state of 2-OtPh⁻, i.e., S₂. Thus, there must be a strong intersystem crossing from S2 to T1. The first peak of X_T is shifted to higher binding energies by 0.042 eV, which is consistent with the S_1 - T_1 splitting (507 cm⁻¹, 0.063 eV), considering the limited accuracy in measuring the binding energies of the X_S and X_T bands. The photoexcitation processes that give rise to band X_T are also schematically shown in Fig. 8. It should be pointed out that S₂ can also relax to S₁ at the same time, and band X_T may contain contributions from electron detachment from both S₁ and T₁ by the second photon, consistent with the observation that the fine features in band X_T in Fig. 6 seem to be broader than those of band X_S in Fig. 5.

3. The constant kinetic energy band S_a and a long-lived autodetaching excited state

The S_a bands in Figs. 5 and 6 all have the same kinetic energy of ~1.3 eV, as illustrated in Fig. S2. This observation suggests that band Sa comes from autodetachment from the same long-lived abovethreshold excited state (shape resonance), which is 1.3 eV above the ground state of neutral 2-OtPh. We designate this shape resonance state as S_{NR}. This state must have the unique property that its relaxation life time is long or comparable to that of autodetachment. Band S_a in Figs. 5 and 6 also suggests that the second photon in the R2PD process can excite the anion to a higher electronic state, which subsequently relaxes to S_{NR}, as schematically shown in process 1 of Fig. 9(d). It is interesting to note that the S_{NR} state is also produced via single photon excitation at 4.661 eV, as shown by the S_a band observed in Fig. 1(c), which is replotted in the kinetic energy scale in Fig. 9(c). We note that the near threshold PE spectrum at 2.7362 eV [Fig. 2(a)] also involves two-photon processes, represented by the high kinetic energy features X' and X''. The X' band is similar to the X_s band in Fig. 5, indicating that the above-threshold excited state of



FIG. 9. Kinetic energy distribution plots for the PE spectra taken at (a) 2.7362 eV [22 069 cm⁻¹, Fig. 2(a)], (b) 2.3329 eV [18 816 cm⁻¹, Fig. 5(a)], and (c) 4.661 eV [37 593 cm⁻¹, Fig. 1(c)]. (d) Schematic energy level diagram illustrating the population of the long-lived autodetaching $S_{\rm NR}$ state that gives rise to the constant kinetic energy band $S_{\rm a}$.

2-OtPh⁻ at 2.7362 eV also relaxes to S_1 , followed by electron detachment by the second photon. At the same time, the second photon can also excite the anion to a higher excited state, which relaxes to S_{NR} to give rise to the weak feature X'', because the X'' band is the same as the S_a band in Figs. 5 and 6, as shown in Fig. 9(a).

The long-lived shape resonance state S_{NR} is ~1.3 eV above the neutral detachment threshold of 2.629 eV, i.e., it is ~3.93 eV above the anion ground state (S_0) , as schematically shown in Fig. 9(d). To probe the nature of the shape resonance state, we took the PE spectrum in Fig. 1(b) at 3.959 eV, which is in resonance with S_{NR} . We indeed observed an autodetachment feature labeled as X_a in Fig. 1(b), which should be due to autodetachment directly from S_{NR} without relaxation. The strong threshold feature [S₀ in Fig. 1(b)] indicates that S_{NR} also undergoes internal conversion or relaxation to the ground state of the anion, leading to the thermionic feature. Thus, the autodetachment lifetime and relaxation lifetime of the S_{NR} state must be comparable to each other. The existence of rich abovethreshold excited electronic states and their fast relaxation to S1 or T₁ suggest that the 2-OtPh⁻ anion can be readily produced from low energy electron attachment to the neutral 2-OtPh radical, although relaxation to the S_{NR} shaped resonance would lead to autodetachment, competing with the formation of the anion. The closed-shell nature of 2-OtPh⁻ and its relatively large electron binding energy of 2.629 eV, which is comparable to that of C_{60}^{-} (2.6835 eV),¹⁰⁴ bode well for its possible existence in PAH-rich environments in the interstellar medium.

