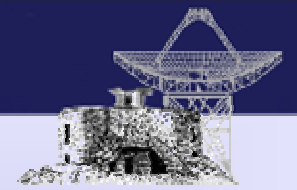


OAC

Osservatorio Astronomico di Cagliari



AstroC-Hemistry Group

PAHs: combined laboratory and observational (and theoretical, and modelling...) approach

■
Giacomo Mulas

Introduzione:

- idrocarburi aromatici policiclici (PAHs)
- la curva di estinzione (ISEC) nell'UV

Perchè

- variazioni della forma dell'ISEC
- variazioni delle sezioni d'urto delle PAH con la carica
- Possibile legame?

Come quantificare?

- modello di estinzione per separare il contributo delle polveri classiche
- fit della componente "PAHs" con una combinazione lineare di sezioni d'urto

Problemi pratici

- 200 parametri liberi nel fit
- 200 vincoli sui parametri liberi
- matrice quasi singolare

Risultati numerici

- geometria del χ^2
- indeterminatezza dei risultati e stima degli errori

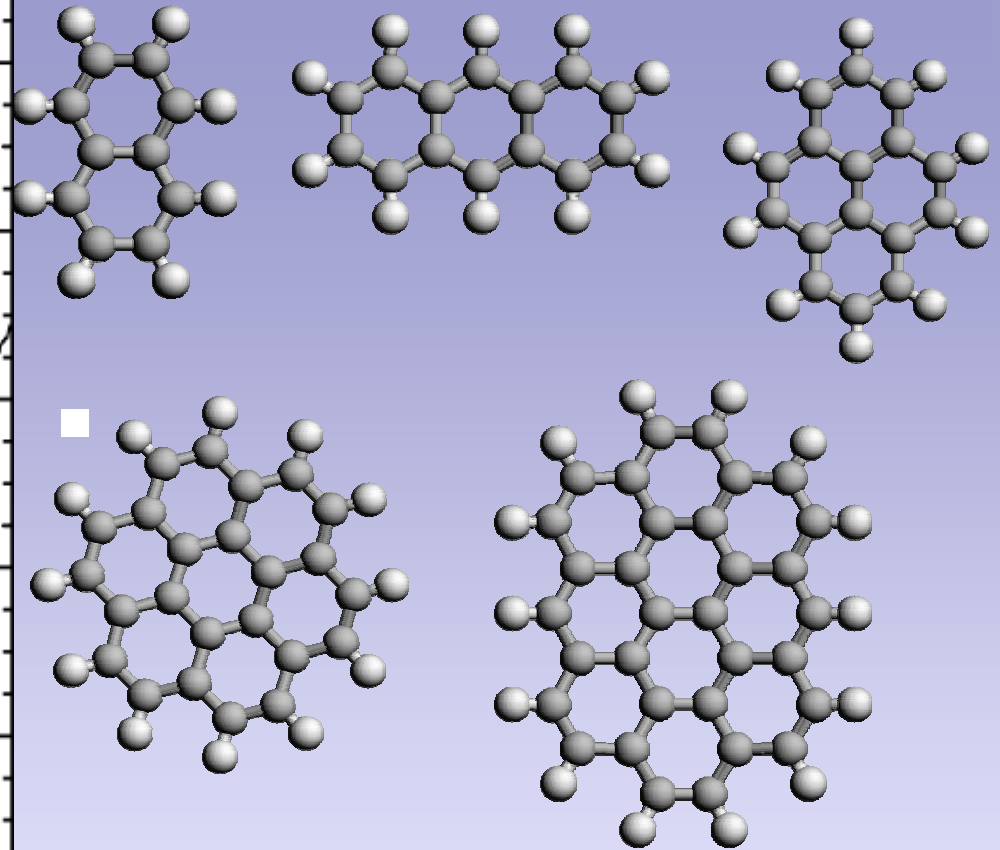
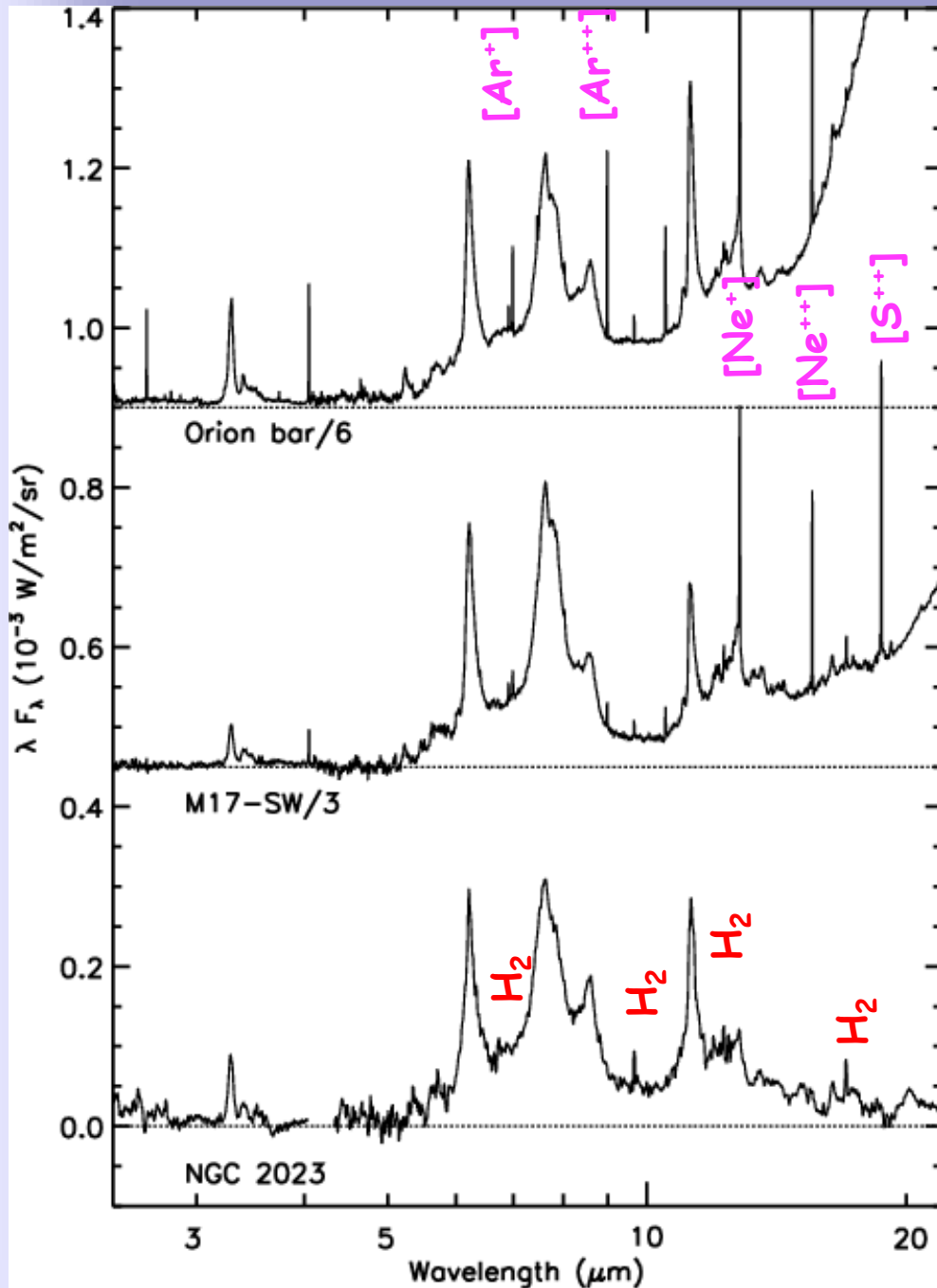
Risultati fisici

- quali quantità fisiche risultano ben determinate e quali no
- relazione tra quantità fisiche e parametri della curva di estinzione

PAHs: who are they?

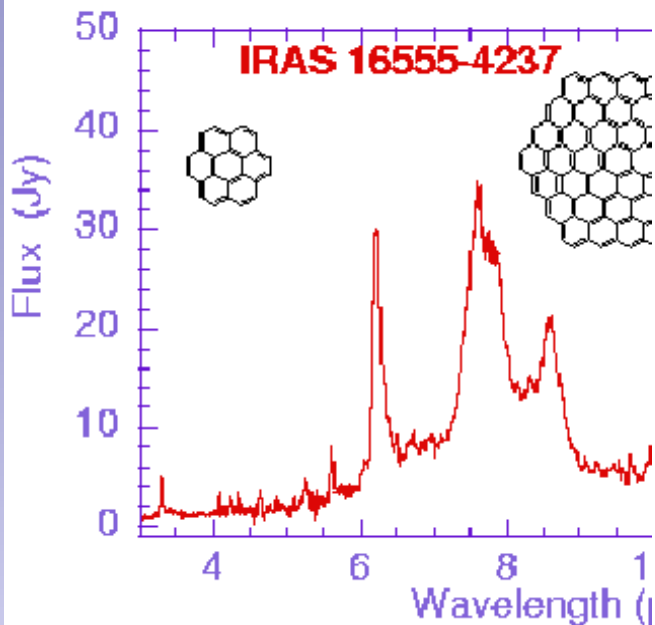
- A component of extremely small carbonaceous dust particles was hypothesised since when the first IRAS results showed that emission in the $12\mu\text{m}$ band required temperatures incompatible with thermal equilibrium conditions
- Particles smaller than a few nm, thanks to their tiny thermal capacity, can be transiently heated to very high temperatures following the absorption of a single UV photon
- When more detailed spectra became available, mid-IR emission turned out to be strikingly similar to the IR spectrum of natural coals. The NASA Ames and Paris groups, independently, came up with the proposal that such extremely small dust “particles” could be free-flying molecules of the polycyclic aromatic hydrocarbon family.

and PAHs

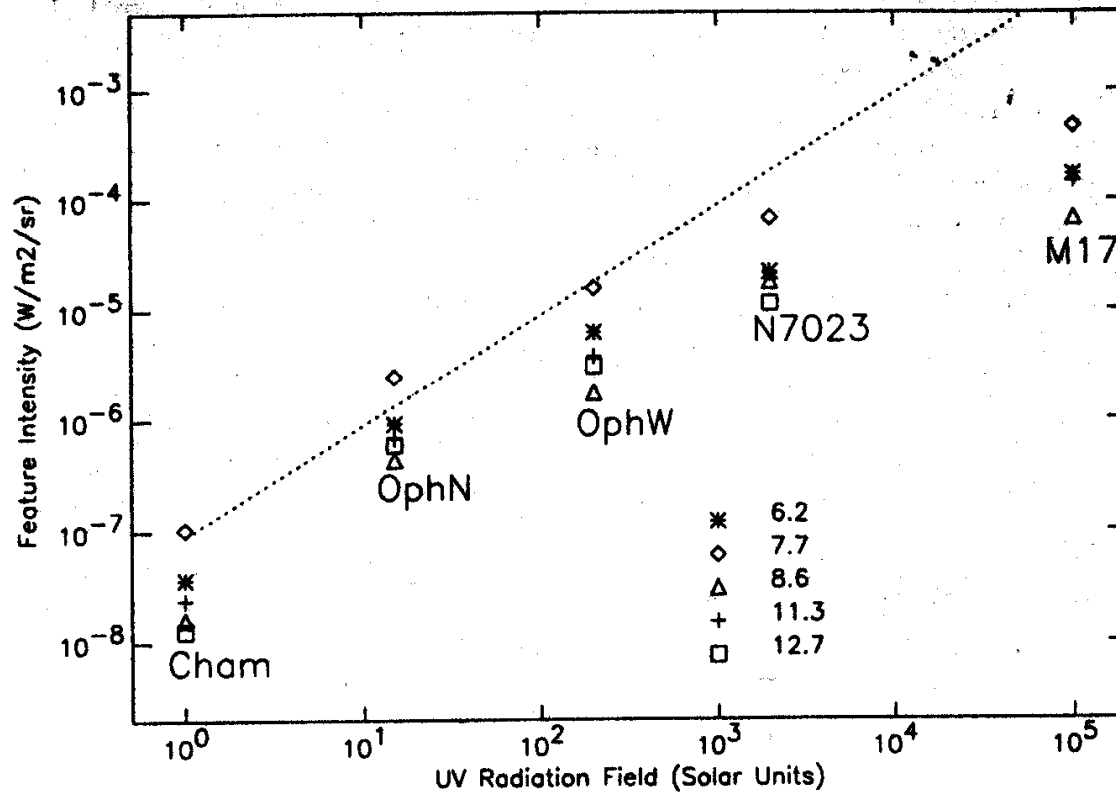


AIBs and PAHs

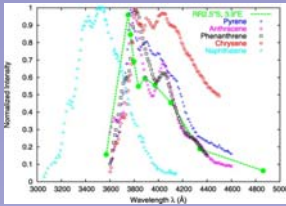
ISO / SWS spectrum



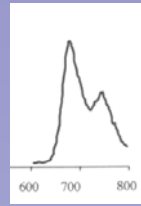
3.3 μm (3050 cm^{-1}); 6.2 μm (1613 cm^{-1});
 " 7.7 " μm (1300 cm^{-1}); 8.6 μm (1149 cm^{-1});
 11.3 μm (890 cm^{-1}); 12.7 μm (787 cm^{-1}),
 aromatic CH and CC vibrational modes



