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On the Electronic Properties of Dehydrogenated Polycyclic Aromatic Hydrocarbons

Damian L. Kokkin and Timothy W. Schmidt*

School of Chemistry, University of Sydney, NSW 2006, Australia

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The electronic excited-state properties of a series of dehydrogenated polycyclic aromatic hydrocarbons from phenyl through to decacyl are reported. The radicals were investigated by use of time-dependent density functional theory in conjunction with the B3LYP functional. The π^* and n orbitals were seen to converge in energy as the system increased in size, yet all radicals were found to have A′ ground states. In addition to the study of the electronic state symmetries, the excited-state transitions and oscillator strengths were investigated with the resulting transitions found within the visible region of the spectrum, placing these radicals in the large group of candidate carriers of the diffuse interstellar bands.

1. Introduction

The family of molecules known as the polycyclic aromatic hydrocarbons (PAHs) has received much attention from a chemical standpoint. The neutral radicals and charged counterparts of these molecules have been known to be of importance in a broad range of chemical processes such as in the formation of soot in combustion[1] and in the processing of organic pollutants.[2]

However, recently, they have been gaining attention in astrophysics as a possible source of the ubiquitous 3.3 μm emission seen in carbon-rich objects and as possible tracers of star-formation.[3] The 3.3 μm is always seen together with features at 6.2, 7.6/7.7, 8.6, 11.3, and 12.7 μm. Collectively they are referred to as the unidentified infrared bands (UIR bands). Their source in PAHs is seen by many as so secure that they refer to these bands as the aromatic IR bands (AIBs).

With the proposed role of PAHs in astrophysics comes a natural postulate of their responsibility for the diffuse interstellar bands (DIBs). The identity of the carriers of the DIBs is the longest standing unsolved problem in chemical spectroscopy.

The DIBs are a series of around 300 absorption features observed in interstellar media, particularly low-density interstellar regions,[4] between 440 and 950 nm.[5] It has been postulated that the origins of these bands are due to the PAH family of molecules either in the neutral, cationic or, anionic form with various levels of hydrogenation,[6] depending on their local environment and photon flux, and that these molecules are the most abundant found within the interstellar medium (ISM) after H_2 and CO.[7]

Though there has been a large range of experiments, observations, and theoretical calculations performed on a vast array of molecules within this group since the PAH model was first proposed in 1984−1985,[8,9] there has been no concise assignment of a DIB. There have been no matches between laboratory and DIB spectra thus far from the study of cationic PAHs,[10−13] these having been studied due to their known ability to absorb in the visible region, in turn due to the open shell nature of the chromophoric π-system. Failure, to date, to identify PAH cations in the interstellar medium turns our attention to other PAH derivatives, such as partially dehydrogenated forms.

With this in mind Vuong and Foing[7] and Le Page et al.[14] have presented a model for the level of hydrogenation of PAHs in the diffuse interstellar medium and found that dehydrogenation effects are dominant. It can be concluded that these effects dominate in intermediate density regions where conditions, molecular hydrogen concentration and UV photon flux are favorable to dehydrogenation.

Of the radicals, to date, the smaller systems of phenyl[1,15,16] and naphthyl[17,18] have been investigated both theoretically and experimentally showing that these systems are stable, are long-lived, and have transitions within the visible, like the cations. In addition to the study of these two systems the neutral fluorene radical has been studied by Wiley, Vala, and co-workers[6] both experimentally through absorption spectroscopy, and computationally, resulting in the assignment of the 0−0 absorption band at 494.6 nm. This species exhibits a similar red-shift in the neutral radical from dehydrogenation as seen upon ionization (from the ultraviolet to the visible as in the case with naphthyl and phenyl). The cavity ring-down spectrum of anthracene at 361.176 nm[5] and gas-phase fluorescence spectra of tetracene at 500 nm[19] and of pentacene at 536.22 nm[20] give hope to studying yet larger species in the gas phase.

It was our proposal that the monodehydrogenated PAHs might, at some size, display open shell π-systems and thus, like the cations, possess strong transitions in the visible region. While this proposal motivated the present study, it will be shown that it is a general property of PAH radicals beyond a certain size to possess strong transitions in the visible region. Given that recent models of PAH chemistry in the interstellar medium predict varying levels of hydrogen coverage for a given size of PAH, we consider that PAH radicals cannot be ignored as potential DIB carriers.