V. CONCLUSION

In conclusion, high-resolution photoelectron imaging and photodetachment spectroscopy of cryogenically cooled anions are utilized to investigate the electronic structure and spectroscopy of a complex PAH species, the deprotonated 2-hydroxytriphenylene

J. Chem. Phys. **160**, 184301 (2024); doi: 10.1063/5.0209948 Published under an exclusive license by AIP Publishing

anion (2-OtPh⁻), and its neutral radical. Rich low-lying excited electronic states of 2-OtPh⁻, including several bound excited states, are observed and studied using single-color resonant two-photon detachment photoelectron spectroscopy. The electron affinity of the 2-OtPh radical is determined to be 2.629(1) eV (21204 \pm 8 cm⁻¹), along with three excited electronic states and vibrational frequencies for several modes for the ground state. Photodetachment spectroscopy revealed rich vibronic features for two bound singlet states (S₁ and S₂) of 2-OtPh⁻, as well as evidence of a bound triplet state (T_1) . Resonant two-photon photoelectron spectroscopy of the bound states reveals rich photophysics of the excited states of the 2-OtPh⁻ anion, including vibrational relaxation, internal conversion, intersystem crossing, thermionic emission, and the existence of a long-lived autodetaching shape resonance 1.3 eV above the neutral ground state. The rich electronic and spectroscopic information and relaxation processes observed in the current study make the 2-OtPh⁻ anion an interesting system for direct pump-probe studies to investigate its rich photophysics and dynamics.

SUPPLEMENTARY MATERIAL

See the supplementary material for the comparison of the Franck–Condon simulation for the $S_0 \rightarrow S_1$ transition with the experiment, the plot in kinetic energies of Fig. 5, the valence molecular orbital picture of 2-OtPh⁻, the vibrational modes and computed frequencies for the neutral and anion ground state and the first singlet excited state, comparison of the shift in the R2PD PE spectra for S_1 and S_2 , the observed binding energies for the vibrational features resolved for the ground state of 2-OtPh and their assignments, the photon energies for the resolved vibronic peaks in S_1 and S_2 and their tentative assignments, and the computed excitation energies for the low-lying triplet and singlet states of 2-OtPh⁻.

ACKNOWLEDGMENTS

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

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jisoo Kang: Data curation (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (lead). Edward I. Brewer: Data curation (equal); Formal analysis (equal); Methodology (equal); Project administration (equal); Writing – review & editing (supporting). Yue-Rou Zhang: Data curation (supporting); Investigation (supporting). Dao-Fu Yuan: Data curation (supporting); Formal analysis (supporting); Methodology (supporting); Writing – review & editing (equal). G. Stephen Kocheril: Investigation (supporting); Methodology (supporting); Writing – review & editing (supporting). Lai-Sheng Wang: Conceptualization (lead); Funding acquisition (lead); Investigation (lead); Methodology (lead); Project administration (lead); Writing – original draft (equal).

DATA AVAILABILITY

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

REFERENCES

¹V. Le Page, T. P. Snow, and V. M. Bierbaum, Astrophys. J. 584, 316–330 (2003).

² R. I. Kaiser and N. Hansen, J. Phys. Chem. A **125**, 3826–3840 (2021).

³M. H. Vuong and B. H Foing, Astron. Astrophys. **363**, L5–L8 (2000).

⁴G. Malloci, G. Mulas, C. Cecchi-Pestellini, and C. Joblin, Astron. Astrophys. 489, 1183–1187 (2008).

⁵N. J. Demarais, Z. Yang, O. Martinez, N. Wehres, T. P. Snow, and V. M. Bierbaum, Astrophys. J. **746**, 32 (2012).

⁶E. Peeters, C. Mackie, A. Candian, and A. G. G. M. Tielens, Acc. Chem. Res. 54, 1921–1933 (2021).

⁷A. G. G. M. Tielens, Annu. Rev. Astron. Astrophys. 46, 289–337 (2008).

