Quantum Chemical Interpretation of Interstellar Infrared Bands

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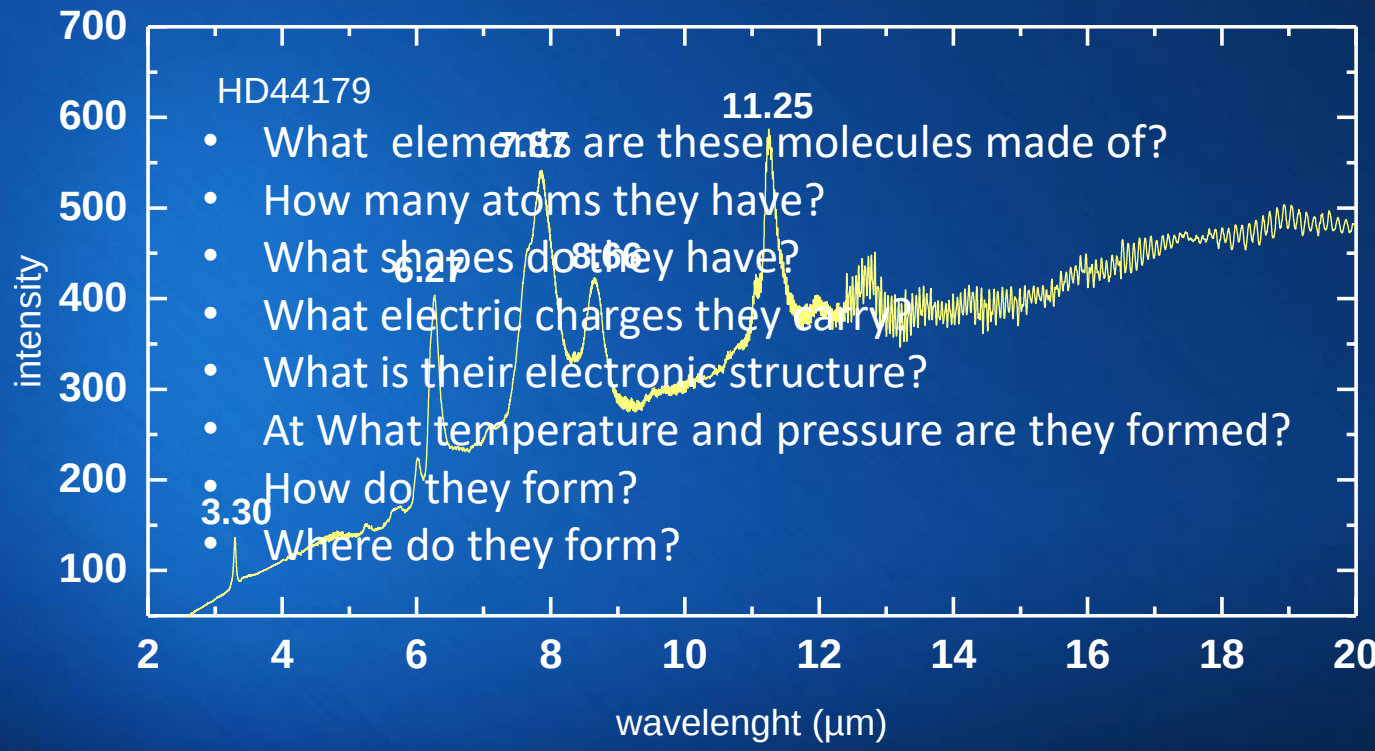
http://www.scifac.hku.hk/kwok/sal/abdi.html

What is(are) this(these) Molecule(s)

Astronomical observations



- What elements are these molecules made of?
- How many atoms they have?
- What shapes do they have?
- What electric charges they carry?
- What is their electronic structure?
- At What temperature and pressure are they formed?
- How do they form?
- Where do they form?

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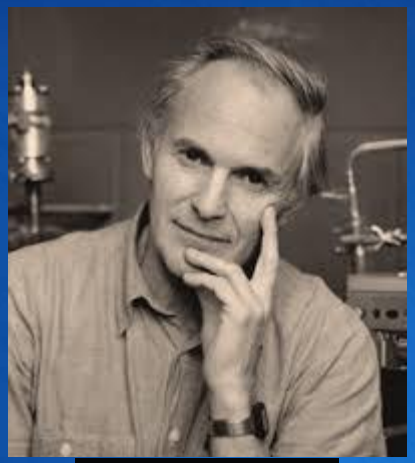
C60 : Buckminsterfullerene



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.
- Fullerenes are not highly "stable" molecules.
- 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

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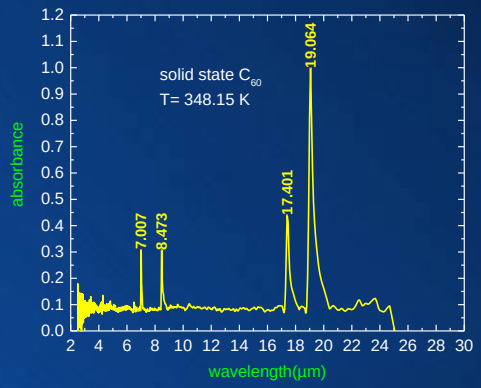
Methods of Interpretation

