



Étude des vibrations intermoléculaires et intramoléculaires de l'indène et de ses analogues hétérocyclés

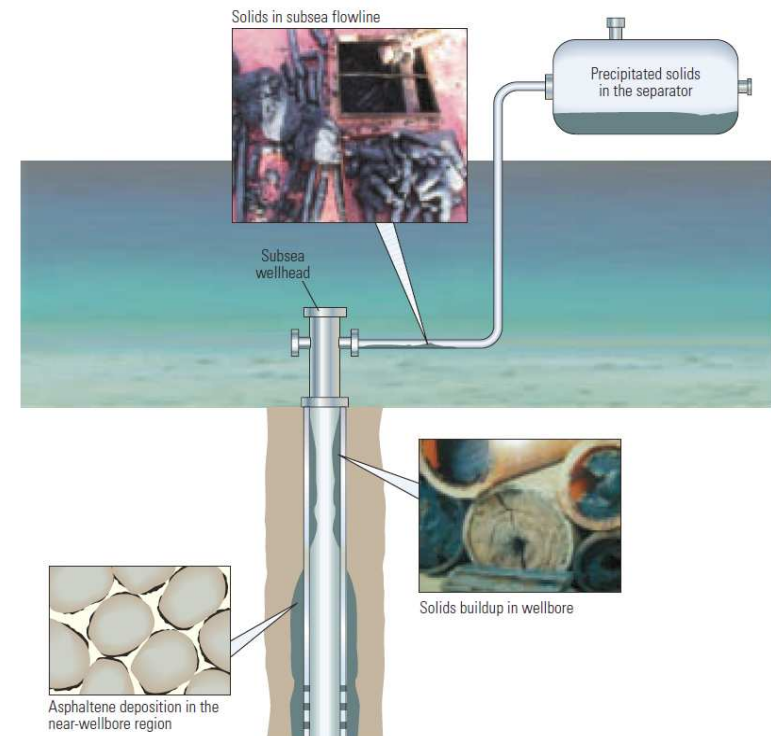
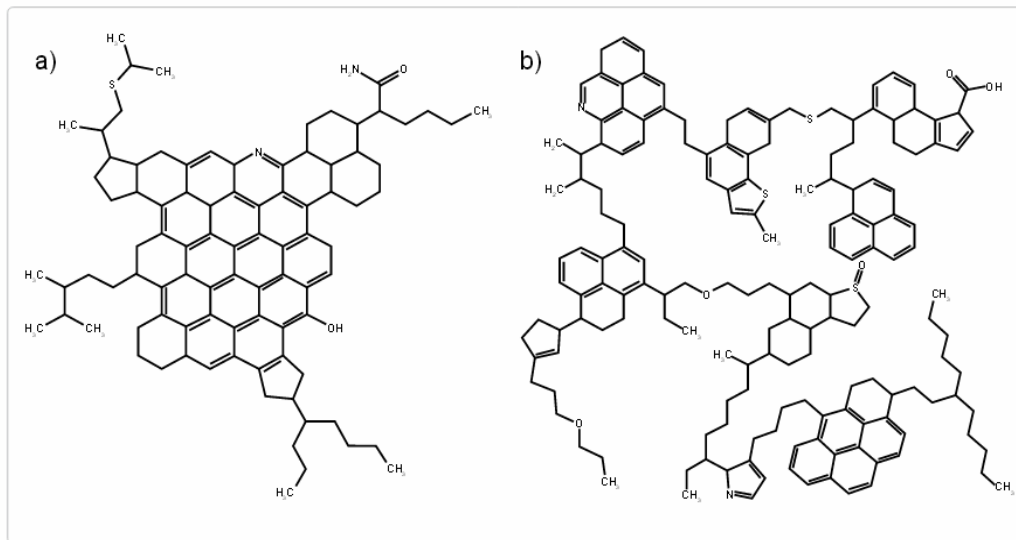
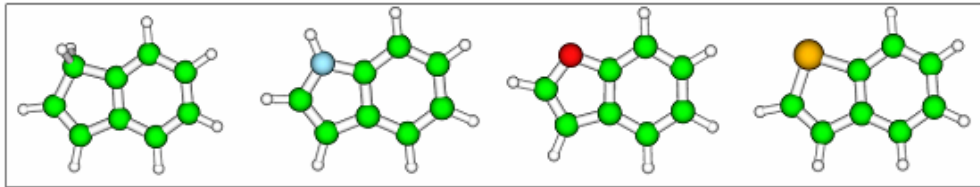
Patricia Guevara, Didier Bégué, John M. Shaw,
K.H. Michaelian, Isabelle Baraille



