Quantum Chemical Interpretation of Interstellar Infrared Bands

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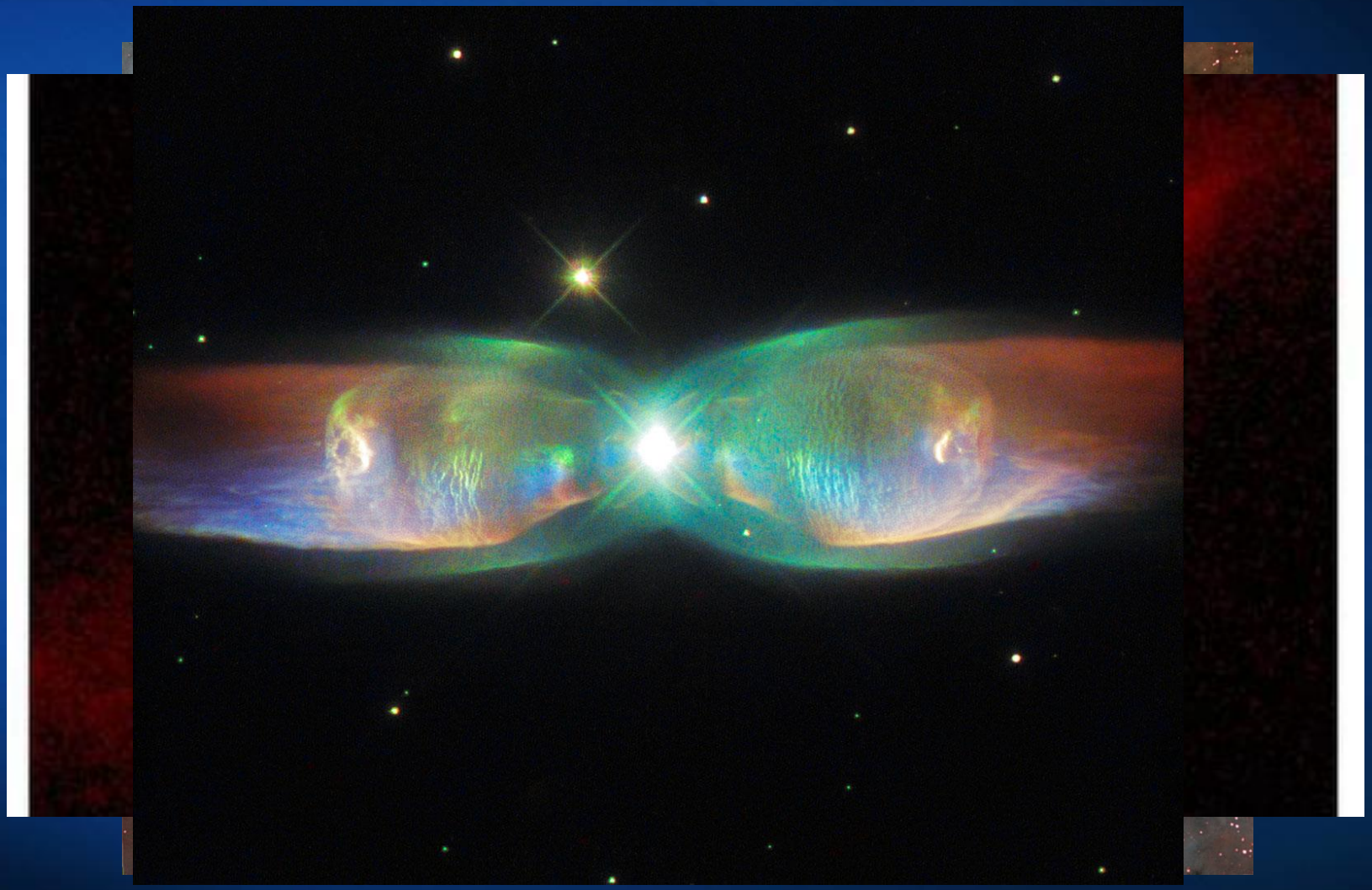
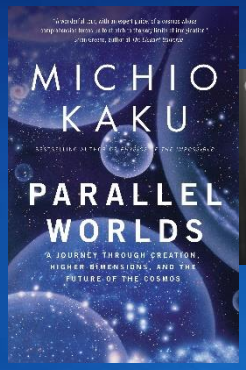
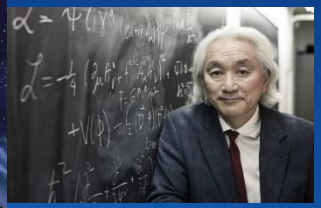
Our Journey



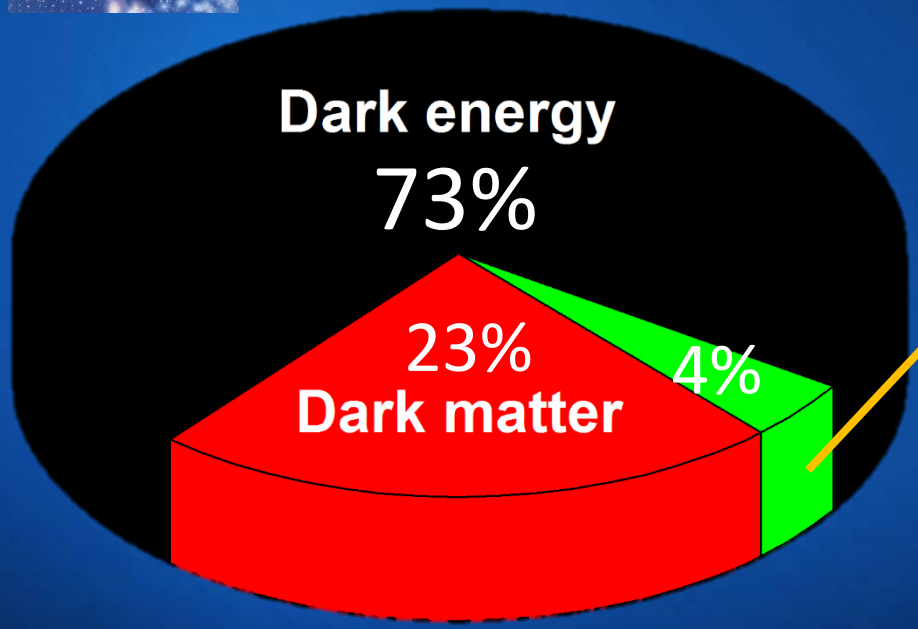
https://www.nasa.gov

Energy and Matter





Usually txt books say that the universe is made of atoms or subatomic particles, well, all those txt books are wrong



Normal mass :
electrons, protons, neutrons

For now lets assume that this tiny piece of Universe is our Universe

Axions, WIMPs, MACHOs

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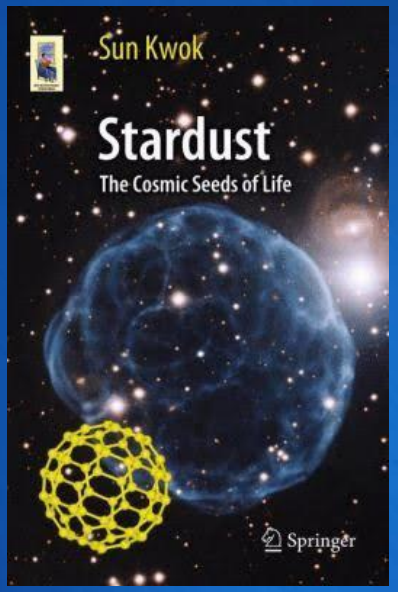
Abundance of Elements in Space



	Mass fraction %			
Elements	**Cosmic**	**Solar**	**Earth**	**Human body**
H	73.9	70.6	0.03	10
He	24	27.5	-	-
O	10.4	5.92	29.7	65
C	4.6	3.03	0.07	18
Ne	1.34	1.55	-	-
Fe	1.09	1.17	31.9	<0.05
N	0.96	1.11	0.003	3
Si	0.65	0.65	16.1	-
Mg	0.58	0.51	15.4	0.05
Si	0.44	0.4	0.64	0.2

Sun Kwok is a leading world authority on the subject of astrochemistry and stellar evolution. He is best known for his theory of the origin of planetary nebulae and death of Sun-like stars.

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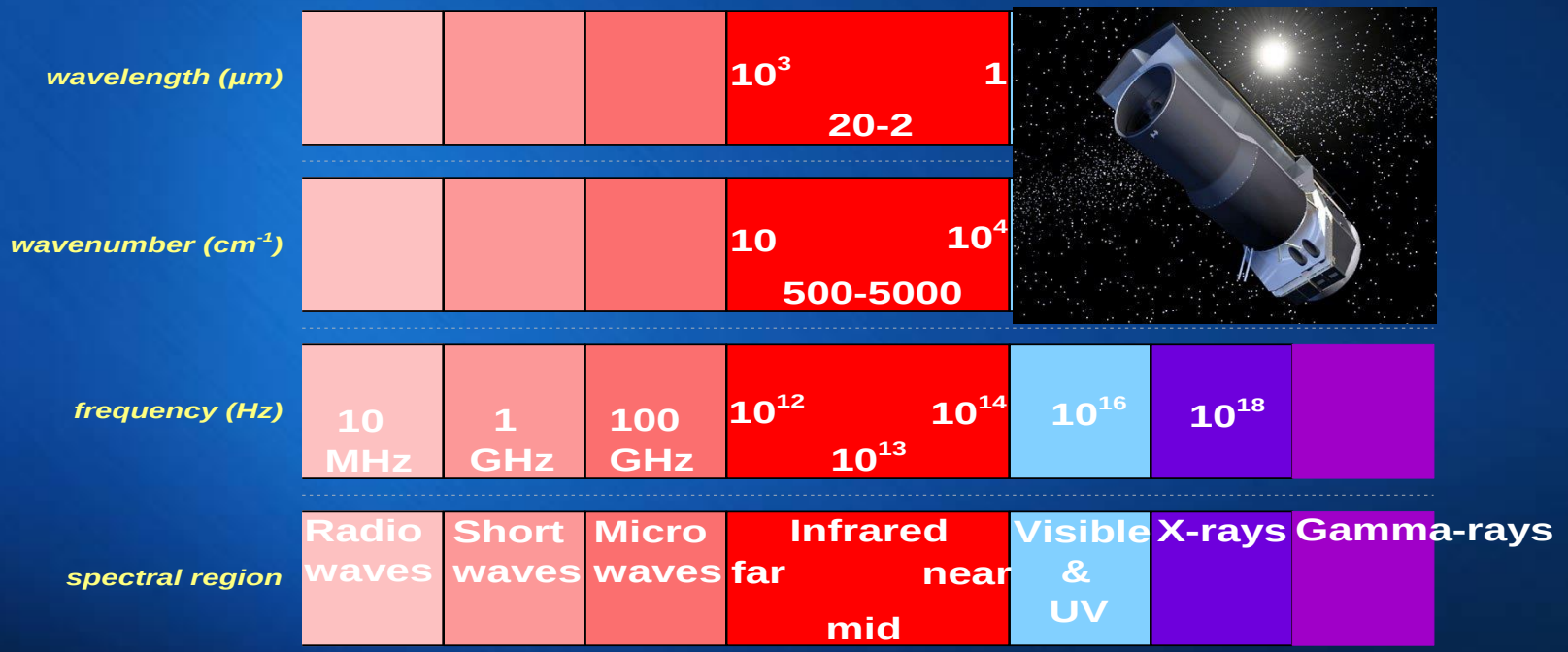
Molecules in Interstellar Space (ISM)

Near 200 molecules have been detected in the interstellar medium or circumstellar shells from 2 to more than 12 atoms like $HC_{11}N$.

Spectroscopy techniques currently applied are: microwave , millimeter wave and infrared

The first molecules detected : CN ,CH and CH+ from their electronic transitions



1-http://www.astro.uni-koeln.de/cdms/molecules

2-Kwok, S., *Complex organics in space from Solar System to distant galaxies.* The Astronomy and Astrophysics Review, 2016. **24**(1): p. 1-27.

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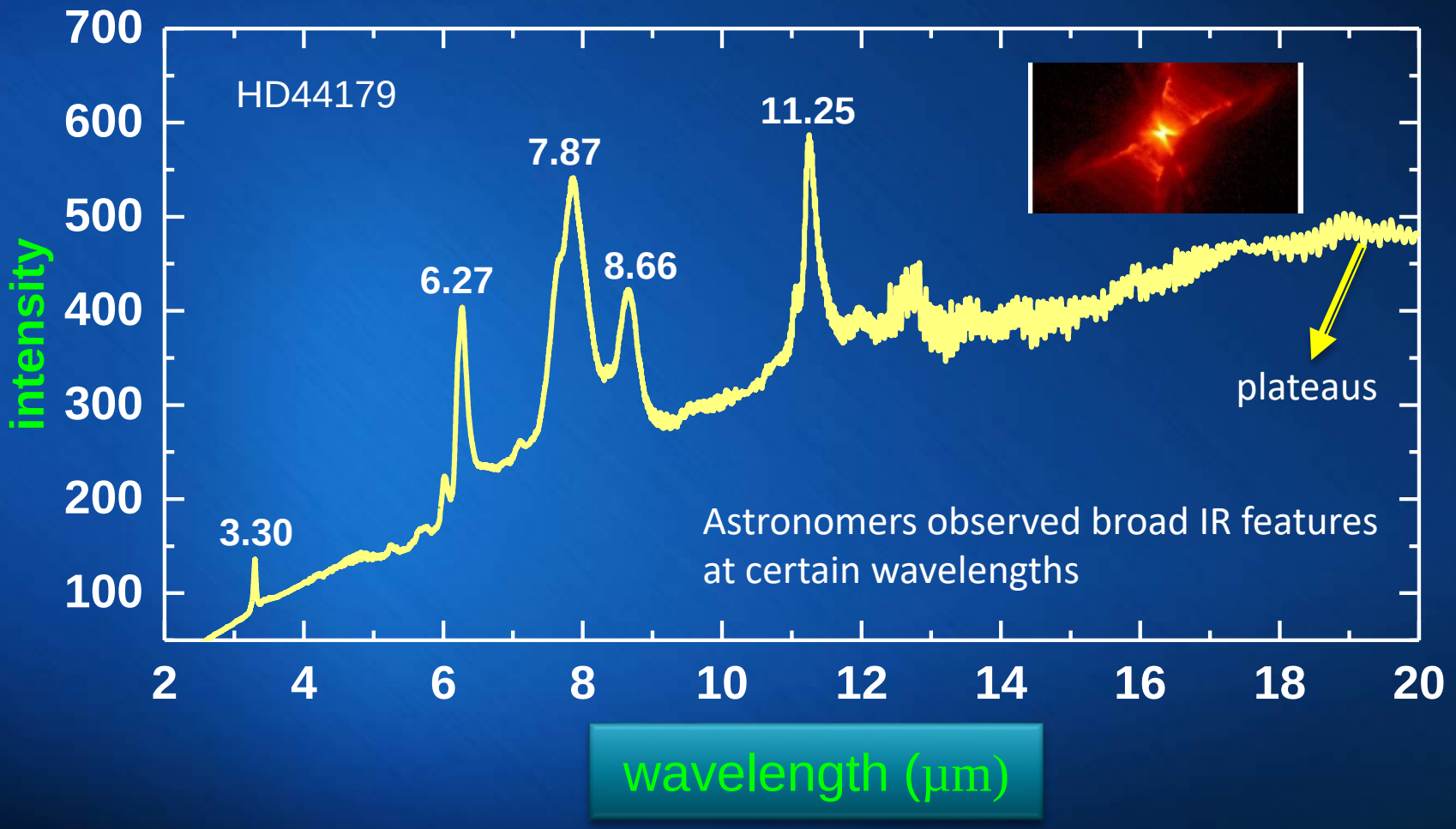
Astronomical UIE Bands