2. Computational Methodology

The ground-state equilibrium structures of the dehydrogenated PAH radicals phenyl, naphthyl, anthracyl, tetracyl, pentacyl, and decacyl were optimized using the Kohn−Sham density functional theory (DFT) employing the Becke3 (B3) exchange integral,[21] the Lee Yang Parr (LYP) correlation functional,[22] and the 6-31G basis set for phenyl to pentacyl and the 3-21G basis set for decacyl. The B3LYP functional has been shown to be the most reliable for this type of system.[23]

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* Corresponding author. E-mail: t.schmidt@chem.usyd.edu.au.

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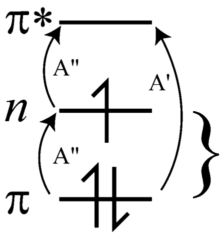

Figure 1. Illustration of the frontier orbitals of the PAH radicals studied here. The HOMO is a nonbonding sp^2 orbtial designated “n” in the above figure and is of A′ symmetry in the C_s point group. The highest fully occupied orbital is of the π type and has A″ symmetry in the C_s point group. Strong transitions of A′ symmetry arise due to $\pi^* \leftarrow \pi$ transitions. Weaker A″ transitions arise due to admixtures of $\pi^* \leftarrow$ n and n $\leftarrow \pi$ transitions. The orbitals swapped to bring about a change in electronic state symmetry, as described in the text, are indicated with a brace: “}”.

Time dependent density functional theory (TDDFT) methods were performed with the 6-31G basis set to determine the excitation frequencies and oscillator strengths from these optimized geometries. These DFT-B3LYP and TDDFT-B3LYP calculations were implemented using the GAUSSIAN 03 program package.[24] Higher basis set TDDFT calculations using the 6-31G(d,p) basis set were carried out on phenyl to tetracyl to check the trend within the 6-31G calculations. To ensure that the correct ground-state symmetry was attained and to explore the energy gap between the A′ and A″ states, the radicals’ frontier orbitals were swapped, resulting in a change of state from the ground to the first excited state (A′ → A″) as indicated in Figure 1. The geometries were optimized for all systems concerned. In addition to these calculations, for the pentacyl and decacyl cases the site of dehydrogenation was changed to explore the effect on the electronic and spectroscopic properties.

Despite having been shown to have problems dealing with extended π systems,[25] TDDFT has been implemented to calculate the excitation spectra of large PAH cations with success.[13] In such a case, the radical is delocalized over the entire PAH structure. In our case, the radical is localized to the nonbonding orbital and the strong transitions of interest emerge as transitions from fully occupied orbitals. As such, we anticipate our calculations to be of similar accuracy to other calculations reported in the literature for similar sized systems.

3. Results and Discussion

All of the PAH radicals in the present study were found to have A′ ground states, with the radical electron localized to a nonbonding sp^2 orbital at the site of dehydrogenation. An important consequence of this is that dehydrogenation will be a barrierless process and that the π-system of the radical is essentially identical to that of the fully hydrogenated parent. The latter point has important consequences for the excitation spectra which will be discussed below. For the remainder of this paper, we shall number the dehydrogenation sites from the outermost carbon(s). The IUPAC scheme may be found in ref 23.

3.1. Equilibrium Geometries. The resulting ground-state optimized geometry for dehydrogenation occurring at the 1-position is shown in Figure 2a for anthracyl (A′), where the site of dehydrogenation is labeled from the outermost hydrogen. By changing the electronic state symmetry to that corresponding to the excited (A″) state for the 1-position, we arrive at the geometry shown in Figure 2b. Where the orbital occupancy is altered, resulting in a state where the lone pair of electrons is favored, the ring on which the dehydrogenation site lies is pinched, resulting in a smaller ring angle (≈15° smaller), and larger C−C bond lengths (≈0.1 Å longer), for the anthracyl system. This is due to the larger coulomb and pauli repulsion forces between the resulting lone pair and the σ-bonding electrons. This effect is similar to that observed upon electron attachment where it was found that the *ipso* bond angle decreased by 14° and the bond lengths increased by 0.04 Å.[23]