Natural Resources Canada

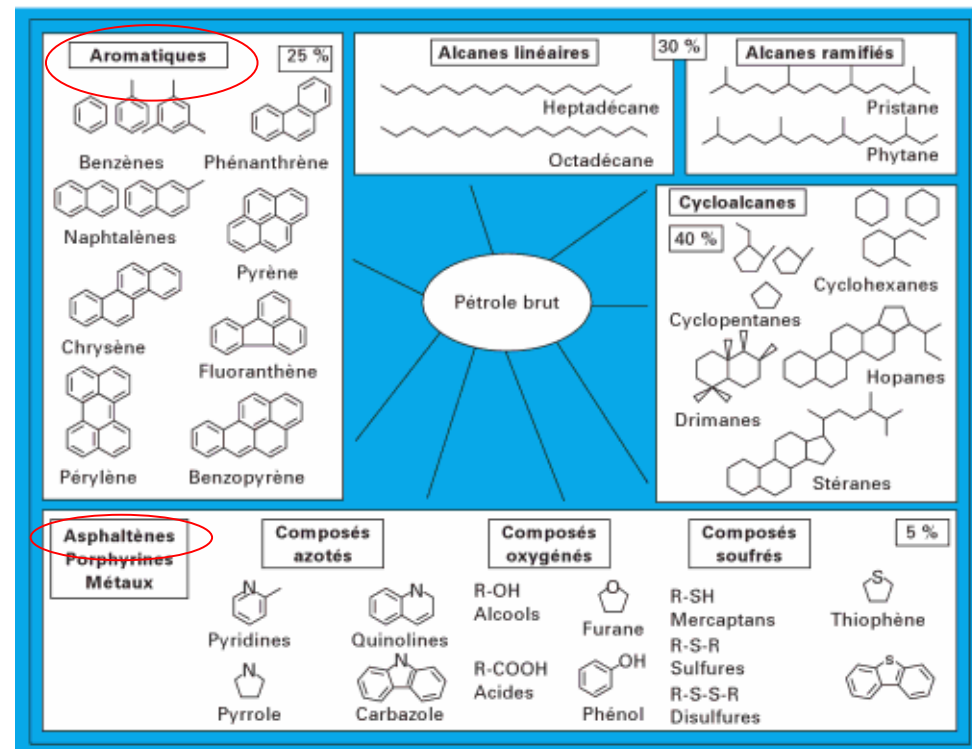
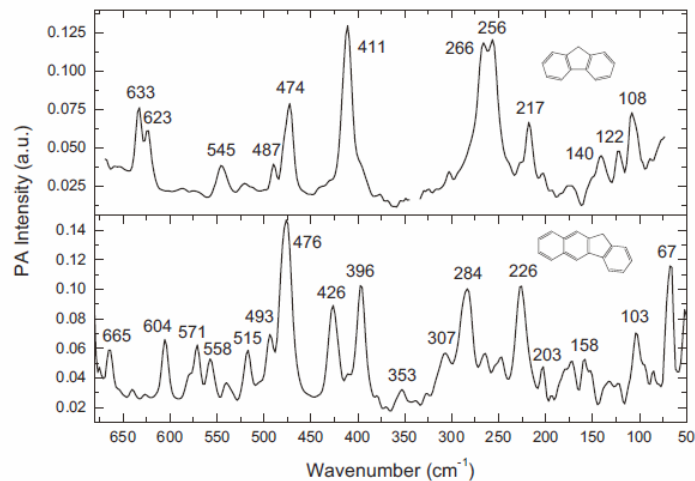


Motivation



Tukhvatullina A, Barskaya E, Kouryakov V, Ganeeva Y, Yusupova T and Romanov G. Supramolecular Structures of Oil Systems as the Key to Regulation of Oil Behavior. *Petroleum & Environmental Biotechnology*.(2013) 4,1-8.

Bibliothèque de spectres



Michaelian, K, Oladepo, S, Shaw, J, Liuc, X, Bégué, D, Baraille, I. Raman and photoacoustic infrared spectra of fluorene derivatives: Experiment and calculations. *Vibrational Spectroscopy* 74 (2014) 33–46.