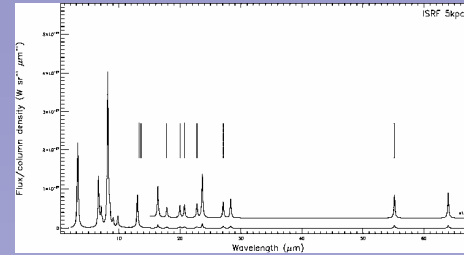
A unified vision of PAH photophysics



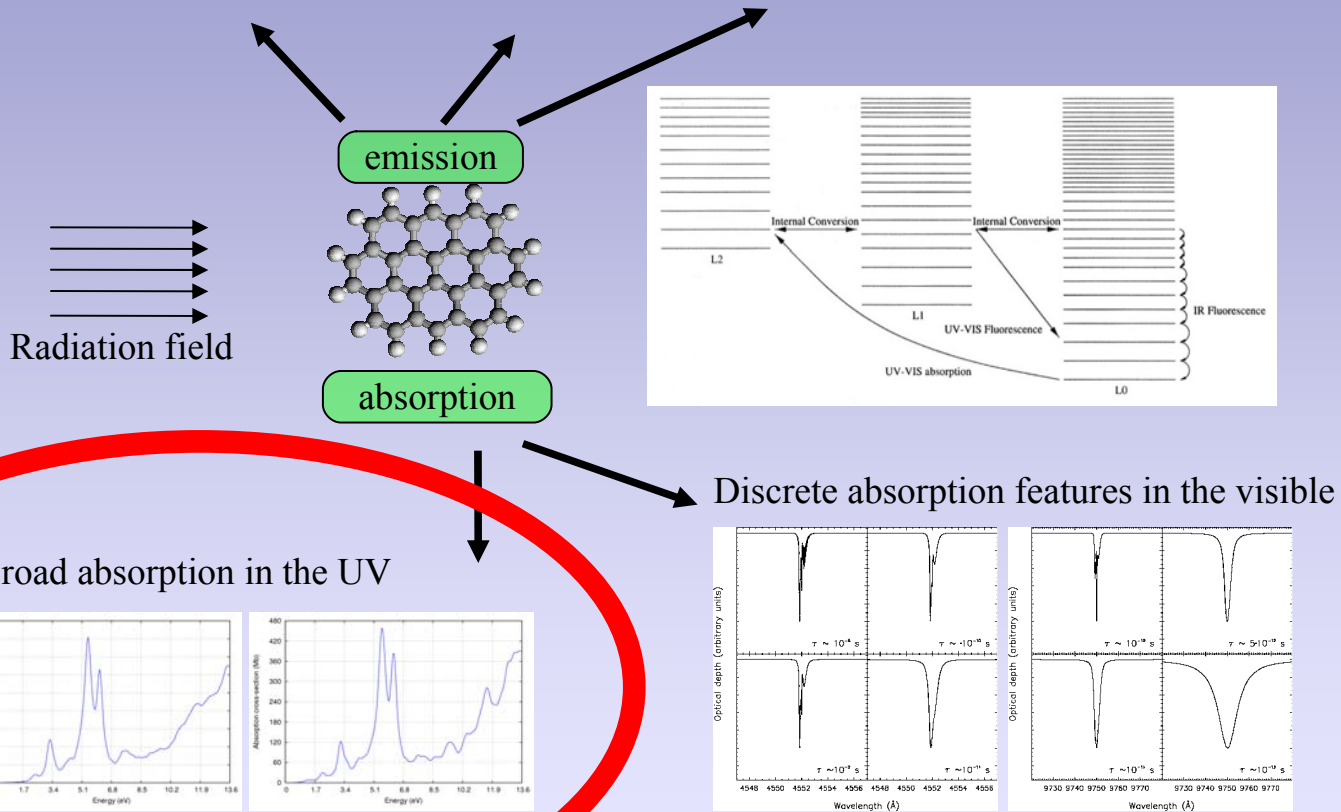
Fluorescence



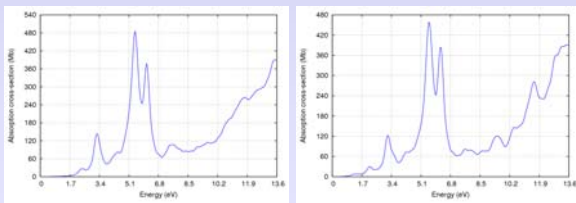
Phosphorescence



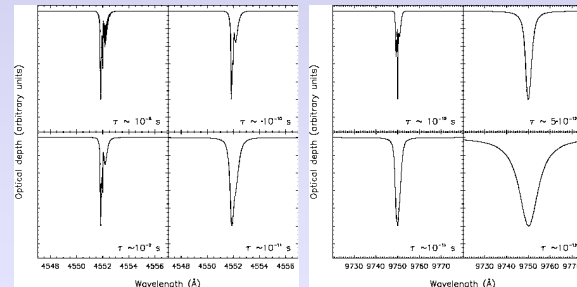
Vibrational emission



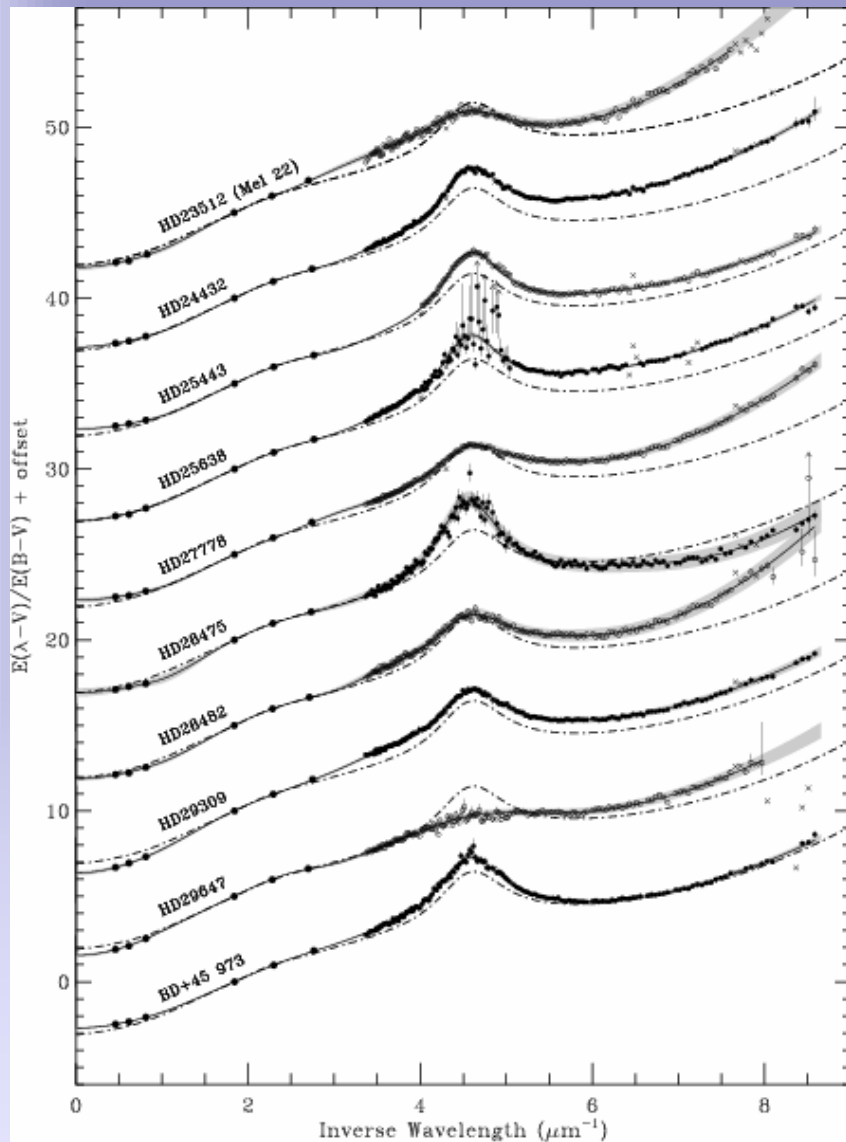
Broad absorption in the UV



Discrete absorption features in the visible



IS extinction curves in the UV



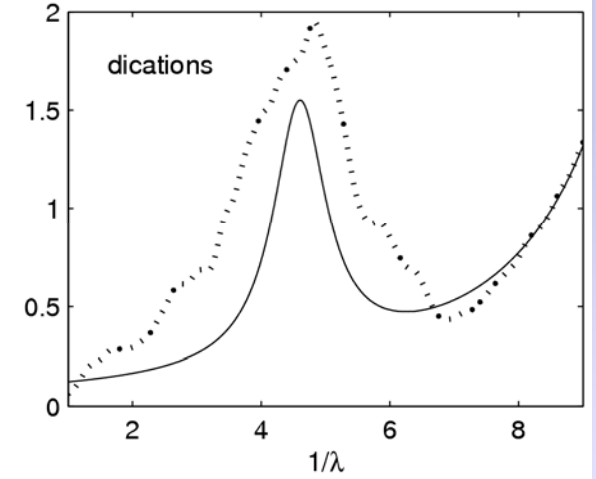
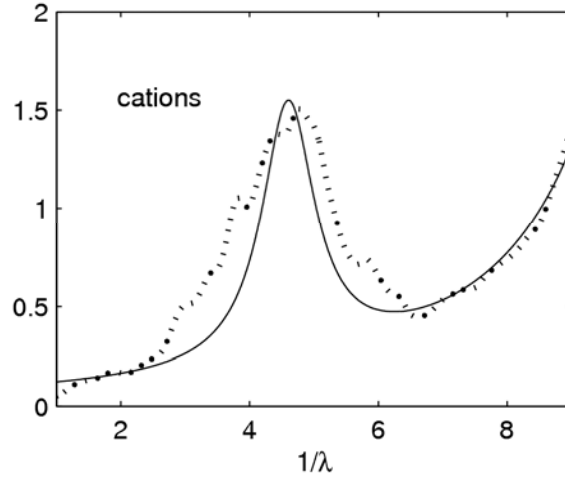
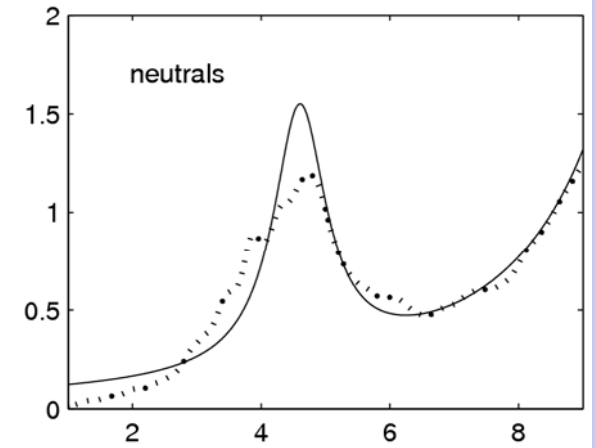
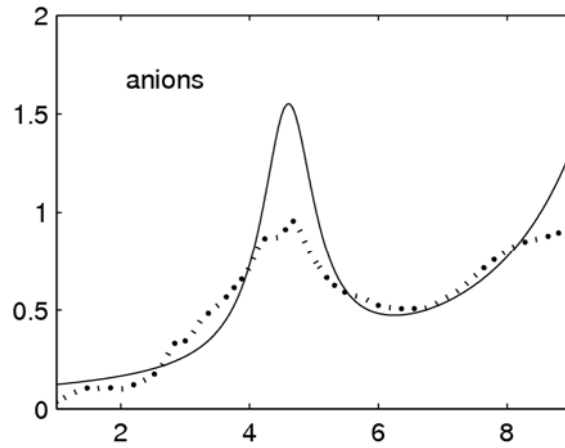
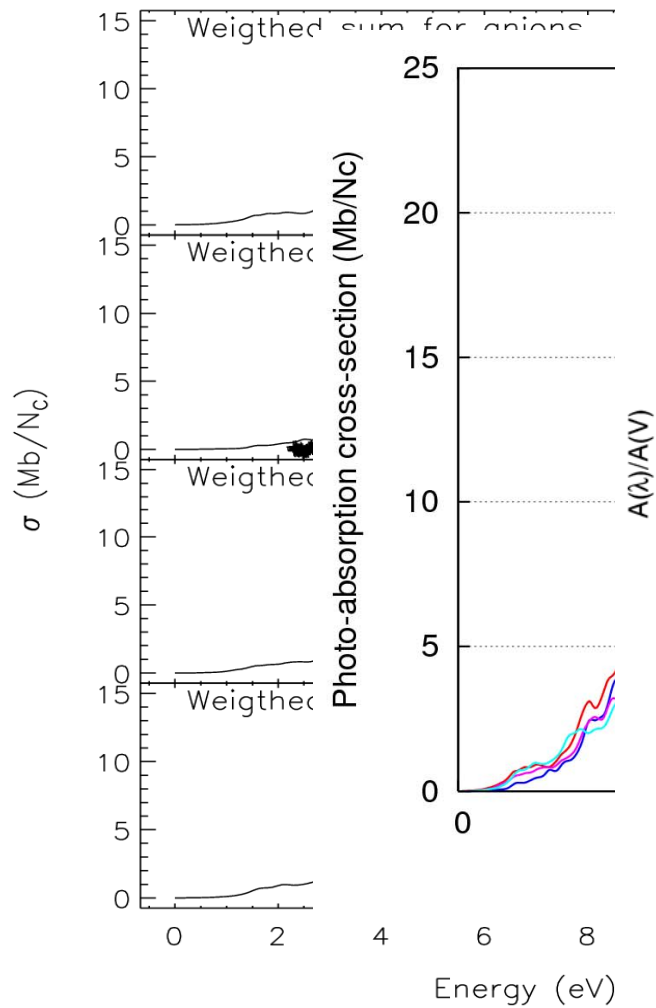
Fitzpatrick & Massa (2007), collecting all the available data, obtained extinction curves along 328 lines of sight, and represented them, in the UV, with the empirical parametrisation:

$$k(\lambda - V) = \begin{cases} c_1 + c_2x + c_3D(x, x_0, \gamma) & x \leq c_5 \\ c_1 + c_2x + c_3D(x, x_0, \gamma) + c_4(x - c_5)^2 & x > c_5 \end{cases}$$