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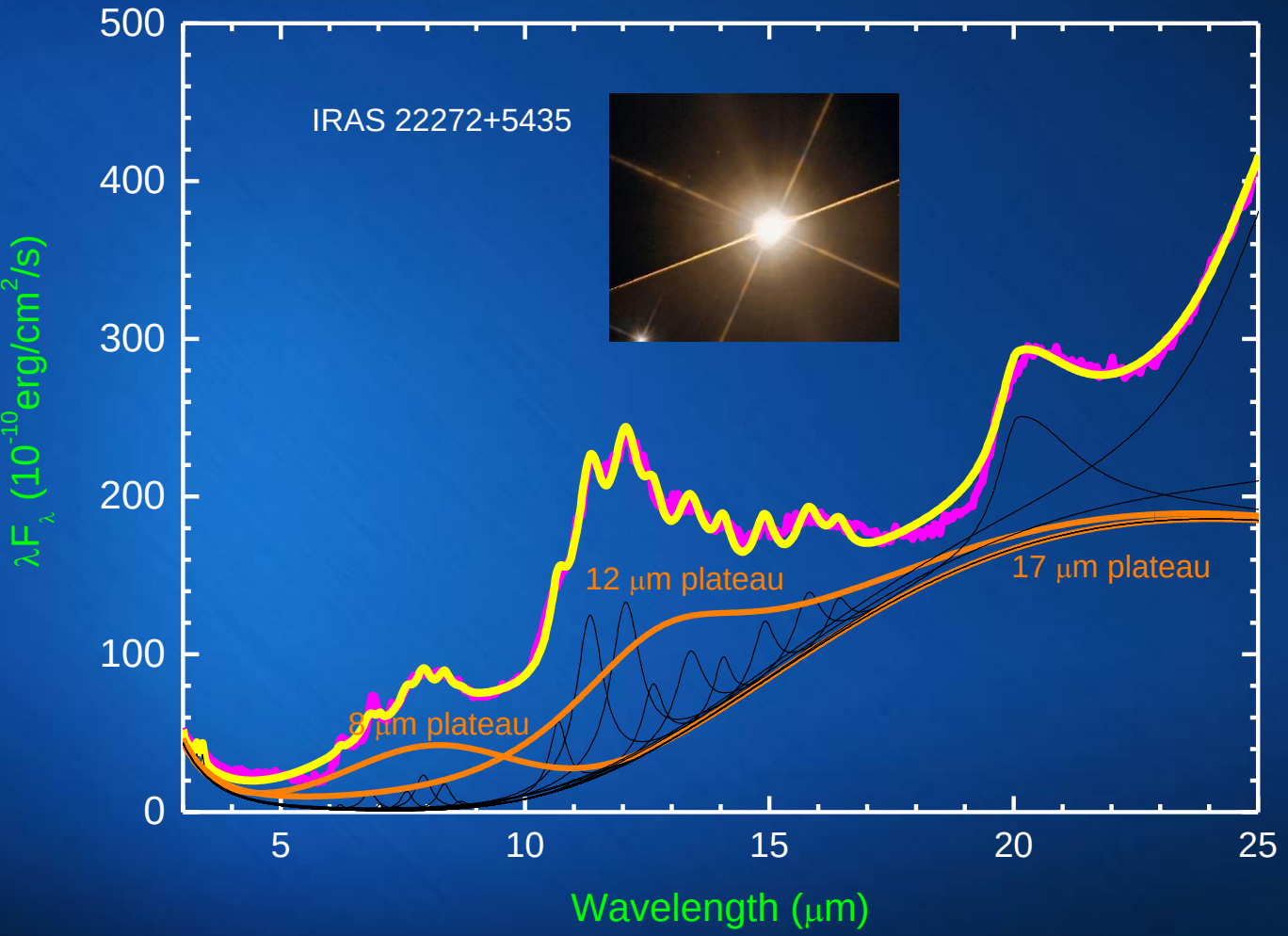
Astronomical UIE Bands



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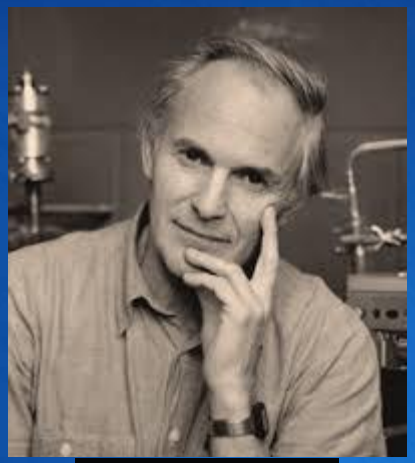
What is unknown?

The first assumption is that these emissions have molecular origin

- What elements are these molecules made of?
- How many atoms they have?
- What are their structures?
- What electric charges they carry?
- What are their electronic states?
- At what temperature and pressure are they formed?
- How do they form?
- Where do they form?. At the center of the stars? or at the Interstellar medium (ISM)

C60 : Buckminsterfullerene



Kroto : At last after nearly 100 years the group of John Maier in Basel has made the first breakthrough by assigning two DIBs unequivocally to C_{60}^{+}.

Paul von Rague Schelyer et al (PCCP, 14, 14886-14891 (2012)):

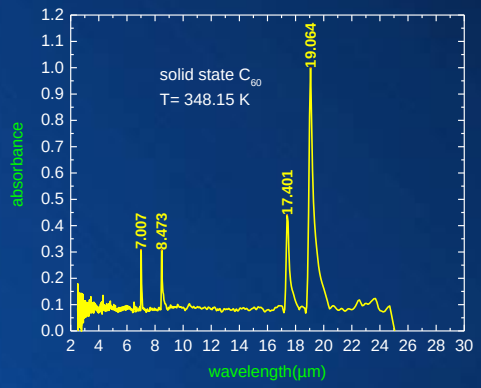
- Buckminsterfullerene is spherically π antiaromatic.
- Fullerene is not highly "stable" molecule.
- Just the opposite is true.
- It is the most strained molecule ever isolated.

Kroto: The main aspect of the discovery was not the fact that C_{60} could be created, but that it self-assembled spontaneously, because this resulted in a reassessment of our perspective on the general dynamic factors which control structure assembly processes at nanoscale dimensions.

This talk is dedicated to the memory of Sir Harold Walter Kroto

Methods of Interpretation

PCR: principle component regression
PLS: partial least square
ANN: artificial neural network
NNS: nearest neighbor searches
CT: classification trees
ES: expert system



Baumann, K. and J. T. Clerc (1997). "Computer-assisted IR spectra prediction — linked similarity searches for structures and spectra." Analytica Chimica Acta 348(1–3): 327-343.

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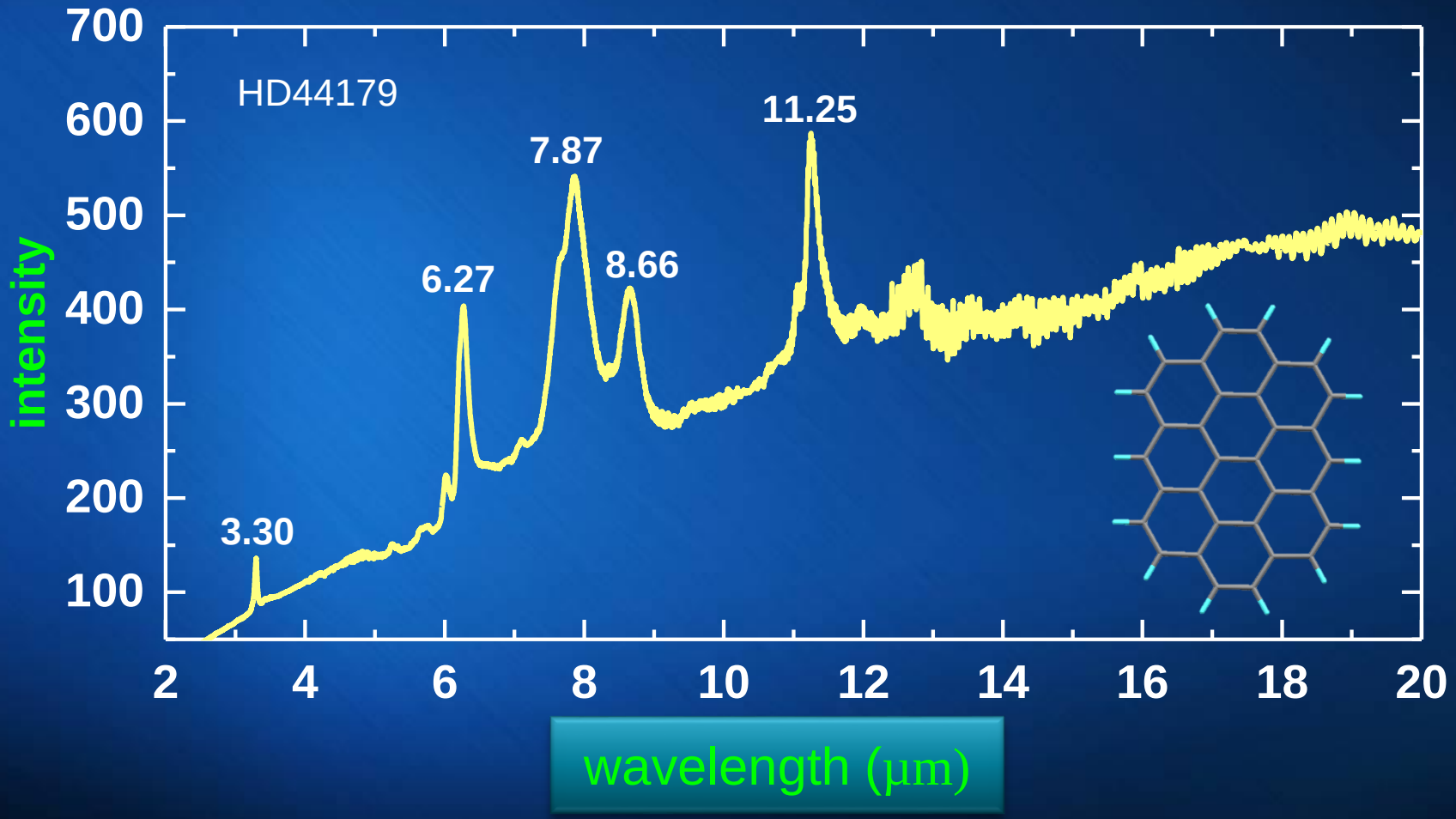
Visual Inspection

Astronomical observations and PAH model



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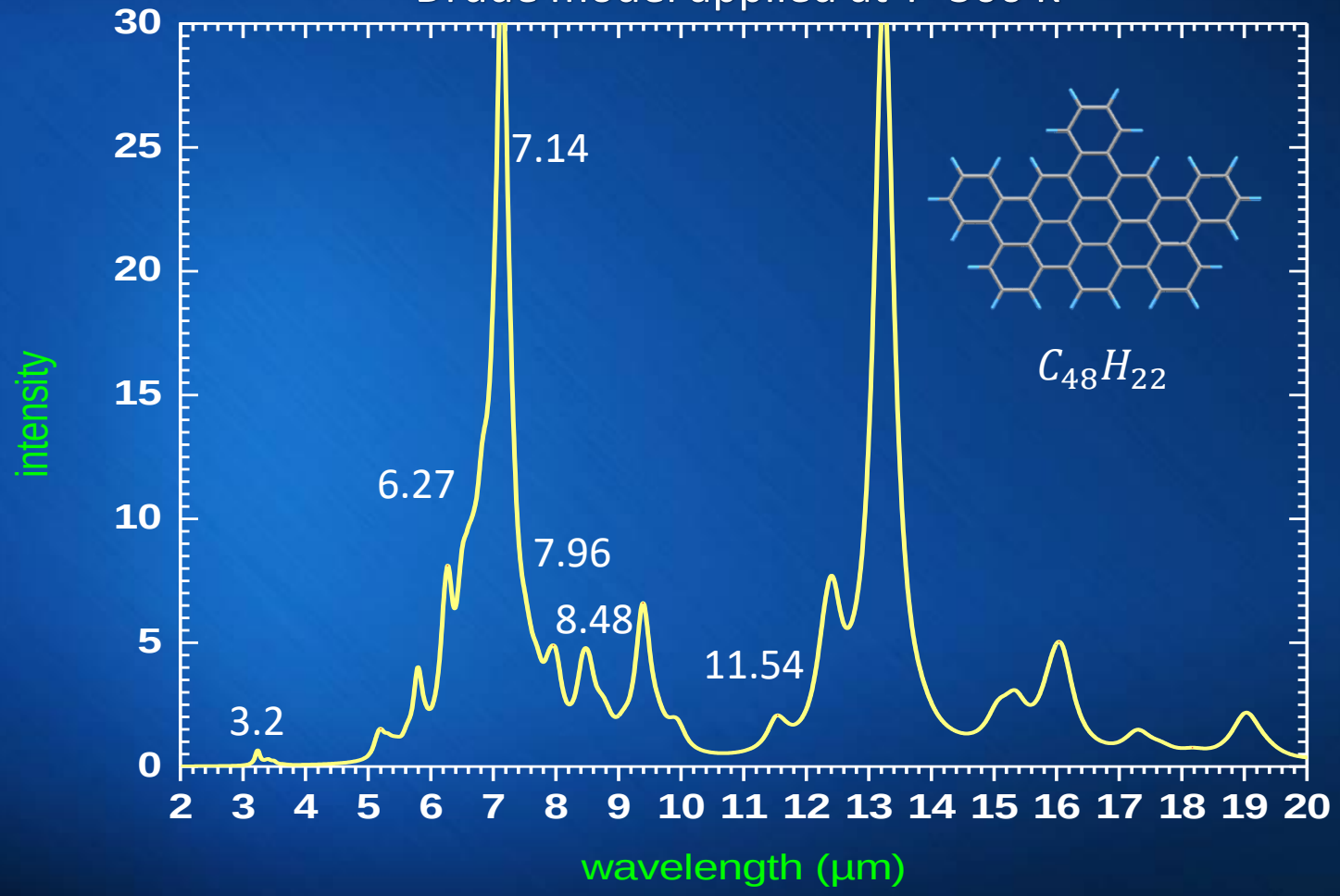
Visual Inspection

