Isomer-specific vibronic structure of the 9-, 1-, and 2-anthracenyl radicals via slow photoelectron velocity-map imaging

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Polycyclic aromatic hydrocarbons, in various charge and protonation states, are key compounds relevant to combustion chemistry and astrochemistry. Here, we probe the vibrational and electronic spectroscopy of gas-phase 9-, 1-, and 2-anthracenyl radicals (C₁₄H₉) by photodetachment of the corresponding cryogenically cooled anions via slow photoelectron velocity-map imaging (cryo-SEVI). The use of a newly designed velocity-map imaging lens in combination with ion cooling yields photoelectron spectra with <2 cm⁻ resolution. Isomer selection of the anions is achieved using gasphase synthesis techniques, resulting in observation and interpretation of detailed vibronic structure of the ground and lowest excited states for the three anthracenyl radical isomers. The groundstate bands yield electron affinities and vibrational frequencies for several Franck-Condon active modes of the 9-, 1-, and 2-anthracenyl radicals; term energies of the first excited states of these species are also measured. Spectra are interpreted through comparison with ab initio quantum chemistry calculations, Franck-Condon simulations, and calculations of threshold photodetachment cross sections and anisotropies. Experimental measures of the subtle differences in energetics and relative stabilities of these radical isomers are of interest from the perspective of fundamental physical organic chemistry and aid in understanding their behavior and reactivity in interstellar and combustion environments. Additionally, spectroscopic characterization of these species in the laboratory is essential for their potential identification in astrochemical data.

polycyclic aromatic hydrocarbons | anion photoelectron spectroscopy | velocity-map imaging | vibronic structure

Polycyclic aromatic hydrocarbons (PAHs) are an important class of species in many areas of chemistry. They are major components in coal (1) and in soot formed from combustion of organic matter (2, 3). PAHs are therefore common environmental pollutants and have well-documented mutagenic and carcinogenic biological activity (4, 5). PAHs are also believed to be abundant in the interstellar medium (6) and may be carriers of the anomalous IR emission bands (7–9). Recent molecular beam studies indicate that PAH growth can proceed through cold collisions of smaller hydrocarbons under interstellar conditions (10, 11). Individual PAH molecules can subsequently provide nucleation sites for amorphous graphitic grains (9). Interstellar PAHs and their clusters therefore bridge the gap between small carbonaceous molecules and larger particles, analogous to their role in soot condensation in combustion environments (12).

In space, PAH species are likely to exist as an equilibrium of neutral and ionic charge states, with varying degrees of hydrogenation and dehydrogenation (13–15). Models of dense interstellar clouds find that anionic PAHs are the major carriers of negative charge, rather than free electrons (16). Closed-shell, singly deprotonated PAH carbanions have large electron affinities compared with radical anionic parent species and may therefore be reasonably robust in the interstellar medium (6, 13). In this article, we investigate the three dehydrogenated isomers of anthracene, the 9-, 1-, and 2-anthracenyl radicals, via slow photoelectron velocity-map imaging (cryo-SEVI) of the corresponding cryogenically cooled, deprotonated anions. Structures of the $C_{14}H_9^-$ isomers are shown in Fig. 1. This cryo-SEVI technique previously yielded highly vibrationally resolved spectra of α - and β -naphthyl (17). We demonstrate here that even larger PAH anions are accessible to detailed characterization with cryo-SEVI and that the three anthracenyl isomers demonstrate strikingly distinct energetics and spectroscopic signatures.

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The anthracene molecule has been well characterized experimentally. Its infrared spectrum has been measured in a rare gas matrix (18, 19) and in the gas phase (20), and its vibrational structure has been largely assigned (21). The $S_1 \leftarrow S_0$ electronic transition in anthracene has been investigated with cavity ring-down spectroscopy (22). The high-temperature oxidation reactions of anthracene with O_2 and OH have been studied experimentally (23, 24). In both cases, H atom abstraction to form the anthracenyl radical intermediate competes with direct oxidation of anthracene. These reaction pathways govern the balance between efficient combustion and soot formation; detailed understanding of the intermediates involved is essential for accurately modeling combustion.

Significance

Polycyclic aromatic hydrocarbons (PAHs) are involved in soot nucleation following inefficient fuel combustion and are considered mutagens and environmental pollutants. They are also suspected to exist in the interstellar medium, although mechanisms for their formation in space are speculative. It is of great interest in these diverse fields to better characterize PAHs, including their dehydrogenated and charged derivatives, which are harder to isolate and probe. We use high-resolution anion photoelectron spectroscopy and quantum chemistry calculations to study the energetics, electronic states, and vibrational frequencies of the three dehydrogenated radical isomers of anthracene. These results provide signatures of these species for potential identification in space and illuminate subtle isomer-specific properties relevant to modeling their behavior in combustion and interstellar environments.

