A theoretical Raman study on Polycyclic Aromatic Hydrocarbons of environmental interest

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We consider the potential use of Raman spectroscopy for the analysis of Polycyclic Aromatic Hydrocarbons (PAHs) that are found in diesel soots (Fetzer et al. 1986). Through first-principles calculations we have simulated the Raman spectra of several PAHs and we have discussed the possible discrimination of different molecular structures based on the analysis of the Raman spectrum.

1. Introduction

PAHs are a concern for human health due to their toxicity (U.S. EPA report, 2002). It is therefore useful considering analytical tools for investigating their presence in day life substances. Among the many analytical techniques available, Raman spectroscopy can provide useful information on the molecular structure of samples with relatively little efforts (*i.e.* minimal sample preparation) and non-destructive probes. On the other hand, the interpretation of experimental data often calls for a theoretical investigation of the spectroscopic features in order to establish a reliable link with the structure of the sample at the molecular level.

In this contribution we explore the potential use of Raman spectroscopy for the characterization of the Polycyclic Aromatic Hydrocarbons (PAH) content in diesel soot. Fetzer et al. (1986) have shown through High Performance Liquid Chromatography (HPLC) analysis that diesel soot may contain rather large PAHs, containing up to 10 fused rings (see Figure 1). Through first-principles calculations we simulate the Raman spectra of the series of 13 PAHs identified by Fetzer et al. (1986) and we carry out a similarity analysis of the spectra in the attempt to correlate the differences in Raman spectra with the different molecular structures of the PAHs considered.
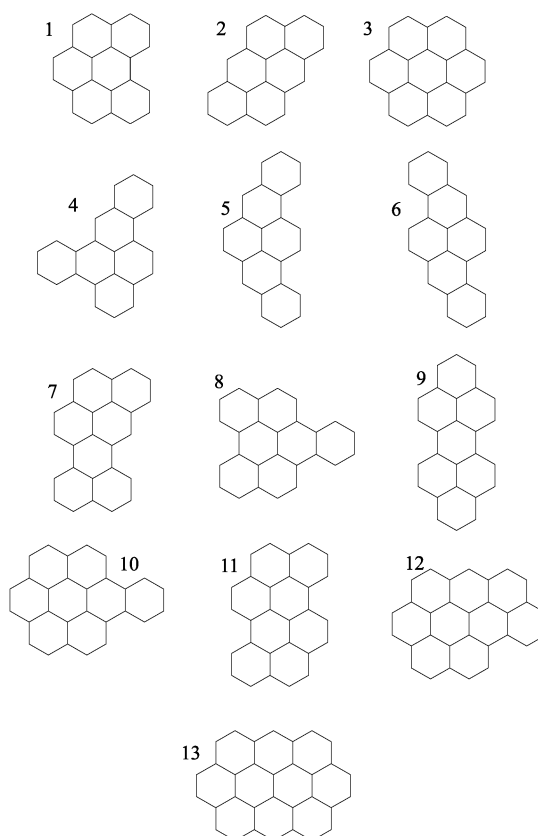
Figure 1. Sketch of the chemical structures of the PAHs found in diesel soot according to HPLC analysis (Fetzer et al. 1986).

2. Raman spectra of selected PAHs

First-pinciples and semiempirical theoretical approaches are of great help in understanding the electronic and vibrational structure of π conjugated materials since they provide a clear picture of the basic ingredients that are responsible of the Raman signal (Castiglioni et al., 2004; Tommasini et al., 2009). Namely, the capability of describing π-π* electronic excitations and their coupling with specific CC stretching normal modes is the key to the modeling of the Raman response of π conjugated and graphitic materials.

Density Functional Theory (DFT) calculations turn out to reliably reproduce the Raman spectrum of π conjugated materials (Castiglioni et al., 2004) as it shown in Figure 2 for two representative large PAH molecules synthesized in the group of Prof. Müllen (Watson et al., 2001). We adopt here the widely used B3LYP/6-31G** method which is deemed a good compromise between accuracy and computational cost when

medium/large size molecules and/or numerous calculations have to be considered, as in the present case.