An example of gas phase IR signature of a typical PAH
Drude model applied at T=500 K



NASA PAH Database V2.00

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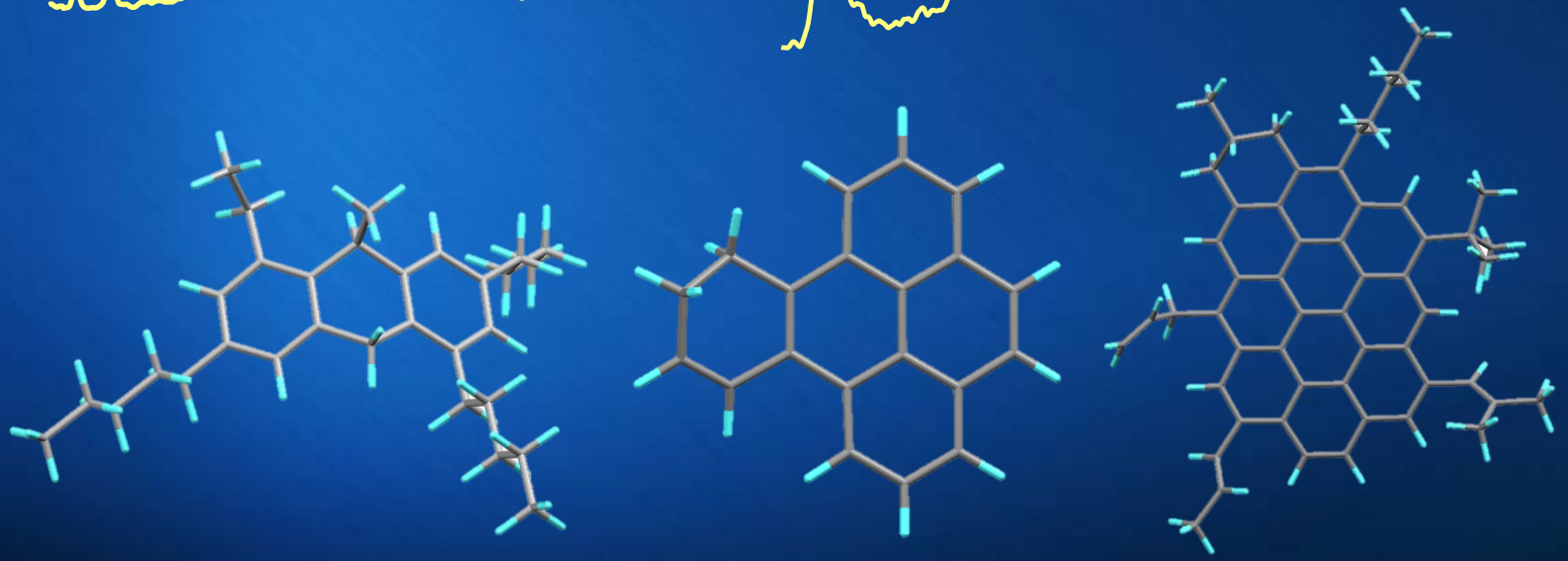
Visual Inspection

Astronomical observations and other proposed models



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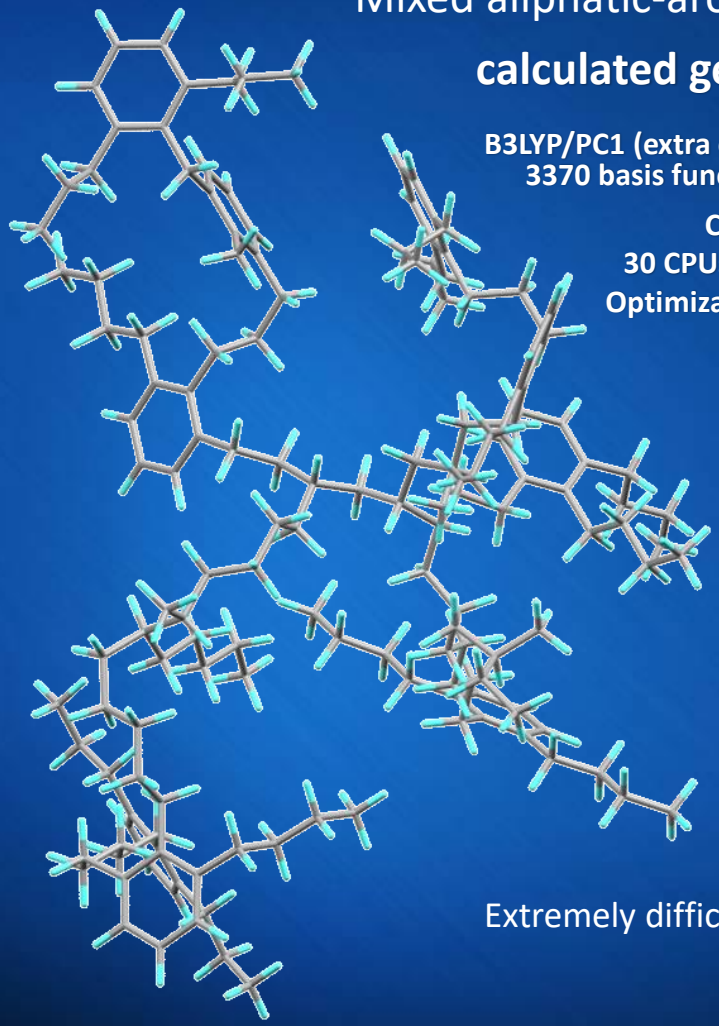
Visual inspection & MAON model

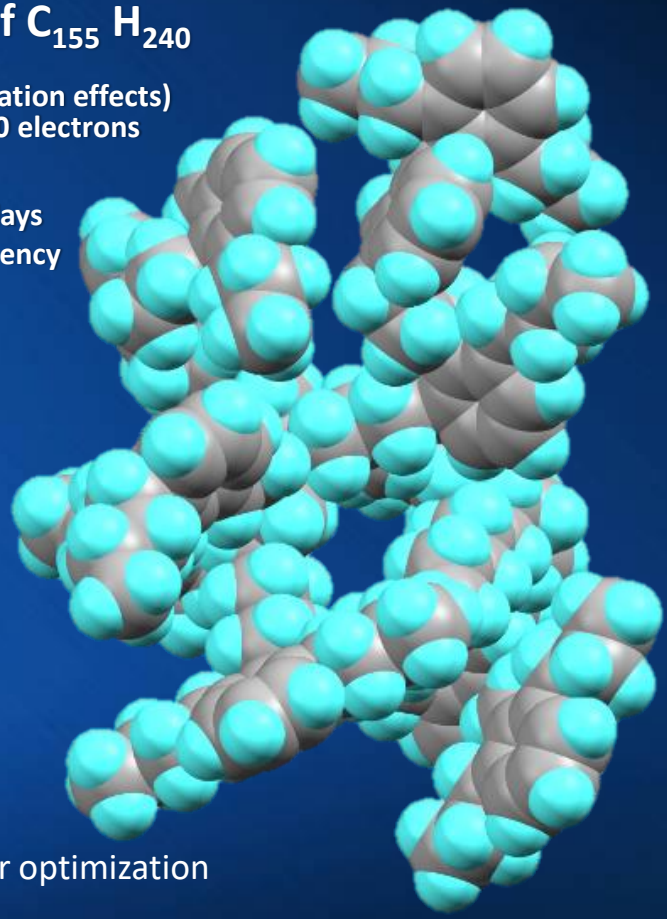
Mixed aliphatic-aromatic organic nanoparticle

calculated geometry of C_{155} H_{240}

B3LYP/PC1 (extra care on polarization effects)
3370 basis functions and 1170 electrons

C1 symmetry
30 CPUs, 3nodes, 20 days
Optimization and frequency



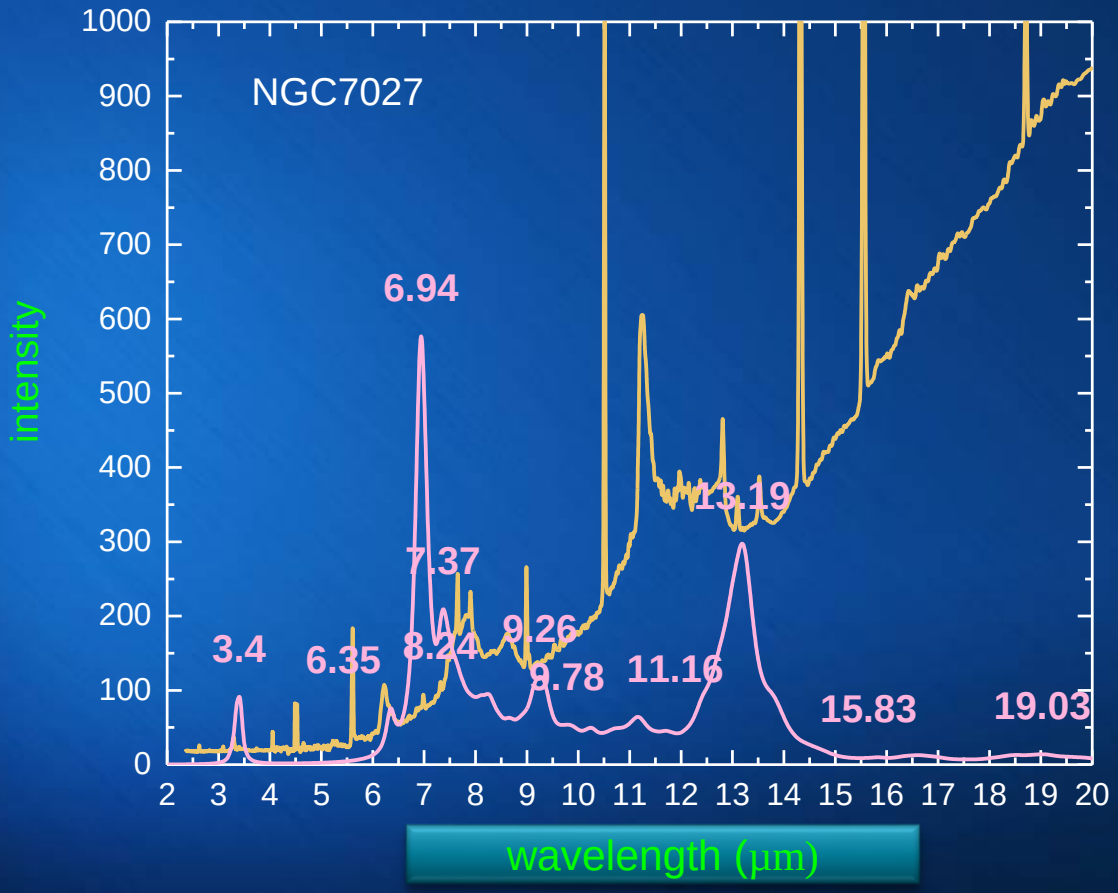


Extremely difficult system for optimization

1-Kwok and Zhang, Nature, 479:80 (2011)
2-Sadjadi, Zhang and Kwok, ApJ, 807:95 (2015 July 1)

MAON Infrared Signature

simulated IR spectra for C_{155} H_{240}, DFT/Drude, T=500 K



Sadjadi, Zhang and Kwok, ApJ, 807:95 (2015 July 1)

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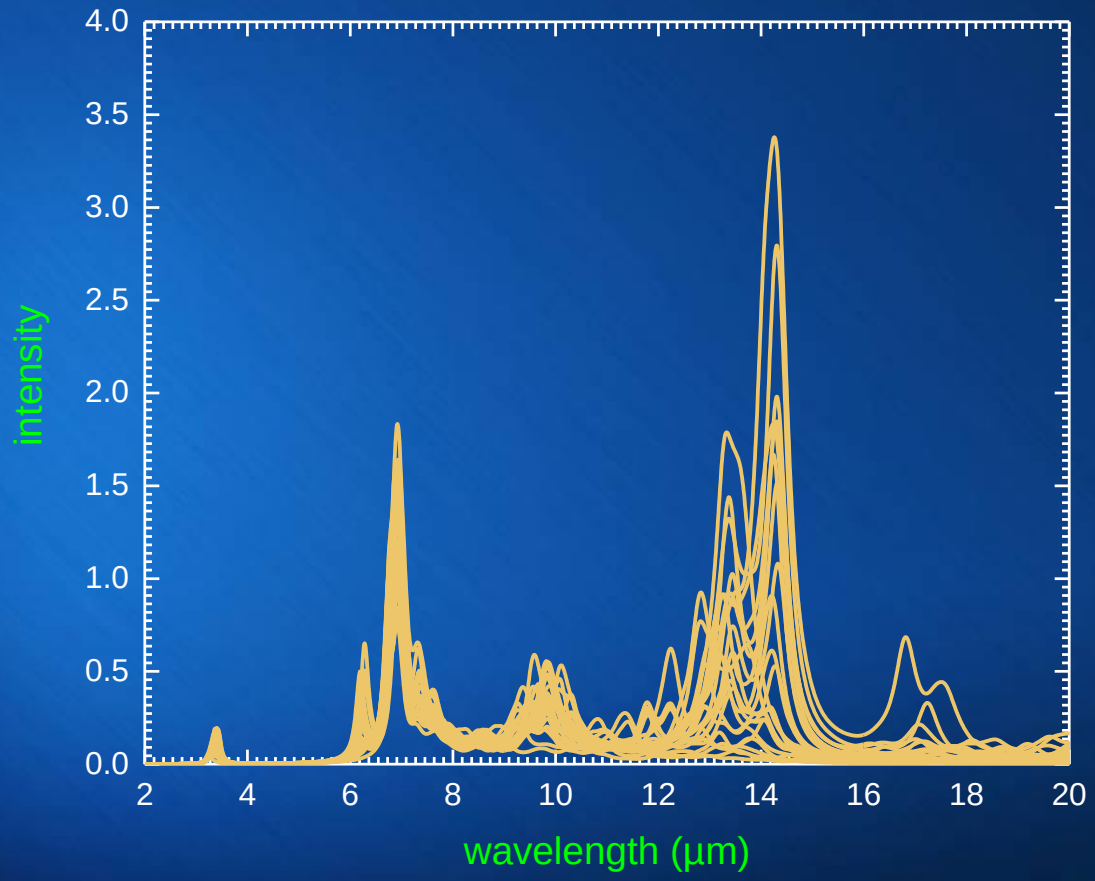
MAON Infrared Signature

simulated IR spectra for 40 MAONs, DFT/Drude, T=500 K



Sadjadi, Zhang and Kwok, ApJ, 807:95 (2015 July 1)