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Fig. 1. (A–C) SEVI spectra of photodetachment to (A) the $\tilde{X}^2 A_1$ ground state of 9-anthracenyl and the $\tilde{X}^2 A'$ ground states of (B) 1-anthracenyl and (C) 2-anthracenyl, with low-resolution overview scans in blue and high-resolution traces in black. Features in the spectrum of 2-anthracenyl appearing due to 1-anthracenyl contamination are plotted in gray. FC simulations are shown in red.

The anthracenvl radical and anion isomers are not nearly as well characterized as the anthracene parent. The 9- and 1-anthracenyl radicals were examined with ESR spectroscopy (25), which suggested that the unpaired electron resides in a σ orbital localized at the site of dehydrogenation. The reactivity of the 9-anthracenyl radical with naphthalene and toluene has also been measured experimentally (26). A recent multiple-photon electron detachment study yielded the infrared action spectrum of the 9-anthracenyl anion (6). Anionic anthracene derivatives in various protonation states are also used in electron transfer dissociation mass spectrometry as an electron source to induce fragmentation of peptide backbones (27). A fair amount of additional theoretical work has been reported detailing the energetics, electronic structure, geometries, vibrational frequencies, and reactivities of the anthracenyl radicals and anions (1, 6, 28–32). The three C-H bond dissociation energies of anthracene are predicted to be very similar, leading to three anthracenyl radical isomers nearly degenerate in energy (1, 28, 29, 31). The anionic isomers are calculated to be more separated in energy, with the 9-anthracenyl anion being the most stable and the 1- and 2anthracenyl anions lying 0.14 eV and 0.18-0.21 eV higher in energy, respectively (6, 29).

Anion photoelectron spectroscopy (PES) is a technique well suited for probing the vibronic structure of neutral radicals through photodetachment of a closed-shell anion (33, 34). The cryo-SEVI technique used here is a high-resolution variant of PES and yields spectra of complex anions with sub-meV resolution (17, 35, 36). Specific anthracenyl anion isomers are prepared using trimethylsilyl-anthracene precursors and cooled to cryogenic temperatures (~10 K) before photodetachment, eliminating hot spectral features and narrowing the rotational profiles of the observed peaks. Cooling is essential for obtaining interpretable spectra of large molecular species with many low-frequency vibrational modes. We also report the use of a newly designed velocity-map imaging (VMI) electrostatic lens with improved energy resolution. This development allows us to observe peaks with 2–3 cm⁻¹ FWHM and resolve splittings as small as 3 cm⁻¹ for the anthracenyl system. Focusing is also improved at higher electron kinetic energy (eKE), yielding narrower features farther from threshold and thus facilitating studies of anions with poor threshold photodetachment cross sections.

We present highly vibrationally resolved, isomer-specific spectra of transitions to the ground and first excited states of the 9-, 1-, and 2-anthracenyl radicals, providing much spectroscopic information and demonstrating the improved capabilities of the cryo-SEVI instrument. We obtain precise electron affinities for three anthracenyl radical isomers and term energies for their excited states, and measure Franck–Condon active fundamental vibrational frequencies. Our results illuminate the distinct spectroscopy, energetics, and potential reactivity of these isomers, with farreaching applications in interpretation of astrochemical data and modeling of combustion chemistry.

Results and Discussion

Experimental Photodetachment Spectra. The cryo-SEVI spectra of 9-, 1-, and 2-anthracenyl presented in Figs. 1 and 2 comprise two well-separated electronic bands, which for each isomer are assigned as transitions from the anion ground state to the ground electronic state (\tilde{X}) and the first excited state (\tilde{A}) of the neutral radical. Franck–Condon (FC) simulations were carried out for



Fig. 2. (*A* and *B*) SEVI spectra of photodetachment to (*A*) the $\tilde{A}^2 B_1$ excited state of 9-anthracenyl and (*B*) the $\tilde{A}^2 A''$ state of 1-anthracenyl, with colored traces taken at progressively lower photon energies and FC simulations in red.

all states and are plotted as red stick spectra. Experimental details are described in *Materials and Methods, Experimental*, and ab initio calculations are described in *Materials and Methods, Electronic Structure Calculations*. Experimental energetics and vibrational frequencies for all anthracenyl isomers are summarized in Table 1 and compared with calculated values. Positions and assignments for the peaks labeled in Figs. 1 and 2 are summarized in Tables S1–S3.

Cryo-SEVI spectra of the 9-, 1-, and 2-anthracenyl \hat{X} bands are shown in Fig. 1 as a function of electron binding energy (eBE). With SEVI, we first measure a low-resolution overview spectrum at a photon energy well above the eBE of the band of interest, plotted in Fig. 1 in blue. We then obtain high-resolution spectra at discrete photon energies tuned above the spectral features of interest and splice them together to create a composite highresolution spectrum of the full region, plotted in black in Fig. 1. The high-resolution trace for a given feature is then scaled to the intensity of that feature in the overview spectrum to minimize any threshold effects that distort relative peak intensities.