Following a well-established practice (Scott et al. 1996), we scaled the computed frequencies to ease the comparison with experimental data. It has been empirically found that the best fit with experimental data is obtained with a factor of 0.98.
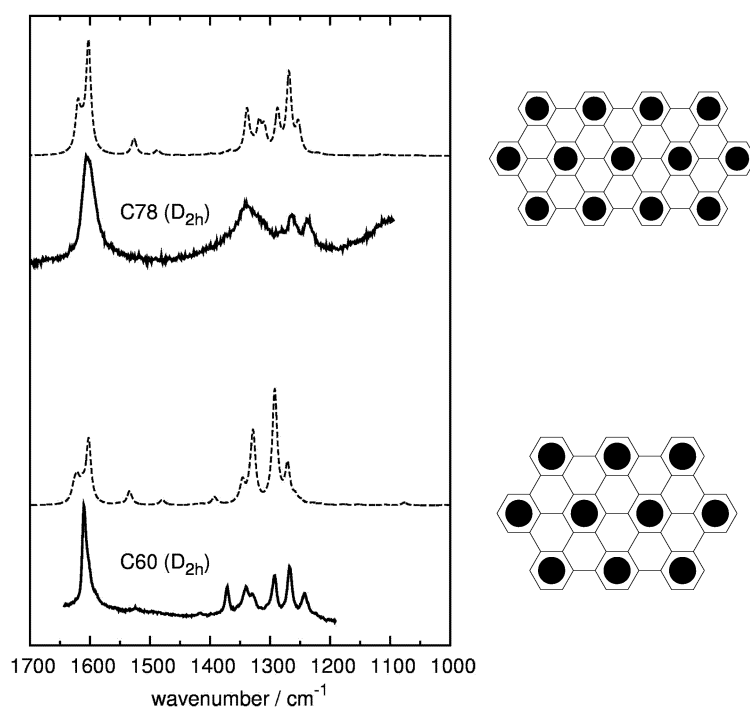

Figure 2. (solid line) Raman spectra of two large PAHs of D_{2h} symmetry (namely $C_{60}H_{22}$, $C_{78}H_{26}$) whose chemical structure is also reported on the right (experimental data have been taken from Di Donato et al., 2004). (dashed line) DFT simulations of the Raman spectra of the two molecules (B3LYP/6-31G**). Vibrational frequencies have been scaled by 0.98.

We report in Figure 3 the simulated Raman spectra of the series of 13 PAHs found in diesel soots by Fetzer et al (1986). The frequency range considered in the plot is the one associated with collective CC stretching vibrations, i.e. the so-called G and D band regions found respectively around 1600 and 1300 cm^{-1} (Castiglioni et al., 2004). The Raman signals in this frequency range constitute a characteristic marker of the vibrations within a confined graphitic domain and are characteristic of both size and shape of the PAH molecule. In particular, the coupling of collective ring breathing vibrations with in-plane CH wagging vibrations makes the Raman features in the D region dependent on the molecular structure of the PAH (Negri et al. 2002). Therefore these Raman data could be considered as the fingerprints of the different PAHs. In fact,

the set of the simulated spectra for the 13 PAHs here considered show marked differences and characteristic Raman spectra, but also shapes which look similar (see Figure 3).
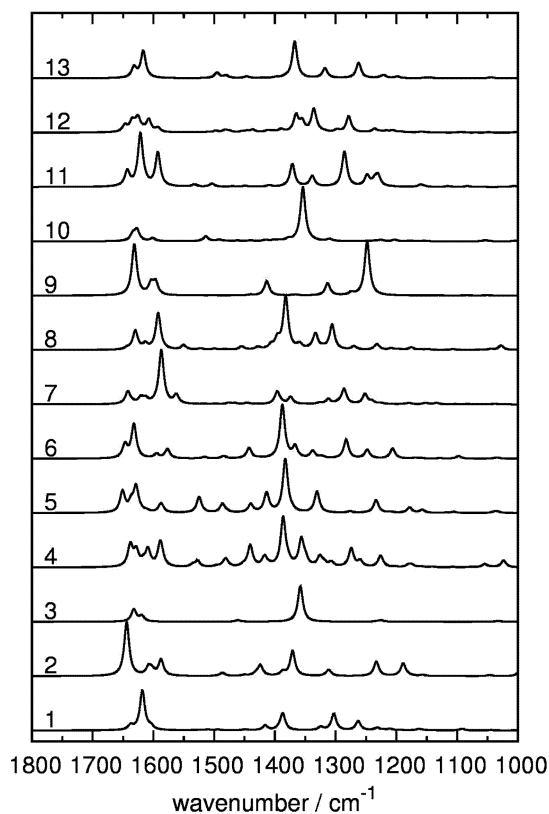

Figure 3. Simulated Raman spectra of the series of 13 PAHs reported in Figure 1. Data from DFT simulations (B3LYP/6-31G**). Vibrational frequencies have been scaled by 0.98.