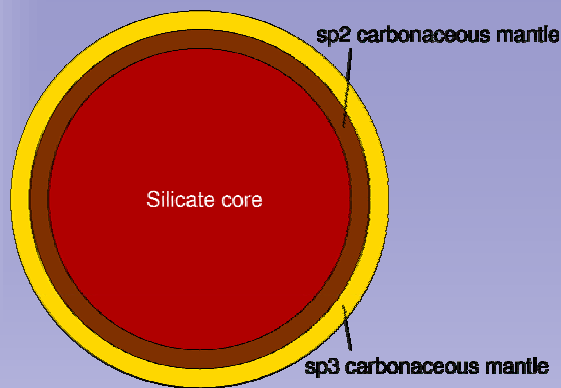
$$D(x, x_0, \gamma) = \frac{x^2}{(x^2 - x_0^2)^2 + x^2\gamma^2}$$

The “bump” is Lorentzian-shaped, its peak position almost constant while intensity and width vary substantially, as does (independently) the intensity of the non-linear far-UV rise

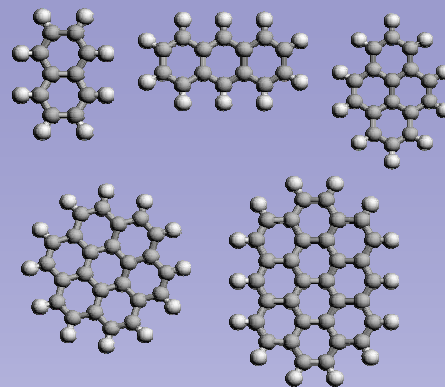
PAHs and IS extinction



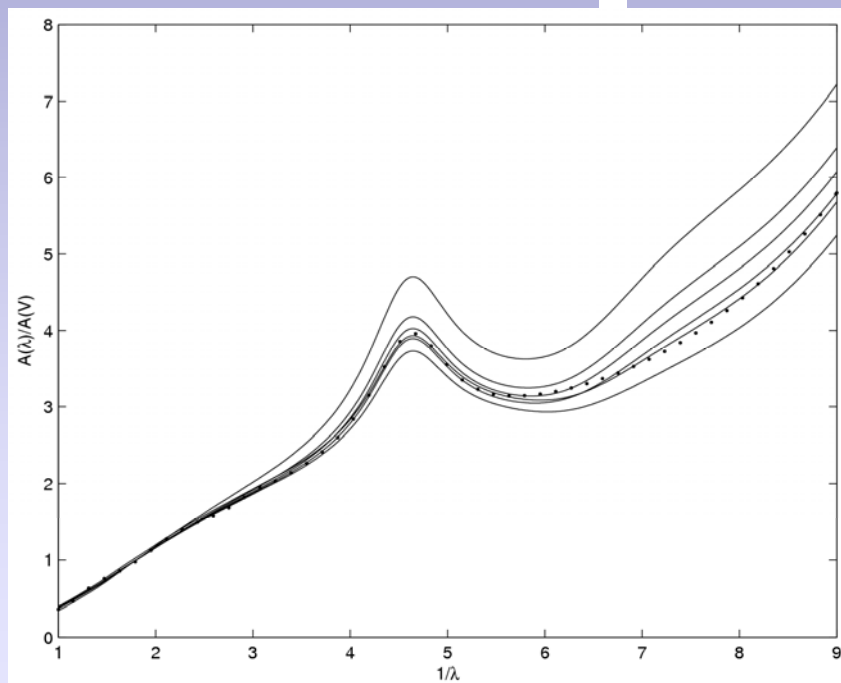
PAHs and IS extinction



+



= IS extinction curve?



maybe, but:

- Can we span the observed variation in IS extinction curves?
- Can we link some parameters of the IS extinction curves with properties of the PAH population?

A complicated fit...

- We use the core+double mantle model of Iatì et al. to separate the contributions of classical dust and “molecular component”
- After subtracting the contribution of the classical component, we perform a detailed fit of the remnant, attributed to the “molecular component”, with a linear combination of all the absorption cross sections in our online database (<http://astrochemistry.ca.astro.it/database/>, 50 species in 4 charge states = 200 cross sections in total)

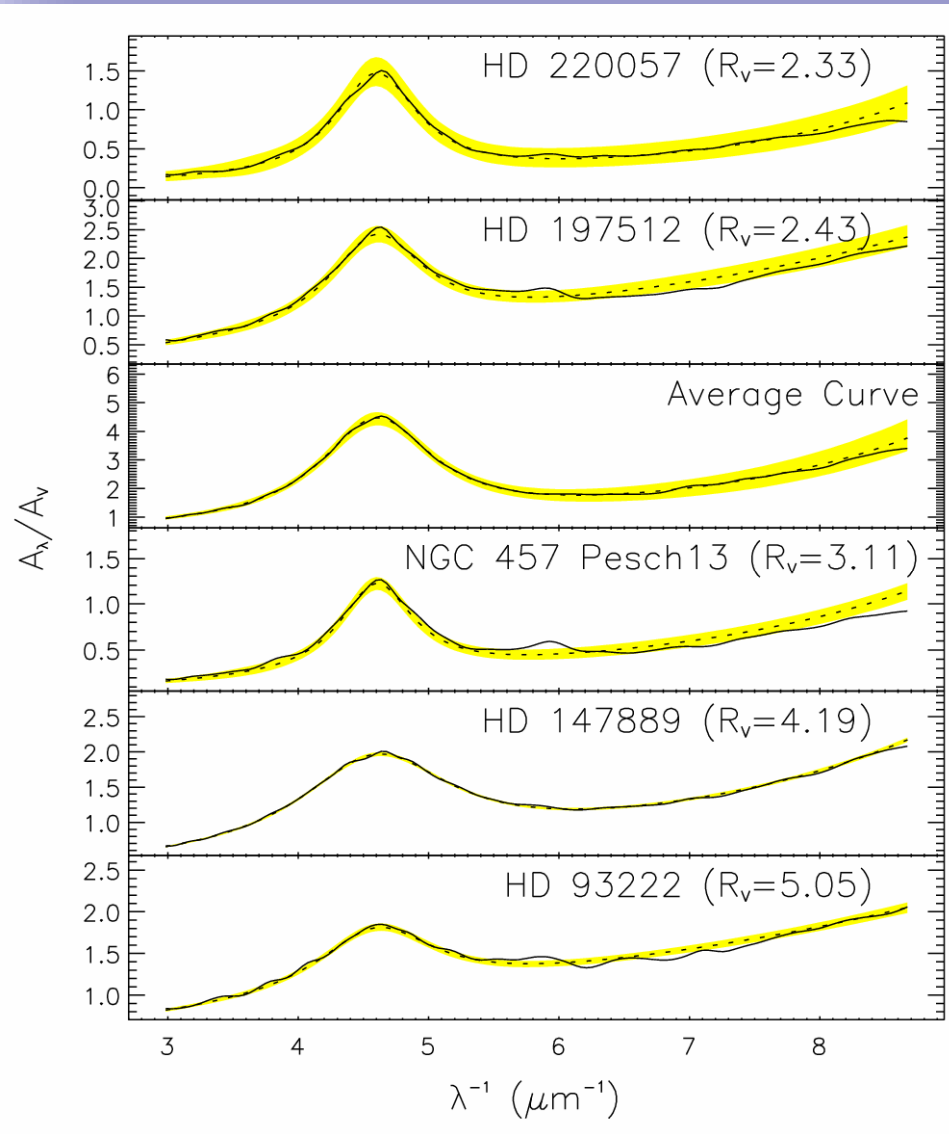
It may sound easy, but...

- 200 free parameters is a very large number!
- The matrix of the quadratic coefficients of the resulting χ^2 , to be minimised to obtain the fit, is very nearly singular (making useless standard linear fitting algorithms which need to invert that matrix)
- This is a conditioned fit: the 200 column densities (i.e. the free parameters) must be non negative. Imposing these conditions by “brute force” scales very poorly (with the factorial of the number of conditions...)

Geometric meaning and numerical solutions

- The χ^2 to be minimised is an N-dimensional paraboloid (with $N=200$ in this case), whose vertex is the formal solution of the fit. The matrix of its quadratic terms is the curvature tensor. If this matrix is almost singular, curvature is negligible in some directions.
- Upon diagonalising this real, symmetric matrix, 180 of the 200 eigenvectors are >20 orders of magnitude smaller than the largest one. The determinant of the matrix, which contains their product, will underflow any machine precision: no surprise that the matrix appears singular, from a numerical point of view.
- After finding the “formal” unconstrained solution of the fit, we look for the acceptable (i.e. constrained) solution closest to it, where “distance” is defined by the curvature tensor.

After all this trickery, does it work?



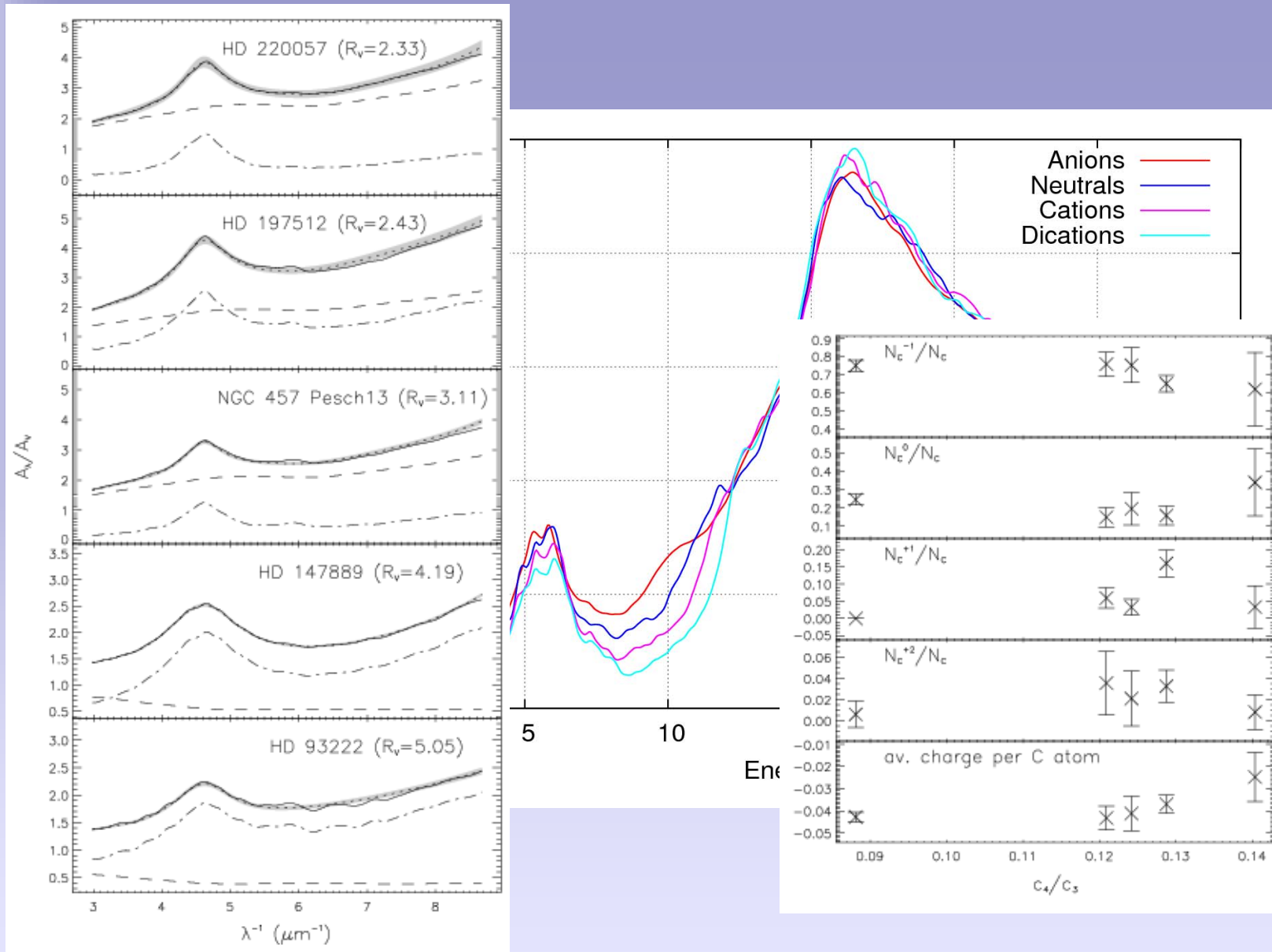
- Despite the relatively small sample of molecules representing “PAHs”, all fits are quite satisfactory, almost always within $1\text{-}\sigma$ from the extinction curves tabulated by F&M!