⁸J. L. Puget and A. Leger, Annu. Rev. Astron. Astrophys. 27, 161–198 (1989).

⁹D. S. N. Parker, F. Zhang, Y. S. Kim, R. I. Kaiser, A. Landera, V. V. Kislov, A. M. Mebel, and A. G. G. M. Tielens, Proc. Natl. Acad. Sci. U.S.A. **109**, 53–58 (2012).

¹⁰ R. I. Kaiser, D. S. N. Parker, and A. M. Mebel, Annu. Rev. Phys. Chem. 66, 43–67 (2015).

¹¹A. Garcia-Sanz, F. Carelli, F. Sebastianelli, F. A. Gianturco, and G. Garcia, New J. Phys. **15**, 013018 (2013).

¹²E. Herbst and Y. Osamura, Astrophys. J. **679**, 1670 (2008).

¹³V. Wakelam and E. Herbst, Astrophys. J. **680**, 371 (2008).

¹⁴ M. C. McCarthy, C. A. Gottlieb, H. Gupta, and P. Thaddeus, Astrophys. J. 652, L141–L144 (2006).

¹⁵J. Cernicharo, M. Guélin, M. Agúndez, K. Kawaguchi, M. McCarthy, and P. Thaddeus, Astron. Astrophys. 467, L37–L40 (2007).

¹⁶S. Brünken, H. Gupta, C. A. Gottlieb, M. C. McCarthy, and P. Thaddeus, Astrophys. J. 664, L43–L46 (2007).

¹⁷P. Thaddeus, C. A. Gottlieb, H. Gupta, S. Brünken, M. C. McCarthy, M. Agúndez, M. Guélin, and J. Cernicharo, Astrophys. J. 677, 1132–1139 (2008).

¹⁸J. Cernicharo, M. Guélin, M. Agundez, M. C. McCarthy, and P. Thaddeus, Astrophys. J. 688, L83–L86 (2008).

¹⁹M. A. Cordiner, J. V. Buckle, E. S. Wirström, A. O. H. Olofsson, and S. B. Charnley, Astrophys. J. 770, 48 (2013).

²⁰ M. E. Strauss, T. J. Santaloci, and R. C. Fortenberry, Chemistry 4, 42–56 (2022).
²¹ T. J. Santaloci and R. C. Fortenberry, Chemistry 3, 296–313 (2021).

²²R. N. Compton, H. S. Carman, C. Desfrançois, H. Abdoul-Carime, J. P. Schermann, J. H. Hendricks, S. A. Lyapustina, and K. H. Bowen, J. Chem. Phys. 105, 3472–3478 (1996).

²³ B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Science 287, 1658–1660 (2000).

²⁴T. Sommerfeld, Phys. Chem. Chem. Phys. 4, 2511–2516 (2002).

²⁵J. E. Turner, Am. J. Phys. 45, 758–766 (1977).

²⁶C. H. Qian, G. Z. Zhu, and L. S. Wang, J. Phys. Chem. Lett. **10**, 6472–6477 (2019).

²⁷C. Desfrancois, H. Abdoul-Carime, and J. P. Schermann, Int. J. Mod. Phys. B 10, 1339–1395 (1996).

²⁸N. I. Hammer, R. J. Hinde, R. N. Compton, K. Diri, K. D. Jordan, D. Radisic, S. T. Stokes, and K. H. Bowen, J. Chem. Phys. **120**, 685–690 (2004).

²⁹D. F. Yuan, Y. Liu, Y. R. Zhang, and L. S. Wang, J. Am. Chem. Soc. 145, 5512–5522 (2023).

³⁰B. A. McGuire, A. M. Burkhardt, S. Kalenskii, C. N. Shingledecker, A. J. Remijan, E. Herbst, and M. C. McCarthy, Science 359, 202–205 (2018).