The ground-state spectra of all isomers show congested but well-resolved structure that is accurately predicted by FC simulations. High-resolution peak widths are typically $4-5 \text{ cm}^{-1}$ FWHM for the ground states of all three anthracenyl radicals and as narrow as $2-3 \text{ cm}^{-1}$ FWHM. This constitutes a notable improvement in instrumental resolution over previous cryo-SEVI studies of aromatic molecules, where the narrowest features were more often $7-8 \text{ cm}^{-1}$ FWHM (17, 36). Peaks indicating some contamination of the 1-anthracenyl isomer in the 2-anthracenyl spectrum are plotted in gray in Fig. 1*C*. This contamination is likely due to decomposition of either the 2-trimethylsilylanthracene precursor or the 2-anthracenyl anions after formation in the ion source. The contamination worsens with increasing temperature of the ion source and over time with use of the same precursor sample.

Spectra of the \tilde{A} bands of 9- and 1-anthracenyl are shown in Fig. 2 A and B. Due to poor threshold cross sections for these bands, we do not plot composite high-resolution spectra, but rather the full traces at progressively lower photon energies. Although we report its term energy in Table 1, the 2-anthracenyl \tilde{A} -state spectrum is not presented due to contamination from 1-anthracenyl structure made worse by relative cross-section effects. The \tilde{A} bands of all isomers have strong vibrational origins

and weak vibrationally excited structure. The profiles of these bands are in qualitative agreement with FC simulations, although more vibrational activity is seen in the spectra than in the simulations.

Compared with the \tilde{X} bands, the \tilde{A} -state vibrational origins are very weak at low eKE, preventing measurements close to threshold where SEVI resolution is best. Hence, peak widths for the \tilde{A} -band origins are limited to ~100 cm⁻¹ FWHM, even with the improved resolution afforded by the redesigned VMI lens. The remaining features in the \tilde{A} bands largely follow this trend of vanishing intensity close to threshold. However, the intensities of some peaks (most notably *b* and *c*) in the 1-anthracenyl spectrum increase dramatically at certain photon energies, evidenced by the purple trace plotted in Fig. 2*B*.

SEVI also provides information about the anisotropy of photodetachment transitions. For a photodetachment process with one photon of linearly polarized light, the photoelectron angular distribution (PAD) is given by (37)

$$I(\theta) = \frac{\sigma_{\text{tot}}}{4\pi} [1 + \beta P_2(\cos \theta)], \qquad [1]$$

where θ is the angle of electron signal relative to the polarization axis of the laser, P₂ is the second-order Legendre polynomial, and β is the anisotropy parameter, which varies between -1 for a PAD aligned perpendicular to the laser polarization and +2 for a PAD parallel to the laser polarization.

Table 1. Experimental and calculated electron affinities,excited-state term energies, and vibrational frequencies forthe 9-, 1-, and 2-anthracenyl radicals

State	Parameter	Experimental	Calculated
9, <i>X</i>	EA,* eV	1.7155 (2) [†]	1.6749
	ν_{15} , cm ⁻¹	1,147 (1)	1,168
	ν ₁₇ , cm ⁻¹	896 (2)	907
	ν ₁₈ , cm ⁻¹	752 (4)	759
	ν ₁₉ , cm ⁻¹	648 (2)	658
	ν_{20} , cm ⁻¹	621 (2)	638
	ν_{21} , cm ⁻¹	390 (2)	398
	ν_{22} , cm ⁻¹	228 (2)	233
9, Ã	T ₀ , [‡] eV	1.205 (6)	1.0382
1, <i>X</i>	EA, eV	1.5436 (2)	1.5287
	ν_{30} , cm ⁻¹	1,091 (4)	1,113
	ν_{34} , cm ⁻¹	891 (2)	902
	ν_{36} , cm ⁻¹	753 (2)	762
	ν_{38} , cm ⁻¹	621 (2)	639
	ν_{39} , cm ⁻¹	599 (2)	618
	ν_{40} , cm ⁻¹	514 (2)	526
	ν_{42} , cm ⁻¹	388 (2)	395
	ν_{43} , cm ⁻¹	232 (2)	236
1, Ã	T ₀ , eV	1.515 (4)	1.3277
	ν_{56} , cm ⁻¹	496 (36)	504
	ν_{60} , cm ⁻¹	255 (33)	256
2, <i>X</i>	EA, eV	1.4671 (2)	1.4734
	ν_{31} , cm ⁻¹	1,013 (2)	1,039
	ν_{34} , cm ⁻¹	882 (2)	894
	ν_{37} , cm ⁻¹	648 (1)	658
	ν ₃₉ , cm ⁻¹	591 (1)	609
	ν_{40} , cm ⁻¹	522 (2)	533
	ν_{41} , cm ⁻¹	389 (1)	398
	ν_{42} , cm ⁻¹	392 (1)	396
	ν_{43} , cm ⁻¹	234 (1)	238
2, Ã	T ₀ , eV	1.755 (8)	1.5580

*Electron affinity.