What physical insight can we obtain?

- Since only ~ 10 eigenvalues of the curvature tensor of the χ^2 are significantly nonzero means that the contribution of PAHs to extinction is quite well determined by a handful of physical parameters, namely those that vary in the subspace spanned by the corresponding eigenvectors of the curvature tensor, hence defined in terms of linear combinations of the column densities of the species included in the fit.
- The eigenvector corresponding to the largest (by far) eigenvalue is very nearly proportional to the total number of carbon atoms contained in the mixture of PAHs. This quantity is therefore quite strongly constrained by the extinction curve.
- Eigenvectors corresponding to almost null eigenvalues (~ 180 on 200!) shuffle carbon atoms among PAHs, but without appreciably changing neither the total carbon contained in PAHs nor the total electric charge of the mixture



In short: it works!

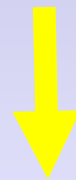


Coming in the near future:

- What other physically meaningful parameters are well constrained by the fit, “hidden” in the combination of eigenvectors with nonzero eigenvalues? E.g. average elongation, symmetry, size?
- Select, in the Fitzpatrick & Massa sample of extinction curves, the most peculiar ones, to check whether we can fit “pathological” cases as well, and with what PAHs
- For those lines of sight for which both the extinction curve and the spectrum of aromatic infrared bands are available, verify whether the average charge properties of PAHs inferred through the two independent observational handles are consistent.
- inclusion of more applicable degrees of freedom in the sample of PAHs (such as e.g. hydrogenation degree, inclusion of heteroatoms...)

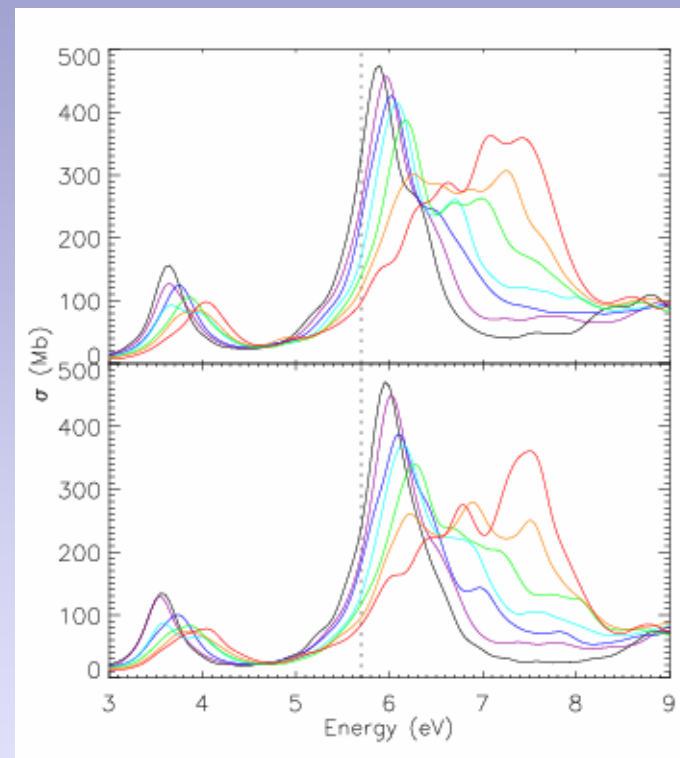
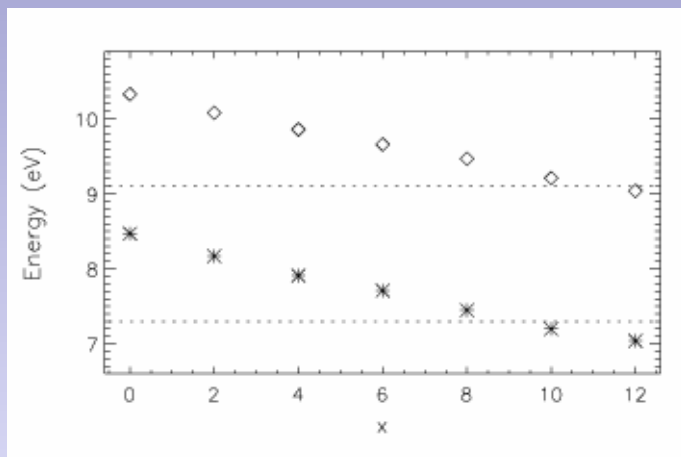
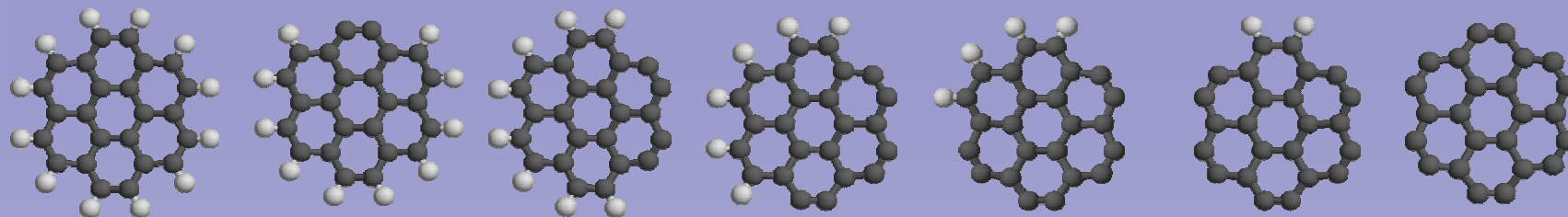
Speaking of which...

- Duley hypothesised that dehydrogenated PAHs, based on discrete dipole approximation calculations, could be the carriers of the UV extinction bump
- Le Page et al. had previously modelled the hydrogenation equilibrium of PAHs in space, as a function of size, concluding that small-sized species would be dissociated, medium-sized ones would be dehydrogenated, large ones would be fully hydrogenated
- Duley further speculated that a specific electronic transition in completely dehydrogenated coronene cation (i.e. C_{24}^+) could account for the 5780 Å DIB, the second transition in the same vibronic sequence involving one of the lowest energy completely symmetric vibration modes would be the 6280 Å DIB, while another electronic transition would match the 4430 Å DIB

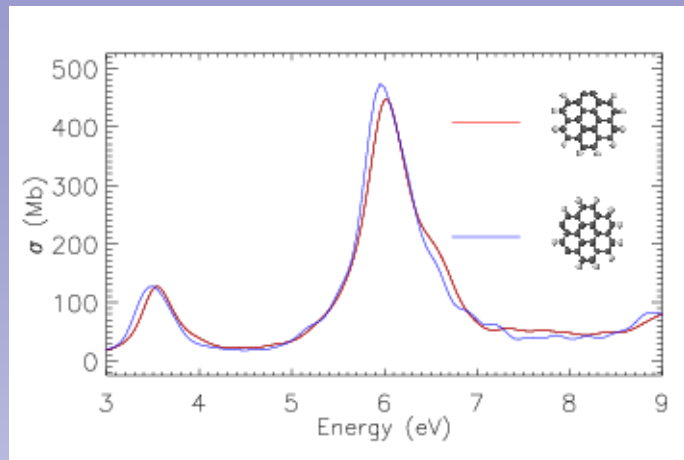


Studying dehydrogenated PAHs looks like a good idea

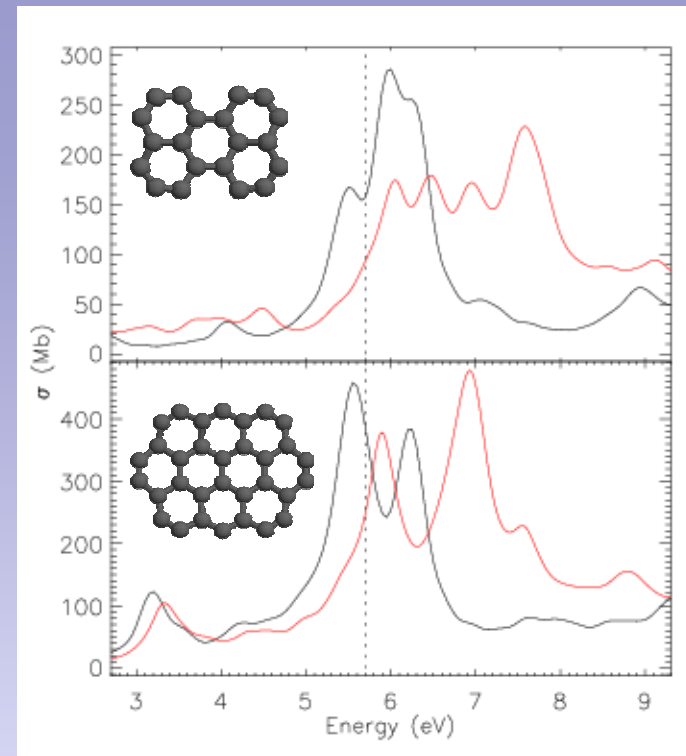
Progressive dehydrogenation...



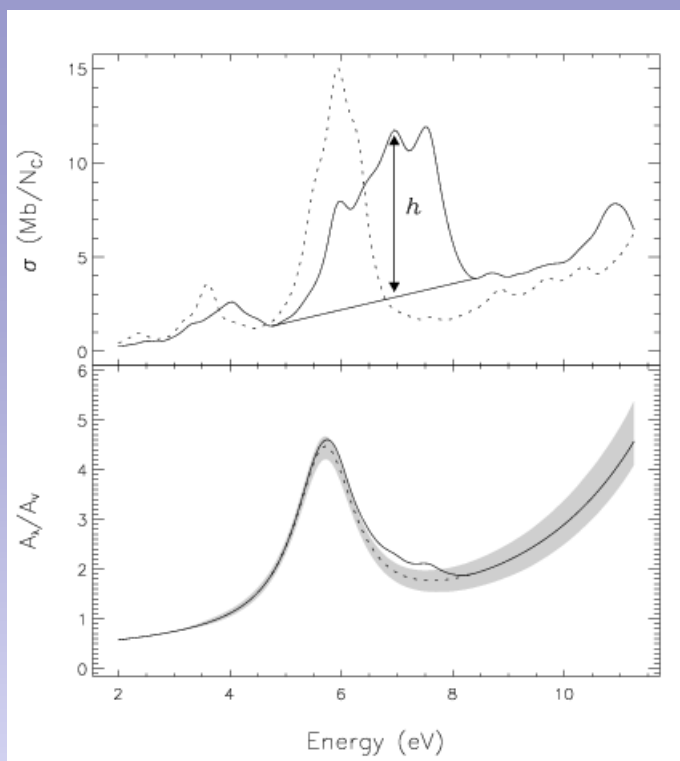
Progressive dehydrogenation...



- The disposition of H atoms seems to be almost irrelevant (at least for coronene derivatives)
- The ~ 2 eV shift of the $\pi \rightarrow \pi^*$ resonance upon complete dehydrogenation seems to be a general effect



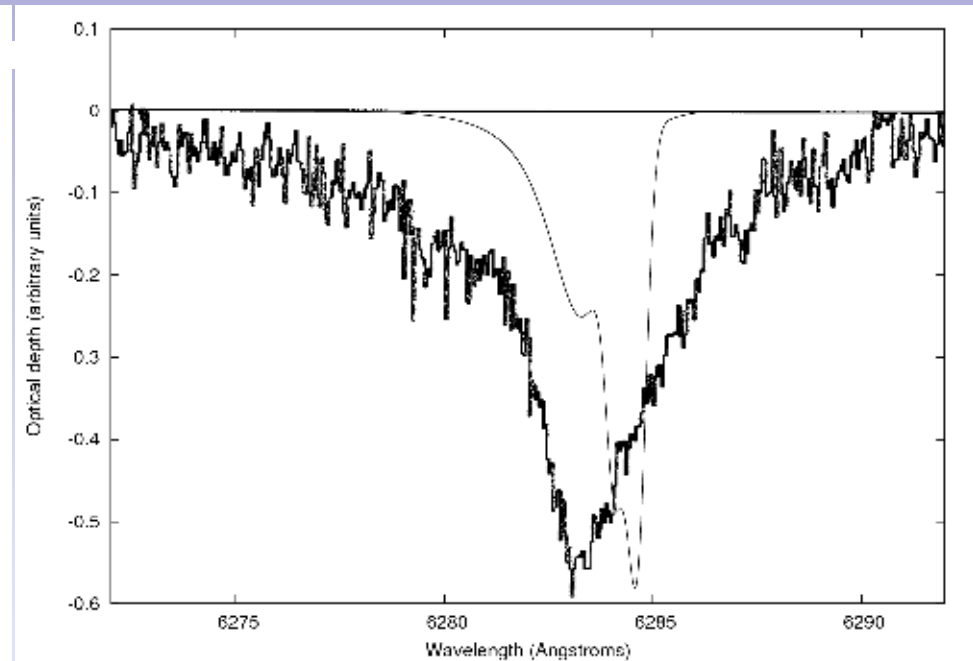
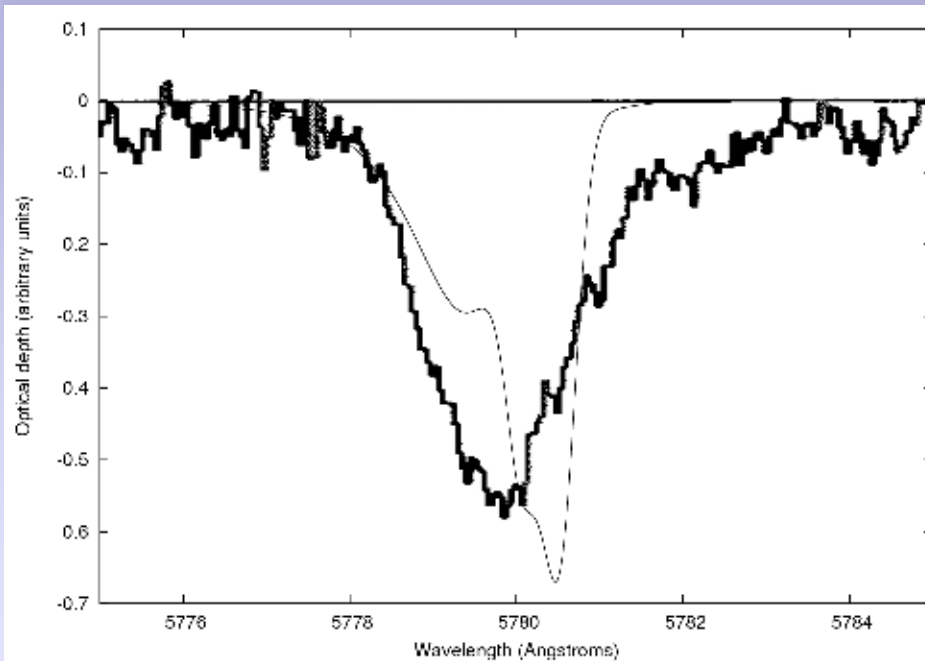
Observational implications of PAH dehydrogenation



