

Locally Aromatic Polycyclic Hydrocarbons (LAPHs) as Prototypes for Particulate Hydrogenated Amorphous Carbon

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We present density functional theory calculations on a group of molecules, encompassing examples ranging from C₁₉H₂₂ to C₃₆H₃₄, which combine structural features of aromatic and alicyclic hydrocarbons. Structural features of these LAPHs (e.g., preferred torsional angles adopted around bonds possessing essentially free rotation) mimic the disorder attributed to particulate hydrogenated amorphous carbon (a-C:H).

The spectroscopy of LAPHs is also explored. Many of the spectrally active modes associated with a-C:H are exhibited also by the small LAPHs for which we have performed vibrational frequency calculations. We therefore suggest that LAPHs may be considered as defining the essential structural elements of a-C:H, particularly with regard to predictions of vibrational spectra of these networks.

1. Introduction

The microscopic properties of amorphous carbon (a-C) and a-C:H are characterized by competition involving various types of bonding between carbon atoms [1-3]. In general, the overall structure is produced by a mixture of sp² and sp³ bonds in a random covalent network (RCN) [4-5]. The proportion of aromatic and aliphatic bonds in a particular solid determines its hardness, optical transparency and chemical properties and therefore yields materials with a range of useful properties [6]. Theoretical studies of the distribution of carbon atom coordination in these solids has shown that the structure can best be described as a mixture of C₆ aromatic rings bridged with tetrahedrally-bonded carbon [7]. This suggests that, in keeping with the RCN formalism, some insight into vibrational spectra of these materials could be obtained from the properties of individual molecules combining benzenoid (aromatic) rings linked by a network of sp³ carbon atoms similar to that in diamond. We adopt this approach in this paper, and show that this method results in a primitive representation of the infrared spectrum of a-C:H.

2. Theoretical Formalism

Various LAPH structures have been subjected to geometry optimization and vibrational frequency calculation using B3-LYP/6-31G* density functional theory as implemented in the GAUSSIAN98 programming suite [8]. This level of theory has been identified [9] as a particularly good compromise between reliability and computational efficiency.

Fig. 1 depicts two conformers (i.e., rotational isomers) of a prototypical LAPH, C₁₉H₂₂. This figure (with aromatic subunits in red) also exemplifies the morphological preferences common to all LAPH structures which we have examined. First, the aromatic subunits are substantially twisted away from a plane-parallel configuration in both structures. Second, the lower-energy conformer (by about 0.1 eV in this instance) is that with the greater separation between aromatic regions. This tendency indicates a repulsive steric or electronic

interaction between the aromatic regions. We suggest that agglomeration of LAPHs is likely to preferentially occur in a disordered fashion, without regular stacking arrangements.

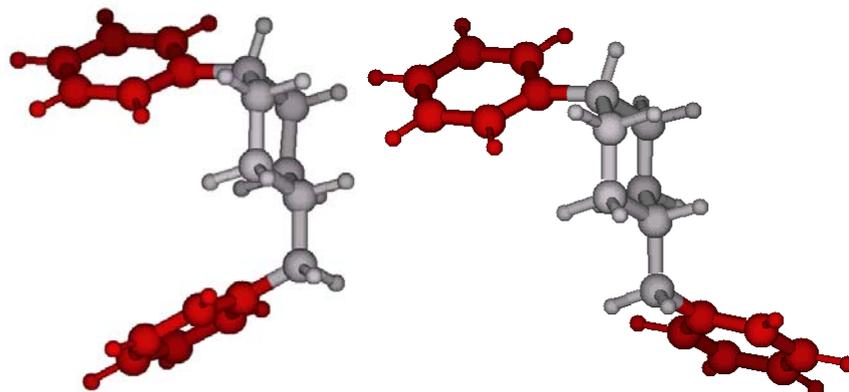


Fig.1 B3-LYP/6-31G* optimized geometries for two conformers of $C_{19}H_{22}$.

3. Vibrational Spectra

Calculated IR spectra for four representative LAPH structures are shown in Fig. 2. Aromatic C-H (centred at $\sim 3.25 \mu\text{m}$), alicyclic C-H ($3.35\text{-}3.50 \mu\text{m}$) and aromatic C-C stretching ($6.25 \mu\text{m}$) features are all apparent for each of these structures; other LAPHs (not shown here) also exhibit analogous features. This combination of alicyclic and aromatic spectral features, not found in (for example) purely aromatic hydrocarbons, is thus characteristic of LAPH vibrational spectra.

