

QUANTUM CHEMICAL INVESTIGATION OF THE IR SPECTRA OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS

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Abstract

In this contribution we wish to assess whether and how Density Functional Theory calculations (DFT) can provide an insight about the link existing between the structure and topology of Polycyclic Aromatic Hydrocarbons (PAHs) and their infrared absorption (IR) spectra. The outcome of the present study is to offer information useful for correlating to possible chemical structures the observed IR features of carbonaceous materials (notably carbonaceous matter of combustion origin [1]). This investigation follows and complements a previous one that considered Raman spectroscopy [2] instead of infrared absorption. While Raman spectroscopy of PAHs is sensible to the π -conjugation of the whole molecule and senses the size of the polyaromatic system [3], IR spectroscopy is more sensitive to edge topology and less to the extension of the sp^2 system.

We have carried out an exploratory quantum chemical study of several PAHs with different topologies and dimensions. We have analyzed in details their IR spectra in the low-frequency region ($600 - 1000\text{ cm}^{-1}$). This is the characteristic range of CH out-of-plane bending vibrations. Our calculations show that these vibrational modes provide spectroscopic signatures that can be used as molecular structure fingerprints.

Computational details

DFT calculations have been carried out with Gaussian09 computer code [4]. Given the exploratory nature of the present study, we have adopted the widely used B3LYP functional because of its generally good performance in vibrational structure calculations. We have considered a flexible enough basis set, namely 6-311G(d,p), still computationally convenient, thus allowing the calculation of the IR spectra of several PAHs in a reasonable amount of time. We envisage that by selecting more accurate basis sets and newer functionals one could optimize further the performance of the quantum chemical calculations (compared to experimental results as a benchmark). However this is out of the scope of the present investigation that aims at finding the relation between the main IR spectroscopic features of PAHs in the CH out-of-plane bending region and the molecular topology. From this point of view it is very encouraging that (with the chosen DFT

approach) the comparison between the experimental and theoretical IR spectrum of benzo[fluorantene] is good (see Fig. 1). The “R” language [5] has been used to represent graphically the vibrational normal modes (see Figs. 1-3).

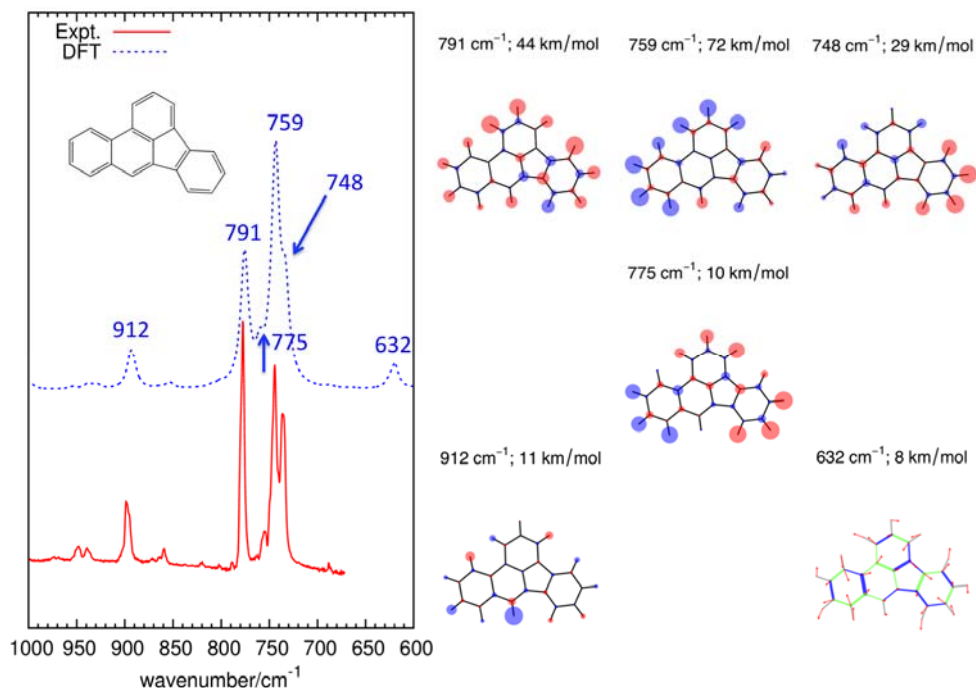


Figure 1. (left) Experimental and theoretical IR spectra of benzo[fluorantene]. In the theoretical spectrum the wavenumber axis has been scaled by a factor 0.98 (as customary in the literature) to ease the comparison with the experimental spectrum. (right) Nuclear displacements associated to the principal IR peaks in the low-wavenumber region. Unscaled wavenumbers are reported both on the theoretical spectrum and on the normal mode plots in order to help assigning the experimental peaks. Computed IR absorption intensities are also reported in km/mol units.