 † Uncertainties represent 1 SD of a Gaussian fit to the experimentally observed peak.

[‡]Term energy.



Fig. 3. (*A* and *B*) Calculated and experimental anisotropy parameters for photodetachment to (*A*) the \tilde{X} -band vibrational origins and (*B*) the \tilde{A} -band vibrational origins of the 9-, 1-, and 2-anthracenyl radicals, as functions of eKE.

Experimental values of β for the vibrational origins of the \bar{X} bands of all isomers are plotted in Fig. 3 as a function of eKE, along with PAD simulations for the \bar{X} and \tilde{A} bands. We do not report quantitative anisotropy parameters for the excited states, because high-eKE photoelectrons from detachment to the ground states create a background that distorts the excited-state anisotropies during image reconstruction. However, it is qualitatively clear that all radical isomers have \tilde{A} -state vibrational origins with slightly perpendicularly polarized PADs ($\beta < 0$). Intriguingly, in the 1-anthracenyl \tilde{A} -state spectrum plotted in purple in Fig. 2*B*, peaks *b* and *c* demonstrate positive β values, in contrast to the vibrational origin *a*.

Assignment of Electronic Structure. Cryogenic cooling ensures, in principle, that we photodetach from the ground vibrational and electronic state of each anthracenyl anion. Our electronic structure calculations indicate that the ground state of each neutral radical is accessed by removing an electron from an in-plane σ molecular orbital (MO) with *s*-*p* character localized on the deprotonated site of the closed-shell anion, whereas the first

excited state of each radical is accessed by removal of an electron from a delocalized π MO of the anion. Calculated Dyson orbitals (38) for the photodetachment transitions for each isomer are shown in Fig. 4.

We assign the low binding energy bands in Fig. 1 to the $\widetilde{X}^2 A_1 \leftarrow \widetilde{X}^1 A_1$ detachment transition of 9-anthracenyl and the $\widetilde{X}^2 A' \leftarrow \widetilde{X}^1 A'$ transitions of 1- and 2-anthracenyl. The peaks labeled A in Fig. 1 represent the vibrational origin of each $\tilde{X} \leftarrow \tilde{X}$ band, yielding precise experimental electron affinities (EAs) for the 9-, 1-, and 2-anthracenyl radicals that are in good agreement with the calculations carried out in the present work (Table 1) as well as in the literature (29). The decrease in EA as the site of deprotonation is moved from C₉ to C₁ to C₂ reflects the energetic ordering of the anions. The isomer energetics calculated in the present work (Table 2) are in good agreement with the literature (1, 6, 28, 29, 31); we find that the 9-anthracenyl anion is lowest in energy with the 1-anthracenyl and 2-anthracenyl anions lying 0.13 eV and 0.18 eV higher in energy, respectively. By contrast, the 9-, 1-, and 2-anthracenyl radicals fall within 0.02 eV of one another.

The higher eBE bands shown in Fig. 2 are assigned to the $\tilde{A}^2 B_1 \leftarrow \tilde{X}^1 A_1$ band of 9-anthracenyl and the $\tilde{A}^2 A'' \leftarrow \tilde{X}^1 A'$ transition of 1-anthracenyl; the peaks labeled *a* are the vibrational origins of these two bands. Experimental and calculated energetics compare favorably (Table 1) and reproduce the trend of increasing \tilde{A} -state term energy from 9- to 1- to 2-anthracenyl. Because the radical ground states are predicted to be nearly degenerate, the differences in T_0 are due to destabilization of the 1- and 2-anthracenyl \tilde{A} states relative to that of 9-anthracenyl. The calculated results in Table 2 place the 1-anthracenyl and 2-anthracenyl \tilde{A} states. Rationalizations for the energetic ordering of the anion and neutral isomers are discussed in further detail below.

Radical Ground States. The \hat{X} bands of the anthracenyl radicals show extensive FC activity, indicative of a large change in geometry upon photodetachment. This FC structure is consistent with detachment of an electron from a highly localized MO (Fig. 4) and with geometry optimization calculations (Tables S4–S6), which indicate that the C–C–C interior bond angle at the deprotonated site widens by ~14° in all three systems upon detachment to the radical ground state.

Several fundamental frequencies of each radical ground state are observed (Table 1). The FC active vibrational modes should be totally symmetric and are therefore attributed to a_1 modes for the $C_{2\nu}$ -symmetric 9-anthracenyl radical and a' modes for the C_s -symmetric 1- and 2-anthracenyl radicals. Schematics for normal mode displacements of all FC active vibrations are given in Fig. S1. The most highly FC active modes for each radical involve



Fig. 4. (A–C) Calculated cross sections and visualized Dyson orbitals for photodetachment to the \tilde{X} and \tilde{A} states of (A) 9-anthracenyl, (B) 1-anthracenyl, and (C) 2-anthracenyl as functions of eKE.