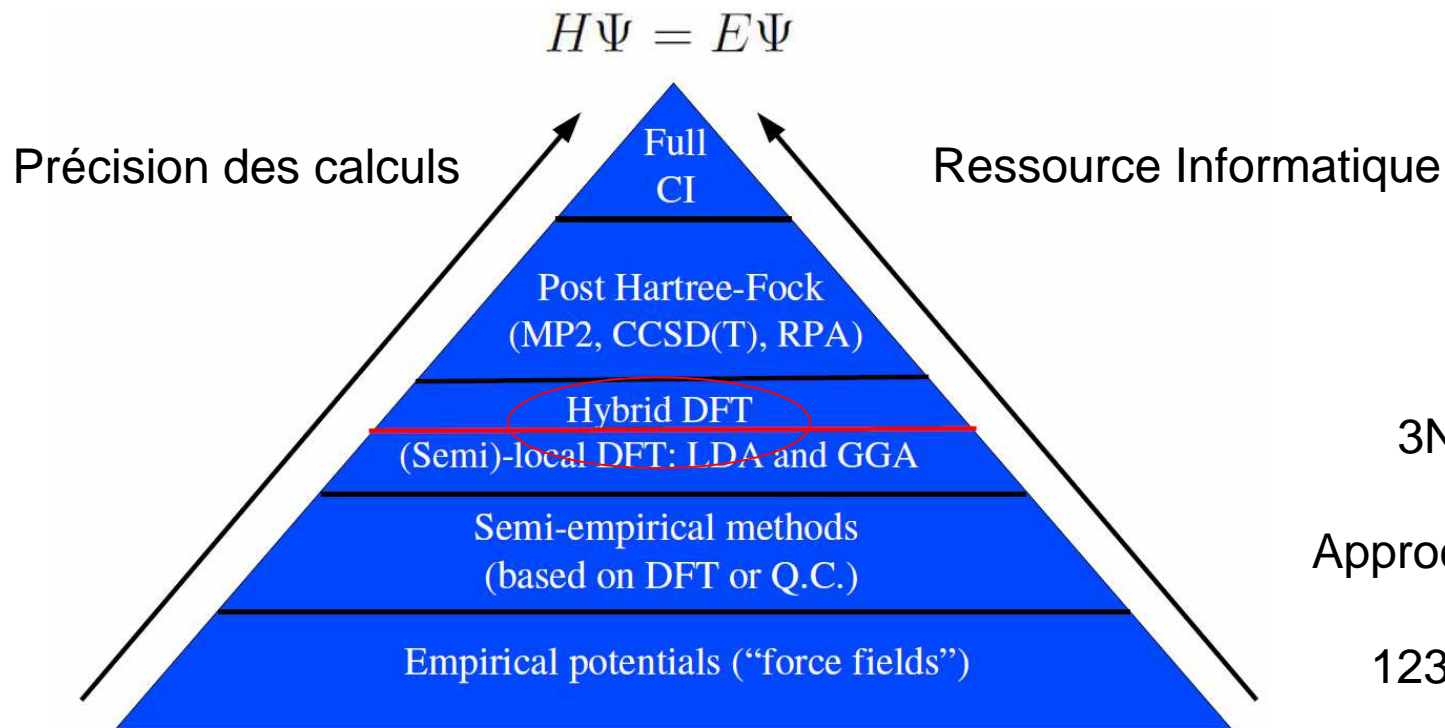
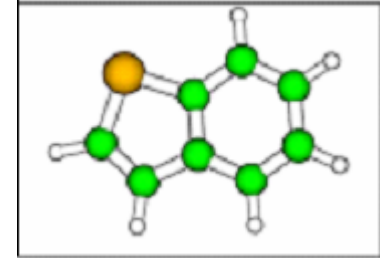
Tocqué, E; Travers, C. *Pétrole*. Editions T.I. (2006) 520



Plan du travail

- Etudier les vibrations moléculaire IR et Raman des différents motifs.
- Etudier les interactions intermoléculaire des dimères et leurs spectres IR Raman.
- Etudier les systèmes périodiques: état solide

