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**Supporting Information for:**

**In situ Resonant UV-Raman Spectroscopy of  
Polycyclic Aromatic Hydrocarbons**

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**Supplementary Information**

Figure S1 UV Raman spectra of naphthalene collected preventing/not preventing photodecomposition.

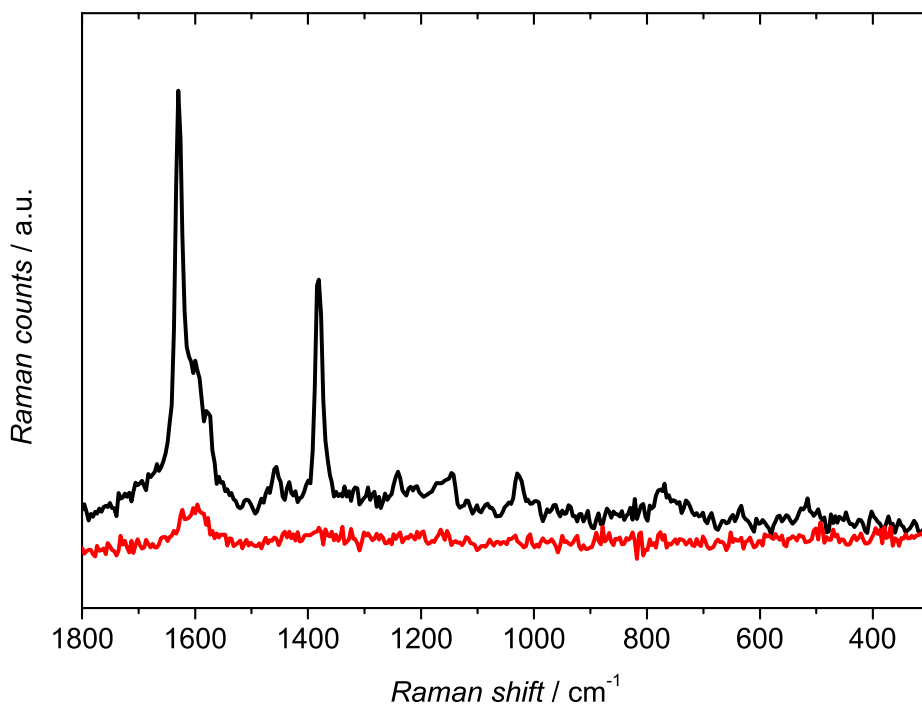
Figure S2 Adsorption spectra of  $10^{-5}$  M solution in acetonitrile of molecules.

Figure S3 Raman spectra of 0.1 M solution in acetonitrile of naphthalene collected with different excitation laser lines.

Figure S4 UV Raman spectrum of 0.1 M solution of benzene in acetonitrile in the  $3100-300\text{ cm}^{-1}$  frequency range.