4th Changsha International Workshop on Theoretical and Computational Chemistry with Materials

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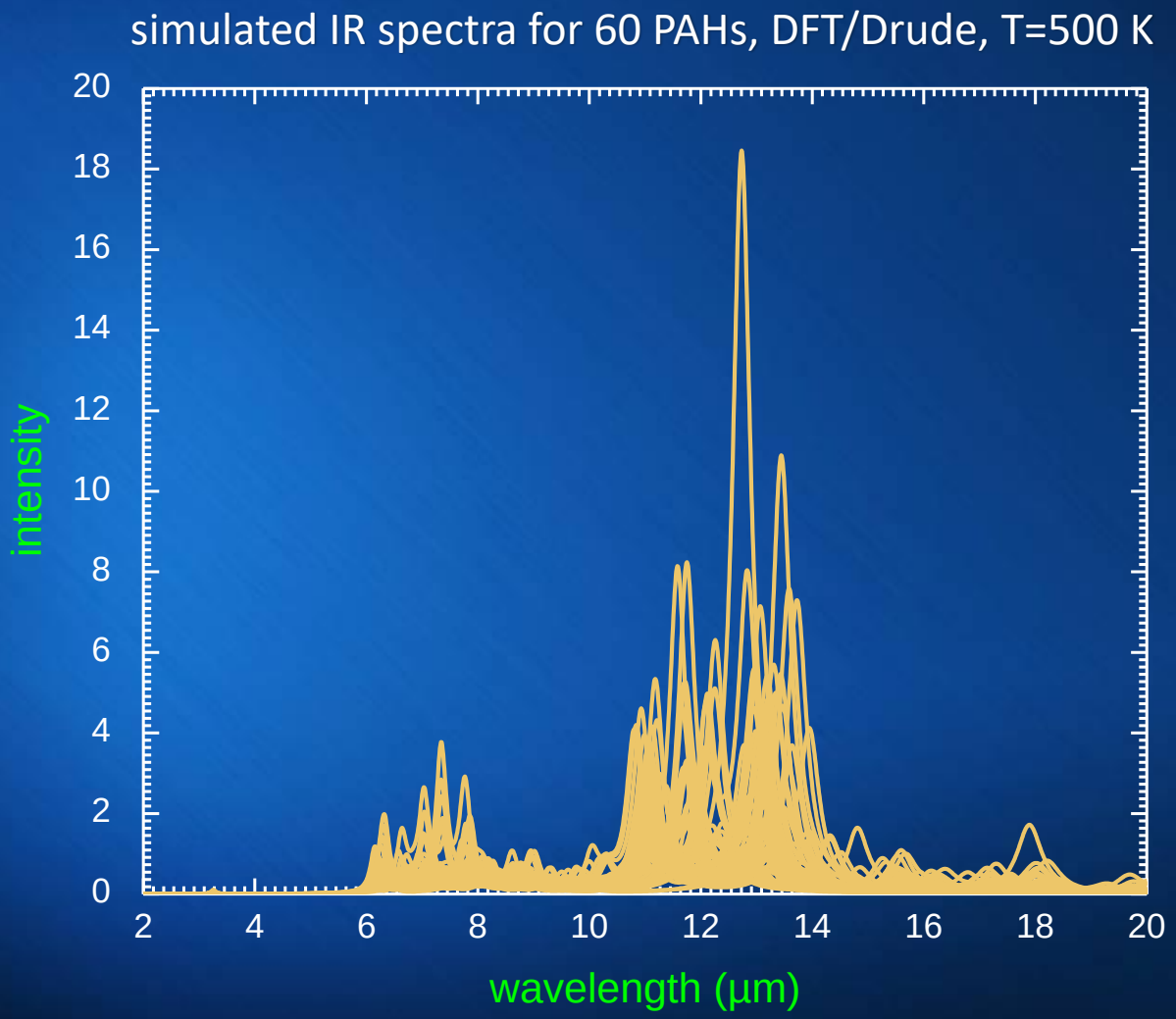
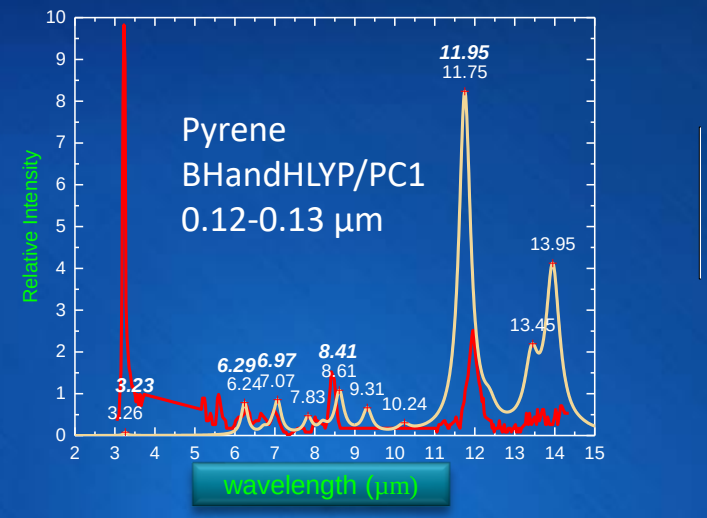
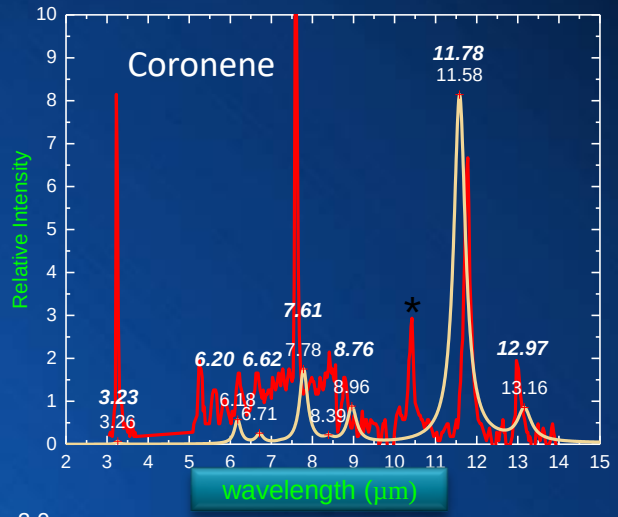
PAHs infrared fingerprint

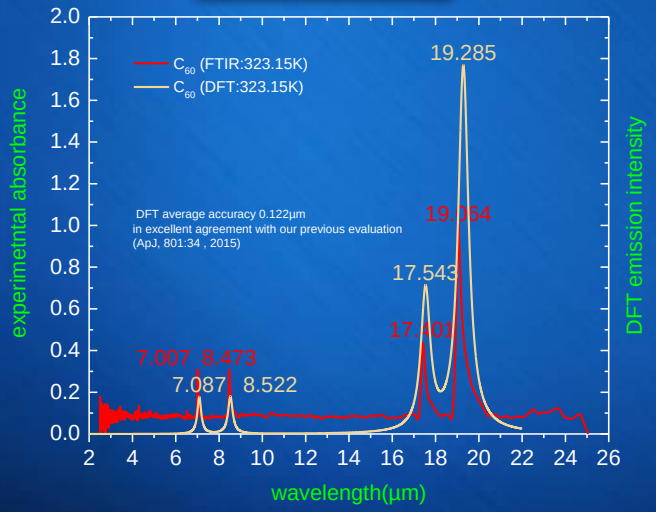


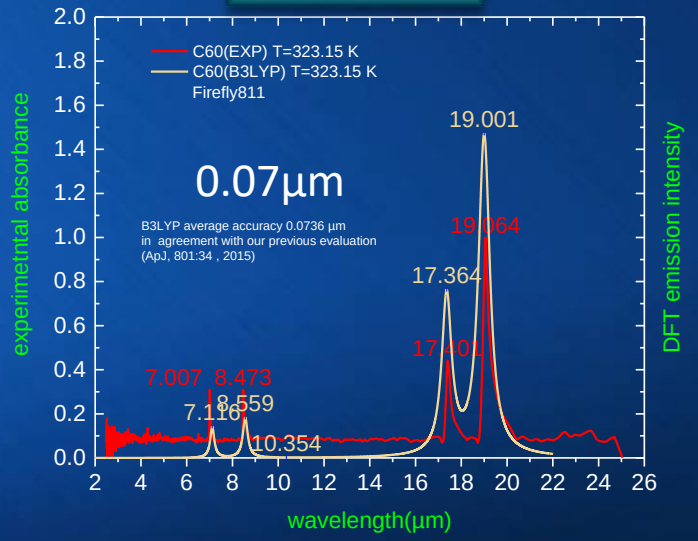
Sadjadi, Zhang and Kwok, ApJ, 807:95 (2015 July 1)

Accuracy of DFT/Drude simulation









SeyedAbdolreza, S., Z. Yong and K. Sun (2015). "A Theoretical Study on the Vibrational Spectra of Polycyclic Aromatic Hydrocarbon Molecules with Aliphatic Sidegroups." The Astrophysical Journal **801**(1): 34.

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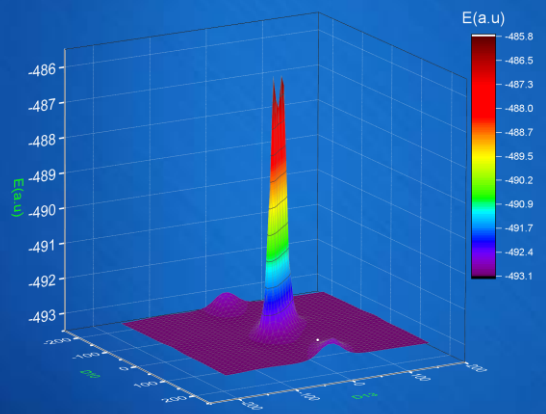
Localized Picture of Vibrational Motions

- First goal : To identify the formula and molecular structure
- Second goal : To understand what kind/type of vibrations could produce such IR features like plateaus
- We seek for the very simple scheme consistent with empirical interpretation of IR spectra (Functional group ideas) and applicable to any molecular sizes.

Potential energy surface



$$T = \frac{1}{2}\sum_{i=1}^{N} m_i[\left(\frac{d\Delta x_i}{dt}\right)^2 + \left(\frac{d\Delta y_i}{dt}\right)^2 \left(\frac{d\Delta z_i}{dt}\right)^2$$

mass-weighted Cartesian

$q_1 = \sqrt{m_1}\Delta x_1\ , q_2 = \sqrt{m_1}\Delta y_1, q_3 = \sqrt{m_1}\Delta z_1$

$$T = \frac{1}{2}\sum_{i=1}^{3N}\left(\frac{dq_i}{dt}\right)^2 = \frac{1}{2}\sum_{i=1}^{3N}\dot{q}_i{}^2$$

$$V = V_0 + \sum_{i=1}^{3N}(\frac{dV}{dq_i})_0 q_i + \frac{1}{2}\sum_{ij}^{3N}(\frac{\partial^2 V}{\partial q_i \partial q_j})_0 q_i q_j + \ldots.$$

$$\frac{d}{dt}\frac{dT}{d\dot{q}_i} + \frac{dV}{dq_i} = 0 \ \ Newton's\ equation\ of\ motion$$

$V_0 = 0\ , (\frac{dV}{dq_i})_0 = 0$ at equilibrium, $F_{ij} = (\frac{\partial^2 V}{\partial q_i \partial q_j})_0 \rightarrow \ddot{q}_j + \sum_{i=1}^{3N} F_{ij}\, q_i = 0$

1-Pulay, P. (2014). "Analytical derivatives, forces, force constants, molecular geometries, and related response properties in electronic structure theory." Wiley Interdisciplinary Reviews: Computational Molecular Science **4**(3): 169-181

2-http://tyr0.chem.wsu.edu/~kipeters/Chem537/schedule.html

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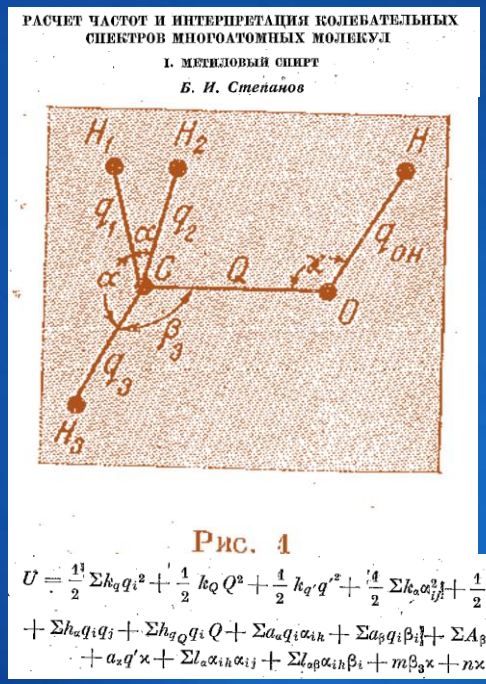
Quantitative visual inspection