Méthodologies adaptées



15 Atomes
 $3N - 6 = 39$ SEP

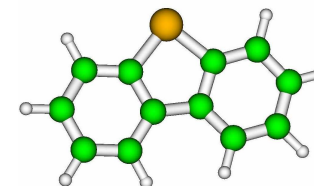
Approche Anharmonique

123410 coefficients

246819 calcul ab initio

28 ans

Approche Anharmonique



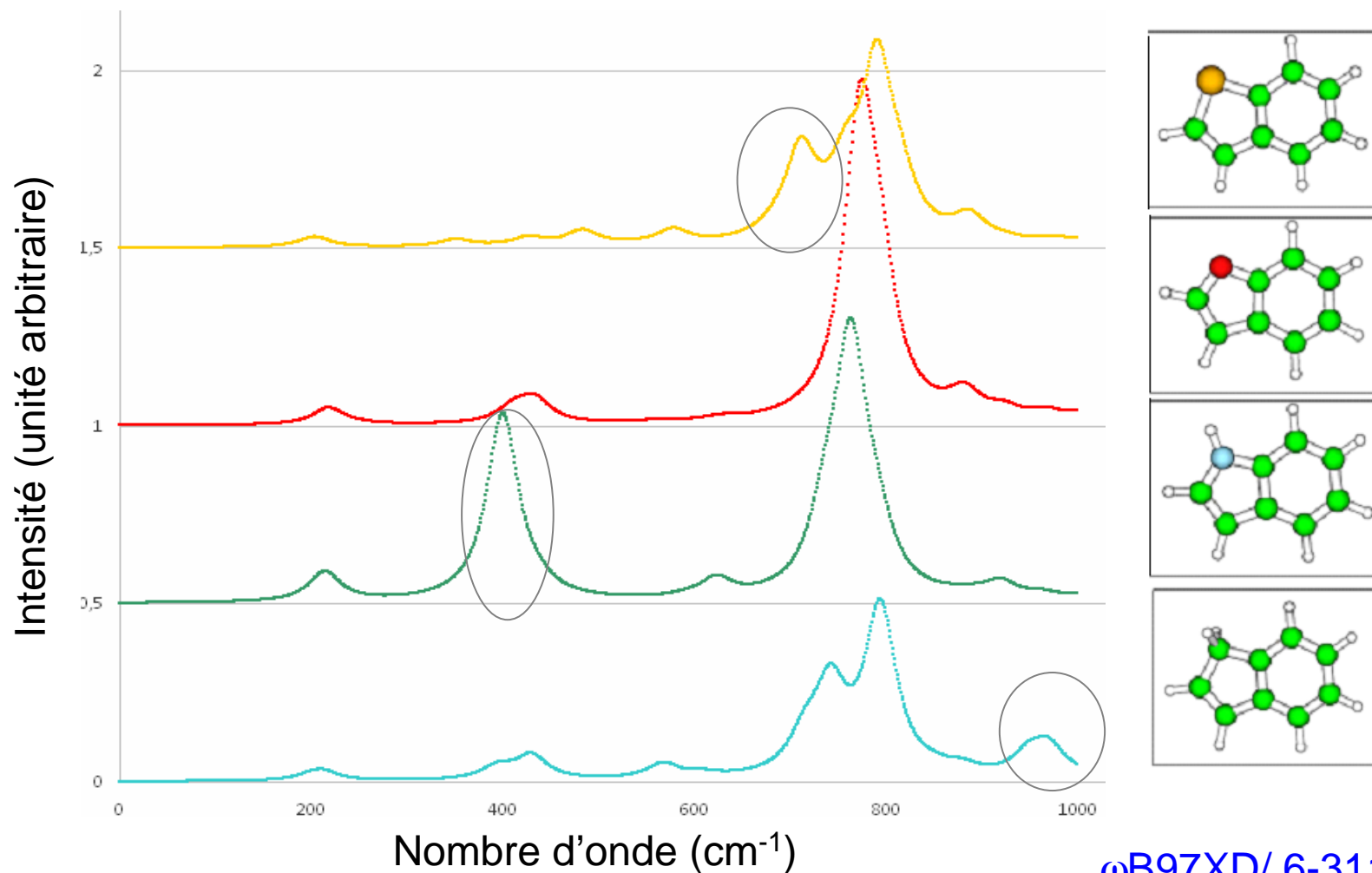
- Le programme P_Anhar.v2.0
- Les corrections d'anharmonicités électrique et mécanique

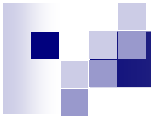
Dibenzothiophene

| Observed | | Mode (Symmetry) | Predicted | | |
|----------|----------|------------------------------------|-------------|------------|-------------|
| Raman | Infrared | | Harmonic | Anharmonic | Combination |
| 138 w | 135 m | $\nu_1 (b_1)$ | 102 (1.54) | 137 (1.66) | |
| 171 w | | $\nu_2 (a_2)$ | 135 (0.00) | 172 (0.00) | |
| 217 m | 213 m | $\nu_3 (a_1)$ | 217 (0.85) | 208 (1.23) | |
| 232 w | 228 m | $\nu_4 (b_1)$ | 221 (1.46) | 223 (1.42) | |
| 282 w | 282 vw | $\nu_5 (a_2)$ | 279 (0.00) | 274 (0.00) | |
| 287 sh | | | | | |
| 410 s | 404 s | $\nu_6 (a_1)$ | 416 (2.83) | 409 (2.80) | |
| 419 m | 419 sh | $\nu_7 (b_2)$ | 428 (0.14) | 425 (0.15) | |
| | 425 s | $\nu_8 (b_1)$ | 433 (7.15) | 425 (5.06) | |
| 437 vw | 436 w | $\nu_9 (a_2)$ | 444 (0.00) | 438 (0.00) | |
| | 460 vw | | | | |
| 496 w | 497 s | $\nu_{10} (a_1)/$ | 505(0.28)/ | 499(0.22)/ | |
| | | $\nu_{12} (b_2)$ | 511(1.23)/ | 497 (1.48) | |
| 504 vw | | $\nu_{11} (b_1)$ | 510(2.74) | 504(1.18) | |
| | 565 w | $\nu_2 + \nu_8 (b_2)$ | 567 | 562 (0.12) | 135+433 |
| | | $\nu_{13} (a_2)$ | 580 (0.00) | 568 (0.00) | |
| | 615 m | $\nu_{14} (b_2)$ | 635 (5.09) | 627 (4.62) | |
| | 667 w | $\nu_{17} (b_1)/ \nu_3 + \nu_{10}$ | 730 (0.82)/ | 675/666 | 217+505 |
| | | (b_2) | 728 (0.15) | | |
| 703 s | 704 vs | $\nu_{15} (b_2)$ | 724 (6.53) | 713 | |