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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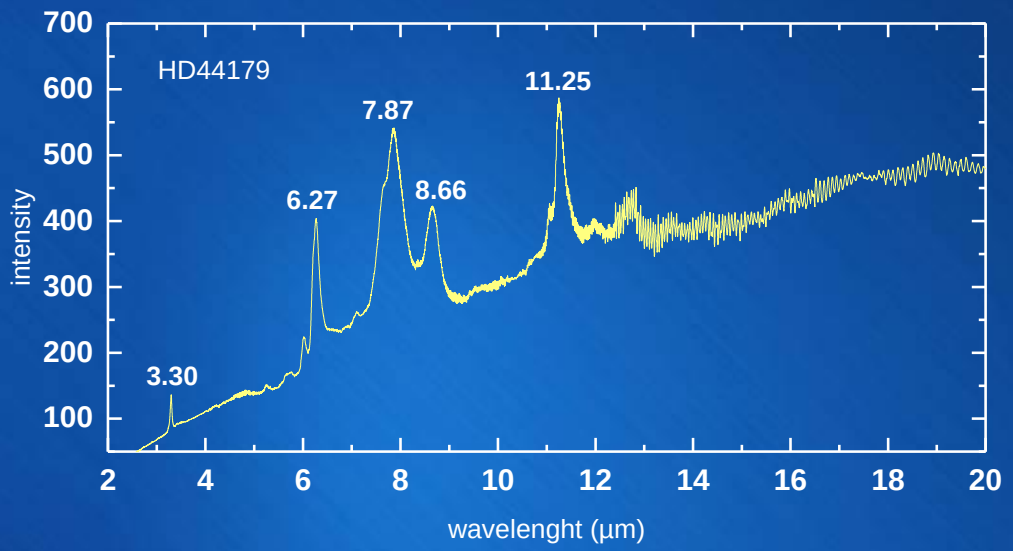
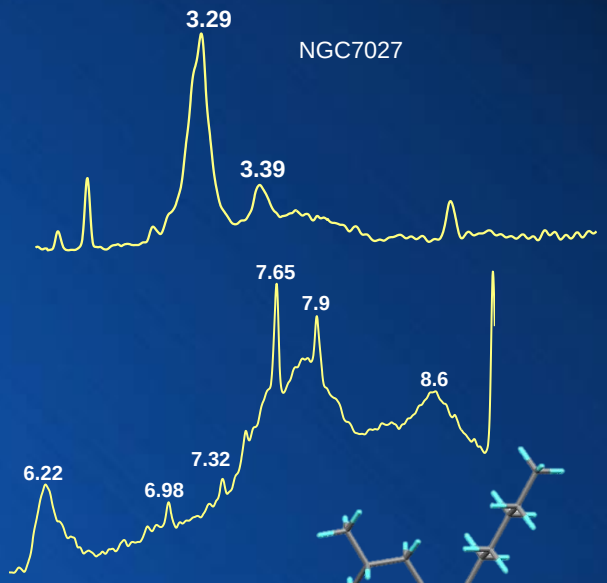
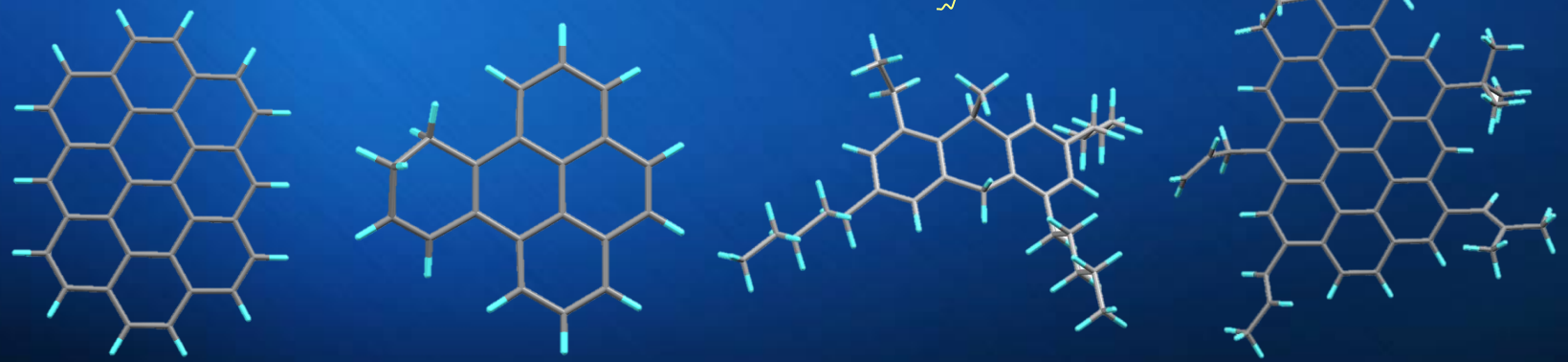
Visual inspection

Astronomical observations and proposed models







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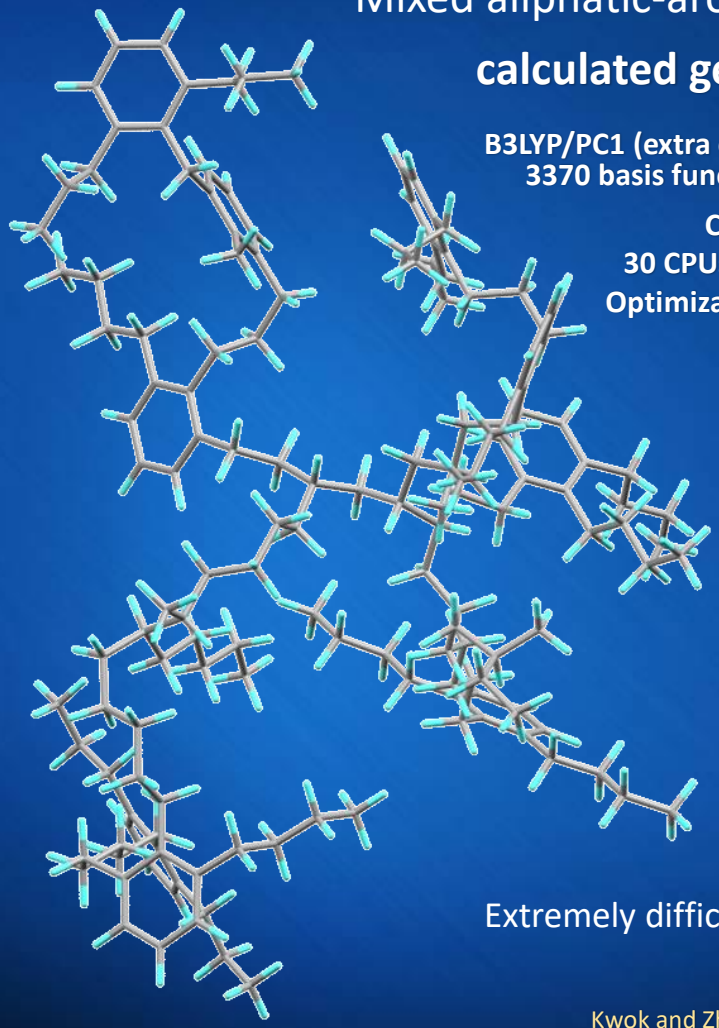
Visual inspection & MAON model