1945



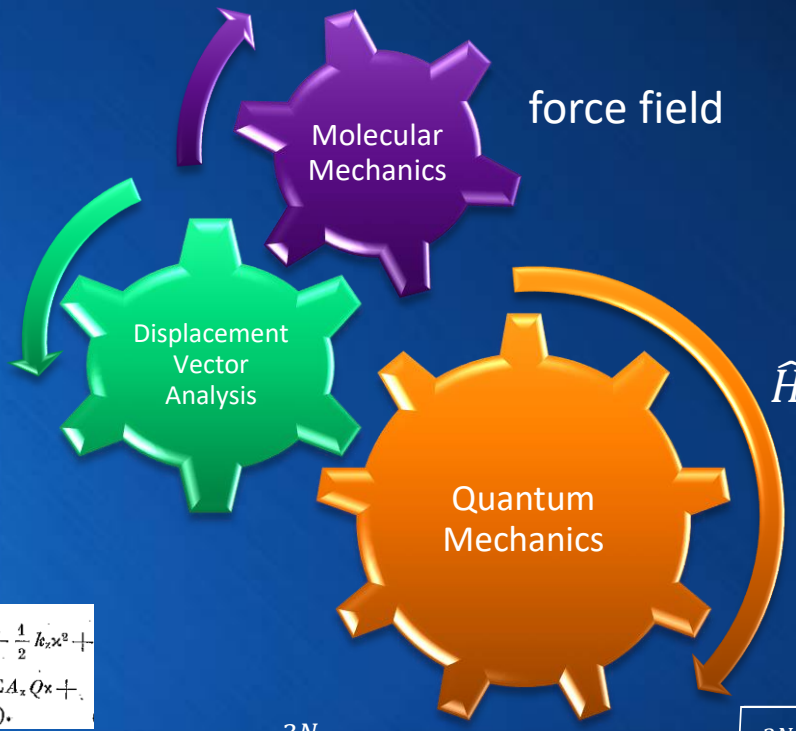
РАСЧЕТ ЧАСТОТ И ИНТЕРПРЕТАЦИЯ КОЛЕБАТЕЛЬНЫХ СПЕКТРОВ МНОГОАТОМНЫХ МОЛЕКУЛ

I. МЕТИЛОВЫЙ СПИРТ

Б. И. Степанов

Рис. 1

$$U = \frac{1}{2}\Sigma k_q q_i^2 + \frac{1}{2} k_Q Q^2 + \frac{1}{2} k_{q'} q'^2 + \frac{1}{2}\Sigma k_\alpha \alpha_{ij}^2 + \frac{1}{2}\Sigma k_\beta \beta_i^2 + \frac{1}{2} k_\chi \chi^2 + \\ + \Sigma h_\alpha q_i q_j + \Sigma h_{q_Q} q_i Q + \Sigma a_\alpha q_i \alpha_{ik} + \Sigma a_\beta q_i \beta_i + \Sigma A_\beta Q \beta_i + \Sigma A_\chi Q \chi + \\ + a_\chi q' \chi + \Sigma l_\alpha \alpha_{ih} \alpha_{ij} + \Sigma l_{\alpha\beta} \alpha_{ih} \beta_i + m \beta_3 \chi + n \chi (\beta_1 + \beta_2).$$



force field

$$\hat{H}\Psi = E\Psi$$

$$I_{k,i}^{CART} = \sum_{j}^{3N} \frac{D_{k,j} L_{j,i}}{\sqrt{m_k}}$$

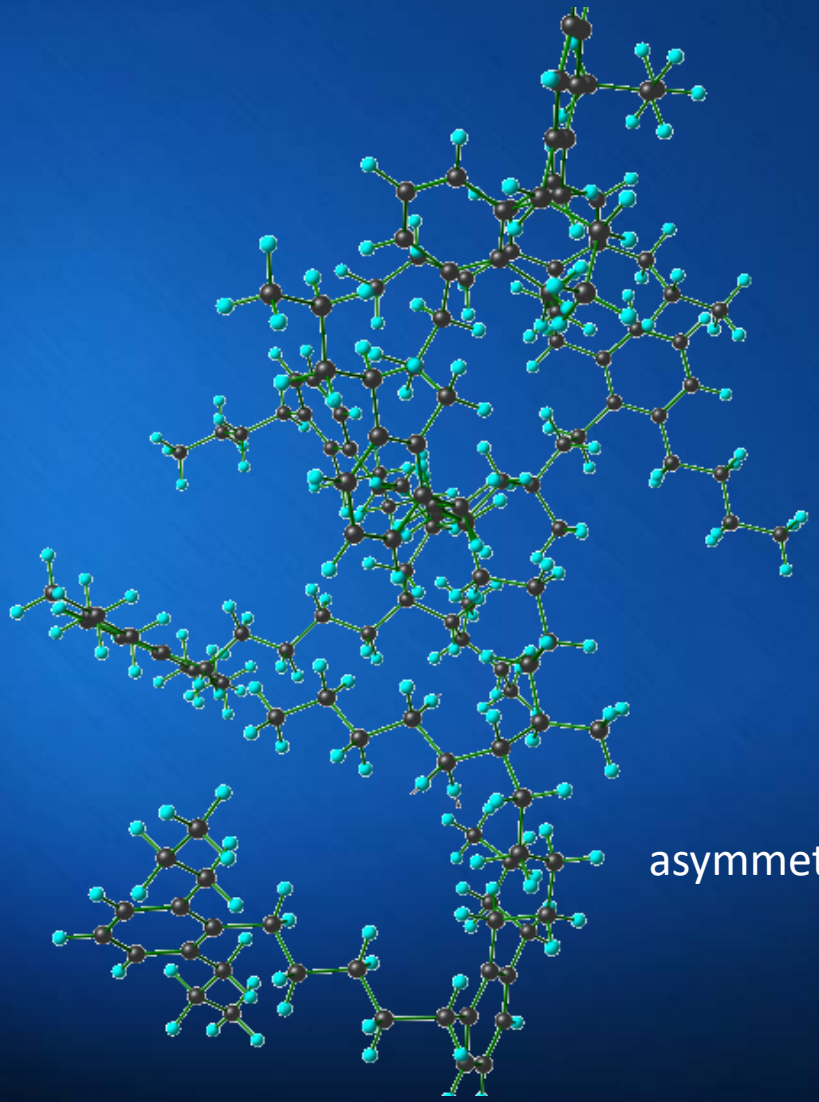
$$N_i = \sqrt{(\sum_{k}^{3N} (I_{k,i}^{CART})^2)^{-1}}$$

$$R = \sqrt{I_x^2 + I_y^2 + I_z^2} \geq 0.1\text{Å}$$

SeyedAbdolreza, S., Z. Yong, and K. Sun, *A Theoretical Study on the Vibrational Spectra of Polycyclic Aromatic Hydrocarbon Molecules with Aliphatic Sidegroups.* The Astrophysical Journal, 2015. **801**(1): p. 34.

Quantitative visual inspection

C_{155} H_{240} (vibrational motion at 3.4 μm)

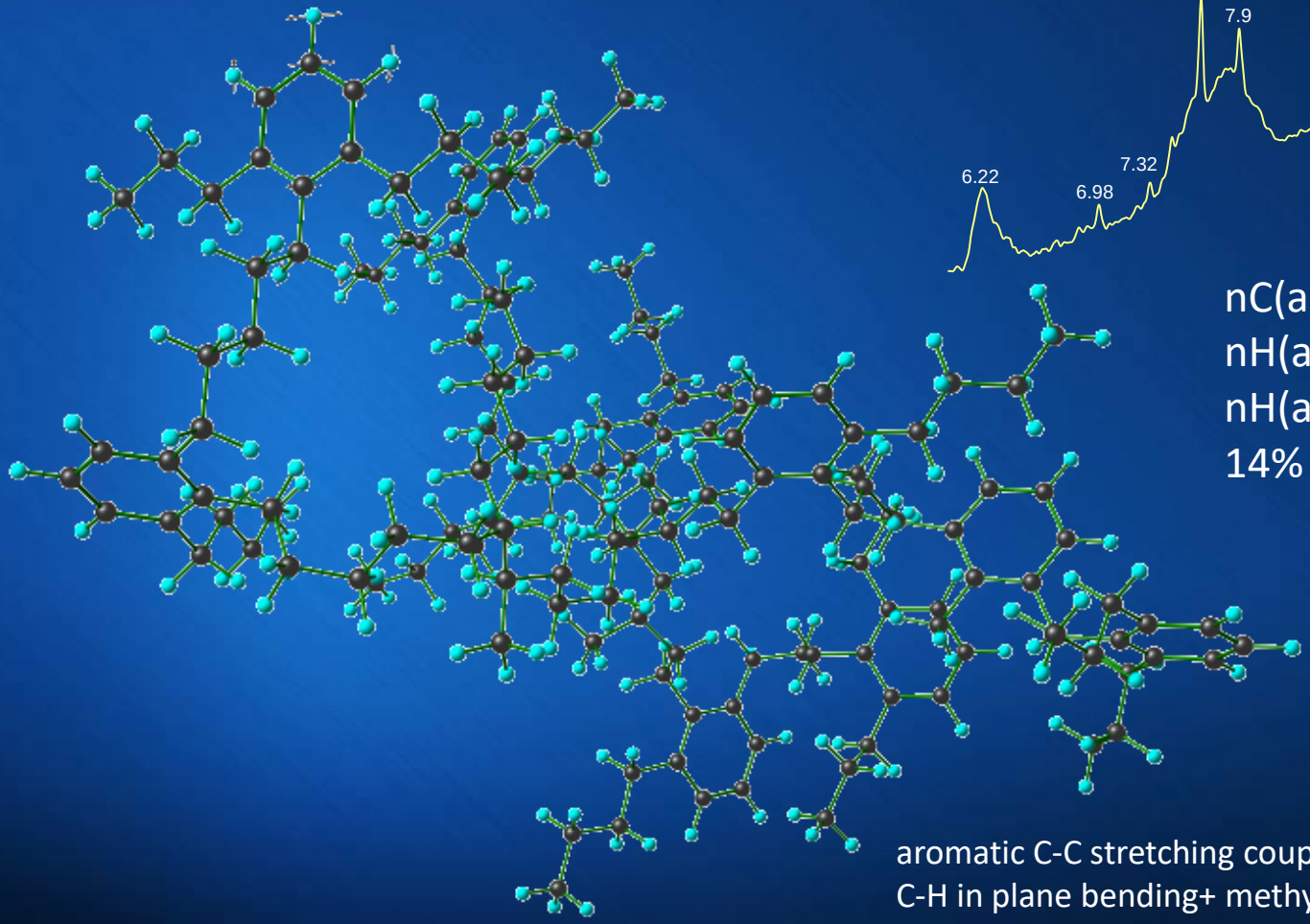


nH(ali): 9
nC: 0
All Aliphatic (100%)

asymmetric methylene C-H stretching

Quantitative visual inspection

C_{155} H_{240} (vibrational motion at 6.35 μm)



nC(ar):8
nH(ar):3
nH(ali):2
14% ali, 86% ar

aromatic C-C stretching coupled with
C-H in plane bending+ methylene twisting

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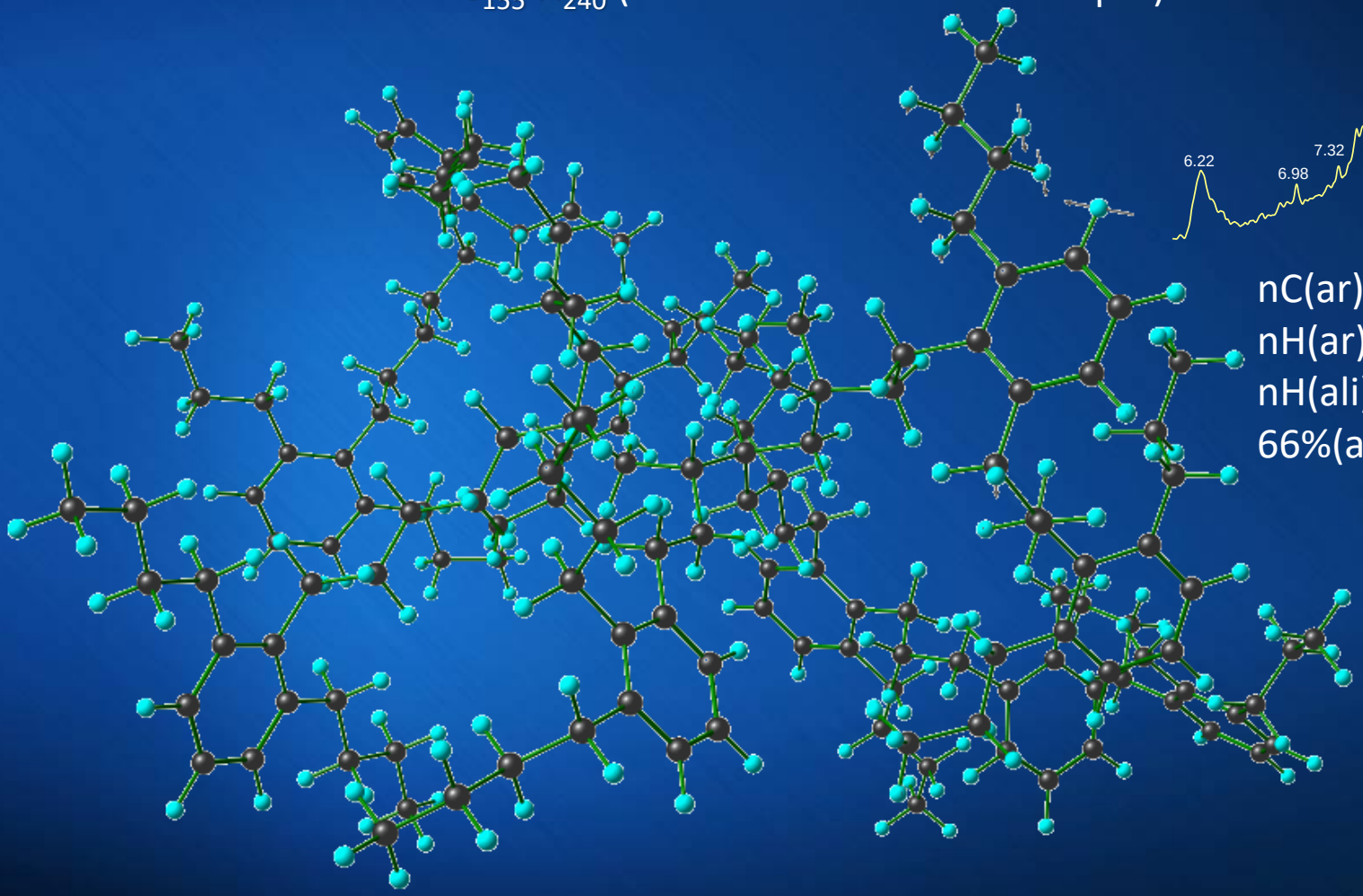
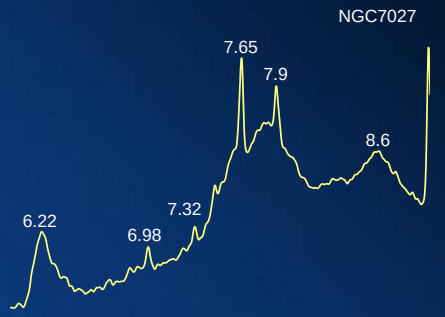
Quantitative visual inspection

C_{155} H_{240} (vibrational motion at 8.25 μm)





nC(ar):3
nH(ar):2
nH(ali):10
66%(ali), 34% (ar)