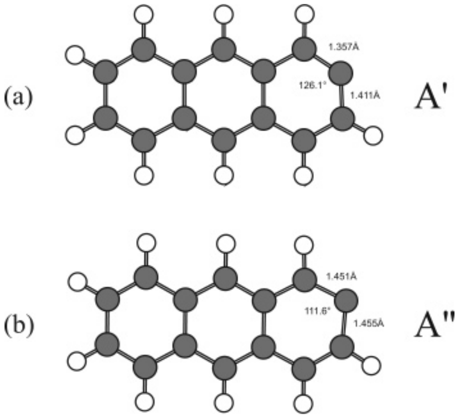

Figure 2. DFT equilibrium geometries for the A′ (ground) and A″ (altered) states of the anthracyl radical. The site of dehydrogenation possesses a lone pair of electrons in the A″ state and thus the ring is pinched and the C−C bond lengths are increased. The site of dehydrogenation is referred to here as the 1-position (see text).

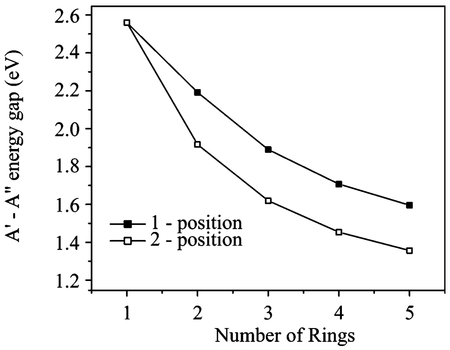

Figure 3. Calculated gap between optimized geometries with A′ and A″ electronic wave functions. For all radicals the ground state was found to be A′.

That the C−C bond lengths increase and the ring is pinched, on the electronic state symmetry going from A′ to A″, is a feature of all the PAH radical structures in the present study. Furthermore, the energy gap between the ground and excited states can be seen to be converging slowly for the 1- and 2-positions with increasing system size (see Figure 3). If the hypothetical infinite radical system were to exhibit zero band-gap, then we would expect that at some stage the ground state to become A″, as the π HOMO exceeds the energy of the A′ nonbonding orbital. As will be seen below, the ground-state remains A′ in systems as large as decacyl, although the gap is smaller than in pentacyl. As such, the strong, in-plane electronic transitions are analogous to those of the closed-shell neutral rather than the cation.

3.2. Bond Length Alternation. The slow convergence of the A′ and A″ states may, in part, be explained in terms of bond length alternation. As can be seen in Figure 4, the bond lengths are seen to alternate strongly at the ends of decacyl, and less in the middle. As has been observed for the polyyne carbon chains,[26] the effect of bond length alternation is to introduce a more pronounced band gap than that expected from simple Hückel considerations. As with the polyynes, the linear PAH radical systems display a decayed bond length alternation

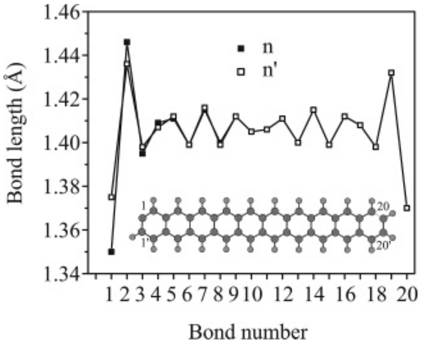

Figure 4. Bond length alternation as calculated for the A′ ground state of decacyl.

toward the center of the molecule thereby implying zero band gap for the infinite system. We do not seek to make predictions about the large systems here but rather seek to comment on the effect of bond length alternation on the propensity toward A′ ground states. It should be noted that the bond length alternation is not a property unique to the PAH radicals, but is known to exist also in the parent PAHs. For example, anthracene exhibits C−C bond lengths of 1.37, 1.42, and 1.39 Å, on going from the end of the molecule to the central carbon atom(s).[27]

3.3. Excitation Spectra. The results of TDDFT calculations on the excited states and oscillator strengths for the 1- and 2-positions show that the phenyl, naphthyl, anthracyl, tetracyl, pentacyl, and decacyl systems have their strongest transition polarized in the molecular plane (A′). These transitions are analogous to those expected for the fully hydrogenated PAHs. They are calculated to occur in the UV region for the phenyl, naphthyl and anthracyl radicals and in the visible region for tetracyl, pentacyl, and decacyl radicals. The strongest transition within the visible region for the phenyl, naphthyl, and anthracyl systems corresponds to an out-of-plane, A″ transition.