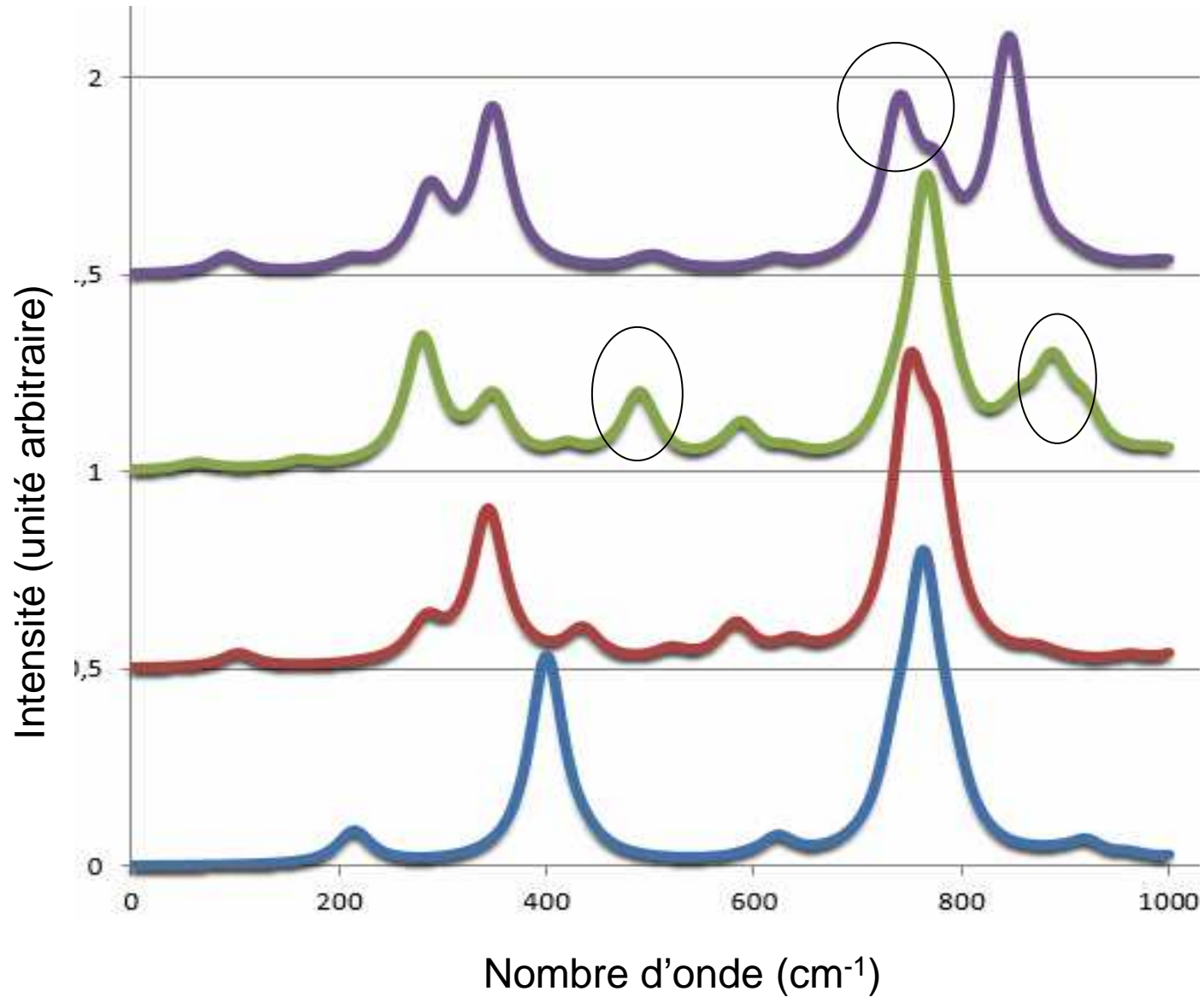
Résultats sur les molécules isolées

Theoretical spectrum Infrarouge d'Indene et ses analogues hétérocycles



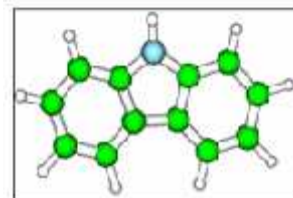
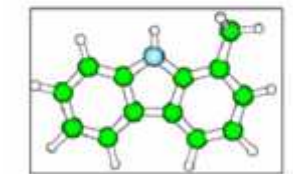
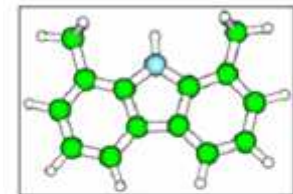
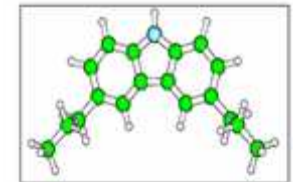
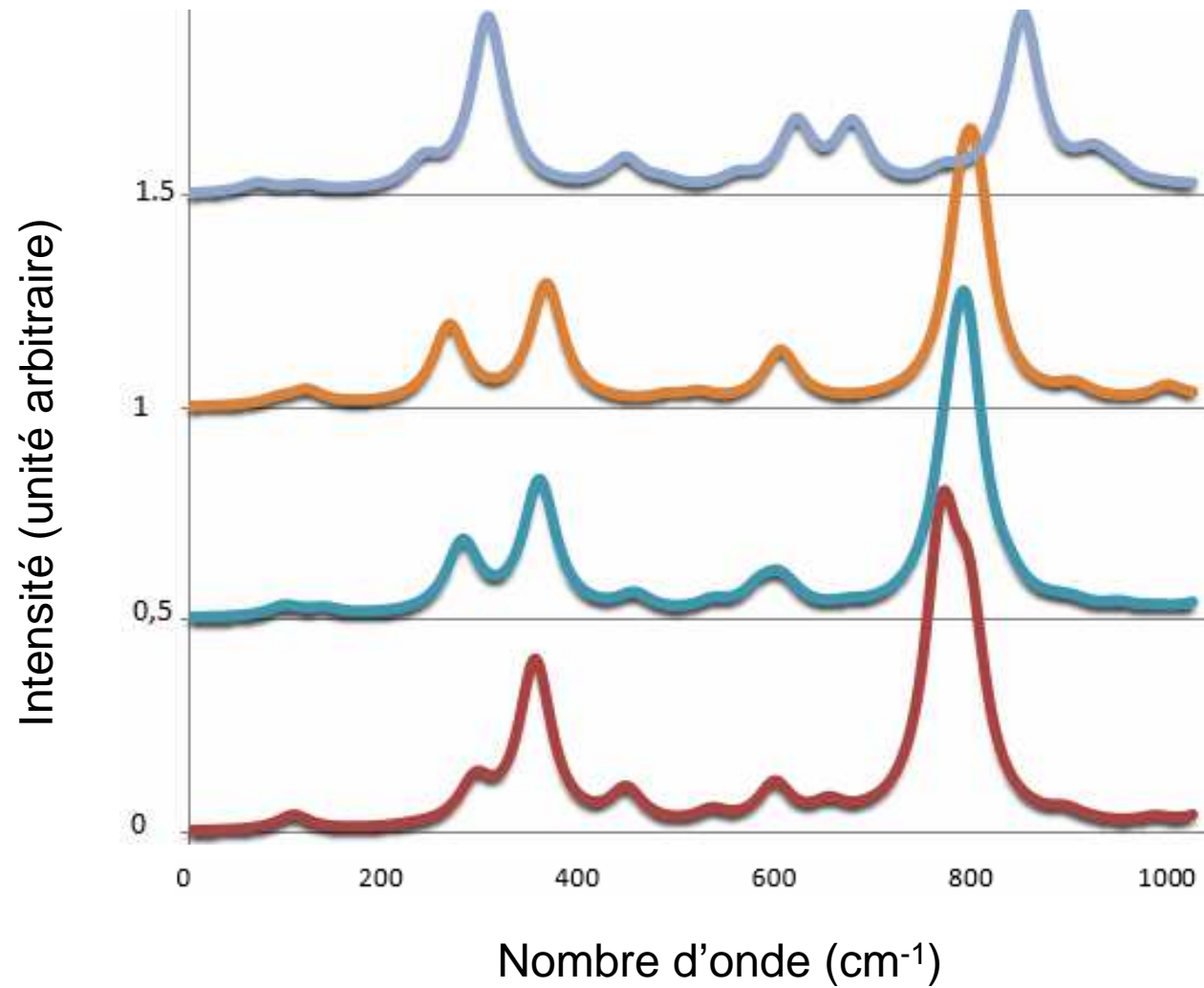


Theoretical spectra Infrarouge





Theoretical spectra Infrarouge



SAPT

(Théorie des perturbations à Symétrie-Adapté pour interactions intermoléculaires)

$$H = F + V + W$$

$$F = F_A + F_B$$

$$W = W_A + W_B$$

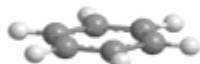
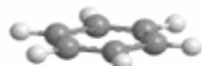
$$E_{int} = \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} (E_{RS}^{(nj)} + E_{exch}^{(nj)})$$

$E_{RS}^{(nj)}$ Corrections à partir de la théorie des perturbations Rayleigh-Schrödinger

$$E_{RS}^{(2j)} = E_{ind}^{(2j)} + E_{disp}^{(2j)} \quad \text{et} \quad E_{exch}^{(2j)} = E_{exch-ind}^{(2j)} + E_{exch-disp}^{(2j)}$$

DFT-SAPT

DFT-SAPT



Sandwich (S)

Parallel-displaced (PD)

Sandwich

Parallel displaced

E_{int}
(kcal/mol)

Distance (Å)

E_{int}
(kcal/mol)

Distance
(Å)

**DFT – SAPT (PBE0)
aug-cc-pVTZ**

-1,47

3,90

-2,35

3,50

CCSD(T)/aug-cc-pVTZ [1]