Methyl deformation+ methylene wagging and twisting+ benzene C-H INP

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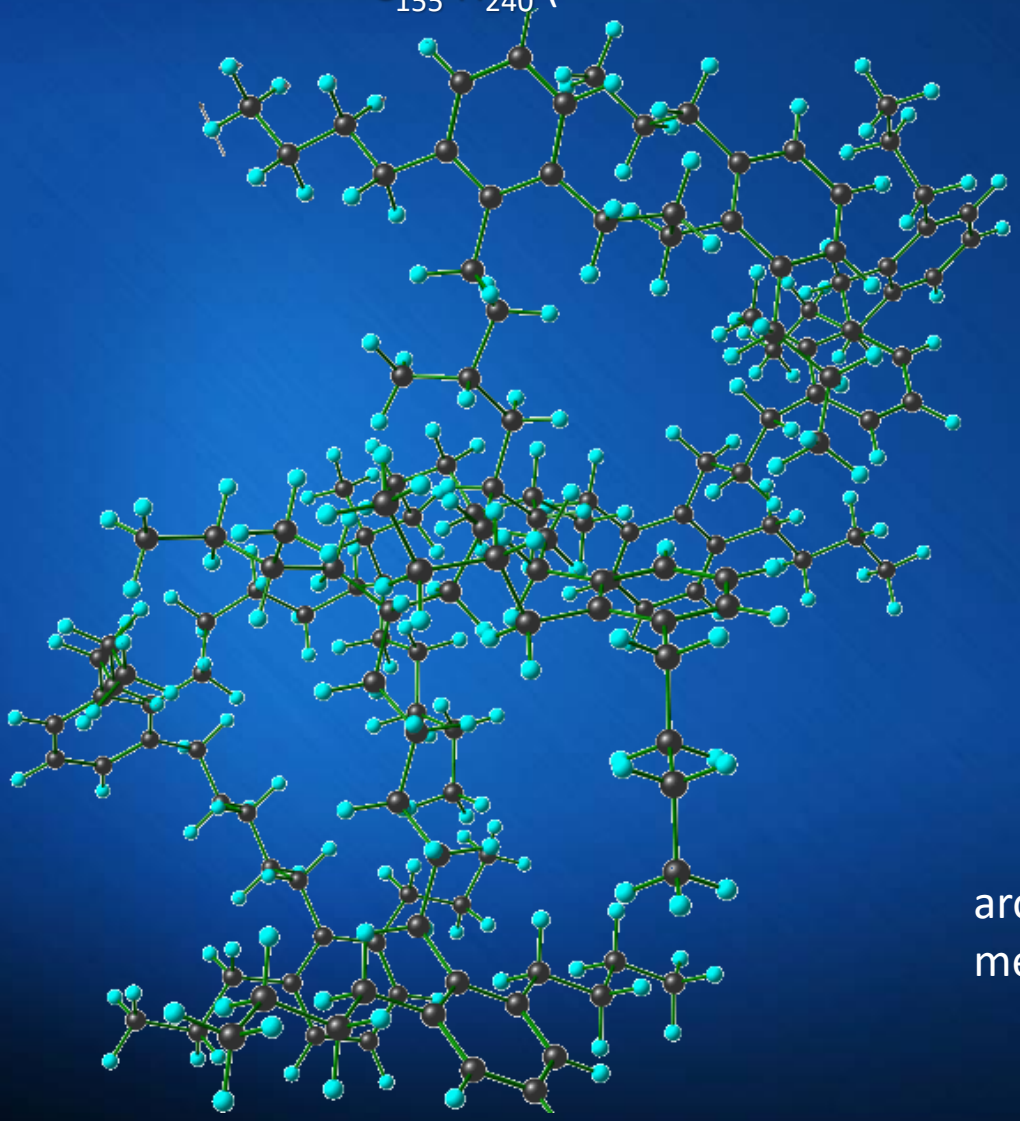
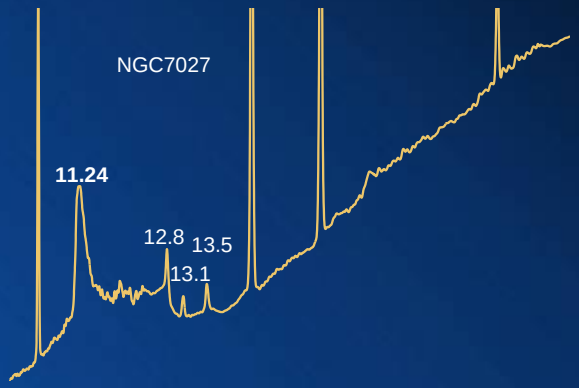
Quantitative visual inspection

C_{155} H_{240} (vibrational motion at 11.16 μm)





nH(ar):2
nC(ali):3
nH(ali): 8
85%(ali), 15% (ar)

aromatic C-H, OOP coupled with methyl & methylene vibrations

Quantitative visual inspection

C_{155} H_{240} (vibrational motion at 13.20 μm)

nH(ali):3
nC(ar): 2
nH(ar):7
75%(ar), 25%(ali)

aromatic C-H, OOP

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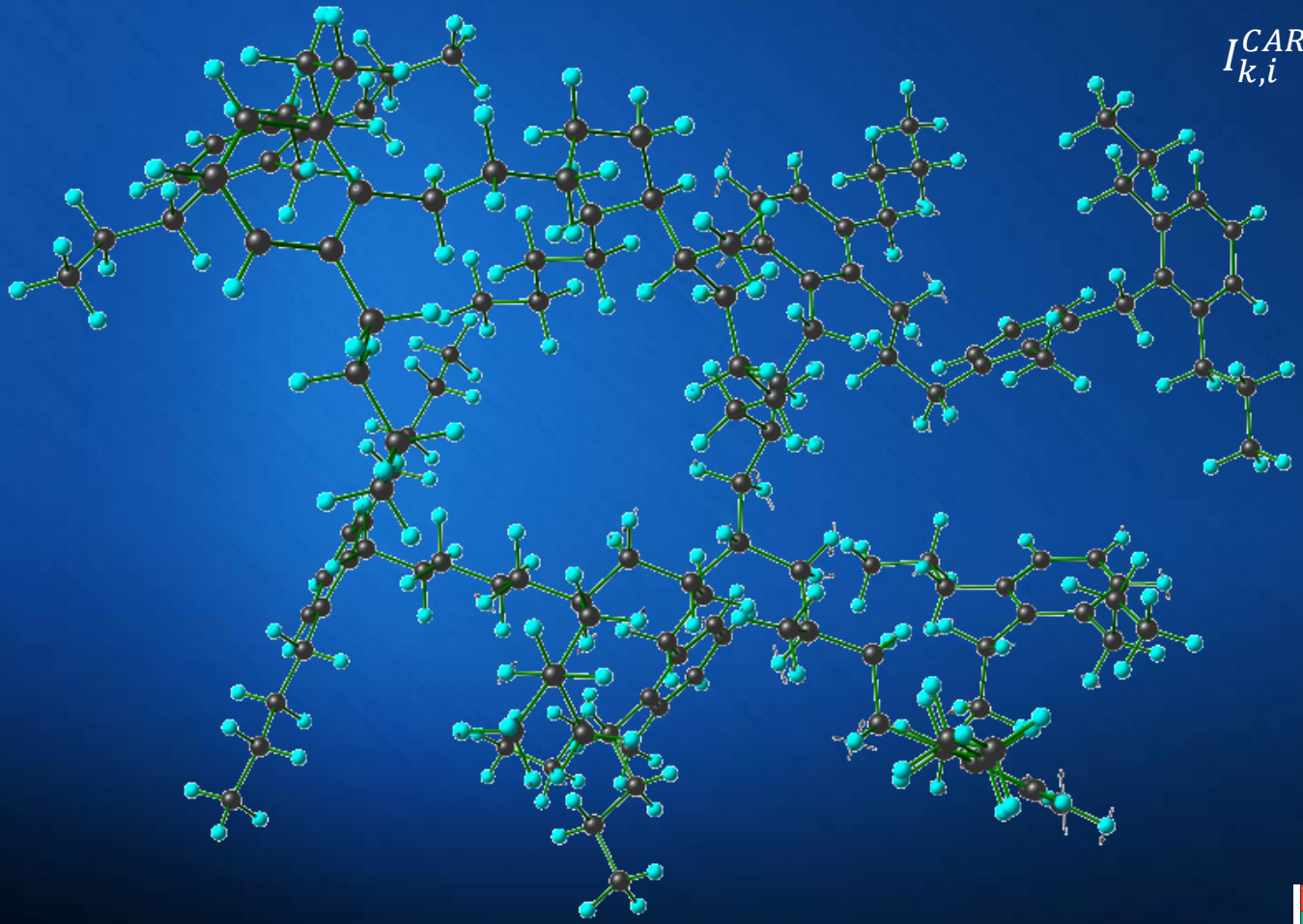
Quantitative visual inspection

C_{155} H_{240} (vibrational motion at 19.06 μm : 32% aromatic, 68% aliphatic)

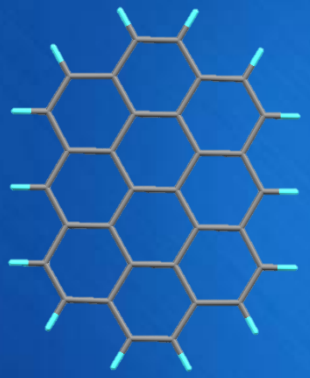
We try to understand which fragments inside molecules are responsible for the observed IR features. Then we can return back to the observations and track the existences of such fragments and perhaps one step ahead to identify the whole molecule(s)

$$I_{k,i}^{CART} = \sum_{j}^{3N} \frac{D_{k,j} L_{j,i}}{\sqrt{m_k}}$$



Quantitative visual inspection

We separated out the vibrations of different peripheral C-H bonds in the skeleton of PAH molecule

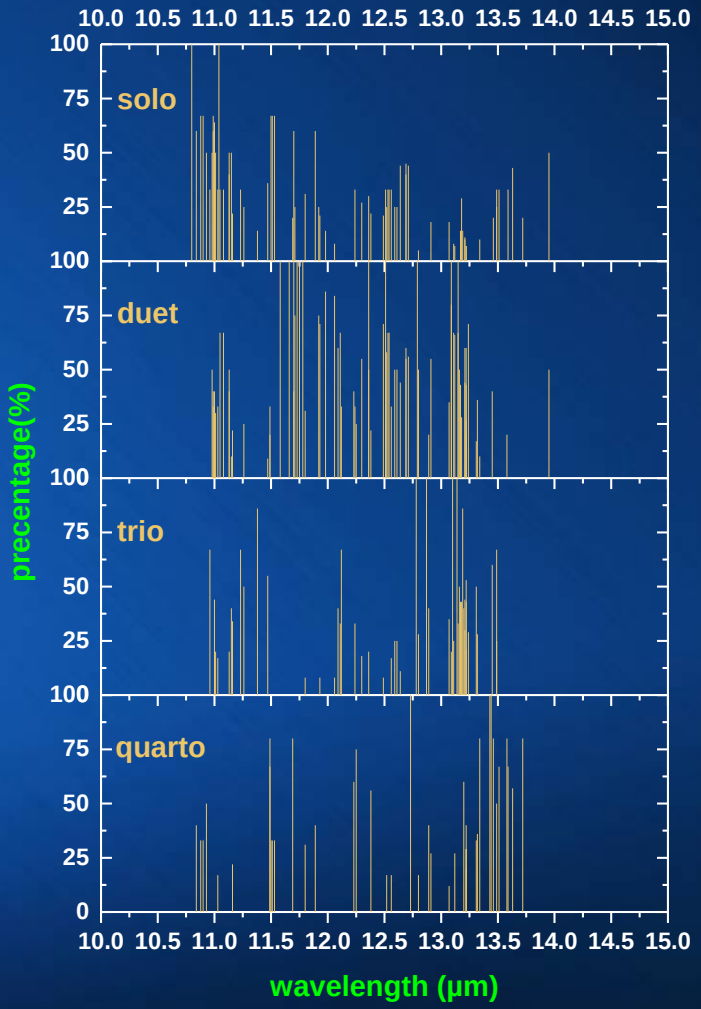


227 vibrations

112
Pure OOP

%solo, %duet, %trio, %quarto

$$I_{k,i}^{CART} = \sum_{j}^{3N} \frac{D_{k,j} L_{j,i}}{\sqrt{m_k}}$$



Sadjadi, Zhang and Kwok, ApJ, 807:95 (2015 July 1)

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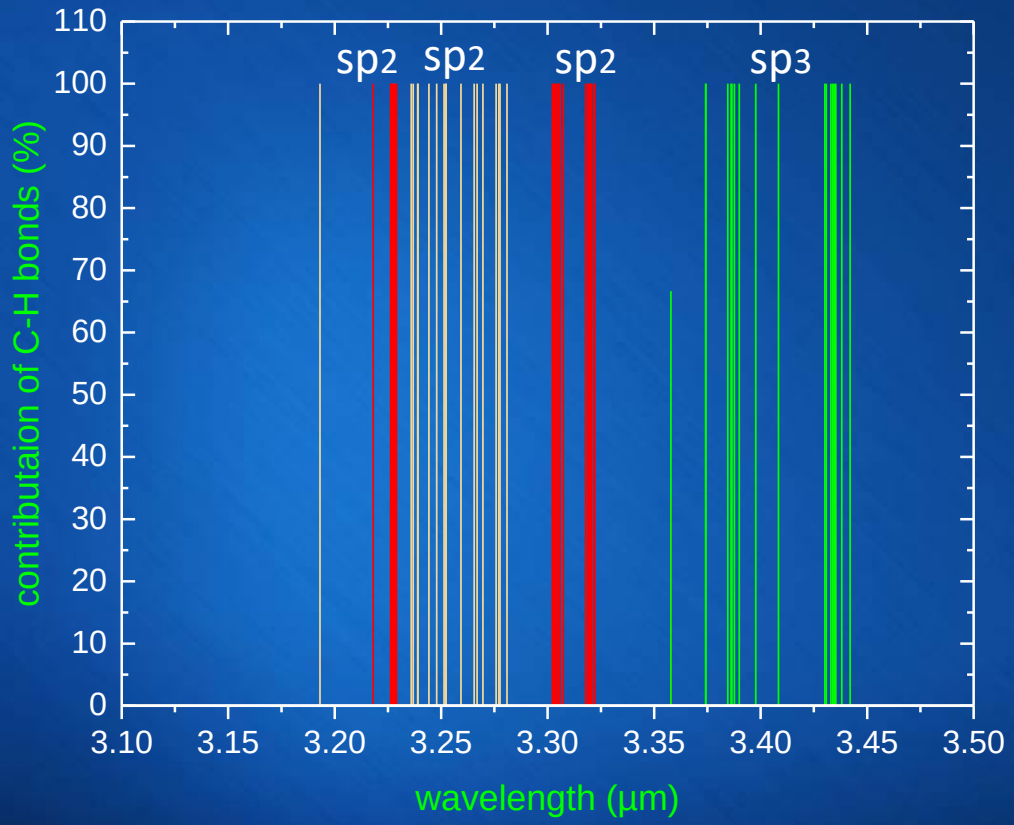
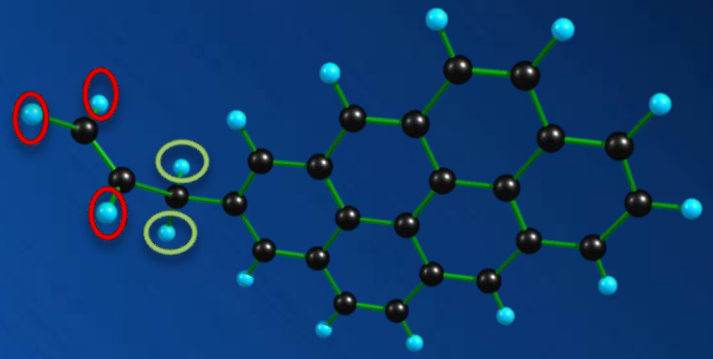
Quantitative visual inspection