Table 2. Calculated energies (eV) for all species at the B3LYP/6-311+G* level of theory, given relative to the 9-anthracenyl anion ground state and corrected for vibrational zero-point energy

State	9-Anthracenyl	1-Anthracenyl	2-Anthracenyl
Anion	0.0000	0.1309	0.1842
Ground	1.6749	1.6596	1.6576
Excited	2.7130	2.9873	3.2156

significant distortion at the deprotonated site, where there is the largest change in geometry upon photodetachment.

For the 9-anthracenyl radical ground state (Fig. 1*A*), all spectral features can be assigned to fundamentals, progressions, and combination bands of the vibrational frequencies listed in Table 1. Full peak assignments are detailed in Table S1. The FC stick spectra are in very good agreement with the experimentally observed features. Only peak B does not appear in the simulation, but it can be assigned unambiguously to v_{22} based on comparison with the ab initio calculated frequencies of FC allowed a_1 modes.

The experimental 1-anthracenyl radical \hat{X} band also largely agrees with the FC simulation (Fig. 1*B*). Peak B again does not appear in the simulation, but it can be assigned to the ν_{43} fundamental as the only FC allowed *a'* mode with a sufficiently low calculated frequency. Additionally, we observe a strong feature (peak F) not predicted by the FC simulation, appearing only 8 cm⁻¹ above ν_{39} (peak E). Elsewhere in the spectrum, similar doublets (e.g., peaks N/O and V/W) appear where the FC simulation predicts only one peak involving excitation of the ν_{39} mode. Nearly all other peaks in the spectrum can be assigned to progressions and combination bands of the observed fundamentals and peak F (Table S2).

The 2-anthracenyl radical \hat{X} band in Fig. 1*C* shows contamination from 1-anthracenyl ground-state features; those peaks that derive from 1-anthracenyl are shaded gray. The distinct binding energies and FC profiles of the two bands permit nearly full assignment of the 2-anthracenyl ground-state features despite the contamination. The instrumental resolution is sufficient to distinguish the ν_{41} and ν_{42} fundamentals (peaks C/D; Fig. 1*C*, *Inset*) that are split by 3 cm⁻¹; this is now possible only with our updated VMI electron optics. Nearly all other bands in the 2-anthracenyl \tilde{X} spectrum can be assigned to progressions and combination bands of the observed fundamentals (Table S3). As was seen in the 1-anthracenyl \tilde{X} band, we observe a feature not predicted by FC simulation (peak G), again 8 cm⁻¹ above the ν_{39} fundamental (peak F).

The source of peaks F and G in the X-state spectra of the 1- and 2-anthracenyl radicals is subtle. The PAD and threshold behavior of these peaks is the same as that of the neighboring peaks, suggesting that they have the same electronic character as the FC allowed peaks. However, the locations of peaks F and G with respect to the vibrational origins of 1- and 2-anthracenyl do not align with any calculated a' fundamentals or combinations of FC active modes. Each of these peaks is most likely a combination band of two a" modes that together have a' vibrational symmetry, as $a'' \otimes a'' = a'$. Such a combination band is FC allowed by symmetry, and if its frequency is very close to that of the ν_{39} fundamental, it can borrow the intensity of the ν_{39} fundamental through a Fermi resonance. Fermi resonances occur when two vibrational states of the same overall symmetry lie very close together and interact, leading to mixing of the two eigenstates and widening of the energy gap as the mixing states repel one another (39). Anharmonic terms in the potential energy provide the perturbation that allows energy levels associated with different normal modes to mix.

Based on calculated harmonic frequencies in Tables S7 and S8, the most likely a'' modes involved in the combination band in Fermi resonance with ν_{39} are modes ν_{59} and ν_{61} for both isomers

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(displacements shown in Fig. S2). In 1-anthracenyl, the ν_{39} mode is strongly FC active, and this Fermi resonance manifests several times, with combination bands and progressions of ν_{39} appearing as doublets and multiplets. The ν_{39} mode is less active in 2-anthracenyl and only the fundamental clearly demonstrates this extra feature. No analogous extra peaks appear in the 9-anthracenyl \tilde{X} spectrum, as the ring distortion mode analogous to ν_{39} (ν_{61} in Table S7) is not FC allowed.

The experimental and simulated values of β describing the anisotropies of the 9-, 1-, and 2-anthracenyl \tilde{X} bands are shown in Fig. 3A. The PADs for detachment to the radical ground states differ based on relative s and p contributions to the s-p hybrid Dyson orbitals of the three isomers (40). Detachment from s-like orbitals yields predominantly l=1 photoelectrons with parallel PADs, whereas detachment from p-like orbitals yields both isotropic l=0 photoelectrons and perpendicularly polarized l=2 photoelectrons. The relative contributions of the s and p detachment channels significantly affect the PAD (41), allowing for very different observed anisotropies for the three isomers.