3.3.1. A″ Transitions. All PAH radicals were found to exhibit A″ transitions whereby a π-electron is promoted to the non-bonding orbital. The oscillator strengths for these transitions are generally low, typically on the order of 10^{-4} (Figure 5). The clearest trend is shown for the first A″ transition whereby the oscillator strength clearly decreases with system size as the absorption position moves to the red. This can be interpreted in terms of a decreased orbital overlap between the localized n-orbital and the more and more delocalized π-orbital as the system size is increased from phenyl to pentacyl.

The general trend for the higher A″ transitions is for the wavelength to shift to the red with increasing system size. Except for pentacyl, all higher A″ transitions lie in the UV region. Because of the expected geometry change upon excitation, and their low oscillator strengths ($f \approx 10^{-4}$), it is unlikely that A″ transitions are responsible for any DIBs (the lack of correlations between DIBs precludes their assignment as transitions other than origin bands, implying very little geometry change upon excitation).

It can be seen that the 1- and 2-positions produce reasonably similar spectra for these radicals, the dehydrogenation site not having a marked effect on the electronic structure so close to the end of the molecular framework. The effects of dehydrogenation site for the pentacyl and decacyl radicals are discussed below.

3.3.2. A′ Transitions. The strongest A′ transition with wavelength above 200 nm is plotted in Figure 6 for phenyl to pentacyl. For both dehydrogenation at the 1- and 2-positions, it is seen that there exist strong transitions which move to the red with increasing system size. Interestingly, the oscillator strength for this transition peaks at anthracyl and then decreases on going to tetracyl and pentacyl. All of these transitions are polarized along the short axis of the molecule, and as such an increase in oscillator strength with system size is not expected. The corresponding transition in decacyl is at 969 nm and has a low oscillator strength of $f = 0.0044$. This decrease for the cases of tetracyl and pentacyl partly arises from the energy term in the expression for oscillator strength. The existence of strong A′ transitions in the visible region implies that these radicals can be considered candidate DIB carriers. However, the strongest transitions are expected to be polarized along the long axis of the molecule. For pentacyl, this transition is calculated to lie to shorter wavelengths than 332 nm. The first radical in the series to exhibit a long axis polarized transition in the visible region is hexacyl, which is calculated to absorb at 470 nm, with a moderate oscillator strength (0.0843).

The decacyl radical was investigated at the TD-DFT/6-31G level (3-21G geometry). It was found to display very strong transitions, polarized along the long axis. The large oscillator strengths ($f > 1$) are of the size required to account for DIBs while not impacting significantly on the interstellar carbon budget.[28] The results for decacyl are discussed in more detail below.

3.4. Comparison to Experimental Results. The A″ transition (B_1) of the phenyl radical was observed by Porter and Ward[15] to lie at 529 nm with the peak of the Franck−Condon envelope lying at 480 nm. This compares favorably with our best TD-DFT result of 431 nm. The electronic spectrum of the phenyl radical between 4000 and 50000 cm^{-1} has been studied by Radziszewski[16] by irradiating nitrosobenzene at 308 nm in an argon matrix. The B_1 state was observed with a Franck−Condon maximum at 450 nm. Two bands were observed at 235.1 nm and 211.5 nm which were assigned to an A_1 and a B_2 state, respectively. Our best TD-DFT results predict an A_1 state at 256.5 nm and a series of B_2 states between 207 nm and 234 nm.

The only other available experimental result for larger PAH radicals studied here is the negative ion photoelectron spectrum of the 1-naphthyl anion.[17] The observed electron affinity of the naphthyl system is 1.4 eV. Our best calculations place the A″ state of the neutral radical 2.26 eV above the ground state. As such, to reach this state would require some ≈3.66 eV of photon energy which is above that implemented in the experiment (3.4 eV).

As can be seen from the above comparisons, employing the current methodology it is impossible to predict transition energies with enough accuracy for a positive identification of a DIB carrier. Such an identification would require an accuracy of ≈0.1 nm or better compared to on the order of ≈10 nm obtained with these calculations.

Interestingly, the PAH radicals absorb in regions of the visible spectrum close to their cationic counterparts (fully hydrogenated). For instance, the phenyl radical and the benzene cation are both seen to absorb near 550 nm. However, the symmetries of the cation transitions are necessarily in-plane (A′), and thus correspondence to the visible spectra of the radicals is coincidental.