-1,59

3,92

-2,54

3,53

MP2/ 6-31++G [1]**

-2,02

3,90

-2,24

3,60

CCSD(T)/aug-cc-pVDZ [2]

-1,21

3,90

-2,00

3,50

Krause et al, $D_0 = 1.6 \pm 0.2$ kcal/mol; Grover et al 2.4 ± 0.4 kcal/mol [4]

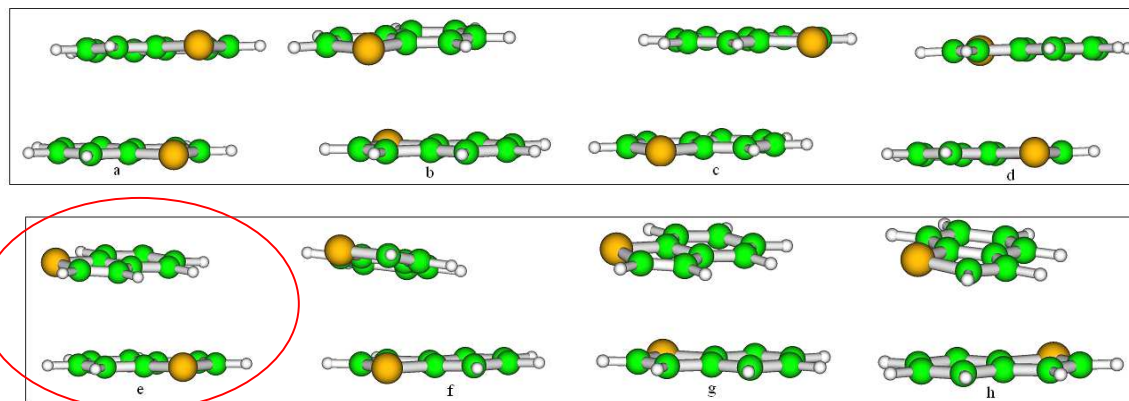
[1] Janowski, T and Pulay, P. Chemical Physics Letters 447 (2007) 27–32

[2] Hobza, P. Selzle, H and Schlag, J. E. Phys. Chem. 1996, 100, 18790 – 18794.

[3] Krause, H., Ernstberger, B., Neusser, C.D. J. Am. Chem. Soc. 2002, 124(36), 10887.

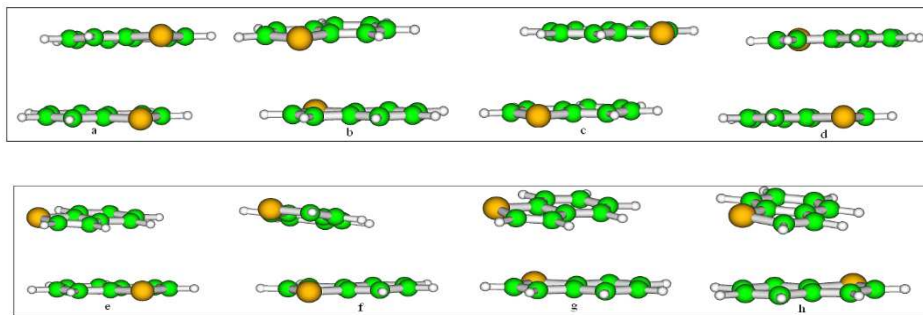
[4] Grover, J.R., Walters, E.A., Hui, E.T. J Phys. Chem. 1987, 91(12), 3233