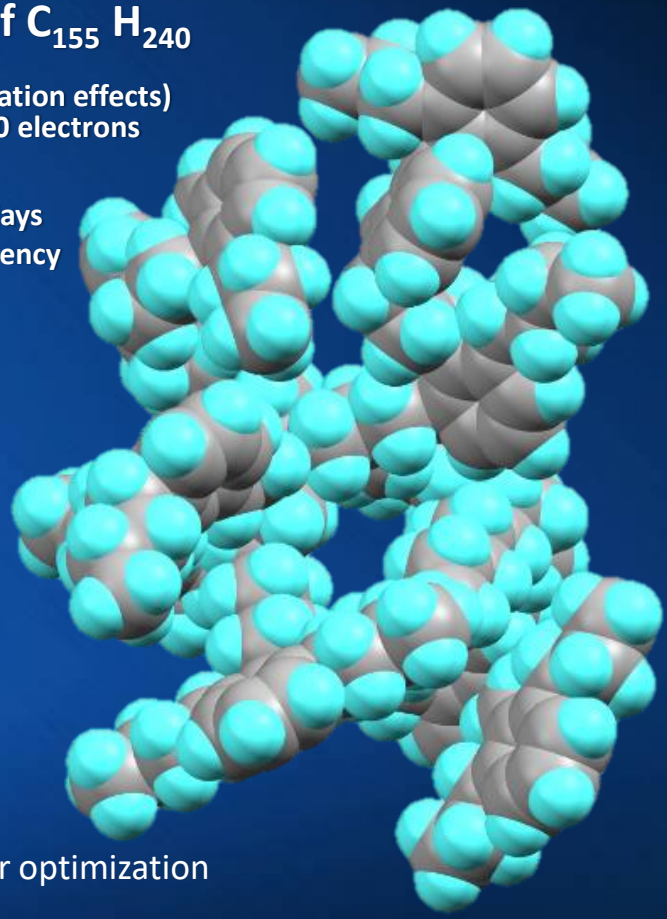
Mixed aliphatic-aromatic organic nanoparticle

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

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

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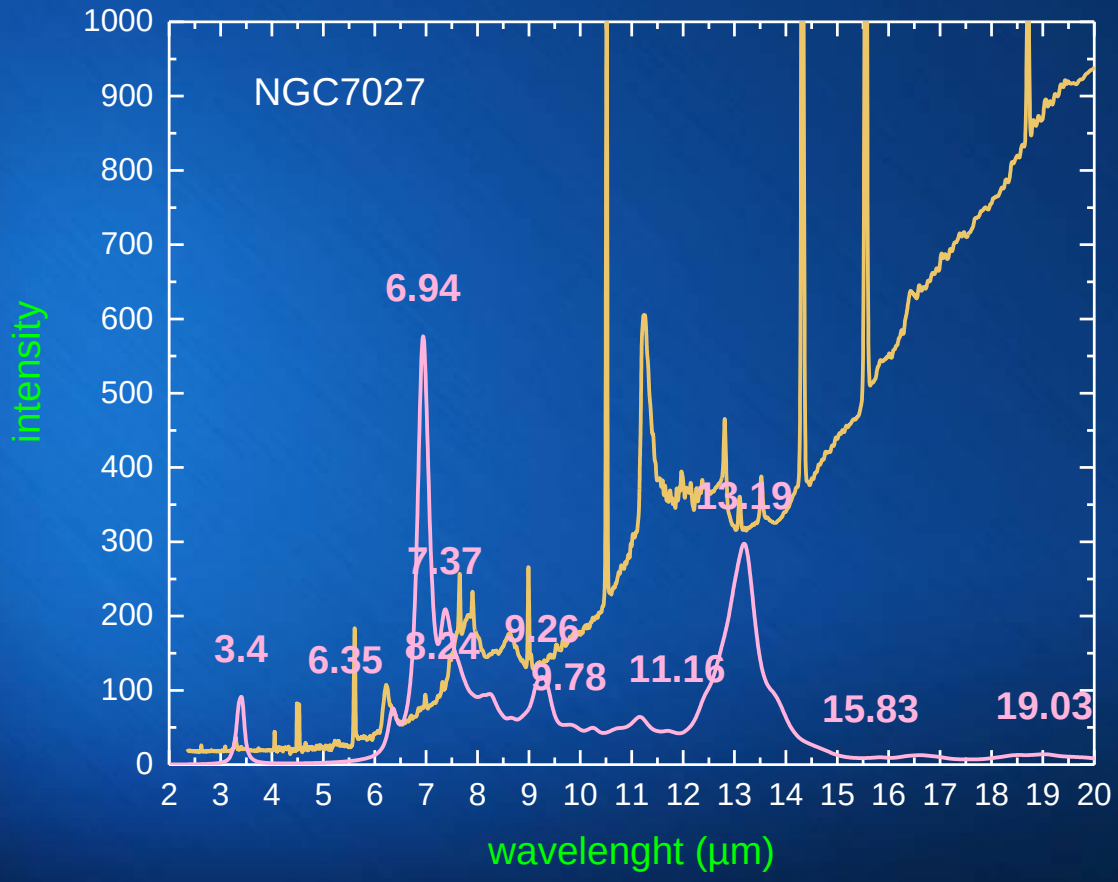
Predictions by visual inspection