To investigate further how the Raman features in the D and G region are correlated with the molecular structure, we introduce the spectral overlap (or spectral similarity index) between the Raman spectra R_i and R_j of two molecular species i and j:

$$S_{ij} = \int_{v_a}^{v_b} R_i(v)R_j(v)dv \tag{1}$$

The spectral overlap is defined over the frequency range $[v_a, v_b]$ and we suppose that each Raman spectrum has been normalized within this range, so that $S_{ii} = 1$. Since the simulated Raman spectra are represented numerically as vectors R(k) over an equally spaced frequency grid v_k, it is more convenient to adopt the discrete version of Eq. (1):

$$S_{ij} = \sum_k R_i(k)R_j(k) \qquad (2)$$

By definition, $0 \leq S_{ij} \leq 1$. Two completely unrelated Raman spectra have $S_{ij} = 0$, while the more similar they look, the larger will be S_{ij}.

It is important to notice that the spectral overlap depends on the Full Width at Half Maximum (FWHM) of the Lorentzian functions used to simulate the Raman spectra. The sharper the Lorentzian functions, the smaller will be the S_{ij} values for a given pair of different Raman spectra. Necessarily, one has to fix a meaningful FWHM parameter in order to obtain useful spectral overlaps. We adopt FWHM = 10 cm^{-1}, which turns out to provide line shapes in good agreement with experimental Raman spectra (see Figure 2).

Table 1 reports the full set of S_{ij} values for the 13 PAHs here considered (see Figure 1). Shaded values of S_{ij} correspond to pairs of PAHs possessing Raman spectra quite similar and for which discrimination based purely on Raman spectroscopy may be difficult. Interestingly, those cases correspond to PAH molecules having similar molecular structures, as for instance **4**, **5**, **6** that display a common pyrene-like core of 4 fused rings. Another interesting case is molecule **8** that can be obtained from molecule **5** by a single ring addition and shows a Raman spectrum similar to that of molecule **5** (see Figure 3). Also, molecule **10** is formed by a coronene core (*i.e.* **3**) fused with one ring (see Figure 1); correspondingly the similarity between the Raman spectra of **3** and **10** is large (see Table 1 and Figure 3).

When the similarity index S drops below 0.70 the Raman spectra can be more easily distinguished. To ease inspection of Table 1 the values of S between 0.60 and 0.70 have been highlighted with a lighter shade. Finally if S_{ij} is less than 0.60 the Raman spectra of the two species i,j becomes significantly different to potentially allow for a good molecular discrimination based on the characteristic Raman spectrum.

3. Conclusions

Through first-principles calculations we have simulated the Raman spectra of several PAHs that have been found in diesel soots via HPLC analysis (Fetzer et al., 1986). We have discussed the possible discrimination of different molecular structures of PAHs based on the analysis of the Raman spectrum. A similarity index S_{ij} has been introduced to quantify to what extent the Raman spectra of two PAHs (i, j) can be reliably distinguished.

We conclude that two Raman spectra are significantly different when the molecular structure of the PAHs considered does differ enough. A common coronene-like or pyrene-like core makes the Raman spectra significantly similar. This theoretical investigation paves the way for an experimental study of the detection of PAHs of environmental interest through resonant Raman spectroscopy and/or Surface Enhanced Raman Spectroscopy (SERS).

Table 1. Similarity indexes S_{ij} among the simulated Raman spectra of the set of 13 PAHs reported in Figure 1. Darker shades denote $S_{ij} \geq 0.70$, while lighter shades denote $0.60 \leq S_{ij} < 0.70$ (see text). Sij values have been computed in the $1800 – 1000\ cm^{-1}$ frequency range.

	1	2	3	4	5	6	7	8	9	10	11	12	13	
1	1.00	0.34	0.28	0.60	0.51	0.52	0.38	0.56	0.41	0.22	0.67	0.52	0.64	**1**
2		1.00	0.28	0.54	0.55	0.51	0.53	0.45	0.37	0.24	0.53	0.53	0.45	**2**
3			1.00	0.54	0.30	0.36	0.16	0.31	0.28	0.85	0.34	0.64	0.54	**3**
4				1.00	0.78	0.80	0.57	0.78	0.43	0.55	0.55	0.70	0.54	**4**
5					1.00	0.77	0.39	0.78	0.43	0.31	0.47	0.58	0.42	**5**
6						1.00	0.44	0.70	0.48	0.32	0.50	0.61	0.46	**6**
7							1.00	0.57	0.39	0.15	0.64	0.40	0.31	**7**
8								1.00	0.37	0.32	0.53	0.55	0.43	**8**
9									1.00	0.24	0.53	0.48	0.39	**9**
10										1.00	0.29	0.60	0.40	**10**
11											1.00	0.69	0.61	**11**
12												1.00	0.67	**12**
13													1.00	**13**
	1	2	3	4	5	6	7	8	9	10	11	12	13	

Acknowledgements

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