By these metrics, the 9-anthracenyl X-state Dyson MO has the largest contribution of s character, whereas 1- and 2-anthracenyl have respectively higher fractions of p character. We propose an explanation by considering a model sp^2 -hybridized σ -bonding network for the anthracenyl anions. In each anion, the deprotonated carbon has three sp^2 orbitals: two participating in C–C σ bonds and one containing the electron lone pair, from which an electron is detached to form the ground-state radical. In the 9-anthracenyl anion, the deprotonated C₉ atom is adjacent to two tertiary carbons, C_{9a} and C_{8a} (Fig. 1A). The two $C_9 sp^2$ bonding orbitals therefore have geometric overlap with the other four C–C σ bonds in which C_{9a} and C_{8a} participate. This overlap delocalizes and stabilizes the longer-range p character of the sp^{2} bonding orbitals, leaving more s character in the lone pair orbital. In the 1-anthracenyl anion, C_1 is bonded to just one tertiary carbon, whereas in 2-anthracenyl, C2 adjoins only secondary carbons. In these anions, the deprotonated carbon sp^2 bonding orbitals therefore have less *p* stabilization due to fewer nearby C–C σ bonds with which to overlap. The lone pair orbital thus exhibits more p character in the 1-anthracenyl anion and more yet in 2-anthracenyl.

The energetic ordering of the anthracenyl anions is closely related to these effects. Papas et al. (29) make the steric argument that the 1- and 2-anthracenyl anions are lifted in energy relative to 9-anthracenyl due to greater repulsion between the excess charge and H atoms bonded to secondary carbons adjacent to the deprotonation site. The repulsion of the lone pair also narrows the C–C–C interior bond angle at the deprotonated site, and the ability of each isomer structure to accommodate this strain contributes to the energetic ordering of the anions. It is compelling that the radical \hat{A} states follow the same energetic ordering as the anions, owing to similar hybridization and steric arguments in accommodate, the ground-state anthracenyl radicals fall much closer together in energy.

Radical Excited States. The anthracenyl radical \hat{A} bands have very intense vibrational origins and weak FC activity beyond the origins, indicating little change in geometry upon photodetachment from the anion to the radical excited state. The calculated excited-state geometries accordingly show little displacement from those of the anions (Tables S4–S6). Dyson MOs for these transitions (Fig. 4) are delocalized over the ring system, consistent with little perturbation in geometry upon removal of an electron.

The \widetilde{A} bands are poorly resolved compared with the \widetilde{X} bands, making spectral assignments challenging beyond identification of the vibrational origin. The low \widetilde{A} -state photodetachment cross sections close to threshold cause features to vanish before they can be narrowly resolved with SEVI. According to the Wigner

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threshold law for photodetachment, the near-threshold cross section (σ) is a function of eKE and *l*, the angular momentum of the nascent photoelectron (42):

$$\sigma \propto (eKE)^{l+1/2}.$$
 [2]

The Dyson MOs for the anthracenyl radical \tilde{A} state, shown in Fig. 4, have nodal structure analogous to that of an atomic g orbital, in which the orbital angular momentum of the electron is l = 4. In a one-photon, one-electron process, a photoelectron is detached from an atomic orbital with $\Delta l = \pm 1$ (43). By extension, after detachment to form the anthracenyl \tilde{A} state, the outgoing photoelectron must have at least l = 3, which yields vanishing σ at small eKE according to Eq. 2. The Dyson orbitals for the \tilde{X} states, on the other hand, have localized *s*-*p* hybrid character, enabling partial l = 0 detachment, and significant intensity at small eKE (40). Photodetachment cross sections calculated as a function of eKE are shown in Fig. 4 and reproduce this difference in threshold behavior for the \tilde{X} and \tilde{A} states of all three isomers.

The 1-anthracenyl A state displays some interesting behavior that warrants additional comment. At photodetachment wavelengths of 27,500–27,600 cm⁻¹, the \tilde{A} band shows increased cross section and enhanced intensity of peaks b and c relative to the origin, demonstrated by the purple trace in Fig. 2B. Additionally, peaks b and c have distinct parallel polarization, in contrast to the consistent slightly perpendicular PAD of the vibrational origin.

The strong wavelength-dependent change in photodetachment cross section in combination with the appearance of features with distinct PADs suggests a contributing autodetachment mechanism. If a metastable anion state is embedded in the neutral-plus-free-electron continuum, resonant transitions to this state can compete with direct photodetachment. The anion excited state can then autodetach, resulting in electron signals whose cross section and anisotropy are not governed by the considerations discussed above. The closed-shell anthracene, whose $S_1 \leftarrow S_0$ band origin lies at 27,687 cm⁻¹ (22), so the presence of a 1-anthracenyl anion resonance at excitation wavelengths of 27,500–27,600 cm⁻¹ is not surprising.