³¹ B. A. McGuire, R. A. Loomis, A. M. Burkhardt, K. L. K. Lee, C. N. Shingledecker, S. B. Charnley, I. R. Cooke, M. A. Cordiner, E. Herbst, S. Kalenskii, M. A. Siebert, E. R. Willis, C. Xue, A. J. Remijan, and M. C. McCarthy, Science **371**, 1265–1269 (2021).

³²J. Cernicharo, M. Agúndez, C. Cabezas, B. Tercero, N. Marcelino, J. R. Pardo, and P. de Vicente, Astron. Astrophys. 649, L15 (2021).

³³M. C. McCarthy, K. L. K. Lee, R. A. Loomis, A. M. Burkhardt, C. N. Shingledecker, S. B. Charnley, M. A. Cordiner, E. Herbst, S. Kalenskii, E. R. Willis, C. Xue, A. J. Remijan, and B. A. McGuire, Nat. Astron. 5, 176–180 (2020).

³⁴ J. Cernicharo, M. Agúndez, R. I. Kaiser, C. Cabezas, B. Tercero, N. Marcelino, J. R. Pardo, and P. de Vicente, Astron. Astrophys. 655, L1 (2021).

³⁵W. C. Lineberger, Annu. Rev. Phys. Chem. **64**, 21–36 (2013).

³⁶L. S. Wang, J. Chem. Phys. **143**, 040901 (2015).

³⁷M. L. Weichman and D. M. Neumark, Annu. Rev. Phys. Chem. **69**, 101–124 (2018).

³⁸J. Schiedt and R. Weinkauf, Chem. Phys. Lett. 266, 201–205 (1997).

³⁹J. Schiedt and R. Weinkauf, Chem. Phys. Lett. **274**, 18–22 (1997).

⁴⁰ J. K. Song, N. K. Lee, J. H. Kim, S. Y. Han, and S. K. Kim, J. Chem. Phys. 119, 3071–3077 (2003).

⁴¹N. Ando, M. Mitsui, and A. Nakajima, J. Chem. Phys. 127, 234305 (2007).

⁴²S. Vosskotter, P. Konieczny, C. M. Marian, and R. Weinkauf, Phys. Chem. Chem. Phys. 17, 23573–23581 (2015).

⁴³J. N. Bull, C. W. West, and J. R. R. Verlet, Phys. Chem. Chem. Phys. 17, 32464–32471 (2015).

⁴⁴L. H. Stanley, C. S. Anstoter, and J. R. R. Verlet, Chem. Sci. 8, 3054–3061 (2017).

⁴⁵G. Mensa-Bonsu, A. Lietard, D. J. Tozer, and J. R. R. Verlet, J. Chem. Phys. 152, 174303 (2020).

⁴⁶J. Meissner, B. Kosper, C. M. Marian, and R. Weinkauf, J. Phys. Chem. A 125, 8777–8790 (2021).

⁴⁷A. Jalehdoost and B. von Issendorff, J. Chem. Phys. 158, 194302 (2023).

⁴⁸M. L. Weichman, J. B. Kim, J. A. Devine, D. S. Levine, and D. M. Neumark, J. Am. Chem. Soc. **137**, 1420–1423 (2015).

⁴⁹M. L. Weichman, J. A. Devine, D. S. Levine, J. B. Kim, and D. M. Neumark, Proc.
 Natl. Acad. Sci. U.S.A. 113, 1698–1705 (2016).

⁵⁰S. J. Kregel, G. K. Thurston, and E. Garand, J. Chem. Phys. **148**, 234306 (2018).

⁵¹S. J. Kregel and E. Garand, J. Chem. Phys. **149**, 074309 (2018).

⁵²C. R. Sagan and E. Garand, J. Phys. Chem. A **125**, 7014–7022 (2021).

⁵³C. R. Sagan, C. S. Anstoter, M. Thodika, K. D. Wilson, S. Matsika, and E. Garand, J. Phys. Chem. Lett. 13, 10245–10252 (2022).

⁵⁴H. T. Liu, C. G. Ning, D. L. Huang, P. D. Dau, and L. S. Wang, Angew. Chem., Int. Ed. **52**, 8976–8979 (2013).