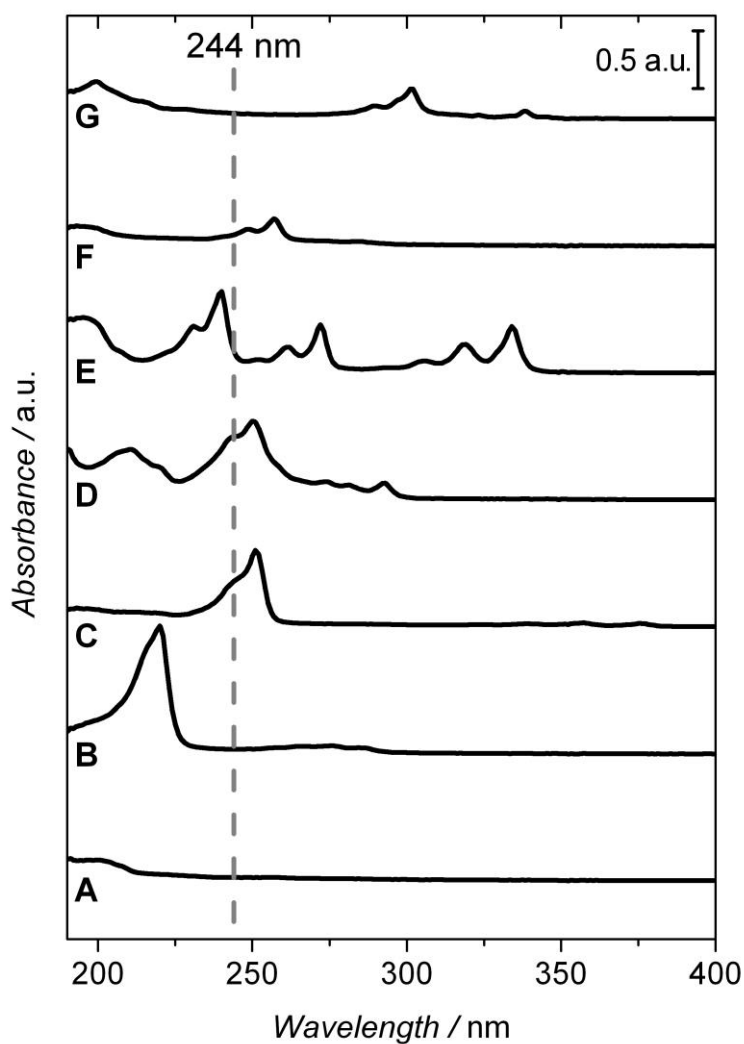
Figure S5 Background subtracted UV Raman spectra of molecules adsorbed from vapor phase on activated carbon.

Figure S1 shows an example of photoinduced degradation due to the excitation laser photons carrying very high energy ( $\lambda = 244$  nm). The use of a specifically designed home-made sample holder avoids the degradation.



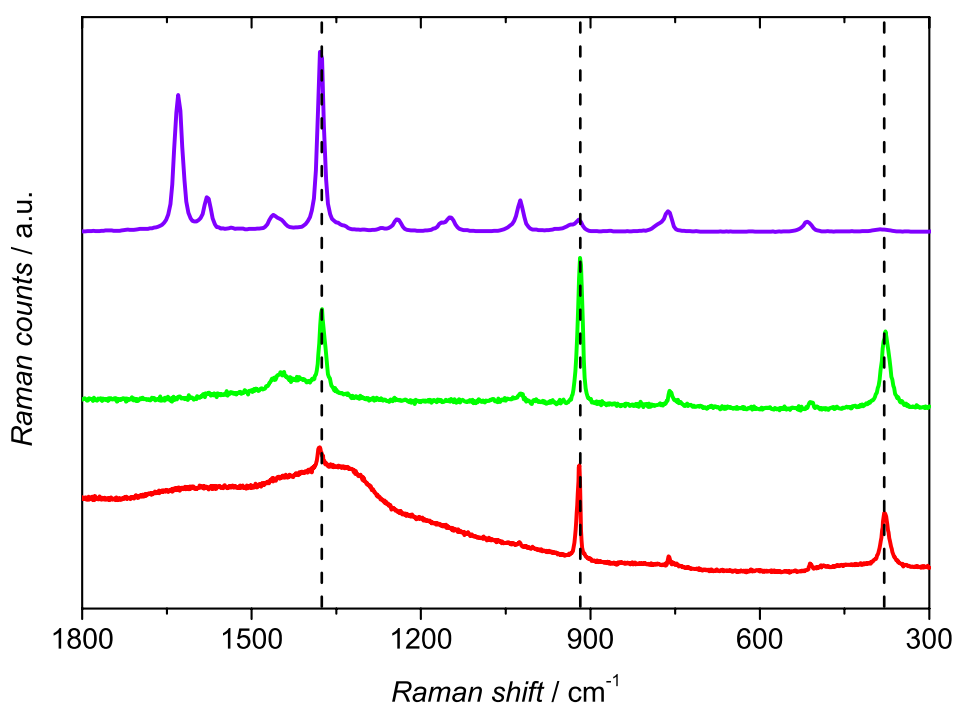
**Figure S1.** UV ( $\lambda = 244$ nm) Raman spectra of naphthalene, collected preventing the sample decomposition thanks to a specific home-made sample holder (solid black line) and without any precaution (solid red line). In this second case, the sample undergoes photodecomposition as testified by the complete transformation of its Raman spectrum.