Conclusions

We have acquired isomer-specific slow photoelectron velocitymap imaging spectra of cold 9-, 1-, and 2-anthracenyl anions, using a newly designed VMI electrostatic lens. We observe detailed vibronic structure of the largely unstudied neutral radicals. The radical ground-state spectra are fully vibrationally resolved, allowing measurement of precise electron affinities and Franck– Condon active vibrational frequencies. Transitions to the radical first excited states are also measured and term energies reported, although poor threshold photodetachment cross sections prevent full vibrational resolution as achieved for the radical ground states.

This work shows how improvements in high-resolution photoelectron imaging, in combination with cryogenic ion cooling and techniques for isomer selection, can be used to untangle the vibronic structure of increasingly complex and diverse radical systems. The subtle structural and electronic differences between the 9-, 1-, and 2-anthracenyl radicals are made clear in the cryo-SEVI spectra and photoelectron angular distributions presented here. These results inform our fundamental understanding of the chemistry of these species, as well as their behavior in the context of astrochemistry and combustion.

Materials and Methods

Experimental. In cryo-SEVI, cold, mass-selected anions are photodetached with a tunable laser. The kinetic energies of the resulting photoelectrons are measured with a velocity-map imaging spectrometer. Low extraction voltages are used to preferentially detect slow electrons, magnifying their image

on a position-sensitive detector. Cryo-SEVI and the current configuration of our instrument have been described elsewhere (33, 44, 45).

Specific anthracenyl anion isomers are prepared by flowing trace NF₃ in helium gas over a reservoir containing 9-, 1-, or 2-(trimethylsilyl)-anthracene heated to 40–60 °C. We expand this mixture through an Even–Lavie pulsed valve (46) operating at 20 Hz and fitted with a circular filament ionizer. Electrons from the ionizer induce dissociative electron attachment of NF₃ to produce F⁻. F⁻ then reacts with 9-, 1-, or 2-(trimethylsilyl)-anthracene, selectively forming the corresponding anthracenyl anion due to the strength of the silicon–fluorine bond (47).

The three trimethylsilyl-anthracene precursors were synthesized from the corresponding bromoanthracenes according to the procedure described by Marcinow et al. (48). The 9-bromoanthracene (TCI; >99%) and 1-bromoanthracene (TCI; >97%) were obtained commercially, whereas 2-bromoanthracene was synthesized from 2-aminoanthracene (Sigma-Aldrich; 96%). The details of these syntheses and NMR characterization of products are reported in *SI Materials and Methods*.

After production, the anthracenyl anions are directed through a radiofrequency (RF) hexapole ion guide and a quadrupole mass filter and into a linear RF octopole ion trap. The trap is held at 5 K and filled with pulsed bursts of precooled buffer gas in a mixture of 80% He and 20% H₂. The ions are stored in the trap for around 40 ms, enabling collisional cooling to their ground vibrational state (45). The cooled ions are extracted from the trap into an orthogonal time-of-flight mass spectrometer.

After mass selection, the anions reach the interaction region inside the VMI spectrometer, where they are photodetached with the output from an Nd: YAG-pumped tunable dye laser. The VMI electrostatic lens focuses the photoelectrons onto an imaging detector comprising a pair of chevron-stacked microchannel plates coupled to a phosphor screen (49). We have recently updated our VMI lens to improve the focusing of photoelectrons onto the detector; the details of this design are described in *Materials and Methods, Modification of the VMI Lens*.

Electron events on the imaging detector are recorded with a $768 \times 1,024$ pixel CCD camera. We use event-counting software to identify single electron events and compute their centroids during data acquisition (50). It is essential to bin centroids into a grid that is fine enough not to limit the resolution of the spectrometer. The radial and angular electron distributions are reconstructed from the accumulated image, using the maximum-entropy velocity Legendre reconstruction method (51).

We calibrate the velocity and hence eKE of the photoelectrons as a function of radial displacement, R, using SEVI images of atomic O⁻ and F⁻ (52, 53) taken at many photon energies. The distance of an electron spot from the center of the reconstructed image is largely linearly proportional to its velocity following photodetachment. However, the added length and lensing properties of the modified VMI design slightly distort the electron velocities, so an additional polynomial term is needed; we calibrate it by fitting $eKE = aR^2 + bR^4$. The eKE spectrum can then be converted to eBE, using the energy conservation expression eBE = $h\nu - eKE$, where $h\nu$ is the photon energy.