- Assuming the ~ 2 eV shift of the $\pi \rightarrow \pi^*$ resonance to be indeed a general effect, a mixture of dehydrogenated PAHs would show up right in the gap between the UV bump and the onset of the far-UV non-linear rise of extinction
- Since the intensity of the $\pi \rightarrow \pi^*$ resonance appears to be unaffected, failure to detect this shifted bump means that the total C in dehydrogenated PAHs must be $\leq 1/8$ of those locked in the bump carriers (for the average ISEC)

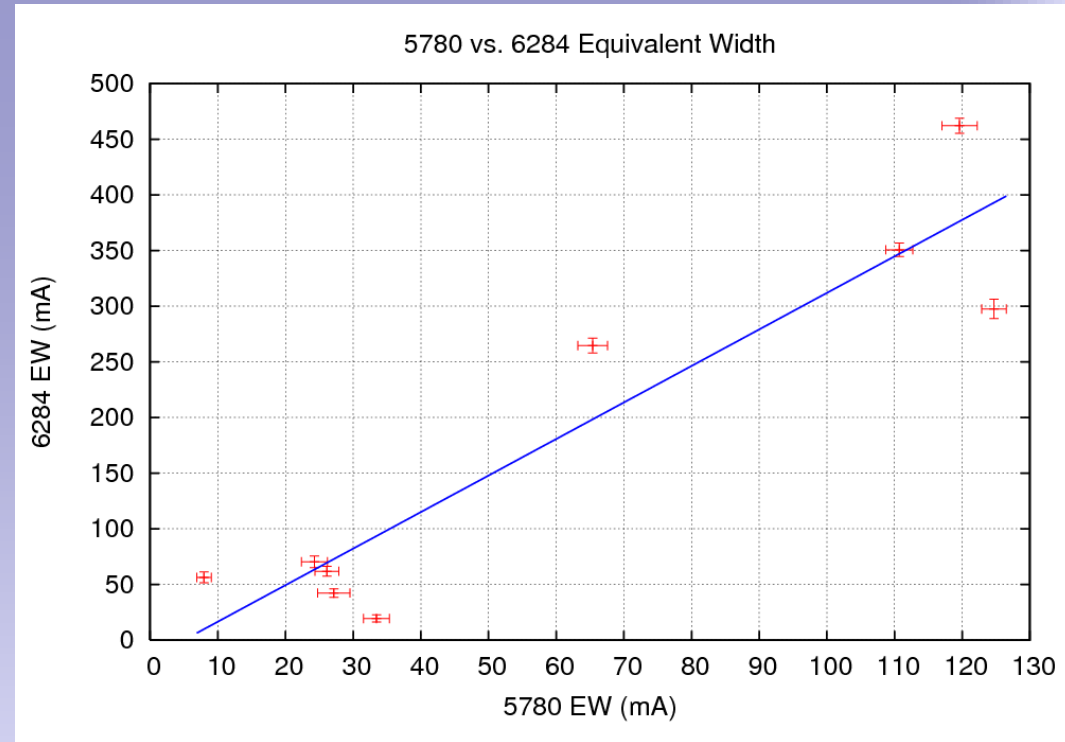
And Duley's C_{24}^+ DIBs hypothesis?

According to the proposal by Duley, the 6284 Å and the 5780 Å bands should be the 0→0 and 0→1 of a vibronic progression of the $\pi_{-4} \rightarrow \pi_0^*$ electronic transition. We calculated the rotational constants in the two electronic states involved by density functional theory (DFT) calculations. The position of the corresponding band as computed using time dependent DFT is at about 1.3 eV (BLYP) and 1.5 eV (B3LYP), to be compared with the observed band position at about 1.97 eV.

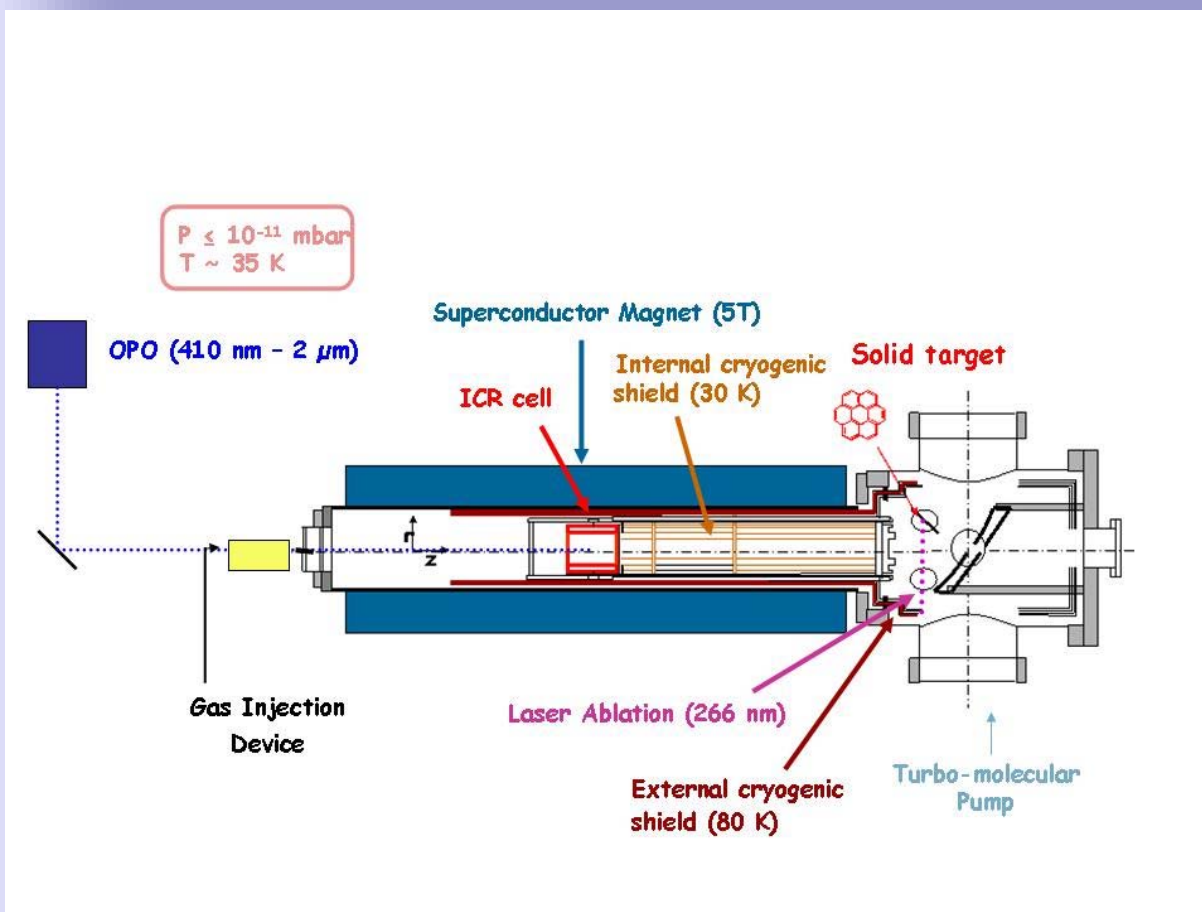


And Duley's C_{24}^+ DIBs hypothesis?

Line of sight	E_{B-V}	EW_{5780} (mÅ)	EW_{6284} (mÅ)
HD56139	0.04	7.957e-03	5.627e-02
HD58343	0.16	1.247e-01	2.974e-01
HD60606	0.15	2.428e-02	7.023e-02
HD88661	0.15	3.345e-02	1.932e-02
HD91465	0.12	2.612e-02	6.173e-02
HD157402	0.12	6.540e-02	2.645e-01
HD167128	0.14	1.107e-01	3.505e-01
HD178175	0.10	1.196e-01	4.620e-01
HD205637	0.05	2.714e-02	4.219e-02

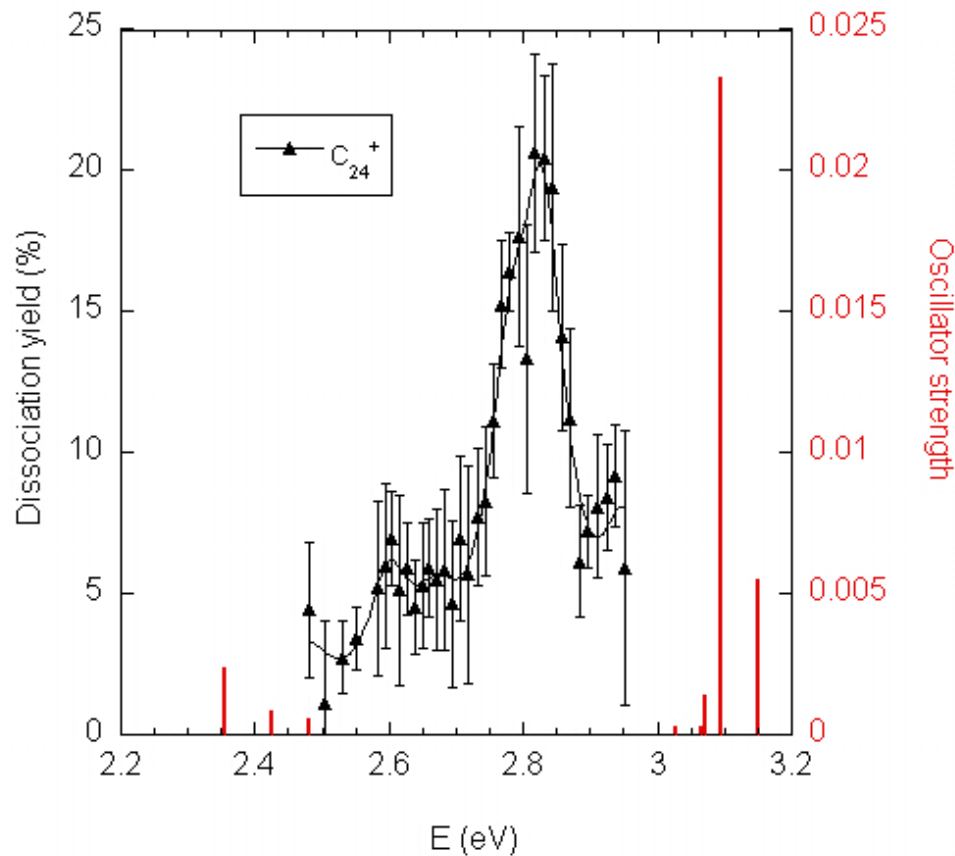


And Duley's C_{24}^+ DIBs hypothesis?



Coronene cations ($C_{24}H_{12}^+$) are produced by laser ablation/ionization of a solid target. The ions are trapped in the ion cyclotron resonance (ICR) cell. C_{24}^+ ions are produced *in situ* by collision induced dissociation with helium buffer gas. Direct spectroscopy is made difficult by the low density of trapped species (about 10^6 ions). We used a tunable laser (broad band OPO from continuum) to perform photo-fragmentation of the isolated cations in the region 420-500 nm. The recording of the fragment ion signal vs laser wavelength gives the fragmentation yield, which depends on the absorption cross section of the cation and the laser intensity ($E = 15$ mJ \pm 20% per pulse between 440 and 500 nm, dropping to 5 mJ at 420 nm).

