

Astrochemistry of Large Carbonaceous Molecules

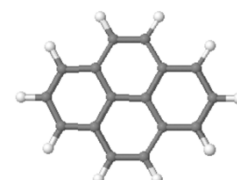
1) IR spectroscopy and emission model



The NASA AMES PAH DATABASE (<https://www.astrochem.org/pahdb/>) contains more than 2000 vibrational spectra of PAHs and PAH-related molecules, calculated using Density Functional Theory (see Lecture on “Electronic Structure”). In this exercise we will make use of the online tools available.

A. Use the Search tool to look up the molecule **pyrene in neutral state** ($C_{16}H_{10}$, uid=334).

You will see the full database entry for pyrene. Select it by checking the small square in front of the formula (orange circle, Fig1)



Pyrene

Select the tab “transitions”, that you find just below the molecular structure (red circle, Figure 2)

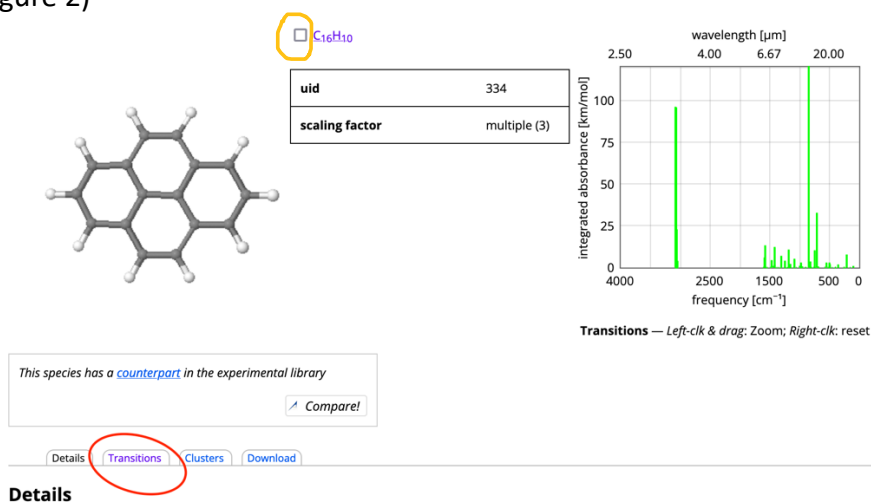


Figure 1: Screenshot from NASA AMES PAH DB

You will find a table containing all the details related to the vibrational modes for the molecule as wavelength/wavenumber and integrated cross-section. Clicking on a specific mode, you can see it animated on the right structure.

1) Can you classify the modes below based on the type of bonds excited (**TIP**: have a look at https://en.wikipedia.org/wiki/Infrared_spectroscopy to name the vibrations)?

- 3069 cm⁻¹ / 3.258 μm
- 1576 cm⁻¹ / 6.34 μm
- 1181 cm⁻¹ / 8.468 μm
- 709.5 cm⁻¹ / 14.09 μm

2) How do the integrated cross-sections of the above modes change? Which are the strongest?

B. Now search in the database for the pyrene cation (C₁₆ H₁₀ cation) and for buckminsterfullerene (C₆₀ neutral). Select both by clicking the small square in front of the formula (orange circle, Fig. 1) Navigate to the “Tools” tab (it is above the molecular search tool). We are going to compare the intrinsic spectra of these three molecules Use the following parameters in the section “General” of the page

- Transition between 3500 and 400 cm⁻¹
- Lorentzian line profile, FWHM = 10 cm⁻¹
- Apply NO emission model

and then click on the button “Stack!”. You will see the convoluted intrinsic spectra of the 3 molecules.

1) Compare the spectra of pyrene and pyrene cation, what are the two most striking differences that you notice? Can you connect these differences to the type of vibrational modes involved? (**TIP:** Go back to list of vibrations and check the Wikipedia entry for Vibrational spectroscopy).

2) Compare the spectra of fullerene and pyrene, what do you notice? Can you connect it to the vibrations of the two molecules?

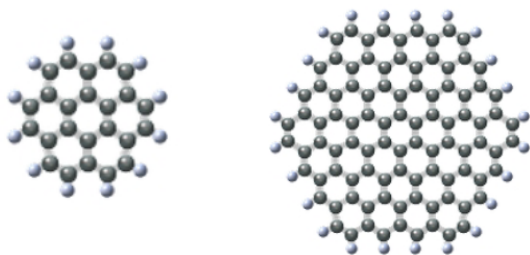
3) During the lecture you saw that vibrational spectroscopy cannot be used to identify single large molecules because the bonds. Do you still agree? And what about “subgroup of molecules”? Explain your reasoning

C. The IR cooling of PAH/fullerene molecules after the absorption of a UV photon of frequency ν_{UV} can be described by the thermal approximation. In this approximation, the max temperature reached after absorption depends on its heat capacity, which can be calculated knowing the ν_i frequencies of the s vibrational modes of the molecule in question, e.g.

$$C_V = k \sum_{i=1}^s \left(\frac{h\nu_i}{kT} \right)^2 \frac{\exp[h\nu_i/kT]}{(\exp[h\nu_i/kT] - 1)^2},$$

After the absorption, these excess energy (which is related to this maximum temperature T) is distributed among the different vibrational modes, which become excited and then molecule cools down emitting a cascade of IR photons, i.e. vibrating.