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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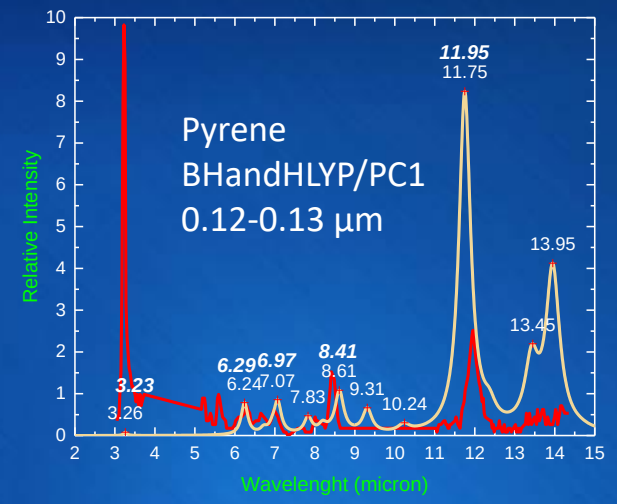
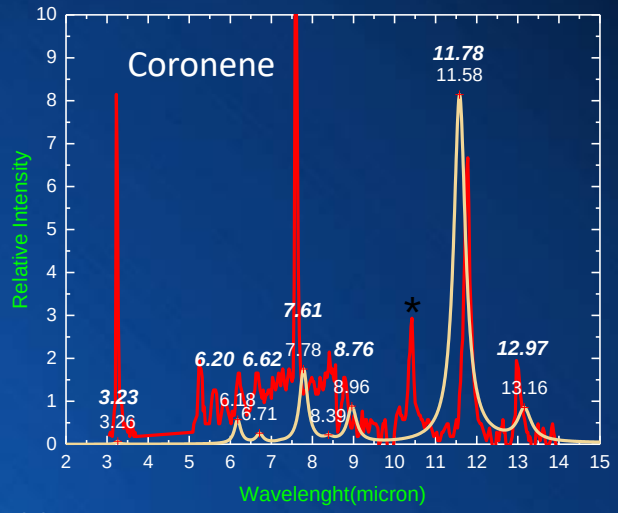
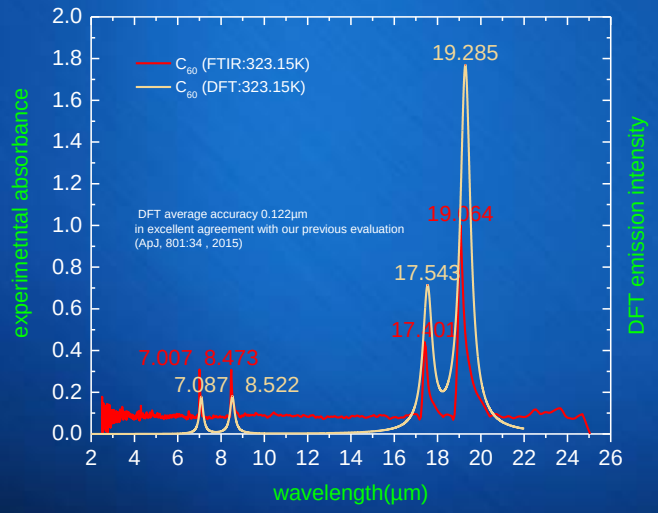
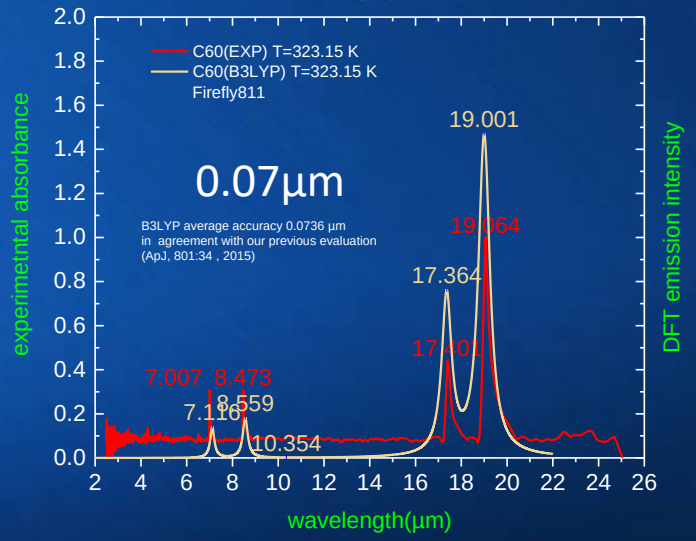
Accuracy of DFT/Drude simulation









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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Theory of vibrations

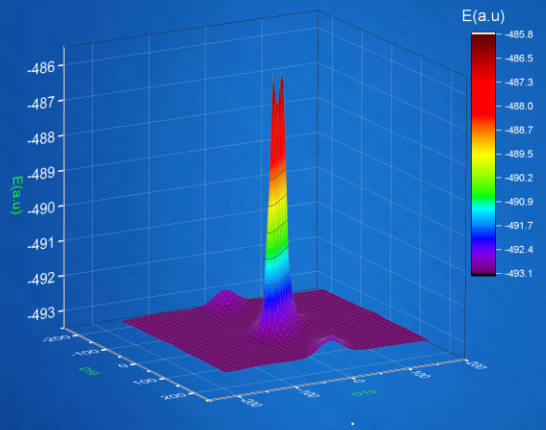
Harmonic vibrational frequencies in classical picture

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

mass-weighted Cartesian

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

Potential energy surface



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

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

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

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

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

Quantitative visual inspection

Theory of vibrations helps to develop a quantitative visual inspection

1945

РАСЧЕТ ЧАСТОТ И ИНТЕРПРЕТАЦИЯ КОЛЕБАТЕЛЬНЫХ СПЕКТРОВ МНОГОАТОМНЫХ МОЛЕКУЛ

I. МЕТИЛОВЫЙ СПИРТ

Б. И. Степанов

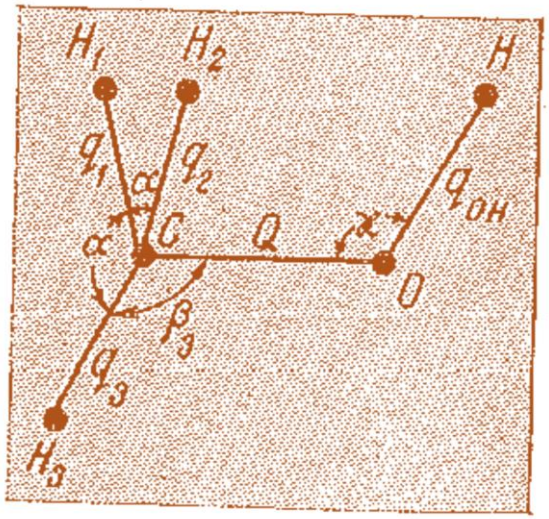
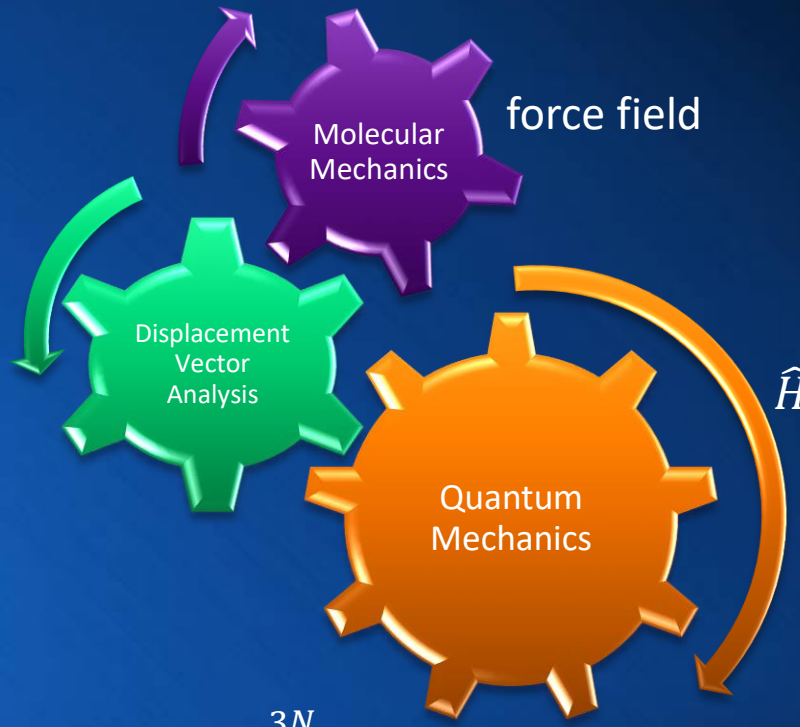