Results and discussion

IR spectra simulated through DFT calculations allow to quickly assigning observed IR bands to specific normal modes. The procedure is illustrated in Fig. 1 for benzo[fluorantene] and leads to the observation that the intense peaks found in the 600-1000 cm^{-1} region are due to out-of-plane bending vibrations with just one exception, represented by the weak in-plane mode computed at 632 cm^{-1} . The main three peaks are assigned to collective CH out-of-plane bending, with different relative phase relations among the CH oscillators and different localization/delocalization patterns. The mode computed at 791 cm^{-1} involves all CH bonds, while the mode at 759 cm^{-1} is more localized on the part of the molecule corresponding to the three condensed aromatic rings. On the opposite, the mode at

748 cm^{-1} is more localized on the isolated ring directly condensed with the pentagonal ring of the molecule. Interestingly, the peak computed at 912 cm^{-1} is a specific marker of the CH bond placed in a sort of “bay” region at the edge of benzo[fluorantene].

Intrigued by the positive match of theory with experiment and by the information carried by the normal modes in the low-wavenumber region we have decided to use DFT to explore further the connection existing between the edge in PAHs and the IR signals. We have thus selected PAHs sharing the topology of a part of their edges and we have inquired whether their simulated IR spectra bear some understandable similarity. In other words, with this procedure, we are trying to find the spectral fingerprints of the selected common topologies. The set of chosen PAHs is shown in Table 1.

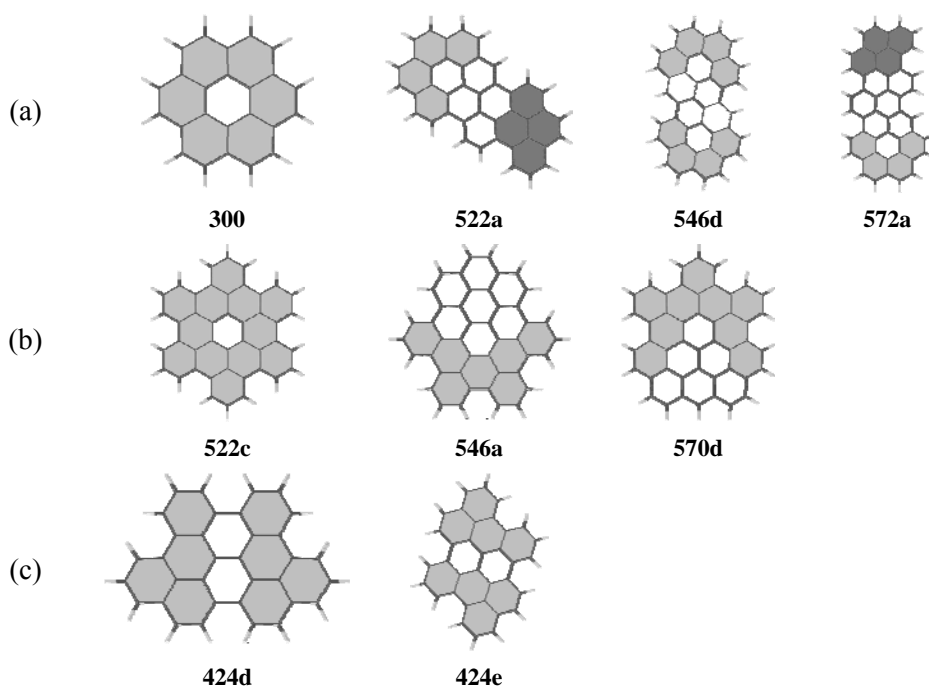


Table 1. Sketch of the selected PAHs for which we have analyzed the IR spectra in the low-wavenumber region ($600 - 1000\text{ cm}^{-1}$). All carbon atoms in these structures have sp^2 hybridization and CH bonds are found at the edges. The shading highlights the common topology of the PAHs belonging to each row. The (informal) label scheme refers to the rounded molecular mass and a one-code letter distinguishes among different isomers.