1) What difference do you expect in the max temperature reached after the absorption of the same photon by a large PAH molecule (such as circumcoronene, right in the figure below) and by a small one (coronene, left in the figure below)?



2) Check if your guess is correct. Search in database for coronene ($C_{24}H_{12}$) and circumcoronene ($C_{96}H_{24}$) (see figure above), select¹ them by clicking the square, and go the “Tools” tab. Use the following parameters in the section “General” of the page

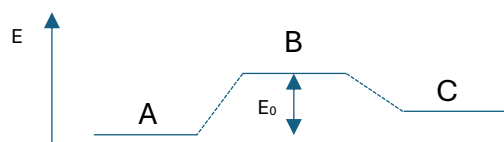
- Transition between 3500 and 400 cm^{-1}
- Lorentzian line profile, FWHM = 10 cm^{-1}
- Apply “Full temperature cascade” with energy of 6.5 eV (the average photon energy absorbed by a PAH in the reflection nebula NGC 7023).

Click on the button “Stack!”. You will see the full emission spectrum of the 2 molecules selected after the absorption of a 6.5 eV photon. On the top right you will see the maximum temperature in K reached by the specific PAH.

3) What major difference do you see when comparing the emission spectra of the two molecules? Connect this difference to the heat capacity of the two PAHs (HINT: Excess energy is distributed among all the modes, starting from the low energy one).

2) Photochemistry of PAHs

We saw that, if internal energy of a PAH is high enough after absorbing a UV photon, chemical reactions can become competitive. In this exercise we will calculate reactions rate for isomerisation for the corannulene molecule using Rice–Ramsperger–Kassel–Marcus (RRKM) theory. Let’s consider a (unimolecular) reaction with the following potential energy surface



where A is the reactant, B the transition state and C the product and the reaction barrier is E_0 . Then the rate constant for this reaction as function of internal energy E of the reactant is given by

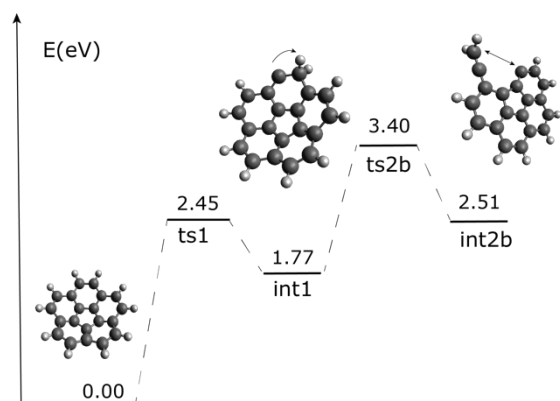
$$k_{RRKM}(E) = \frac{W^*(E - E_0)}{h\rho(E)},$$

where the denominator is the sum of states for the transition state B between 0 and $E - E_0$ and $\rho(E)$ is the vibrational density of states of the reactant molecule A. Density and sum of

¹ If you still have some molecules selected from the previous exercise, go to the “Selection” tab and deselect them.

states can be calculated knowing the vibrational modes of the molecules in question, and this can be achieved through quantum chemistry calculations².

A Let's consider the following potential energy surface, showing isomerisation reaction of the corannulene cation



where the energies are in eV and are given with respect to corannulene cation. You can find the full potential energy surface in the paper *Phys. Chem. Chem. Phys.*, 2024, **26**, 19332-19348

In the folder / PAH_mol_proc /data/QC_output/ there are five output files corresponding to the 5 stationary points (intermediates and transition states) of the potential energy surface above. Open each of them (separately) with the software Avogadro and look at the structures. On the right-hand side of Avogadro's window, there is a list of the vibrational modes (frequency in cm^{-1} and intensity in km/mol) of the molecule you are visualising. If the first vibrational mode has a minus sign, you are looking at a transition state.

1) Assign each output file to the corresponding stationary point.

A.log =>

B.log =>

C.log =>

D.log =>

E.log =>

Animate the frequency with a negative sign to see how the transition state connects the reactant and product.

2) Using the figure above, calculate the energy barrier E_0 for the reactions

back_to_cora Int1 -> corannulene :

to_int2b Int1 -> int2b :

B. Now you will calculate the RRKM using the python notebook `Exercise2_rates` which is in the folder / PAH_mol_proc /scripts.

1) Calculate the RRKM rate for the first reaction named "**back_to_cora**", using E_0 calculated in the previous exercise. Make sure to change the path to file accordingly. Do the same for the second reaction "**to_int2b**". Plot the rates (you can use your own script or the script `plot_rrkm_rates` in the folder / PAH_mol_proc /scripts. What is probability of the

² A good resource to learn more about RRKM is *Baer and Mayer, J. Am. Soc. Mass Spectrom.*, 1997, 8, 2, 103-115

molecule int1 to become either the molecule int2b or corannulene as function of its internal energy E ? (TIP: $\text{probability} = \text{rate} / \text{sum of rates}$)

The reliability of the RRKM rate depends on the quantum chemistry calculations required for it, in particular the energy barriers. Calculate the RRKM rates for the same reactions as in B.1 and B.2 exercise but now changing both E_0 by ± 0.2 eV (which is the accuracy on the energy coming from these DFT calculations). Plot all the rates.

2) What change in the reaction rate do you observe and where is it more relevant?

3) Can you put forward a strategy to obtain RRKM rates accurate enough for astrochemical modelling?