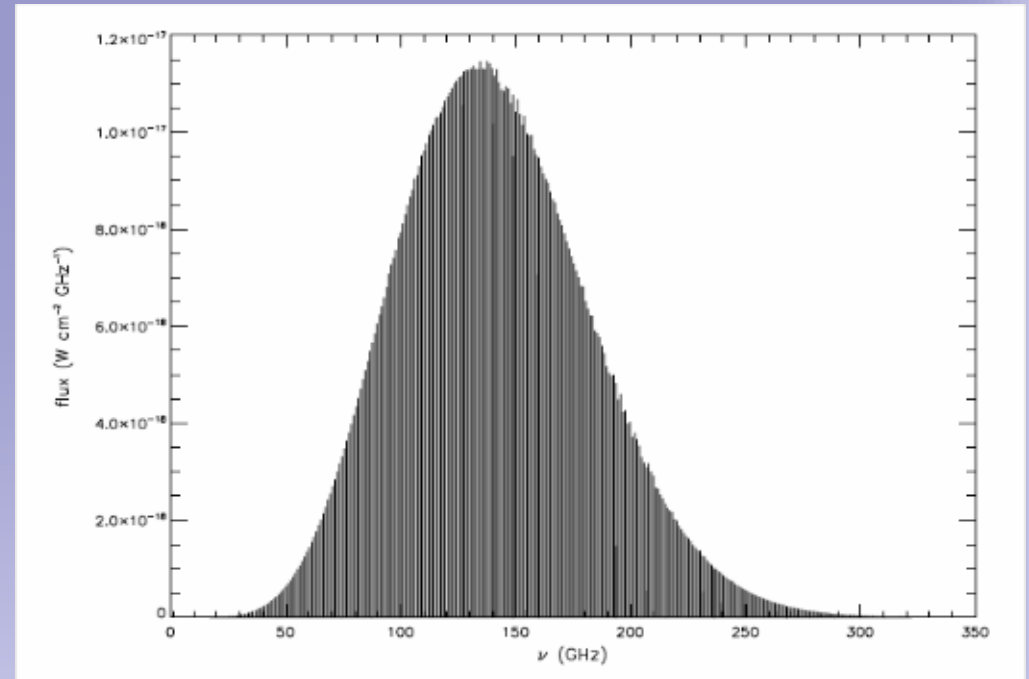
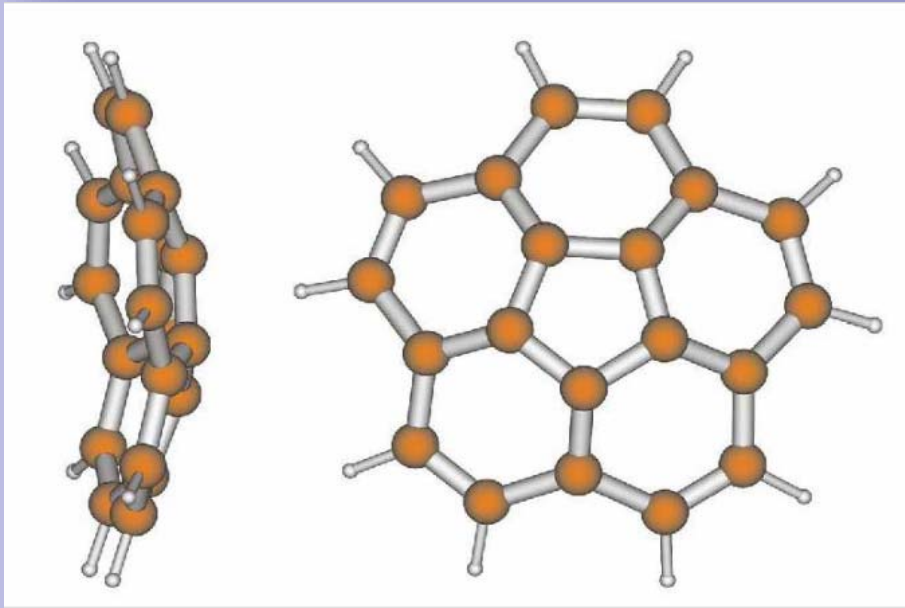
And Duley's C_{24}^+ DIBs hypothesis?



Our dissociation spectrum of C_{24}^+ has a broad peak compatible, in position, with the 4430 Å DIB. It is also compatible with the absorption spectrum of the aromatic form of C_{24}^+ calculated via TD-DFT.

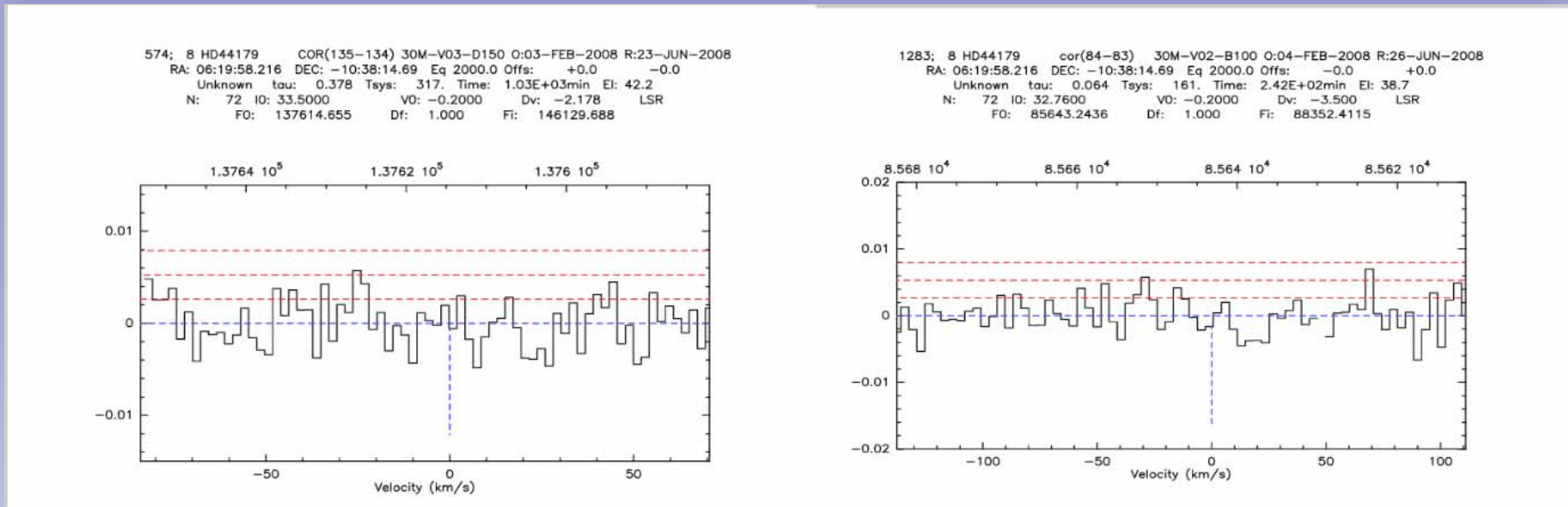
Result: we cannot rule this one out (yet?)

Back to PAH rotation: radio spectra?



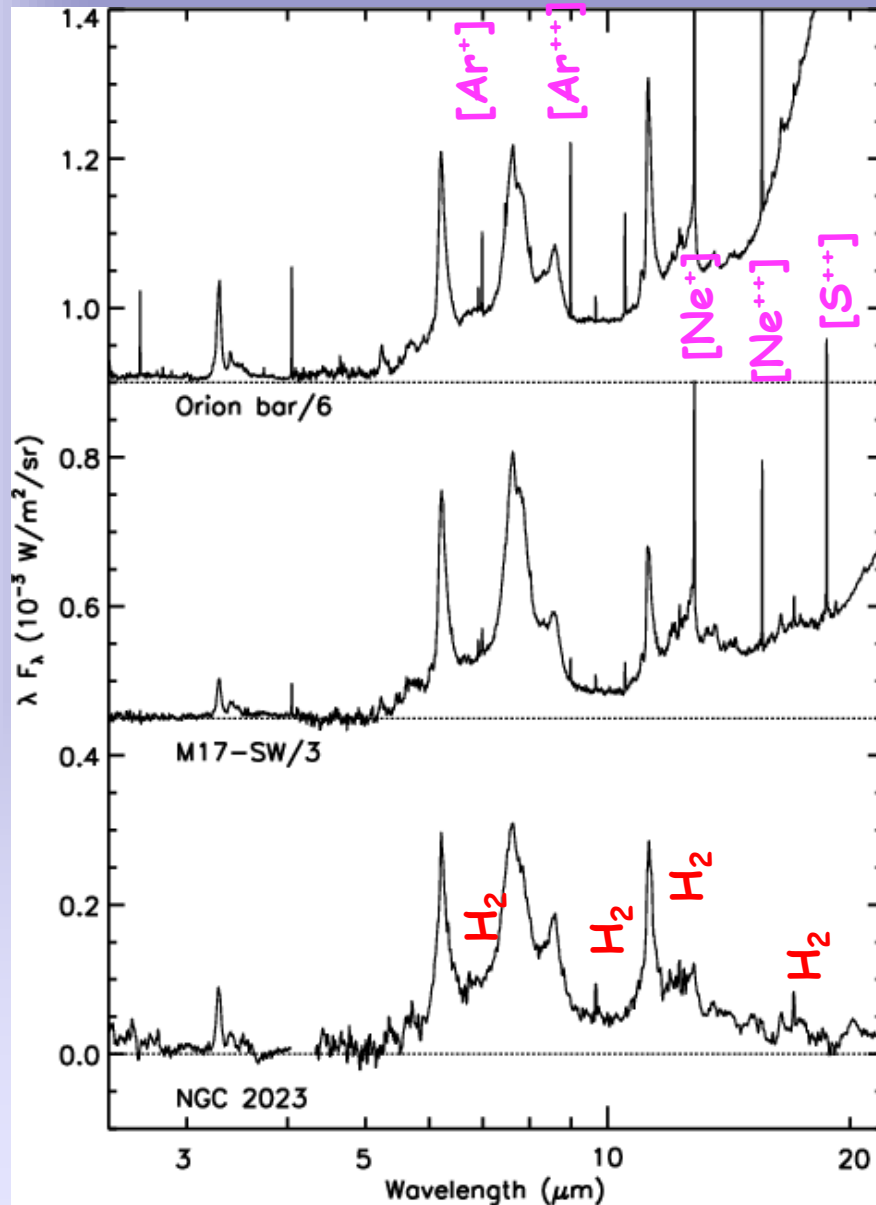
Most “normal” PAHs have either no or a very small permanent electric dipole moment, in the order of ~ 0.1 Debye. An exception to this is corannulene ($C_{20}H_{10}$), with a moment of 2.6 Debye. Its pure rotational spectrum was measured in the laboratory up to $J \sim 100$, yielding very accurate rotational constants. $C_{20}H_{10}$ appears to behave as a perfect symmetric top, with no hint of splitting in its K stacks, which therefore superimpose producing very sharp and intense lines. This makes this molecule, which is also a chemical progenitor of the “buckyball” C_{60} , an ideal candidate for the detection of PAH through radio observations

Back to PAH rotation: radio spectra?



We carried out observations of the Red Rectangle at the IRAM 30m telescope in Pico Veleta, looking for the 135→134 (137.615 GHz) and 84→83 (85.643 GHz) transitions of $C_{20}H_{10}$. In total, we used roughly 1500 minutes on source. Prominent CO 2→1 and lines of several small hydrocarbon were observed, from the dense circumbinary disk, ensuring proper calibration and pointing. Since we could not detect the corannulene lines, we infer that the fraction of C atoms contained in corannulene, versus the number of C atoms contained in all PAHs contributing to the AIB emission in the Red Rectangle, is $<10^{-6}$

From rotation back to vibrations...



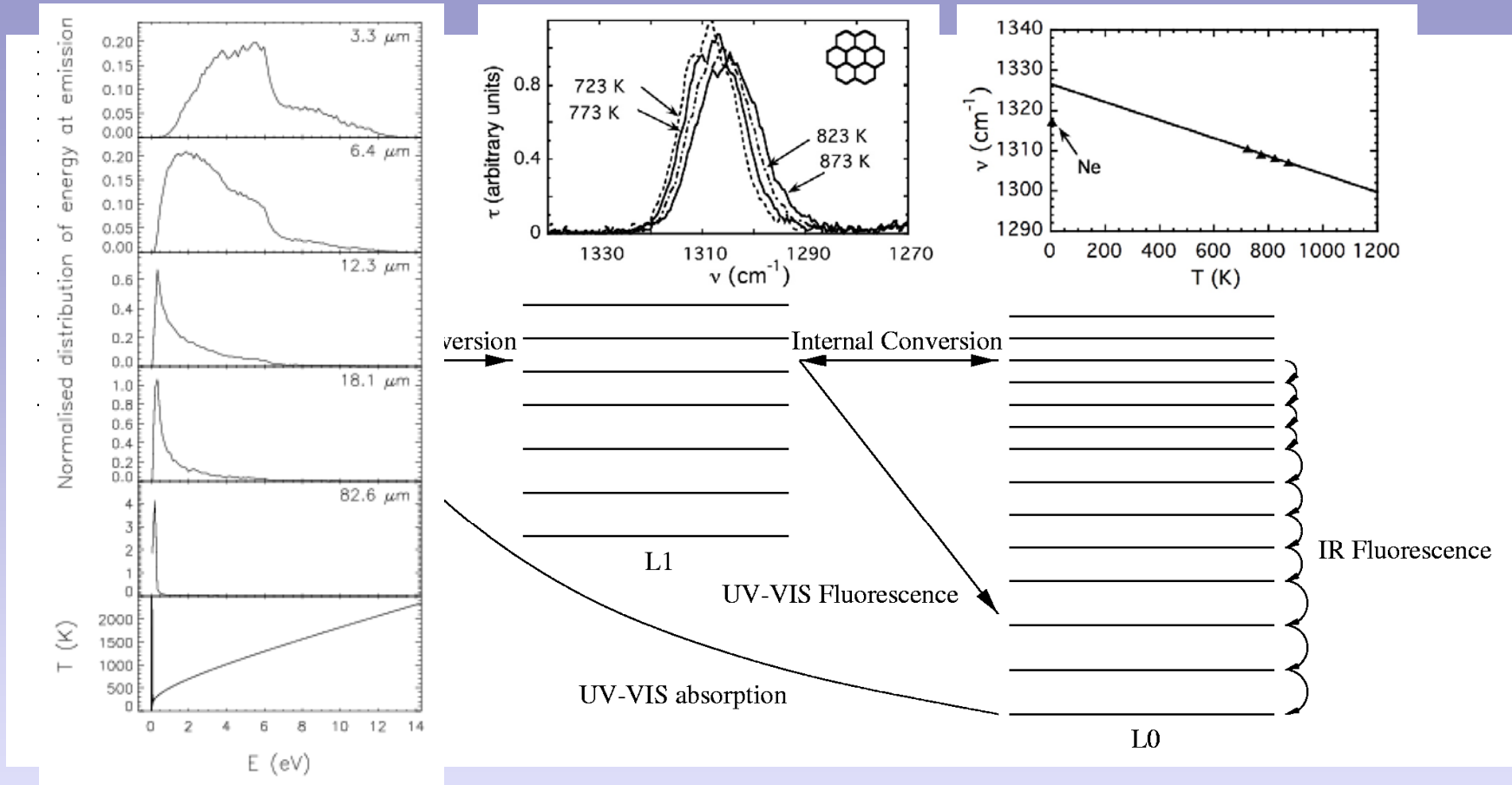
While in recent times aromatic infrared bands are increasingly being called “PAH bands”, there are two embarrassingly big problems with this, namely:

- No single PAH identified yet in space
- No way to simultaneously match the aromatic spectrum in band positions, profiles and (relative) intensities with any given mixture of the available spectra (many hundreds in the NASA Ames database!)