Figure S2 shows the absorption spectra of the  $10^{-5}$  M solutions of PAHs in CAN, measured in transmission on a Varian Cary300 spectrometer in the 200-800 nm range. The vertical bar shows the frequency of the UV laser used for excitation in the UV-Raman measurements: it is possible to observe that most of the analyzed molecules present an electronic transition falling close to the laser frequency, allowing to achieve the resonance conditions.



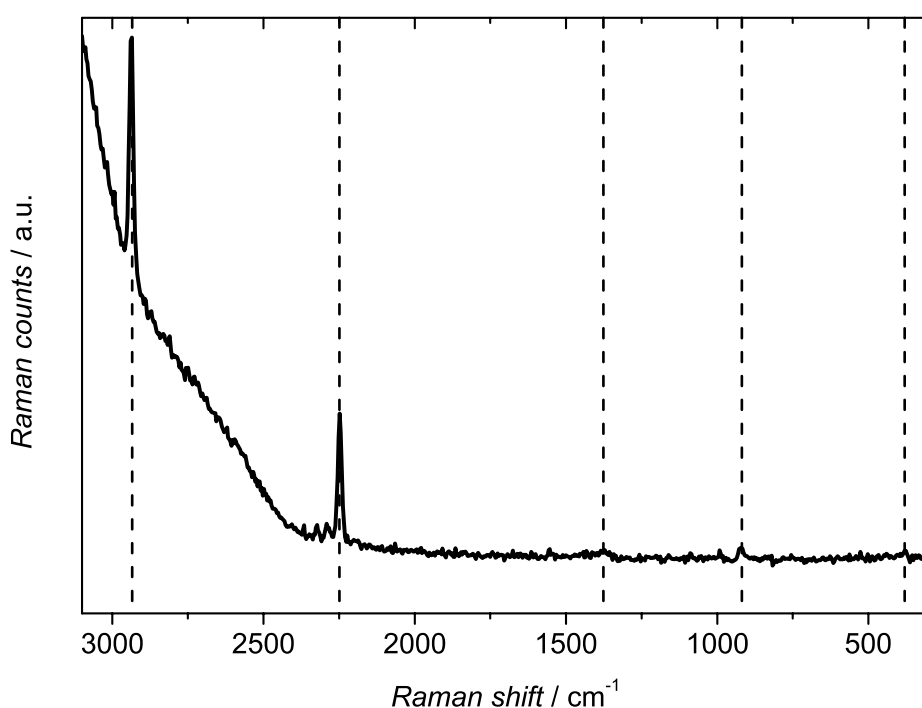
**Figure S2.** Absorption spectra of  $10^{-5}$  M solutions in ACN of benzene **A**, naphthalene **B**, anthracene **C**, phenanthrene **D**, pyrene **E**, triphenylene **F** and coronene **G**. Spectra have been vertically shifted for a better comparison.

Figure S3 shows the Raman spectra of the 0.1 M solution of naphthalene in acetonitrile collected both with visible ( $\lambda = 785$  nm and  $\lambda = 514$  nm) and UV ( $\lambda = 244$  nm) laser lines. The spectra collected with the visible excitation lines show very weak signals ascribable to naphthalene and most intense modes are related to the solvent. Conversely the sample vibrations are selectively enhanced by the resonant Raman effect when the spectrum is collected with the UV excitation source. In this way naphthalene can be detected, even if diluted, without relevant interferences from the solvent.