Let us consider the subset (a) of the PAHs reported in Table 1. The associated simulated IR spectra are reported in Fig. 2 and, even at first sight, demonstrate a similar shape, especially considering the more intense signals. The reason of this similarity becomes clearer when considering the nuclear displacement patterns

shown in the right hand side of Fig. 2. The three columns (1-3) group the nuclear displacements that are characterized by a similar pattern. Column (1) shows collective in-phase out-of-plane vibrations of the regions with a topology corresponding to that of coronene (**300**). The wavenumbers associated to these normal modes are rather stable and range from 873 cm^{-1} in **572a** to 877 cm^{-1} in **546d**. Column (2) shows nuclear displacements that are remarkably similar, with the same associated wavenumber (848 cm^{-1}) and are localized at the pyrene-like substructures of molecules **522a** and **572a**. Column (3) shows nuclear displacements somewhat localized in the middle of the armchair edge of molecules **572a** and **522a**.

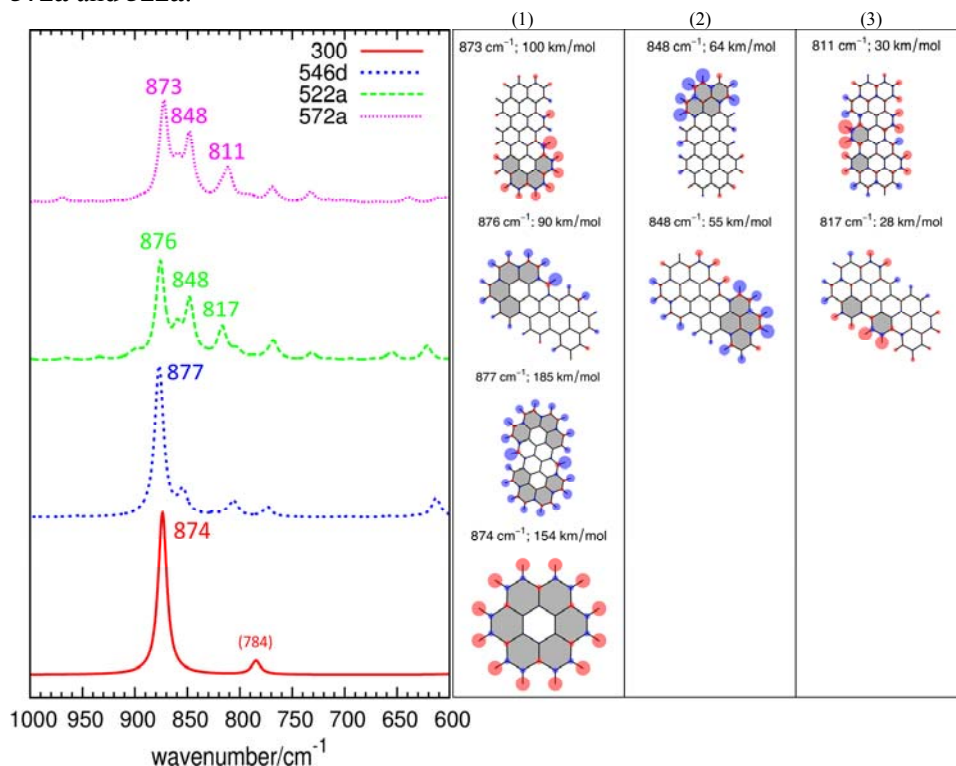


Figure 2. (left) IR spectra simulated by DFT of molecules belonging to the (a) group of Table 1. (right) Nuclear displacements of the principal IR bands. The size of the circles is proportional to the amplitude of the nuclear displacement along the out-of-plane direction (z -axis). The weak IR mode computed at 784 cm^{-1} in coronene (**300**) corresponds to a doubly degenerate in-plane vibration mainly involving CCC bending along the edge.