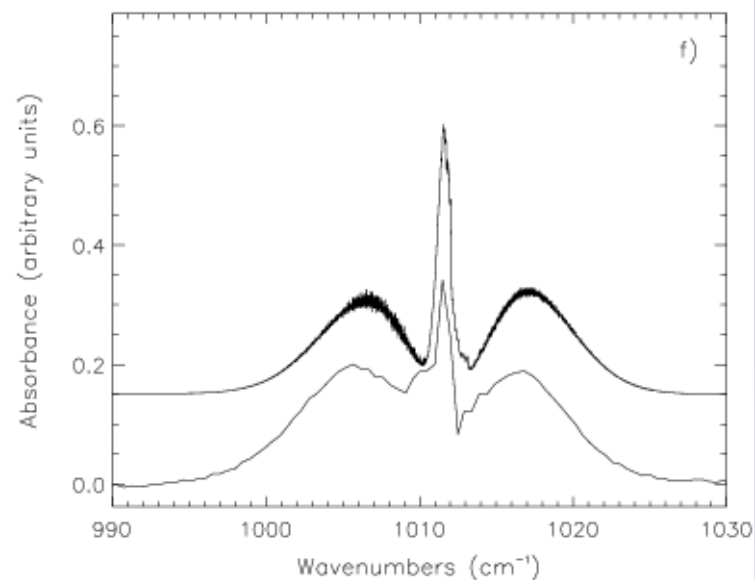
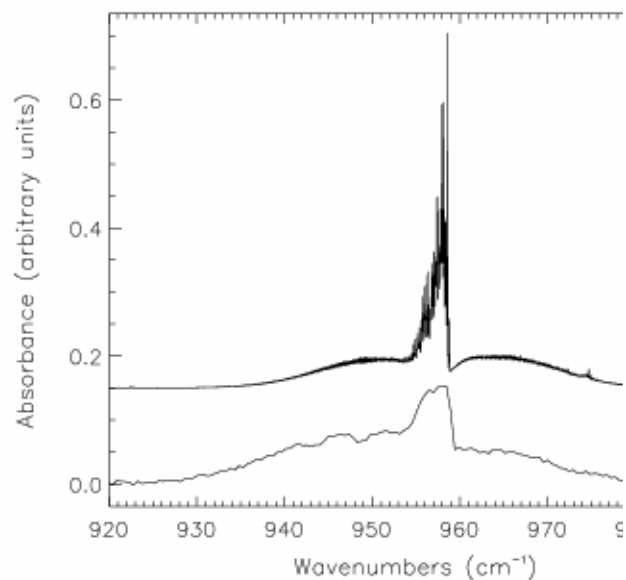
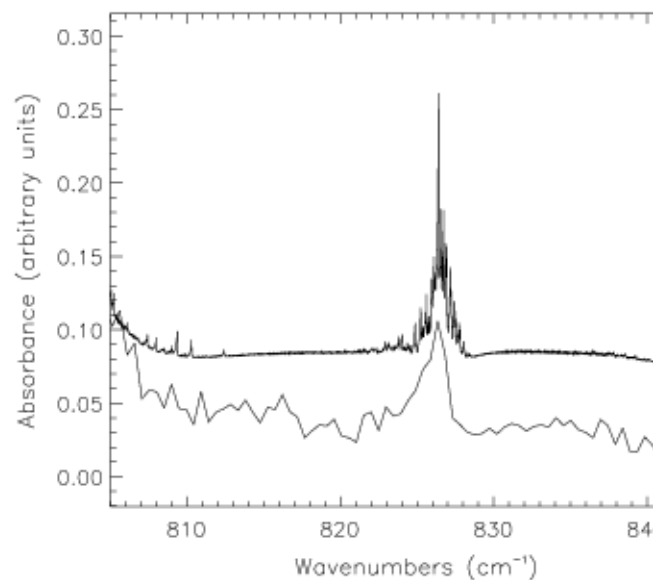
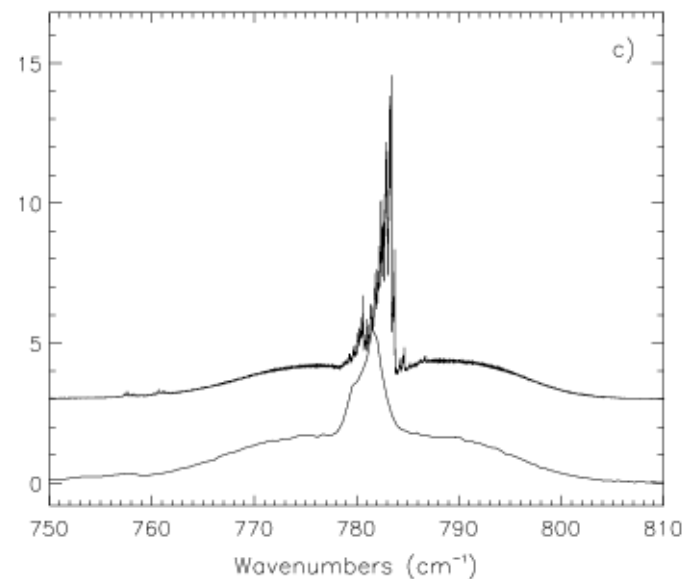
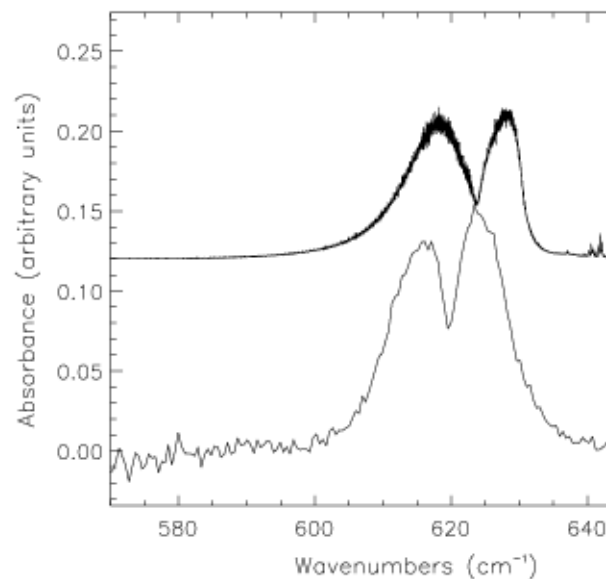
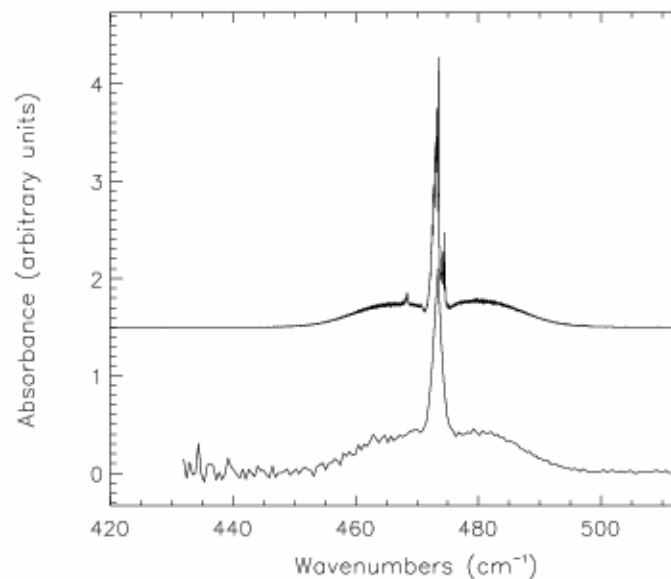
The likely reasons are

- Some important ingredient is still missing from the database
- Some important molecular physics has yet to be properly included in PAH emission models

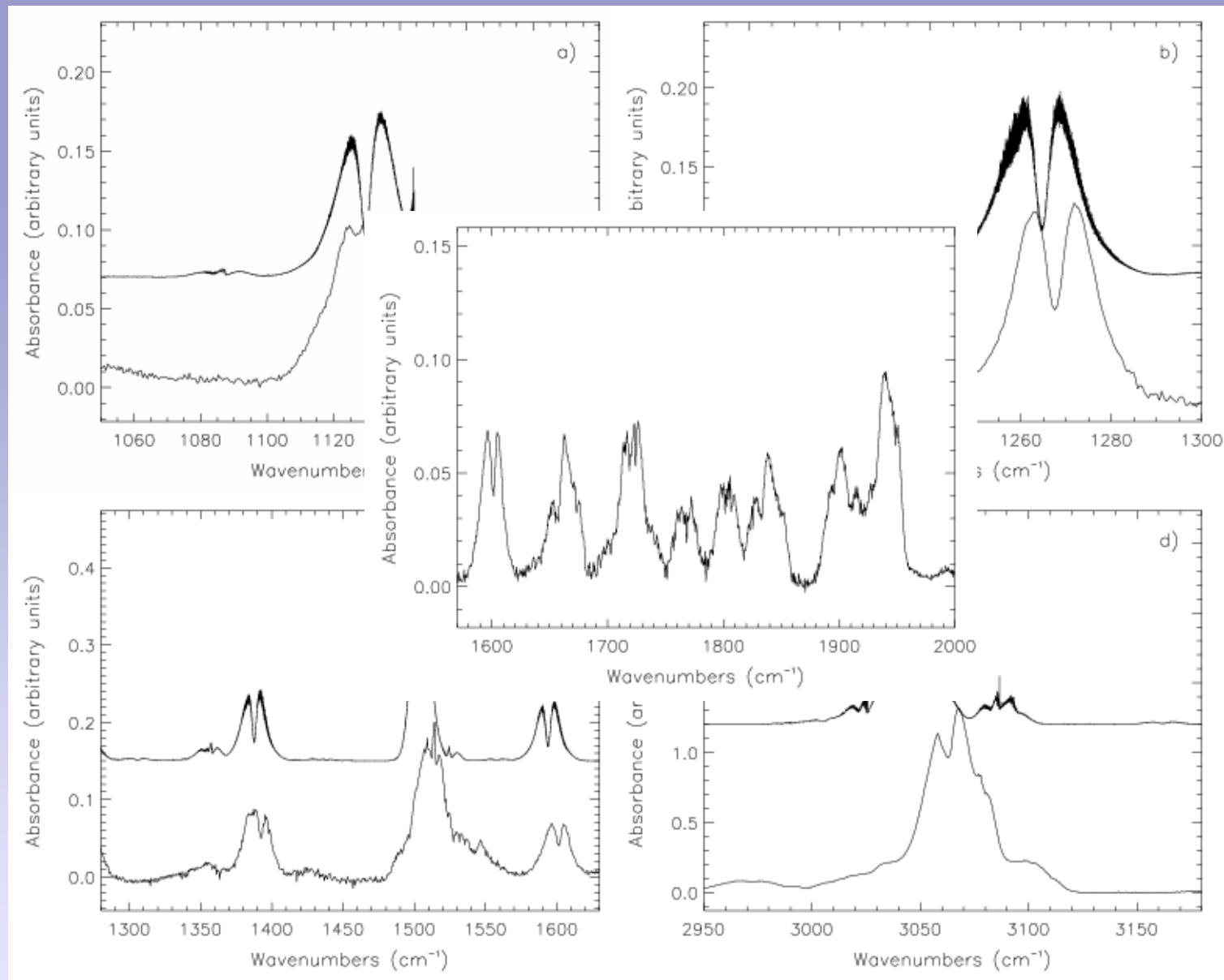
From rotation back to vibrations...