3.5. Dehydrogenation Site. The dehydrogenation site in pentacyl and decacyl was moved toward the center of the molecule to investigate the effect on the stabilities, excitation energies and oscillator strengths (Figure 7). For pentacyl, the dehydrogenation site was seen to have little bearing on the oscillator strength and absorption position, the latter being

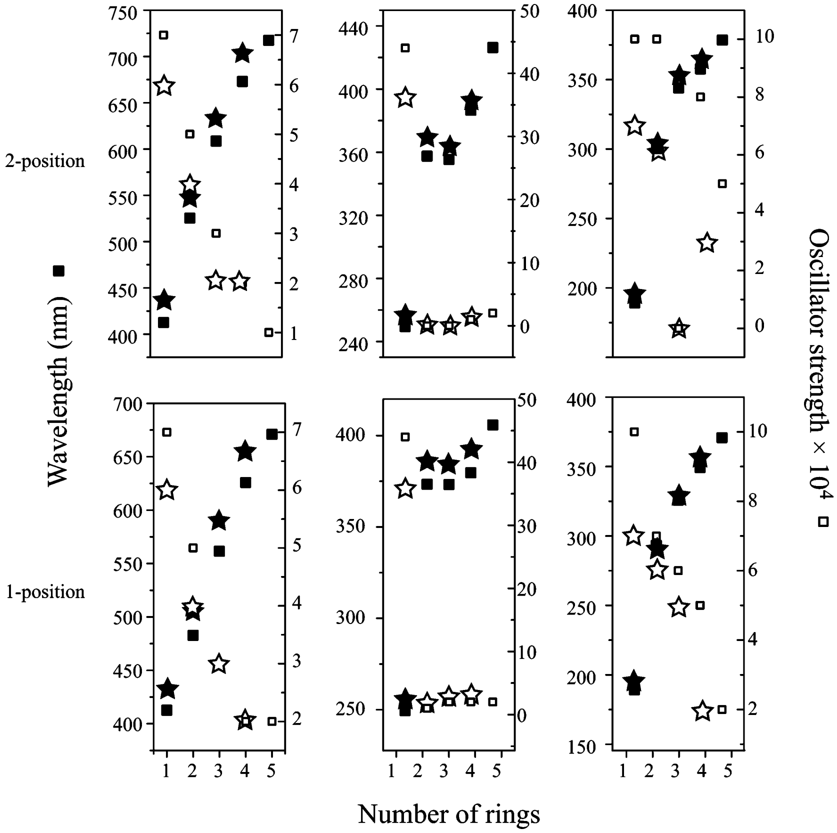

Figure 5. Wavelengths and oscillator strengths for the three least energetic A″ ← A′ transitions for phenyl through pentacyl with dehydrogenation at the 1- and 2-positions. Wavelengths are plotted as filled symbols (square, 6-31G; and star, 6-31G[d,p]) and oscillator strengths as open symbols.

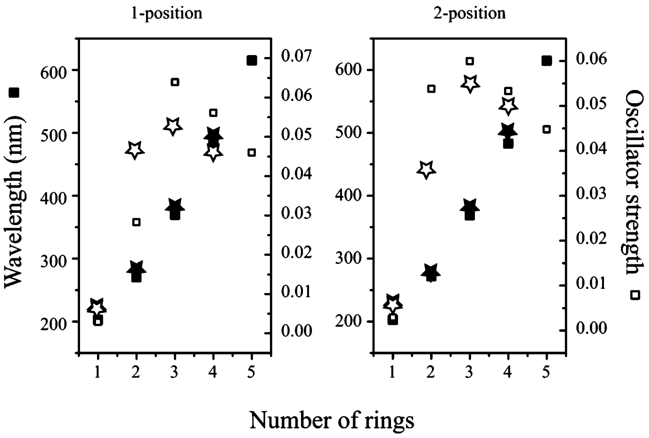

Figure 6. Wavelengths and oscillator strengths for the strongest A′ ← A′ transitions above 200 nm for phenyl through pentacyl with dehydrogenation at the 1- and 2-positions. Wavelengths are plotted as filled symbols (square = 6-31G and star = 6-31G[d,p]) and oscillator strengths as open symbols. All of these transitions are polarized along the short axis of the radical.