Рис. 1

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



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

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

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

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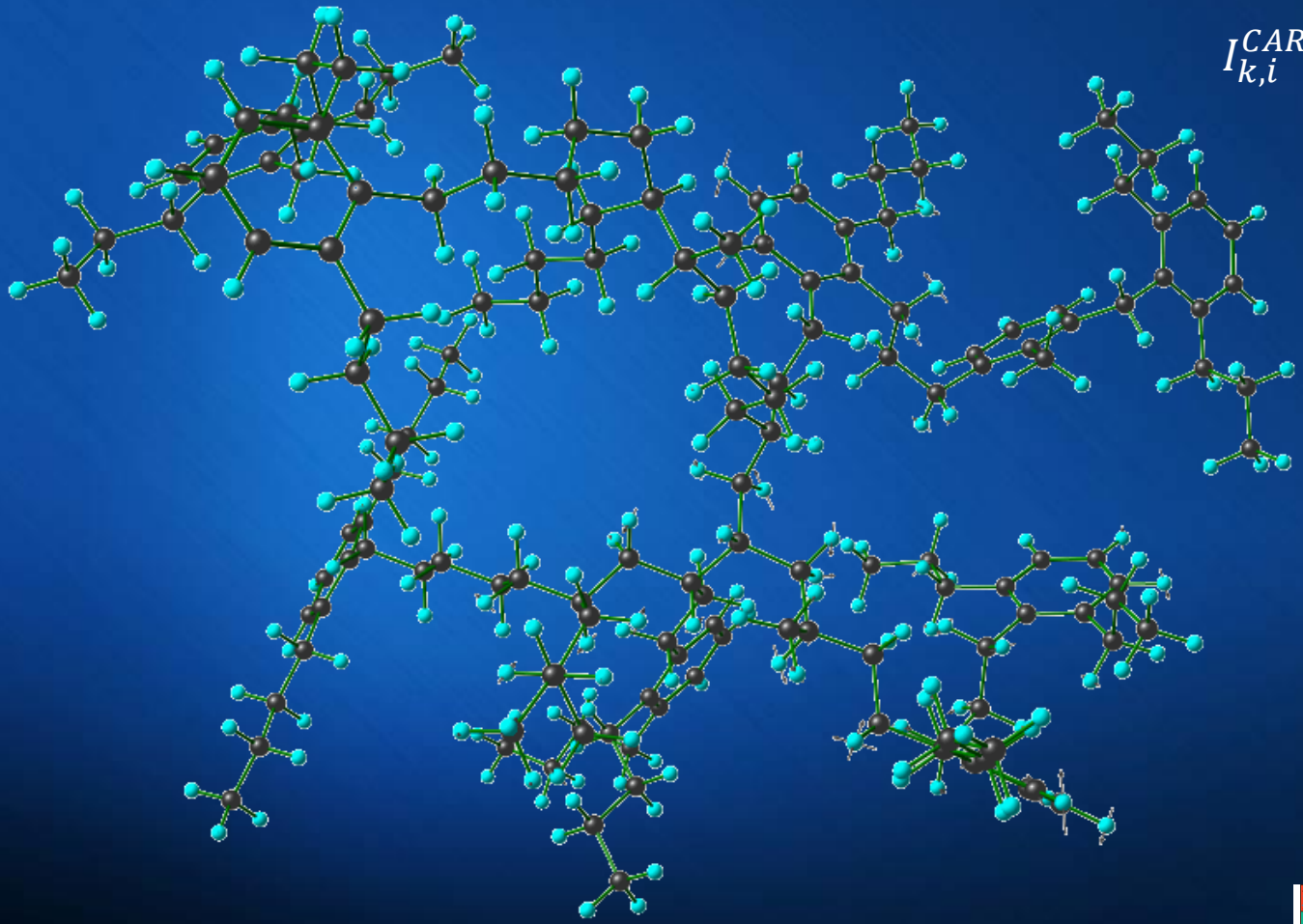
Quantitative visual inspection

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)

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



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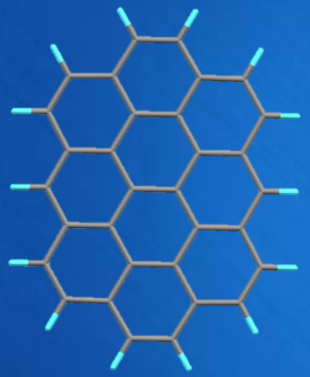
Quantitative visual inspection

