Conformational testing of nitrophthalic acids using quantum chemistry and experimental methods

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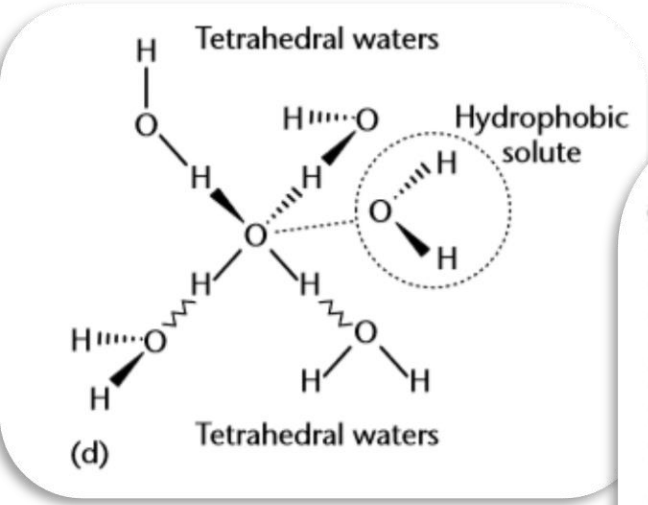
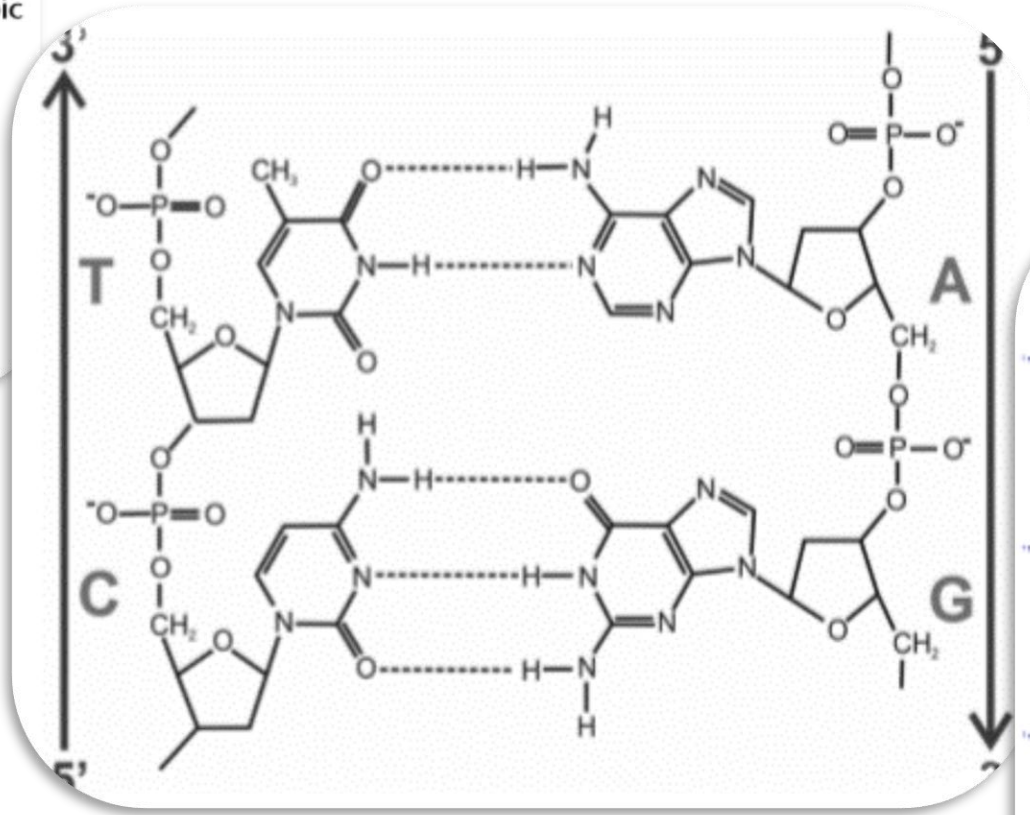
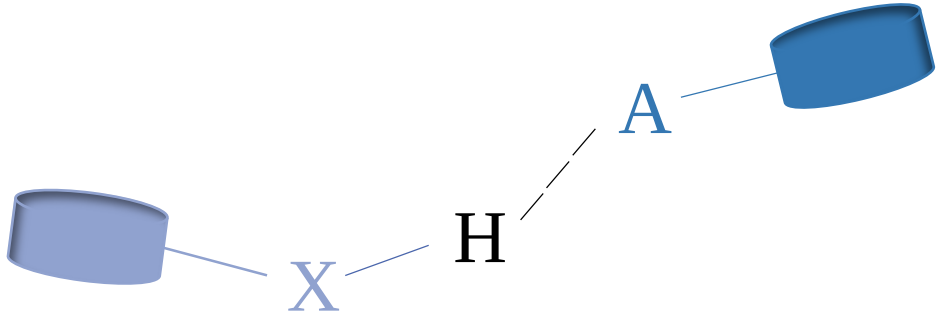
Theoretical introduction