⁵⁵H. T. Liu, C. G. Ning, D. L. Huang, and L. S. Wang, Angew. Chem., Int. Ed. **53**, 2464–2468 (2014).

⁵⁶G. Z. Zhu and L. S. Wang, Chem. Sci. **10**, 9409–9423 (2019).

⁵⁷Y. R. Zhang, D. F. Yuan, and L. S. Wang, J. Am. Chem. Soc. **144**, 16620–16630 (2022).

⁵⁸Y. R. Zhang, D. F. Yuan, and L. S. Wang, J. Phys. Chem. Lett. **14**, 7369–7381 (2023).

⁵⁹C. H. Qian, G. Z. Zhu, Y. R. Zhang, and L. S. Wang, J. Chem. Phys. **152**, 214307 (2020).

⁶⁰D. F. Yuan, Y. Liu, C. H. Qian, Y. R. Zhang, B. M. Rubenstein, and L. S. Wang, Phys. Rev. Lett. **125**, 073003 (2020).

⁶¹C. H. Qian, Y. R. Zhang, D. F. Yuan, and L. S. Wang, J. Chem. Phys. **154**, 094308 (2021).

⁶²D. F. Yuan, Y. R. Zhang, C. H. Qian, Y. Liu, and L. S. Wang, J. Phys. Chem. A 125, 2967–2976 (2021).

⁶³Y. R. Zhang, D. F. Yuan, C. H. Qian, G. Z. Zhu, and L. S. Wang, J. Am. Chem. Soc. 145, 14952–14962 (2023).

⁶⁴L. S. Wang, C. F. Ding, X. B. Wang, and S. E. Barlow, Rev. Sci. Instrum. 70, 1957–1966 (1999).

⁶⁵X. B. Wang and L. S. Wang, Rev. Sci. Instrum. **79**, 073108 (2008).

⁶⁶I. León, Z. Yang, H. T. Liu, and L. S. Wang, Rev. Sci. Instrum. **85**, 083106 (2014).

⁶⁷G. A. Garcia, L. Nahon, and I. Powis, Rev. Sci. Instrum. 75, 4989–4996 (2004).
 ⁶⁸V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, Rev. Sci. Instrum. 73, 2634–2642 (2002).

⁶⁹J. Cooper and R. N. Zare, J. Chem. Phys. 48, 942–943 (1968).

J. Chem. Phys. 160, 184301 (2024); doi: 10.1063/5.0209948

⁷⁰ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Jyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *GAUSSIAN 09, Revision D.01*, Gaussian, Inc., Wallingford, CT, 2016.

⁷¹ I. Pugliesi and K. Müller-Dethlefs, J. Phys. Chem. A **110**, 4657–4667 (2006).

⁷²L. S. Wang, J. Conceicao, C. Jin, and R. E. Smalley, Chem. Phys. Lett. **182**, 5–11 (1991).

⁷³Y. Zhao, E. de Beer, C. Xu, T. Taylor, and D. M. Neumark, J. Chem. Phys. 105, 4905–4919 (1996).

⁷⁴J. C. Pinare, B. Baguenard, C. Bordas, and M. Broyer, Phys. Rev. Lett. 81, 2225–2228 (1998).

⁷⁵S. K. Lower and M. A. El-Sayed, Chem. Rev. 66, 199–241 (1966).

⁷⁶S. M. Casey and D. G. Leopold, J. Phys. Chem. **97**, 816–830 (1993).

⁷⁷X. B. Wang, C. F. Ding, and L. S. Wang, J. Chem. Phys. **110**, 8217–8220 (1999).
 ⁷⁸J. Li, X. Li, H. J. Zhai, and L. S. Wang, Science **299**, 864–867 (2003).

⁷⁹J. Simons, J. Phys. Chem. A **112**, 6401–6511 (2008).

⁸⁰G. Herzberg, Science 177, 123–138 (1972).

⁸¹W. C. Lineberger and T. A. Patterson, Chem. Phys. Lett. 13, 40-44 (1972).