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

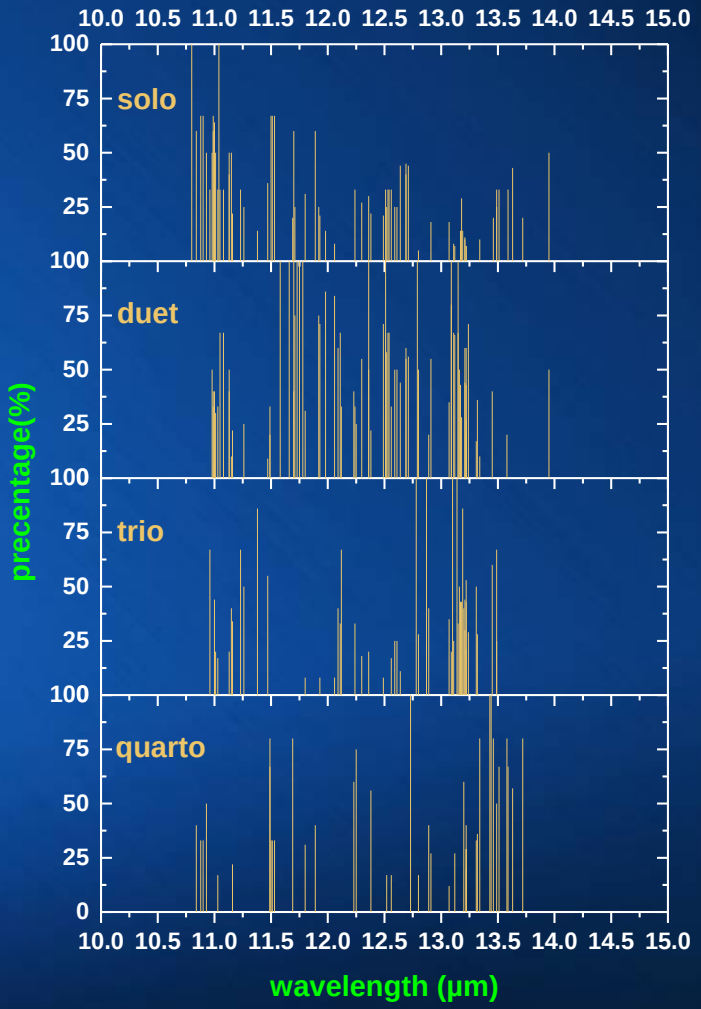


227 vibrations

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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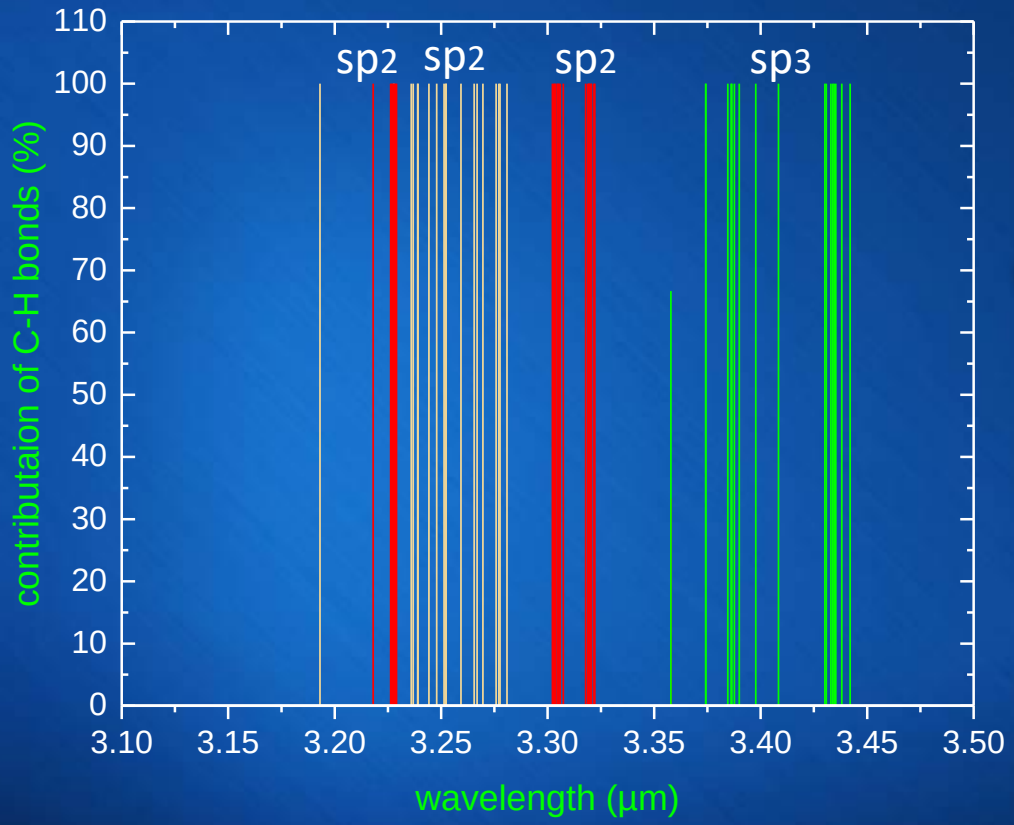
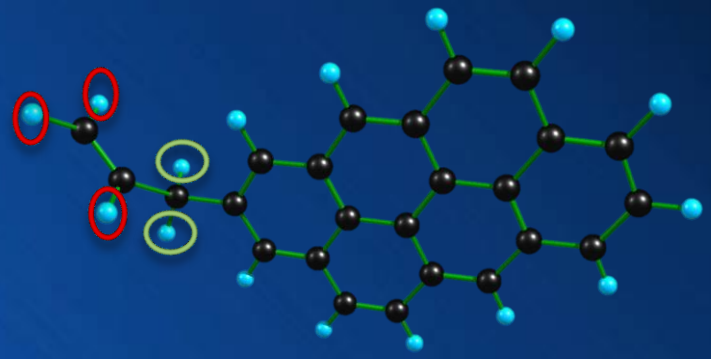
Quantitative visual inspection

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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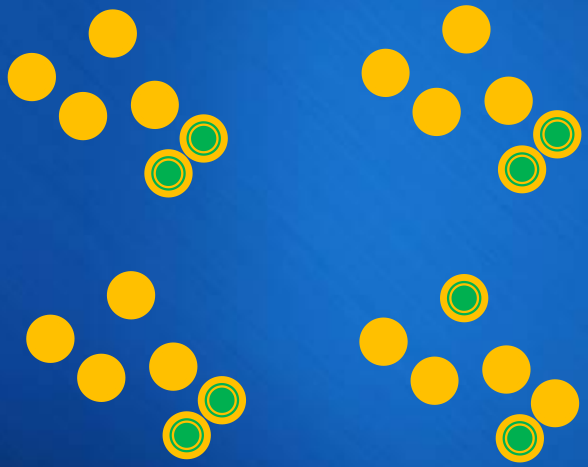
Spectral similarity

$Properties = f(strcutue)$

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.