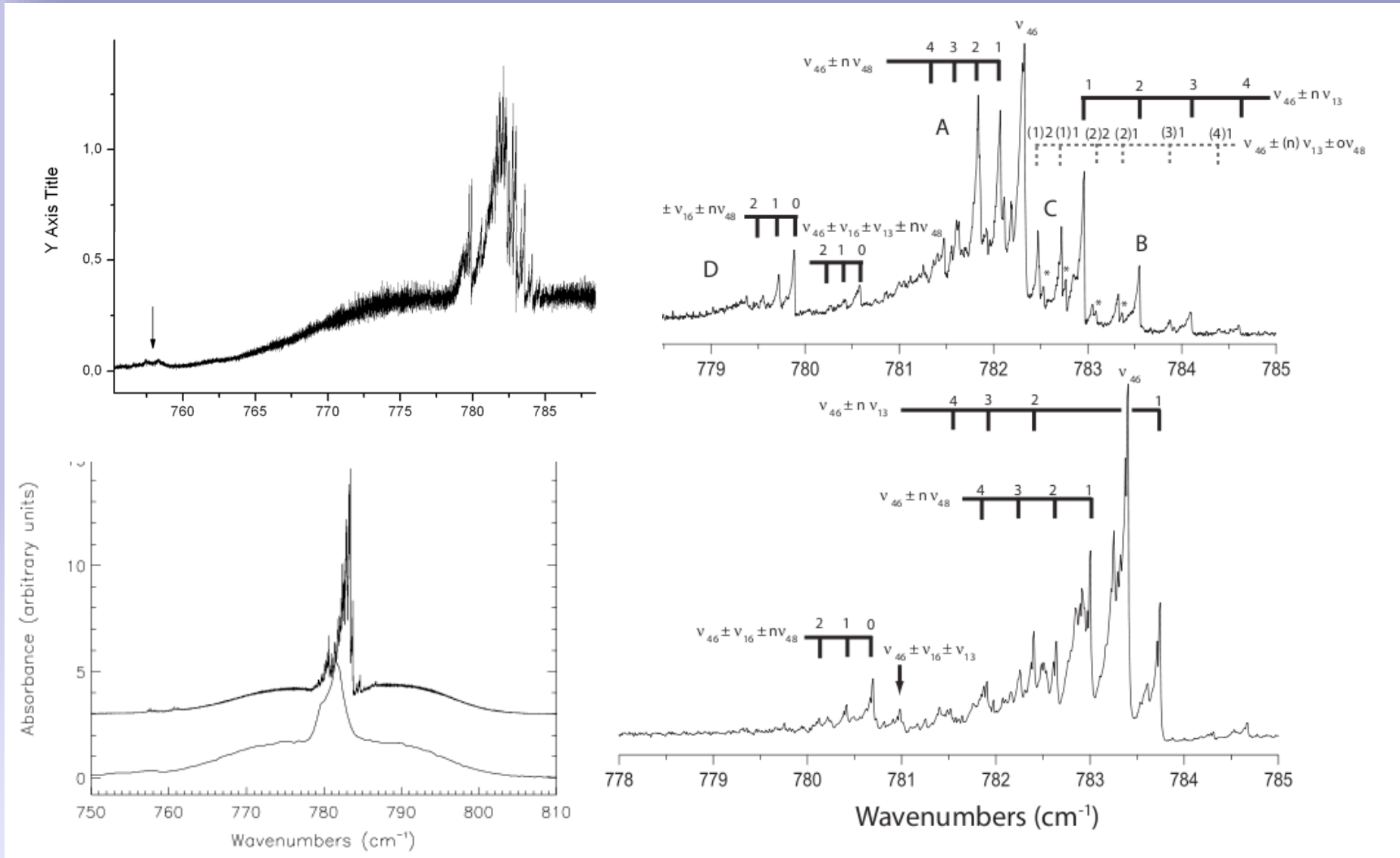
We need to include anharmonicity



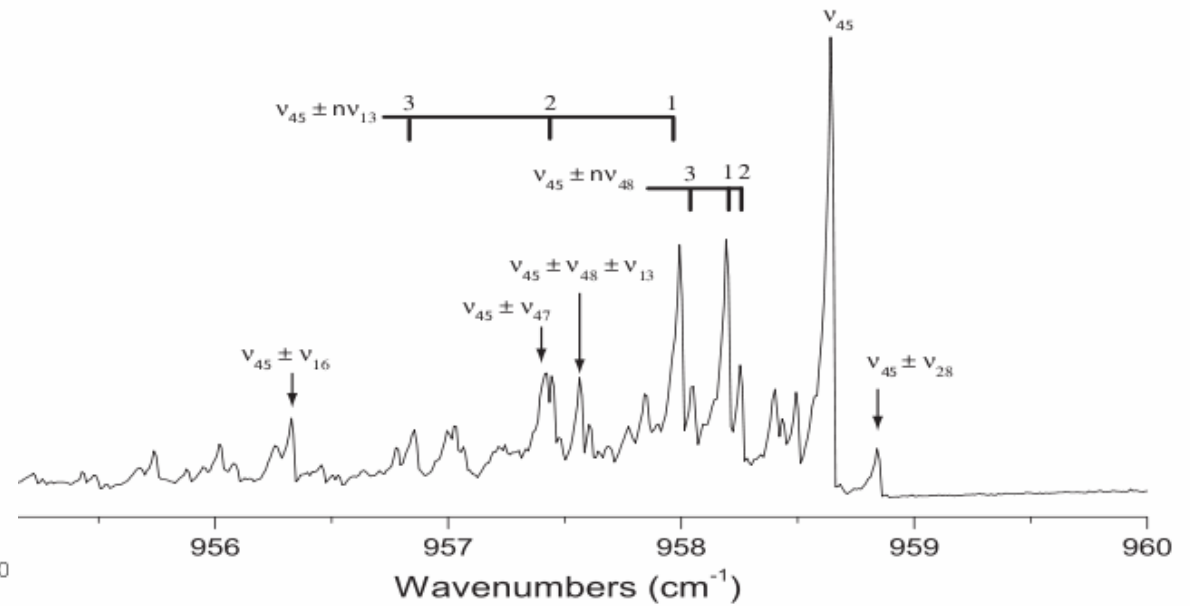
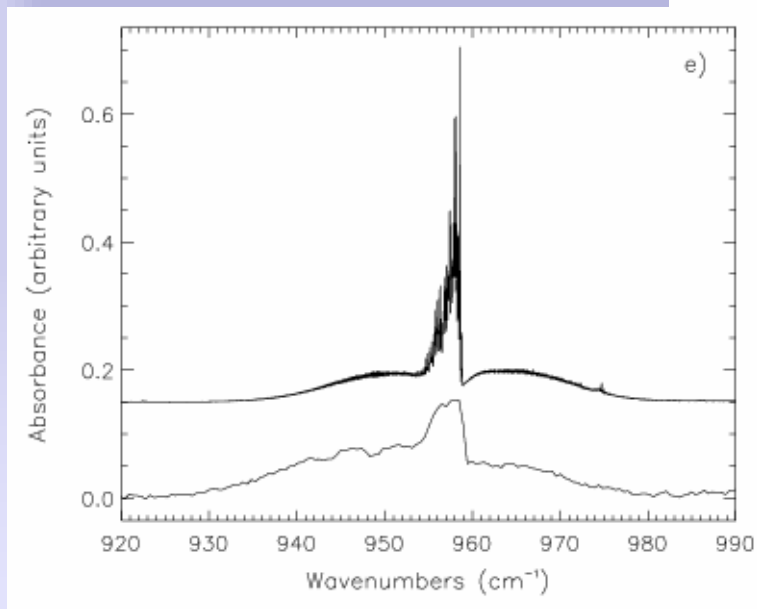
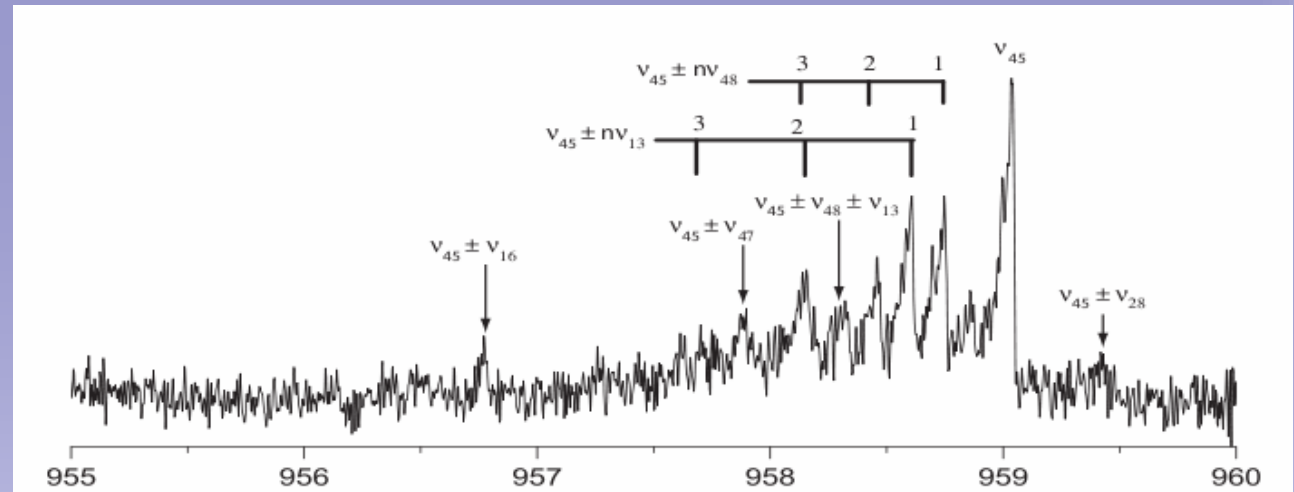
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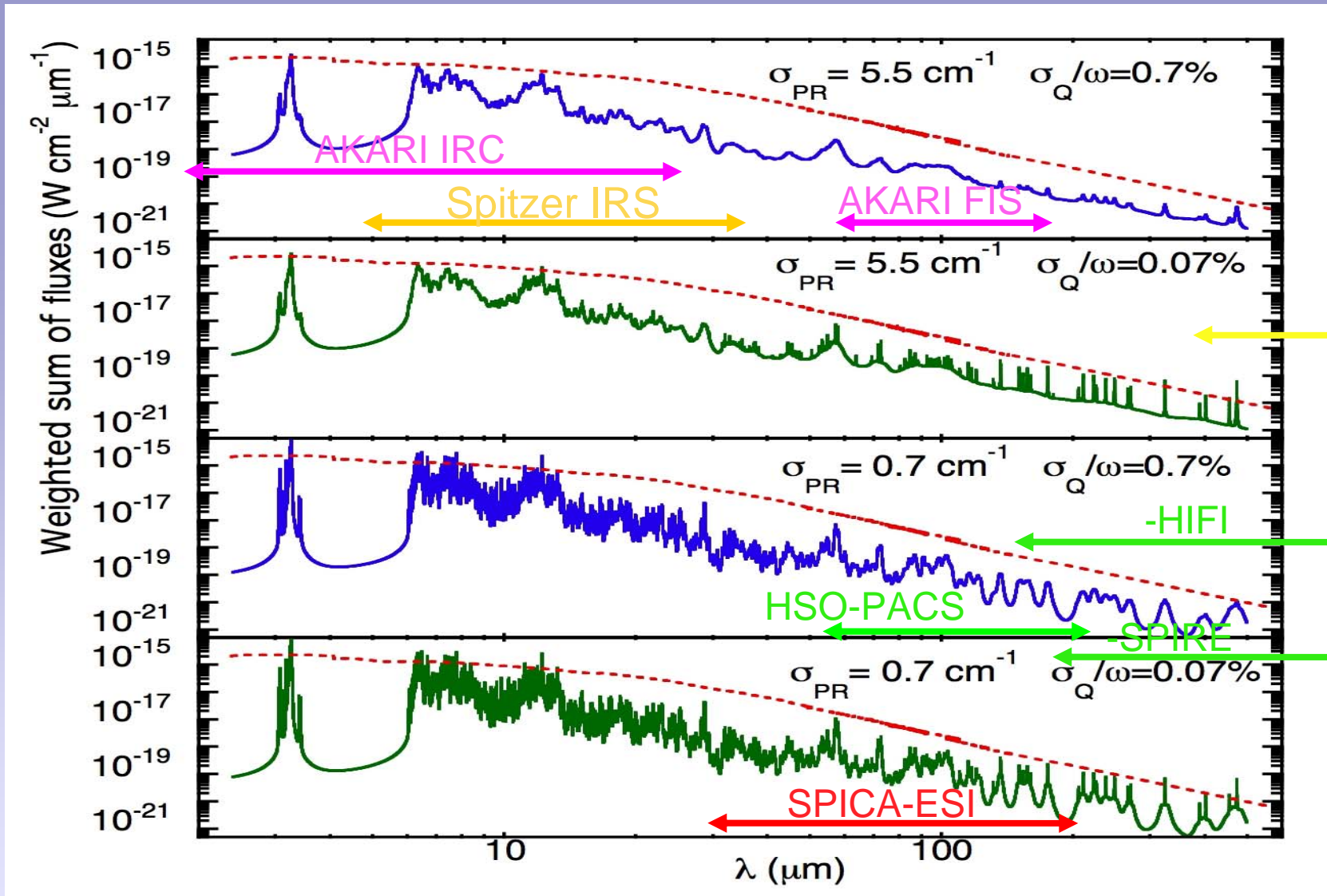
We need to include anharmonicity



We need to include anharmonicity



Keep your fingers crossed for Herschel



Thanks to:

Osservatorio di Cagliari

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