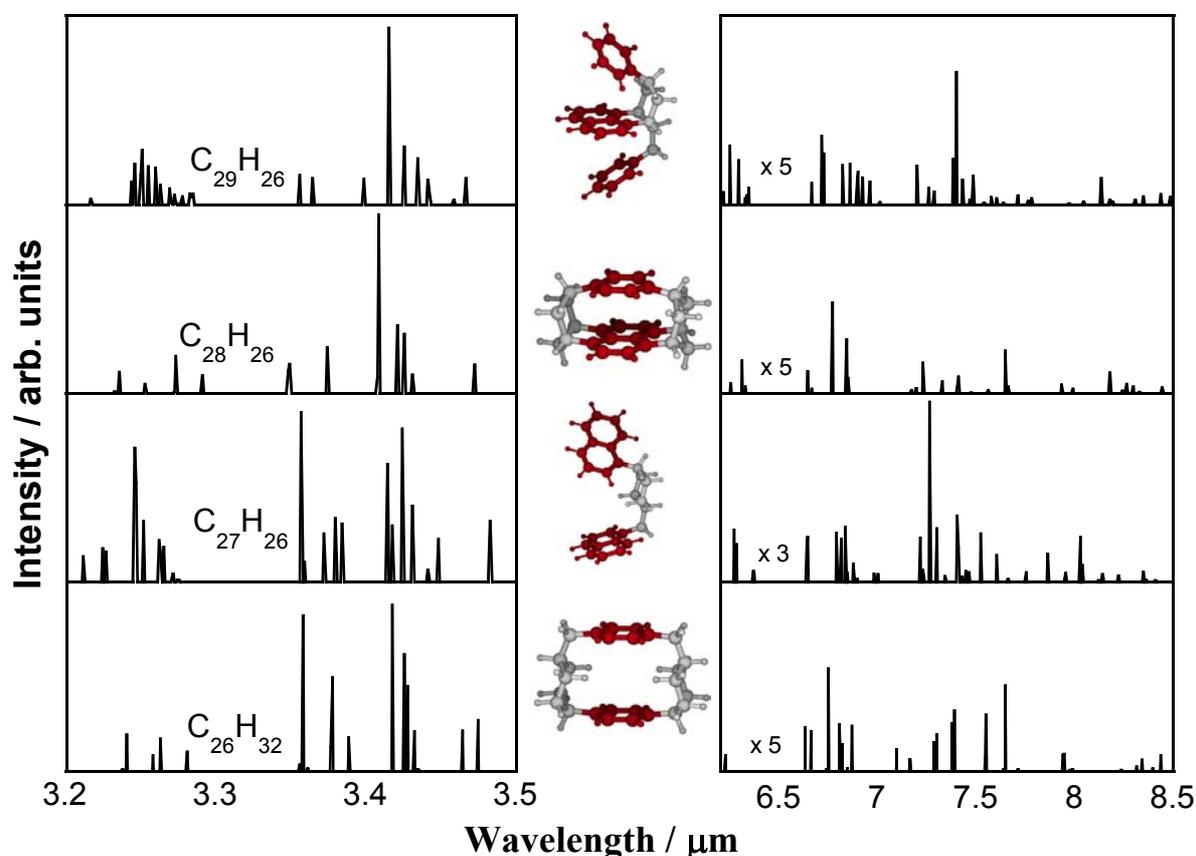


Fig. 2. Vibrational spectra of four typical LAPHs (structures shown, with aromatic regions in red) obtained at the B3-LYP/6-31G* level of theory.

4. Discussion

Laboratory studies show that the dominant features of the infrared spectrum of a-C:H arise from vibrational modes of sp^2 and sp^3 hybridized bonded carbon [3, 10]. These include the stretching (3.38 – 3.50 μm) and deformation (6.8 – 8.8 μm) vibrations of aliphatic C-H, the stretching vibration (3.29 μm) of aromatic C-H, as well the C=C aromatic stretch (at 6.25 μm). Our simulated spectra (fig.2) show that these features also appear in calculated vibrational spectra of LAPHs. While a detailed comparison between theoretical and laboratory spectra is unjustified at this time because of limitations in the accuracy of predicted vibrational frequencies and intensities, it is apparent that the B3-LYP/6-31G* level of theory applied to these LAPHs does reproduce the general features of the spectrum of a-C:H. This suggests that LAPH structures, containing both aromatic and diamond-like carbon bonds, replicate the dominant structural elements of extended amorphous carbon networks. We plan to extend these calculations to larger molecules and to molecules containing heteroatoms.

Acknowledgments

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References

- [1] J. Beeman, J. Silverman, R. Lynds, and M. R. Anderson, *Phys. Rev. B.* **30**, 870 (1984).
- [2] C. Z. Wang and K. M. Ho, *Phys. Rev. Letters*, **71**, 1184 (1993).
- [3] Z. L. Akkerman, H. Efstathiadis, and F. W. Smith, *J. Appl. Phys.*, **80**, 3068 (1996).
- [4] J. C. Angus, and F. Jansen, *J. Vac. Sci. Technol.*, **A6**, 1778 (1988).
- [5] G. Dadswell and W. W. Duley, *Astrophys. J.*, **476**, 184 (1997).
- [6] J. Angus, P. Koidl, and S. Domitz, *Plasma Deposition of Thin Films* (Boca Raton: CRC), (1986).
- [7] J. Robertson and E. P. O'Reilly, *Phys. Rev. B.* **35**, 2946 (1984).
- [8] M. J. Frisch et al., GAUSSIAN98, Gaussian, Inc., Pittsburgh, PA (1998).
- [9] A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).
- [10] J. Biener, A. Schenk, B. Winter, U. A. Schubert, C. Lutterloh, and J. Koppers, *Phys. Rev. B.*, **49**, 17307 (1994)