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%

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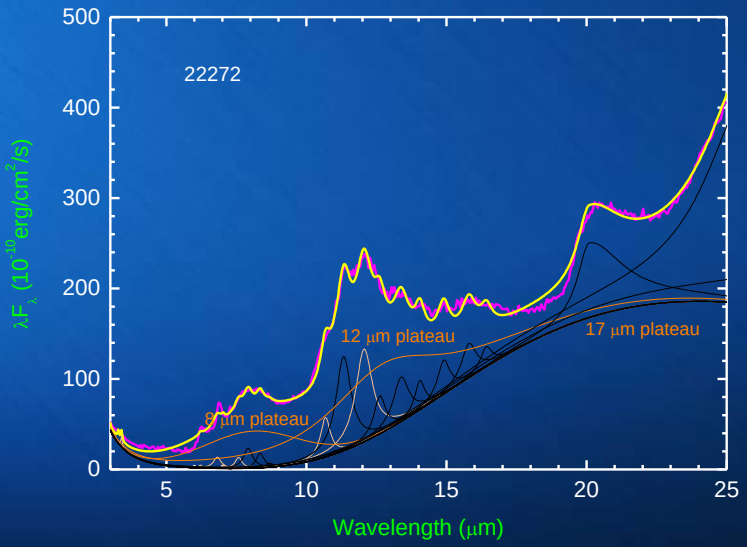
Astronomical spectra and spectral similarity

Astronomical spectra are recoding in Emission

- 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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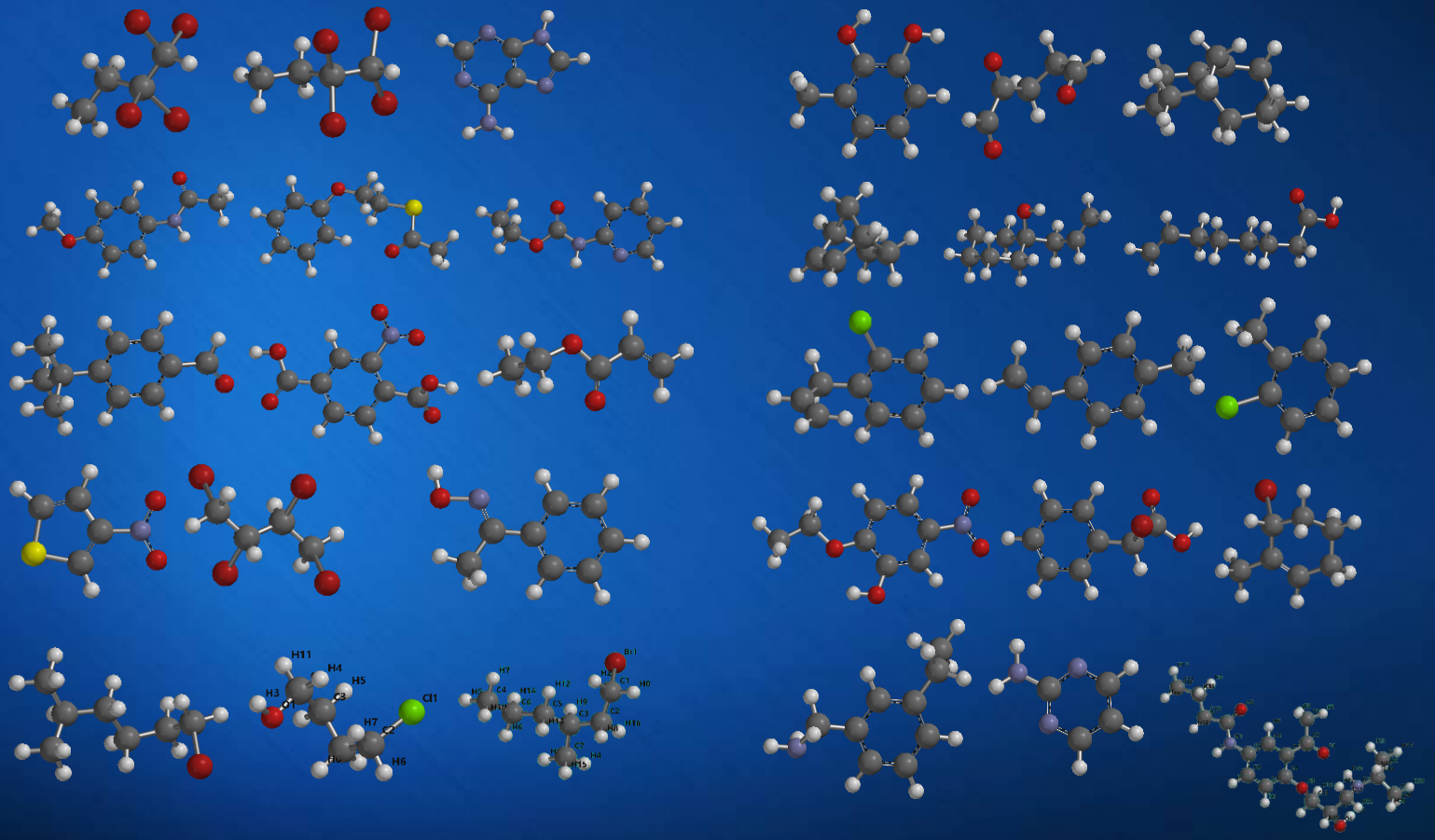
Astronomical spectra and spectral similarity

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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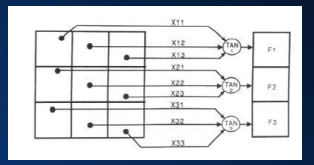
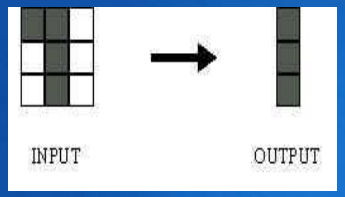
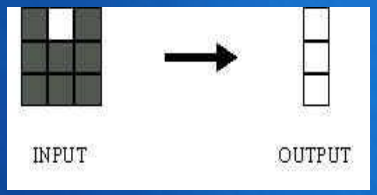
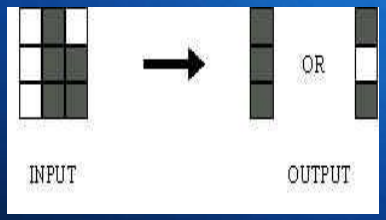
Training tables in neural networks