Separation of the vibrations of C-H stretching modes in 3μm region





$$I_{k,i}^{CART} = \sum_{j}^{3N} \frac{D_{k,j} L_{j,i}}{\sqrt{m_k}}$$

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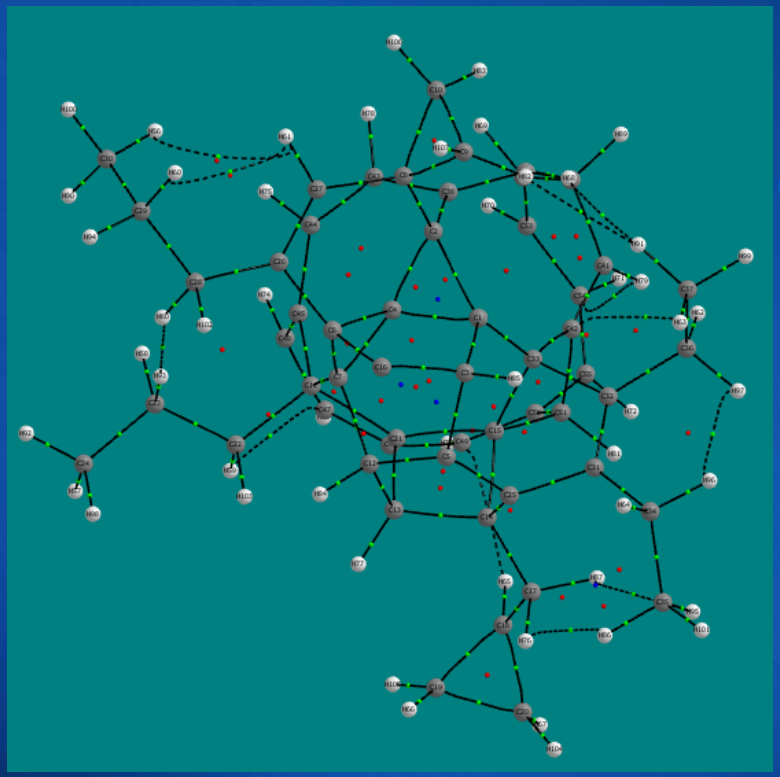
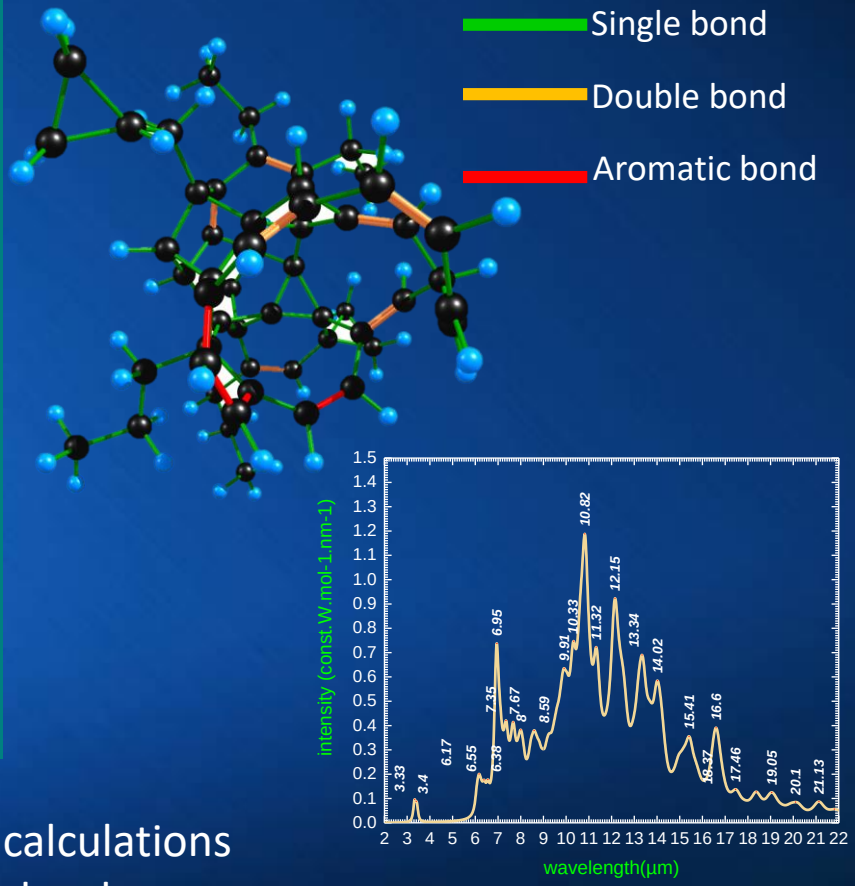
The QTAIM Role in Interpretation of IR spectra

Amorphous hydrocarbon (C55H52) non classical structure at B3LYP/PC1





comparison with the same type of calculations on C6H6, C2H6, C2H4 and C2H2 molecules.

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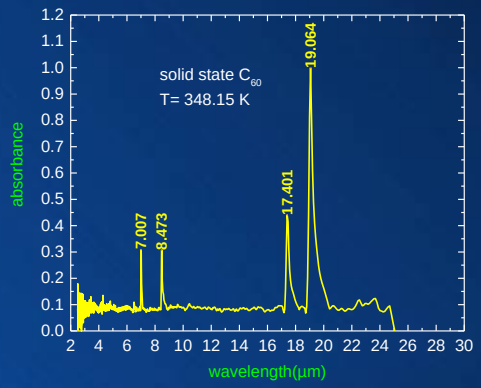
Methods of Interpretation

PCR: principle component regression
PLS: partial least square
ANN: artificial neural network
NNS: nearest neighbor searches
CT: classification trees
ES: expert system



Baumann, K. and J. T. Clerc (1997). "Computer-assisted IR spectra prediction — linked similarity searches for structures and spectra." Analytica Chimica Acta 348(1–3): 327-343.

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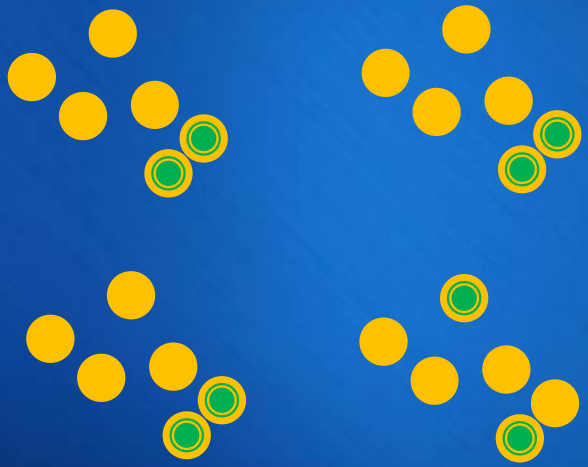
Spectral similarity

$Properties = f(strcutue)$

structure space properties space



$X = \{x_1, x_2, \ldots, x_i, \ldots, x_n\}$ target molecule intensity or wavelengths

$Y = \{y_1, y_2, \ldots, y_i, \ldots, y_n\}$ reference molecule intensity or wavelengths

$$r_p = \frac{\sum_i (x_i - \overline{x}).(y_i - \overline{y})}{\sqrt{\sum_i (x_i - \overline{x})^2 . \sum_i (y_i - \overline{y})^2}}$$ Pearson's product moment correlation coefficient.

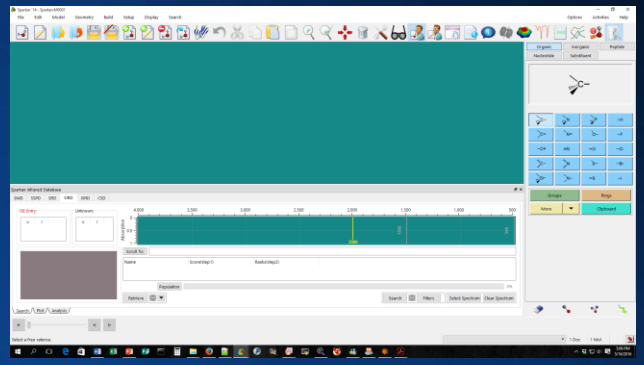
r_p=1 prefect linear correlation or similarity.

For performing similarity we need

1- a pool of reference spectra with same wavelength resolution and normalized intensities with respect to the strongest peak.

2- the unknown spectra should be prepared to match The conditions of reference spectra.

Spartan a tool for spectral similarity



Spartan Spectra and Properties Database (SSPD)
Theoretical database with more than 250,000 molecules
Calculated IR spectra at EDF2/6-31G*
EDF2 stands for Empirical density functionals

$$E^{EDF2} = a_1 E^{HF} + a_2 E^{LSDA} + a_3 E^{BLYP} + a_4 E^{B3LYP} + a_5 E^{EDF1}$$

a_i: is determined by least-square fit of HF, LSDA, BLYP, B3LYP and EDF1 harmonic frequencies to experimental data

$$E_{XC}^{EDF2} = b_1 E_X^{F30} + b_2 E_X^{D30} + b_3 E_X^{B88} + b_4 E_X^{EDF1} + b_5 E_C^{VWN} + b_6 E_C^{LYP} + b_7 E_C^{EDF1}$$

Overall RMS: $34\ cm^{-1}$,

Lin, C. Y.; George, M. W.; Gill, P. M. W., EDF2: A Density Functional for Predicting Molecular Vibrational Frequencies. *Australian Journal of Chemistry* **2004,** *57* (4), 365-370.
Adamson, R. D.; Gill, P. M. W.; Pople, J. A., Empirical density functionals. *Chemical Physics Letters* **1998,** *284* (1–2), 6-11.

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Reliability of similarity methodology

Experimental	Formula	Results
allene	C3H4	2nd
1-3-butadiene	C4H6	1st
1-4 pentadiene	C5H8	1st
acetone	C3H6O	1st
anthracene	C14H10	1st
styrene	C8H8	Not found
tetrahydrofuran	C4H8O	1st
acetonitrile	C2H3N	4th
2-ethyl-3-methyl-1-butene	C7H14	Not found
acetylene	C2H2	1st
ethylene	C2H4	1st
ethane	C2H6	Not found
1-butyne	C4H6	Not found
1-pentene	C5H10	1st
2,4-dimethyl-1,4-pentadiene	C7H12	Not found
acrolein	C3H4O	1st
Diethyl ether	C4H10O	Dimethyl ether
1-propene	C3H6	2nd

Target: Experimental IR gas phase (NIST)
Reference: EDF/6-31G* data base

Total: 35 tries
Successful hit: 13
Reliability : 37%

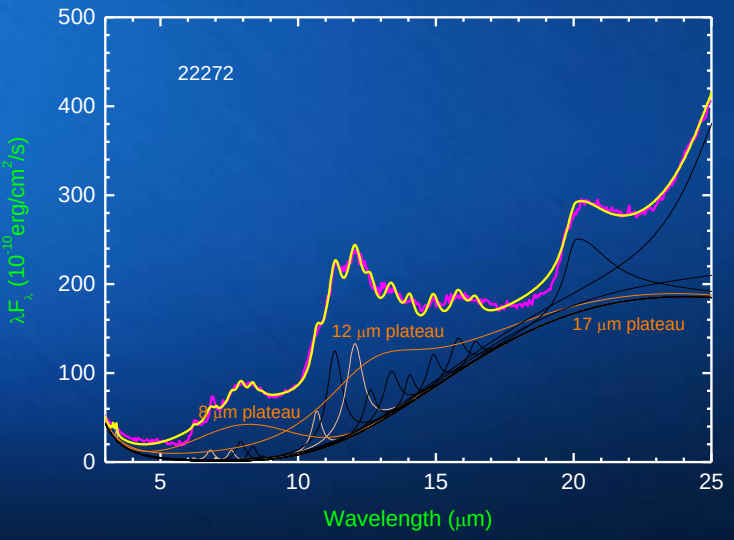
Astronomical spectra and spectral similarity

Astronomical spectra are recoding in Emission

- Continuum Emission
- Hubble Red shift for the galaxies moving away from us
- They contains very strong atomic emission lines interfere with IR emission bands.
- There is no base line for astronomical IR spectra.

We combined different mathematical techniques in signal/noise processing

- To deal with sharp atomic lines.
- Extracting the true IR features and smoothing the spectrum.
- Non linear baseline corrections.
- Finally convert this astronomical spectrum to a mathematical analogue in laboratory spectrum format.