⁸² P. I. Jones, R. D. Mead, B. E. Kohler, S. D. Rosner, and W. C. Lineberger, J. Chem. Phys. **73**, 4419–4432 (1980).

⁸³ R. D. Mead, U. Hefter, P. A. Schulz, and W. C. Lineberger, J. Chem. Phys. 82, 1723–1731 (1985).

⁸⁴C. C. Arnold, Y. Zhao, T. N. Kitsopoulos, and D. M. Neumark, J. Chem. Phys. 97, 6121–6135 (1992).

⁸⁵ P. Freivogel, J. Fulara, M. Jakobi, D. Forney, and J. P. Maier, J. Chem. Phys. 103, 54–59 (1995). ⁸⁶Y. Zhao, E. de Beer, and D. M. Neumark, J. Chem. Phys. **105**, 2575–2582 (1996).
 ⁸⁷M. Ohara, H. Shiromaru, and Y. Achiba, J. Chem. Phys. **106**, 9992–9995 (1997).

⁸⁸C. Frischkorn, A. E. Bragg, A. V. Davis, R. Wester, and D. M. Neumark, J. Chem. Phys. **115**, 11185–11192 (2001).

⁸⁹T. Andersen, K. R. Lykke, D. M. Neumark, and W. C. Lineberger, J. Chem. Phys. 86, 1858–1867 (1987).

⁹⁰T. N. Kitsopoulos, C. J. Chick, Y. Zhao, and D. M. Neumark, J. Chem. Phys. 95, 1441–1448 (1991).

⁹¹J. E. Mann, S. E. Waller, D. W. Rothgeb, and C. C. Jarrold, Chem. Phys. Lett. 506, 31–36 (2011).

⁹²H. T. Liu, D. L. Huang, Y. Liu, L. F. Cheung, P. D. Dau, C. G. Ning, and L. S. Wang, J. Phys. Chem. Lett. **6**, 637–642 (2015).

⁹³E. A. Brinkman, E. Gunther, O. Schafer, and J. I. Brauman, J. Chem. Phys. 100, 1840–1848 (1994).

⁹⁴G. Baryshnikov, B. Minaev, and H. Ågren, Chem. Rev. 117, 6500–6537 (2017).

95 G. Y. Zheng, D. P. Rillema, J. DePriest, and C. Woods, Inorg. Chem. 37, 3588–3592 (1998).

⁹⁶ J. Yuan, R. Chen, X. Tang, Y. Tao, S. Xu, L. Jin, C. Chen, X. Zhou, C. Zheng, and W. Huang, Chem. Sci. 10, 5031–5038 (2019).

⁹⁷S. Kunishige, M. Kawabata, M. Baba, T. Yamanaka, Y. Morita, S. Higashibayashi, and H. Sakurai, J. Chem. Phys. **139**, 044313 (2013).

⁹⁸D. L. Kokkin, N. J. Reilly, T. P. Troy, K. Nauta, and T. W. Schmidt, J. Chem. Phys. **126**, 084304 (2007).

⁹⁹C. Harthcock, J. Zhang, and W. Kong, J. Chem. Phys. **140**, 244308 (2014).

¹⁰⁰D. F. Yuan, Y. R. Zhang, and L. S. Wang, J. Phys. Chem. A **126**, 6416–6428 (2022).

¹⁰¹A. Kunin and D. M. Neumark, Phys. Chem. Chem. Phys. 21, 7239–7255 (2019).

¹⁰²J. R. R. Verlet, C. S. Anstöter, J. N. Bull, and J. P. Rogers, J. Phys. Chem. A **124**, 3507–3519 (2020).

¹⁰³D. H. Kang, J. Kim, H. J. Eun, and S. K. Kim, Acc. Chem. Res. 55, 3032–3042 (2022).

¹⁰⁴D. L. Huang, P. D. Dau, H. T. Liu, and L. S. Wang, J. Chem. Phys. **140**, 224315 (2014).