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







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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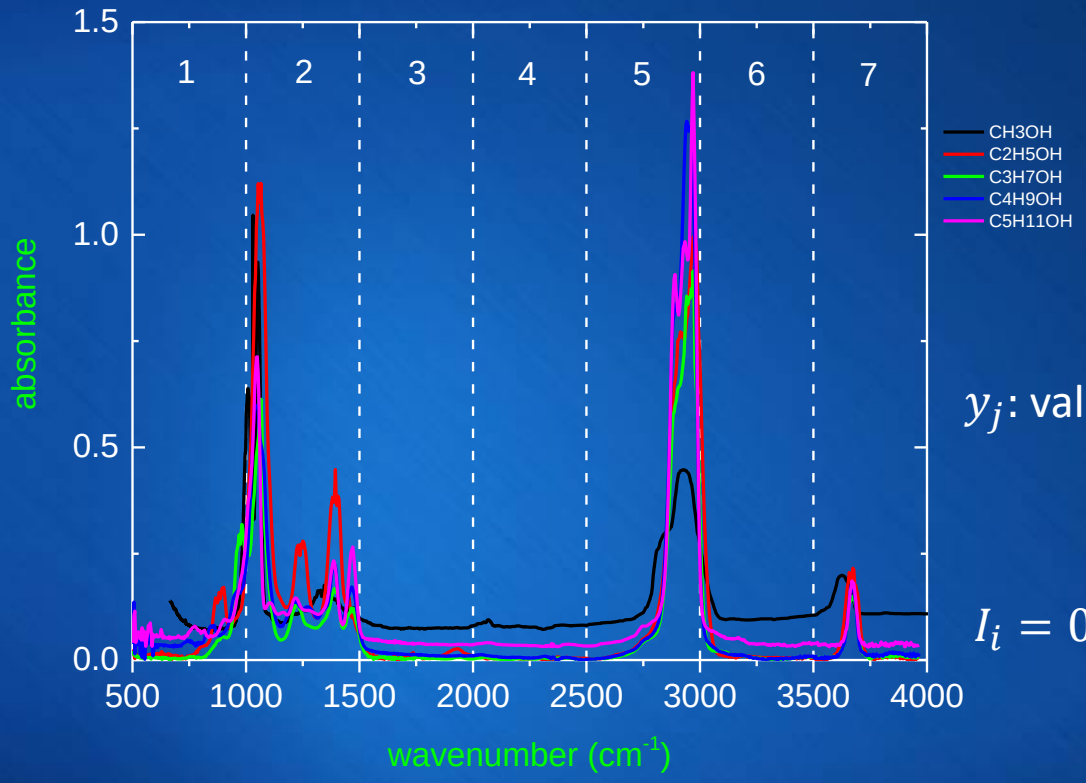
First steps for training the neural networks



Experimental IR spectra, gas phase

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

y_j: value at output unit

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

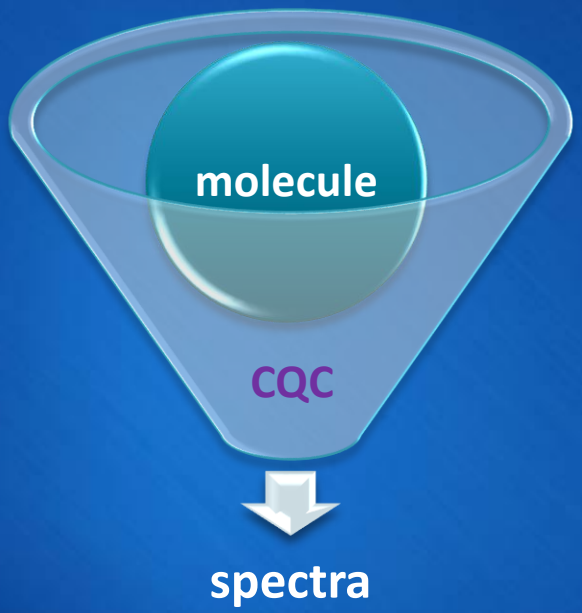
$$I_i = 0 \; if \; there \; is \; no \; peak \; at \; ith \; section$$

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

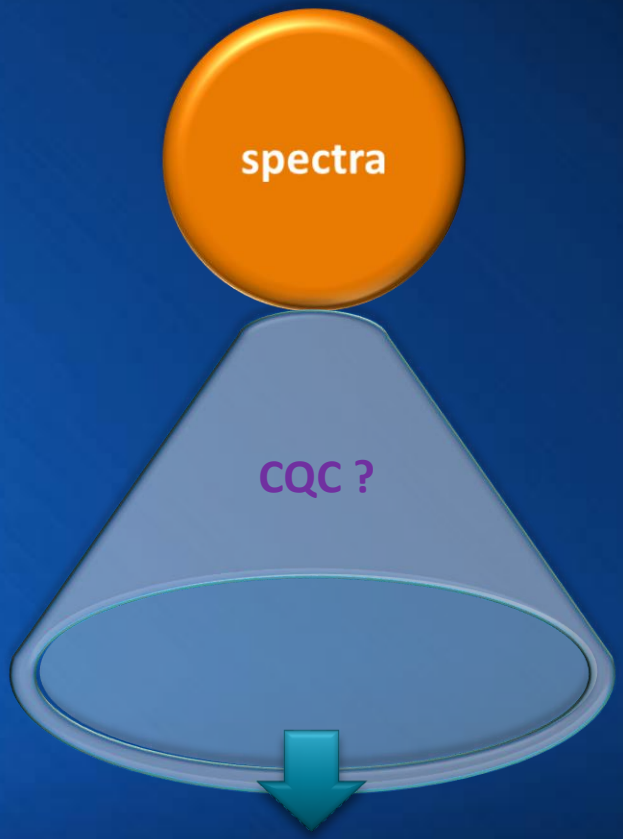
$$i = \frac{\vartheta - 400}{5.625} \; or \; i = 6.0(\vartheta)^{0.5} - 120.0 \; rounded \; to \; the \; neasrt \; integer$$

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



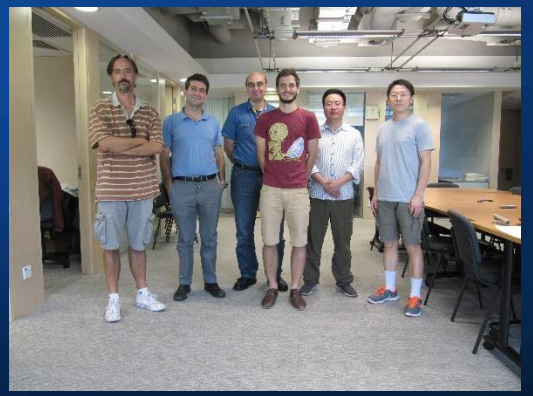
backward transformation
of spectra to its molecular origin

Acknowledgments

Thank you for listing to this talk

I would like to thank my supervisor Professor Sun Kwok
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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