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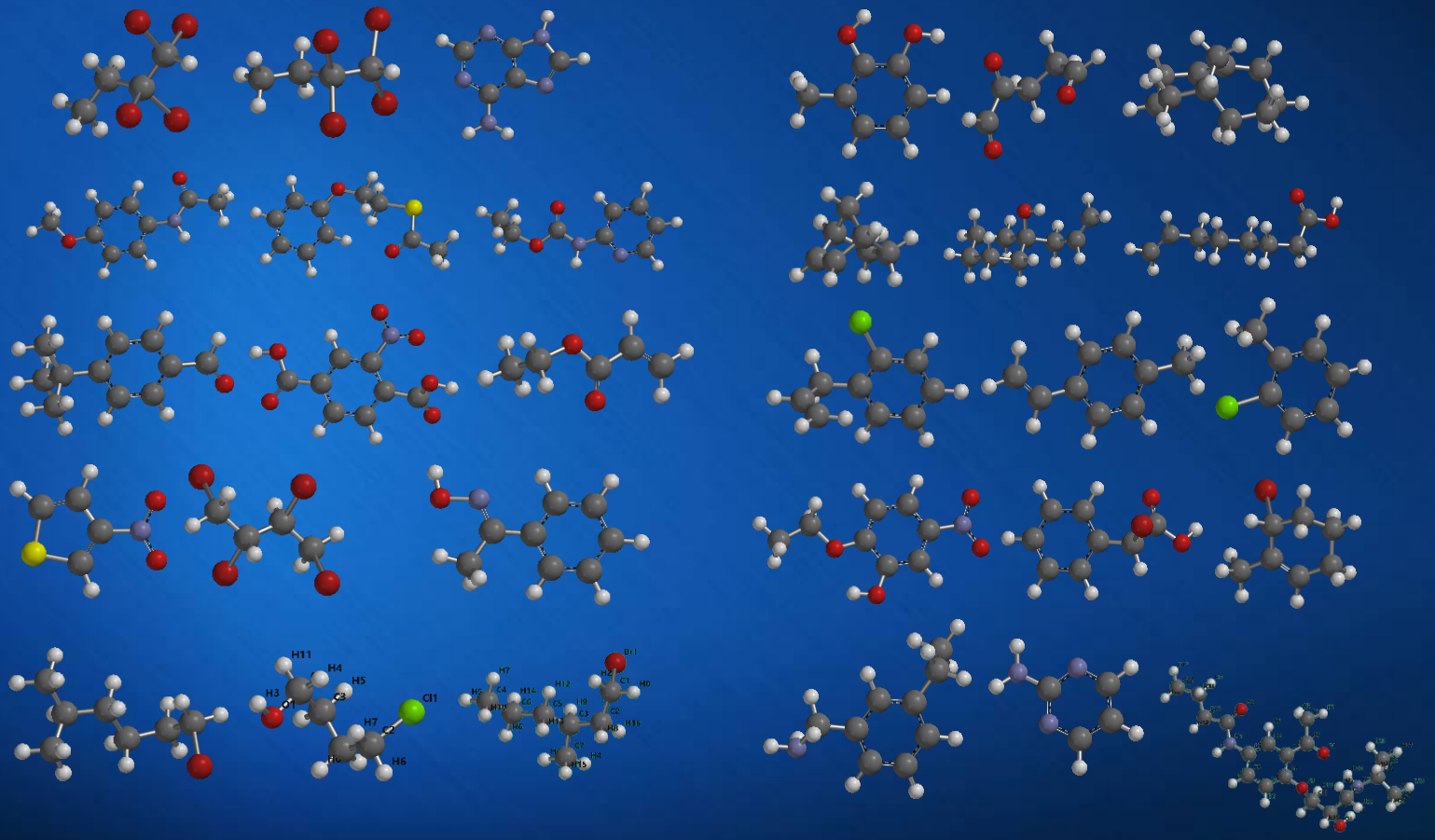
Astronomical spectra and spectral similarity

Results of our search over a pool of 250,000 molecule by similarity method

First results of our mathematical explorations on the chemical composition of the PDS100.

elemental composition is predicated as : H, C, N, O, S, Cl, Br



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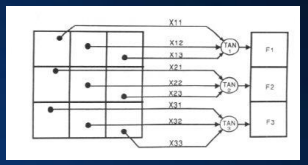
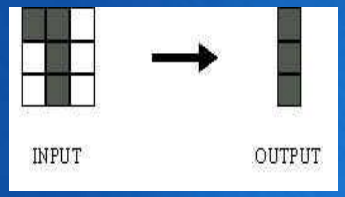
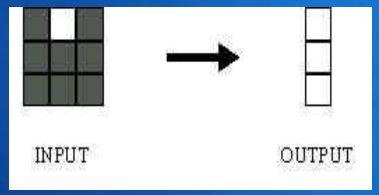
Training tables in neural networks

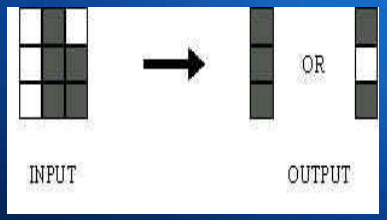
BLACK=0, WHITE=1,
Network after training and applying the firing rule
Generalized tables of neural network



T H







X11:	0	0	0	0	1	1	1	1	TAN1
X12:	0	0	1	1	0	0	1	1	
X13:	0	1	0	1	0	1	0	1	
OUT:	0	0	1	1	0	0	1	1	
X21:	0	0	0	0	1	1	1	1	TAN2
X22:	0	0	1	1	0	0	1	1	
X23:	0	1	0	1	0	1	0	1	
OUT:	1	0/1	1	0/1	0/1	0	0/1	0	
X31:	0	0	0	0	1	1	1	1	TAN3
X32:	0	0	1	1	0	0	1	1	
X33:	0	1	0	1	0	1	0	1	
OUT:	1	0	1	1	0	0	1	0	

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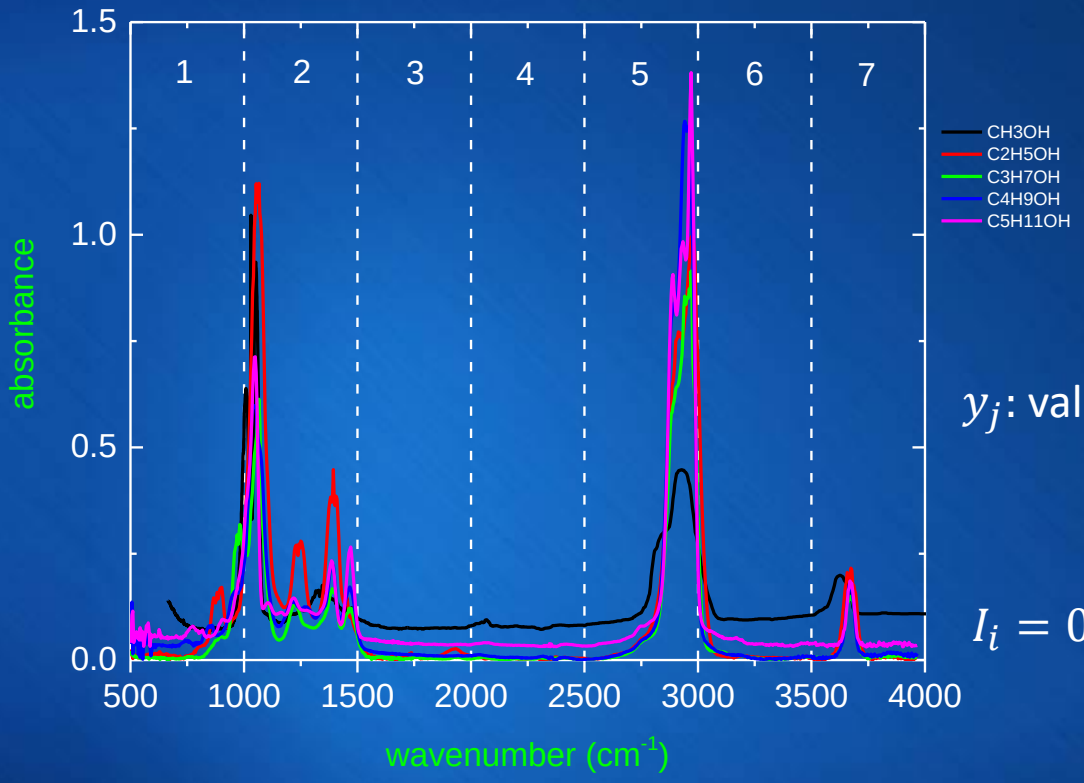
First steps for training the neural networks



Experimental IR spectra, gas phase

$$i = \frac{\vartheta - 500}{500} \; (section\ number)$$

y_j: value at output unit

$$y_{OH}^{CH3OH} = \sum_{i=1}^{7} I_i^{CH3OH} \, C_{i,OH}^{CH3OH}$$

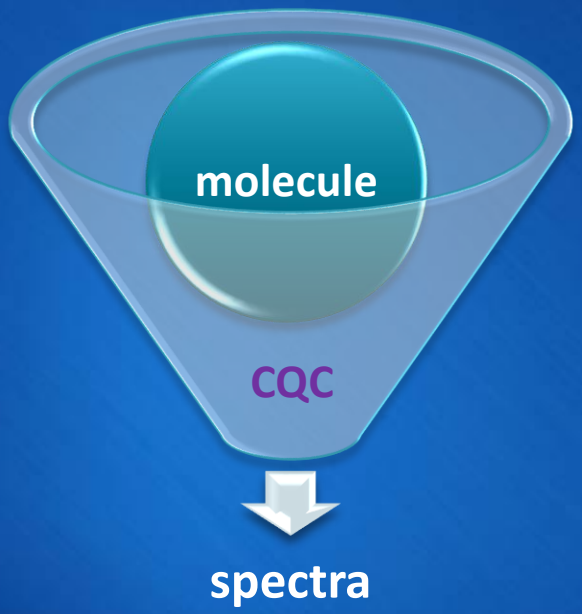
$$I_i = 0 \; if \; there \; is \; no \; peak \; at \; ith \; section$$

$$\overline{y}_{OH} = \sum_{m=1}^{N=5} y_{OH}^{m}$$

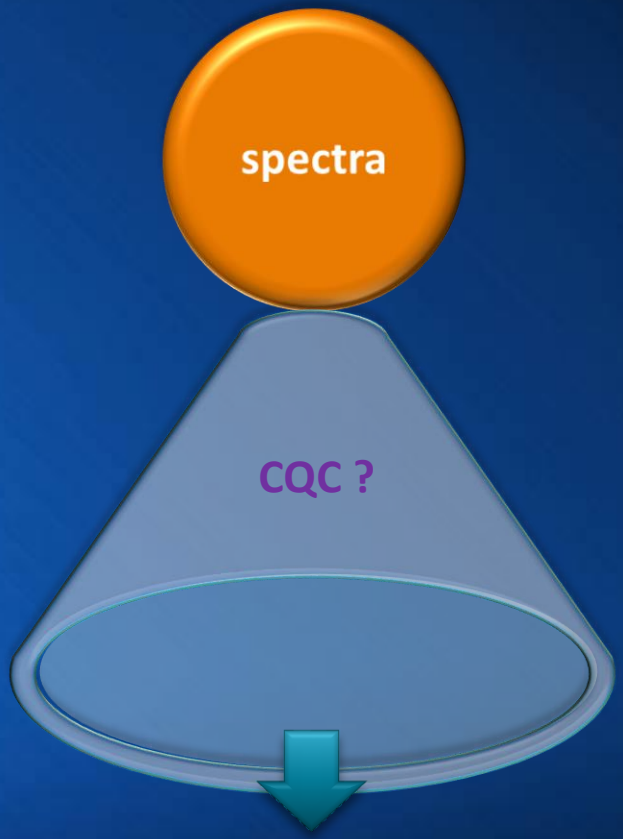
$$i = \frac{\vartheta - 400}{5.625} \; or \; i = 6.0(\vartheta)^{0.5} - 120.0 \; rounded \; to \; the \; neasrt \; integer$$

Robb, E. and M. Munk (1990). "A neural network approach to infrared spectrum interpretation." Microchimica Acta **100**(3-4): 131-155.

Pictorial conclusion



forward transformation
of molecule(s) to the spectra



backward transformation
of spectra to its molecular origin

Hong Kong and Its Culture

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Acknowledgments

Thank you for listing to this talk

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and all my colleagues in LSR and HKU Chemistry Department
And
my special thank to Professor Quentin Andrew Parker
for organizing PSHK 2016 at HKU

谢谢

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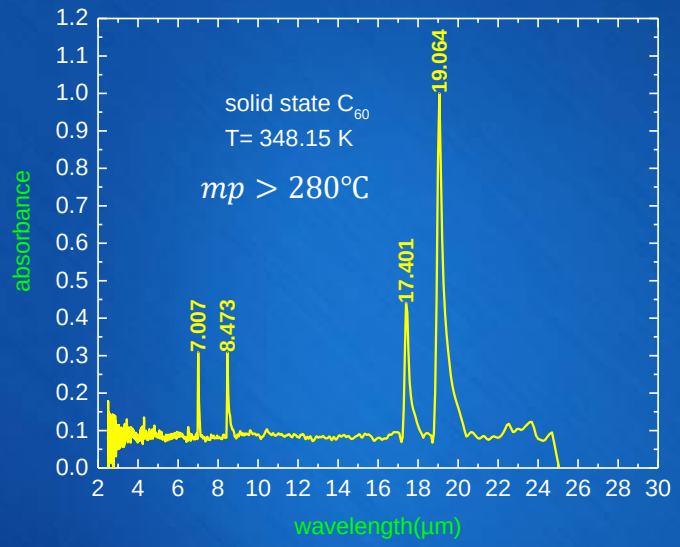
Introduction to Infrared Spectroscopy



Advantages of FT spectroscopy

a) Multiplex advantage: All wavelengths are measured simultaneously in interferometer. substantial reduce of the noise.

b) Throughput advantage: Greater radiation power , 100 times greater in mid-IR at 2000 1/cm in comparison to conventional spectrometers.

c) Connes advantage : High wavenumber stability of the spectra obtained

C60 spectrum obtained from Professor Franco Cataldo
INAF–Osservatorio Astrofisico di Catania, via S. Sofia 78, 95123 Catania, Italy
& Actinium Chemical Research srl, via Casilina 1626/A, 00133 Rome, Italy

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Theory of vibrations

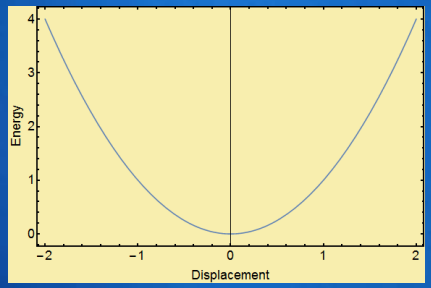
Classical harmonic oscillator

$$F = -kx$$

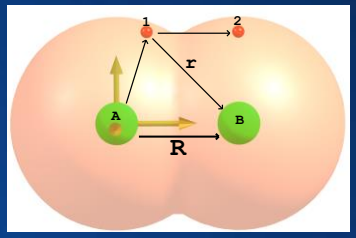
$$V = -\frac{\partial F}{\partial x} = \frac{1}{2}kx^2$$

$$E = V + T = \frac{1}{2}kA^2$$

$$A: amplitude$$



Quantum mechanical Rotation-vibration

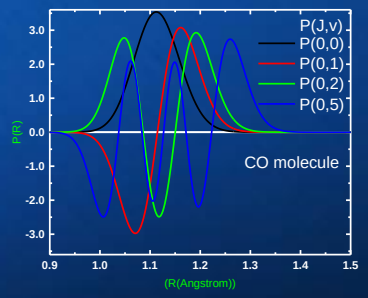


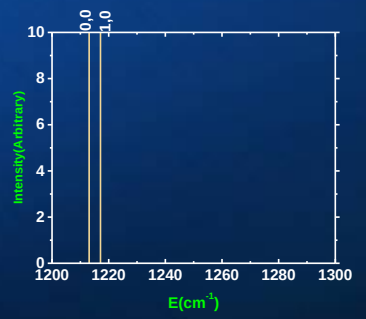
$$\frac{\partial^2 P_R(R)}{\partial R^2} + \{\frac{-2\mu}{\hbar^2} E^e_{gr}(R) + \frac{J(J+1)}{R^2} + \} P_R(R) + \frac{2\mu}{\hbar^2} E^{rv} = 0$$

$J = 0$ are the vibrational levels without the effect of rotation

$J \neq 0$ coupling between rotation and vibration

Numerov method
(free download is available from our LSR)





1-Sadjadi 2013, PhD Thesis (Appendix), HKU Department of Chemistry

2-http://www.scifac.hku.hk/kwok/sal/abdi_rovibrational.html

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Overtones and combination bands

Vibrational Self-Consistent Field (VSCF) calculations
perturbation theory, MP2/DZ or TZ