In Fig. 3 we plot the simulated IR spectra corresponding to the sets of PAHs (b) and (c) reported in Table 1. Again, one finds a remarkable similarity among the spectra, with the presence of well-defined marker bands that, by analyzing the nuclear displacement patterns, turn out to be associated to specific edge topologies shared by these molecules. This is for instance the case of the band computed at

782-783 cm^{-1} in set (b) which is associated to the out-of-plane bending motion of CH bonds as they are found in hexabenzocoronene (**522c**). Other vibrations in set (b) are more specific to each PAH. For instance this is the case of the band computed at 898 cm^{-1} in **570d**, which is mainly due to the central CH bond placed along the short zig-zag edge of the molecule.

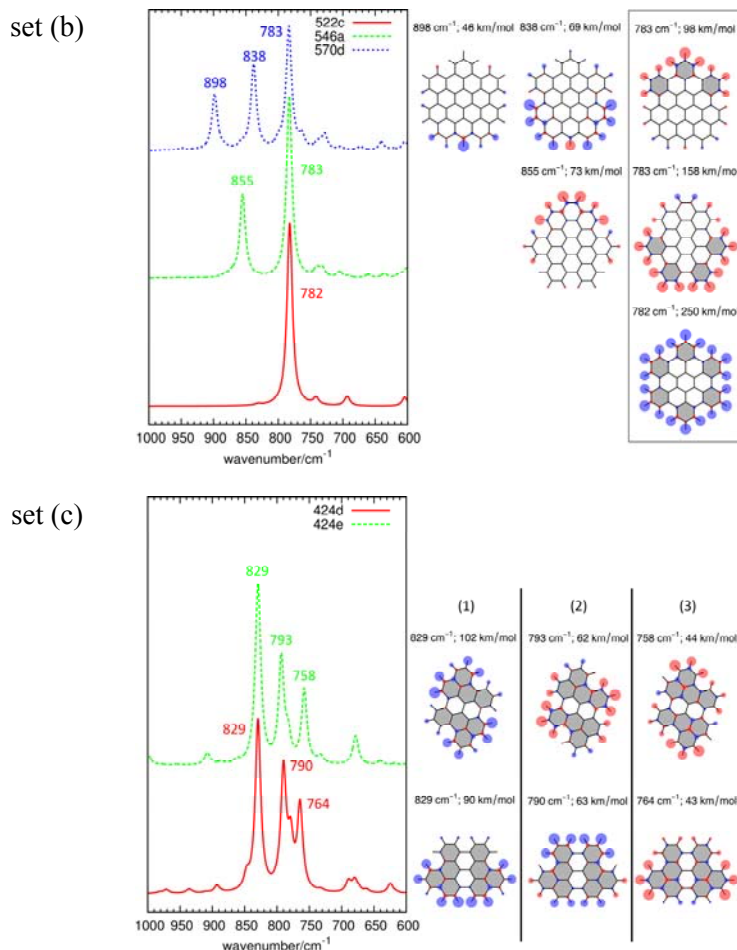


Figure 3. Simulated IR spectra of molecules belonging to the (b) group of Table 1 (top) and the (c) group of Table 1 (bottom). The nuclear displacements of the principal IR bands are also reported on the right-hand side (see also Fig. 2 caption).

Finally, set (c) is remarkable; the correspondence of the nuclear displacements associated to the three principal IR bands is very good, as one easily realizes by checking in Fig. 3 the pattern of the CH motions at the highlighted ring positions.

Conclusions

With the help of DFT calculations able to reproduce the low-wavenumber IR absorption ($600\text{--}1000\text{ cm}^{-1}$) of a benchmark PAH (benzofluorantene) we have shown the nice potential of IR spectroscopy for the characterization of edge topology in PAHs. DFT simulations carried out on a selection of different PAHs sharing common edge motifs show the rise of marker IR bands. These can be associated to specific common topologies at the PAH edge and are assigned to collective out-of-plane CH bending vibrations. We have also found interesting indications of marker bands which are associated to vibrations rather localized on peculiar hydrogen atoms along the molecular edge, as the CH “bay” position in benzofluorantene. Further analysis of the IR spectra of a wider set of PAHs is being carried out in our lab, aiming at the interpretation of IR absorption data of combustion products [1] on a molecular structure basis. The present results complement spectroscopic assignments in the CH out-of-plane region successfully used in the past [6].

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