Modification of the VMI Lens. We have recently modified the original threeelectrode Eppink–Parker VMI design (54) to improve the energy resolution of our cryo-SEVI spectra. The redesigned VMI lens is shown in Fig. 5. The major goal of this modification was to improve the energy resolution for eKEs in the range of a few hundred to a few thousand wavenumbers. This is the regime in which SEVI is forced to operate for anions with poor threshold photodetachment cross sections. Additionally, a SEVI spectrum over a particular energy range can now be obtained with fewer high-resolution windows.

Several alternative VMI designs with excellent focusing capability for photoelectrons have been reported in the literature (55–57). The key changes made in these designs include adding a fourth electrode whose voltage is adjusted to optimize focus (55, 57) and increasing the total length of the VMI stack (56). Increasing the length of the VMI lens along the electron flight axis can significantly improve its focusing ability, as the volume of the interaction region is smaller relative to the size of the lens. Additionally, lengthening the stack while maintaining a fixed repeller voltage results in a lower electric field gradient in the interaction region, which can reduce the importance of laser positioning and stabilize the velocity calibration of the resulting images (58). However, adding distance between electrodes allows fringe fields to penetrate into the lens and distort electron trajectories. This effect can be corrected for either by adding guard rings to the existing electrodes (56) or by adding additional guarding plates to maintain a smooth voltage gradient in each acceleration region (57).

We chose to implement a design comprising three electrodes and four guarding plates for simplicity and ease of optimization. The seven-plate geometry shown in Fig. 5 keeps the repeller (plate 1), extractor (plate 4), and grounding (plate 7) electrodes of the Eppink–Parker design, but adds four guarding electrodes (plates 2, 3, 5, and 6). The plate apertures and spacings were optimized using electron trajectory simulations in SIMION 8.0 (59). All VMI plates were machined from stainless steel 304 and are coated with colloidal graphite. Four sets of Vespel spacers maintain the gap between neighboring plates. Using resistors wired in series, the guarding plates are held at voltages linearly interpolated between the repeller, extractor, and ground electrodes. The VMI is focused by tuning the ratio of the extractor voltage ($V_{\rm E}$) to the repeller voltage ($V_{\rm R}$).

The VMI spectrometer has a roughly constant value for $\Delta eKE/eKE$, yielding the narrowest features for the lowest-eKE transitions. Using detachment of atomic O⁻ and F⁻ to characterize the lens, we obtain our narrowest feature with a 1.2-cm⁻¹ FWHM at eKE = 5 cm⁻¹ and V_R = -170 V. Farther from threshold, V_R = -340 V provides the best compromise between image magnification on the detector and invulnerability to stray fields and yields typical resolution of 6 cm⁻¹ FWHM at eKE = 190 cm⁻¹ and 20 cm⁻¹ FWHM at eKE =

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1,350 cm⁻¹, comparable to the performance reported by Wang and coworkers (57). Our resolution with the original Eppink–Parker design with a comparable V_R was 14 cm⁻¹ FWHM at eKE = 180 cm⁻¹ and 36 cm⁻¹ FWHM at eKE = 1,000 cm⁻¹. With V_R = –670 V, we can achieve Δ eKE/eKE ~ 1.4% for faster electrons, compared with an optimal resolution of ~3% with the Eppink–Parker lens.

Electronic Structure Calculations. Density functional theory calculations were carried out at the B3LYP/6-311+G* level of theory to find the energetics, optimized geometries, normal modes, and harmonic vibrational frequencies for the 9-, 1-, and 2-anthracenyl anions and the ground and first excited states of the corresponding radicals. The maximum overlap method (60) was used for the radical excited states. Dyson orbitals for photodetachment transitions were calculated with EOM-IP-CCSD/6-311G. All ab initio work was done using Q-Chem 4.0 (61, 62).

Calculated energetics corrected for vibrational zero-point energy and relevant harmonic vibrational frequencies are summarized in Table 1; isomer energetics are summarized in Table 2. Full lists of optimized geometries and harmonic frequencies can be found in Tables 54–59. All states considered were found to have planar equilibrium geometries, in agreement with the literature (6, 29, 31).

Photoelectron spectra for detachment to the ground and excited states of the 9-, 1-, and 2-anthracenyl radicals were simulated at 0 K, using the ezSpectrum program (63). The ab initio geometries, normal modes, and harmonic frequencies were given as input, and Franck–Condon overlap factors were calculated in the harmonic approximation with Duschinsky mixing of all modes (64). The vibrational origins of all bands were shifted in eBE to align with their experimental values. Those frequencies of the neutral ground states that were observed in the high-resolution SEVI spectra were scaled to their experimental values; the others were left at their calculated B3LYP/6-311+G* values.

The photoelectron angular distributions and photodetachment cross sections for transitions to the neutral ground and excited states were calculated as functions of eKE with the ezDyson program (38, 65). ezDyson takes as input the ab initio Dyson orbitals for the relevant photodetachment transitions and finds the contribution of partial spherical waves with angular momentum $l \le 4$ to the wavefunction of the outgoing photoelectron.

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