DFT-SAPT



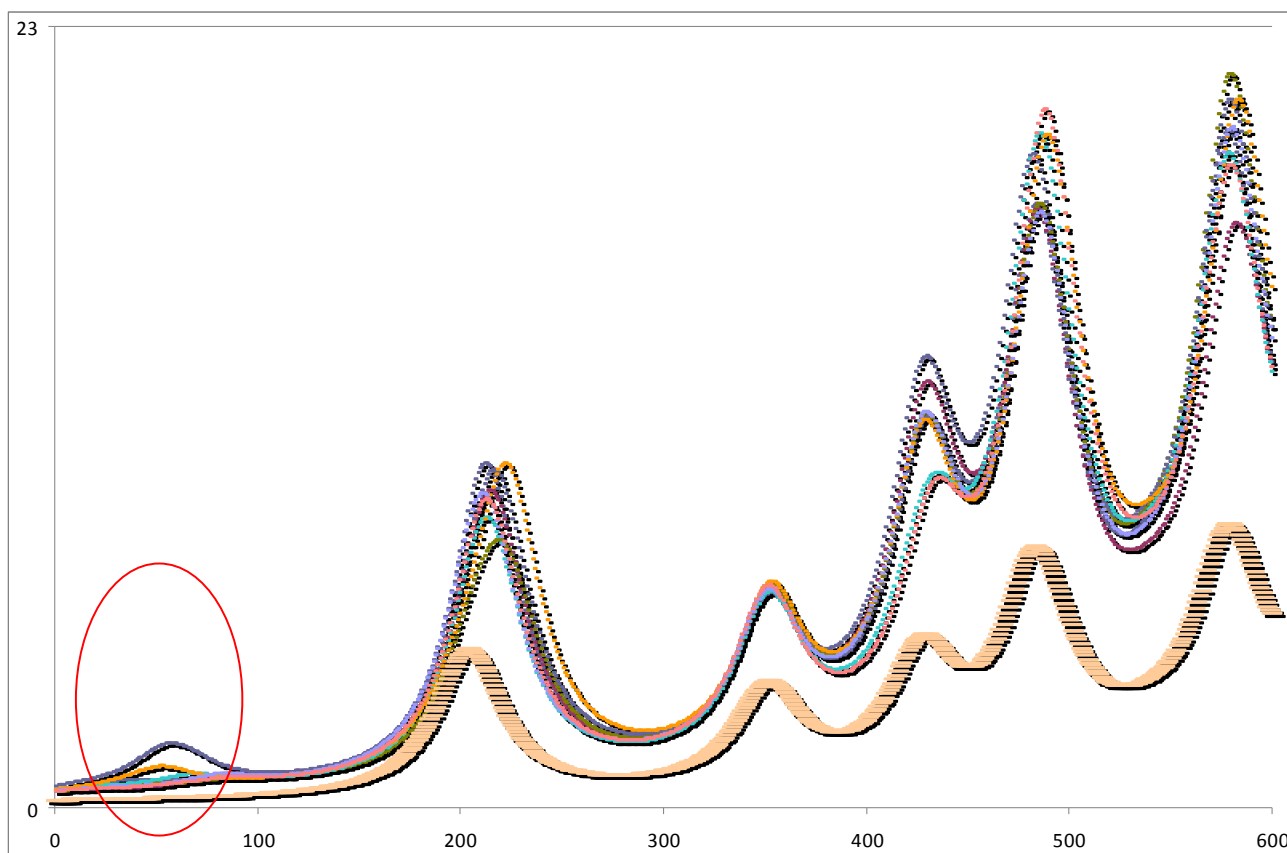
Énergie d'interaction (kcal/mol)

| | A | B | C | D | E | F | G | H |
|----------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| ω B97XD/ 6-311++G** | -6,41 | -7,05 | -6,83 | -7,11 | -7,23 | -7,01 | -7,02 | -7,00 |
| DFT – SAPT (PBE0) aug-cc-pVTZ | -5,33 | -5,73 | -5,56 | -5,95 | -5,83 | -5,87 | -5,72 | -5,63 |



Benzothiophene

Intensité (unité arbitraire)



Nombre d'onde (cm⁻¹)

État solide

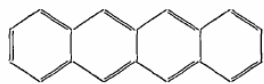
- DFT-D2 méthode de Grimme
- DFT-D3 méthode de Grimme
- Méthode Tkatchenko-Scheffler
- Méthode Self – consistent screening in Tkatchenko – Scheffler

$$E_{DFT-disp} = E_{KS-DFT} + E_{disp}$$

Collaboration avec Dr Sébastien Lebègue



Tetracène

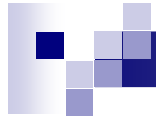


| EXP | V (Å ³) 583.0 | (a) 7.90 | (b) 6.03 | (c) 13.53 | α 100.30 | β 113.20 | γ 86.30 |
|----------|---------------------------|----------|----------|-----------|----------|----------|---------|
| PBE | 1007.16 | 9.25 | 7.21 | 16.62 | 101.36 | 112.14 | 85.67 |
| D2 | 531.41 | 7.54 | 5.96 | 13.28 | 102.10 | 114.33 | 85.20 |
| D3 | 572.96 | 7.92 | 6.00 | 13.38 | 101.21 | 113.26 | 85.89 |
| TS | 554.74 | 7.71 | 5.99 | 13.38 | 101.36 | 113.61 | 85.74 |
| TS + SCS | 563.74 | 7.70 | 6.08 | 13.47 | 100.97 | 114.39 | 85.68 |



Conclusions

- La méthode DFT ω B97XD/6-311++G** permet faire un etude théorique des vibrations intermoleculaire et intramoleculaire d'une serie de hydrocarbure aromatiques susceptible d'être presents dans les molecules des asphaltènes avec une bonne approximation.
- L'étude des dimeres de l'indene et ses analogues hétérocycles montre qui ces molecules sont liés par des interactions type pi-stacking.
- L'etude des modes de vibrations inferieur a 400 cm^{-1} dans spectres infrarouge et Raman permet l'identification de vibrations intermoleculaires.
- Caractérisation des hydrocarbures aromatiques est possible grâce à l'etude des bandes de vibration infrarouge et Raman inferieur a 1000 cm^{-1} , et l'attribution de quelques modes propre des motifs permet leur elucidation dans des systems complexes.



**Merci de votre
attention**