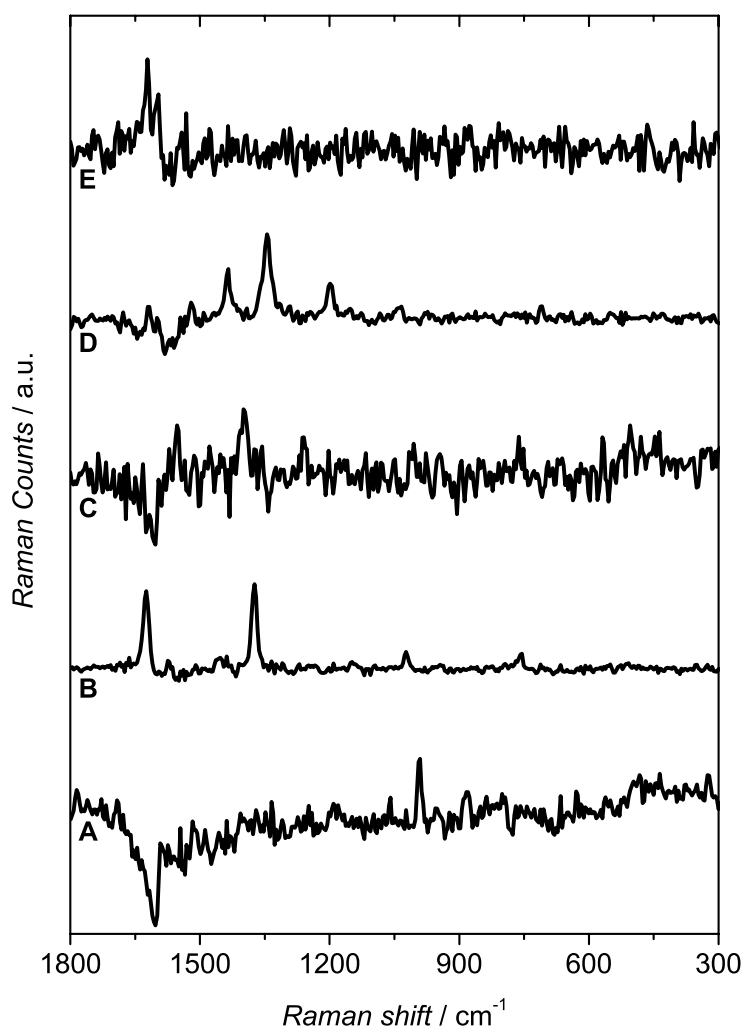
**Figure S3.** Raman spectra of 0.1M solution in acetonitrile of naphthalene, collected with different excitation laser lines:  $\lambda = 785$  nm (solid red line);  $\lambda = 514$  nm (solid green line); and  $\lambda = 244$ nm (solid violet line). The vertical dashed lines label the vibrational modes of the acetonitrile. Spectra have been rescaled and shifted for a better comparison.

The UV Raman spectrum of the 0.1M solution of benzene in acetonitrile is reported in an extended frequency range (3100-300  $\text{cm}^{-1}$ ) in Figure S4. The pronounced slope of the background in the high wavenumber region is due to the benzene emission (i.e. fluorescence) competing with the Raman signal of both acetonitrile and benzene itself. Moreover benzene absorbs most of the incident light, as the excitation wavelength ( $\lambda = 244 \text{ nm}$ ) matches with an electronic transition of the molecule. This results in an overall poor quality of the spectrum, where no signal related to the benzene can be identified.



**Figure S4.** UV ( $\lambda = 244\text{nm}$ ) Raman spectra of 0.1M solution of benzene. The vertical dashed lines label the vibrational modes of the acetonitrile.

The UV Raman spectra of PAHs adsorbed on activated carbon suffer the interference of the G band of carbon itself around  $1600\text{ cm}^{-1}$ . In order to try to extract the information related to the molecules even from this region, the spectrum of the bare activated carbon has been subtracted from the ones of PAHs adsorbed on it. The results are reported in Figure S5. The subtraction procedure allowed to better discriminate the vibrational modes of PAHs around the carbon G band, although the heavy noise makes the obtained spectra not fully reliable in terms of relative intensities.



**Figure S5.** Background subtracted UV ( $\lambda = 244\text{nm}$ ) Raman spectra of benzene **A**, naphthalene **B**, anthracene **C**, phenanthrene **D** and pyrene **E** adsorbed from vapor phase on activated carbon. Spectra have been rescaled and shifted for a better comparison.

## Extendend references

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