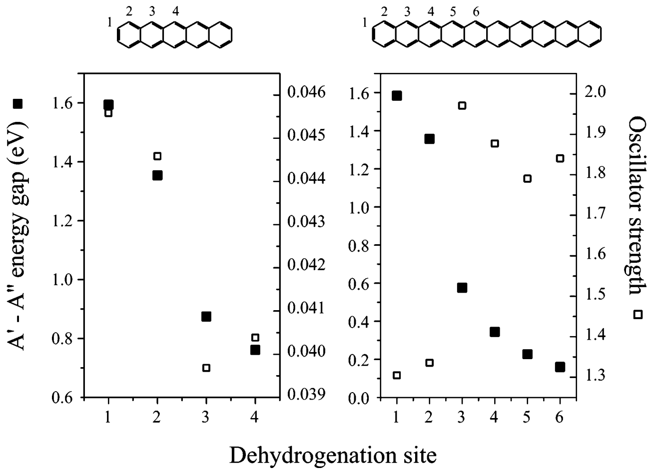

Figure 7. A′−A″ energy gap and oscillator strengths of dominant transitions as a function of dehydrogenation position as indicated at the top.

calculated as 615 ± 1 nm. Both the energies of the A′ and A″ states of the pentacyl radical decreased on moving the dehydrogenation position toward the center of the molecule: the A′−A″ gap also more than halving. These results for the ground states contradict those reported by Papas et al.,[23] who noted the opposite trend. However, our differences span only 0.13 kcal mol^{-1}, with those of Papas (who employed a more extensive basis set) spanning only 0.62 kcal mol^{-1}. As such, the radicals may be considered more or less isoenergetic. The excited state is stabilized most at the innermost dehydrogenation site. Papas et al., show that the anion is most greatly stabilized toward the center of the molecule, and rationalize this in terms of steric interactions with hydrogen atoms bound to neighboring carbons.

For decacyl, the dominant electronic transition was calculated to be at 589 nm for the 1-position and 2-position but 709, 708, 718, and 732 nm for the 3-, 4-, 5-, and 6-positions, respectively. The corresponding oscillator strengths are very large and vary considerably with dehydrogenation position, a possible consequence of the radical site modulating the extent and pattern of bond length alternation in the structure. As distinct from pentacyl, the A′ energies for decacyl are seen to increase on moving the dehydrogenation position toward the center of the molecule. In this case, the energy differences span 10 kcal mol^{-1}. However, the small basis set implemented for decacyl geometry optimization is likely to render these results less reliable than the excitation energies. Like pentacyl, the A′−A″ gap is seen to decrease markedly upon moving the dehydrogenation site inward. The likely interpretation of this is the same as pentacyl: that the energy is lowest when neighboring carbon atoms are devoid of hydrogen. This hypothesis is supported by the large drop in energy observed on moving the dehydrogenation site from the 2-position to the 3-position in decacyl.

4. Conclusion

The ground-state electronic structure for a range of PAH radicals was investigated. It was found that PAH radicals up to decacyl all have A′ ground states, and that they exhibit transitions in the visible and UV regions. The in-plane transitions up to decacyl are thus analogous to those of the closed-shell neutrals.

It was found that the gap between the A′ ground and the A″ excited state decreased on moving the radical position inward from the end of the molecule. As such, we may conclude that, if a “linear” PAH radical of a given size were to possess an A″ ground state, the radical site would occur toward the center of the molecule.

Since the larger PAH radicals have excitation frequencies in the visible region, they may be considered candidate carriers of the diffuse interstellar bands (DIBs). These transitions are of in-plane A′ symmetry and arise due to the similarity of the electronic structure of the radical to the parent. The oscillator strength of the strong transition in the visible peaks at anthracyl for the radicals up to pentacyl. But, these transitions are polarized perpendicularly to the molecular axis and therefore do not possess the property of increasing in strength with system size. However, extremely strong transitions are predicted for decacyl in the visible region. These transitions are polarized along the molecule and can be expected to be exhibited by a range of linear PAHs radicals, making these excellent candidates for DIB carriers. That DIBs are only observed in sparse interstellar regions with an appreciable UV flux lends credence to this hypothesis. We conclude that due to the significant geometry change upon excitation and low oscillator strengths, the A″ transitions will not be responsible for the DIBs. Positive identification of PAH radicals in the interstellar medium will require an excellent match between a gas-phase laboratory spectrum and that obtained with high-resolution astronomical observation. Any match must then be reconciled with known interstellar conditions, and their effects on PAH populations.

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