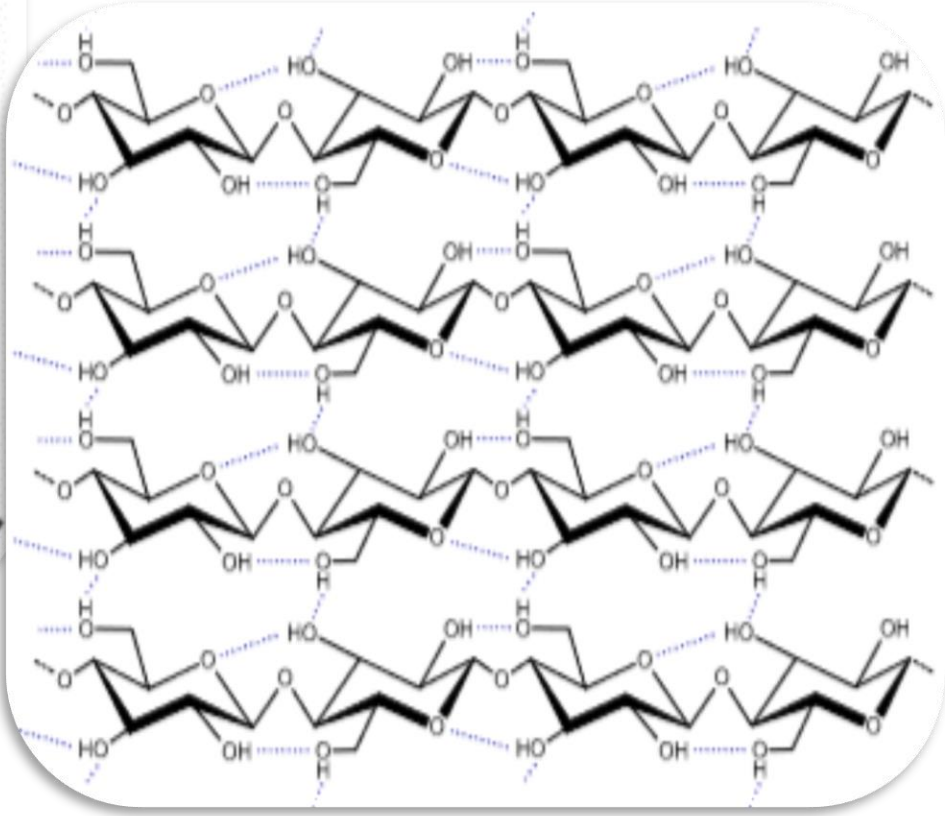
The most important information related to the experiment

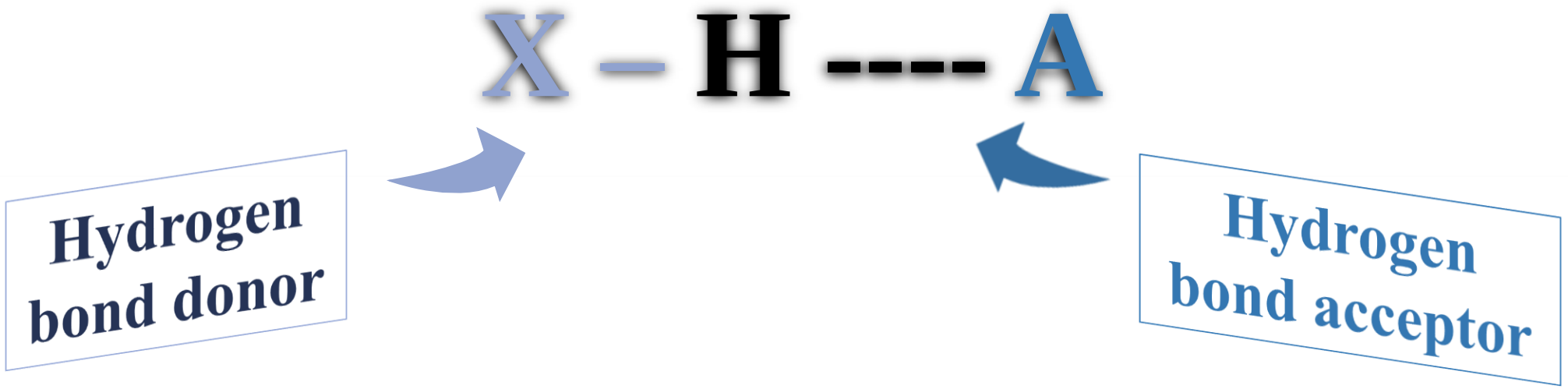
HYDROGEN BOND







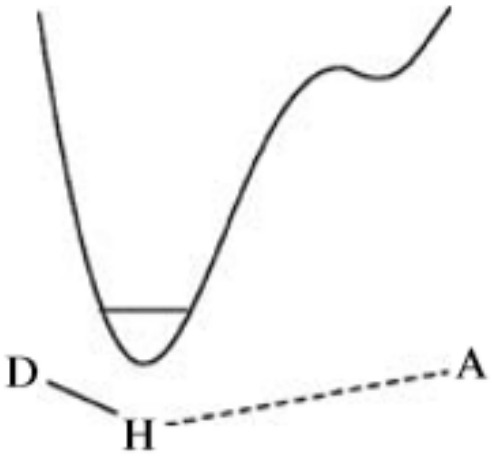


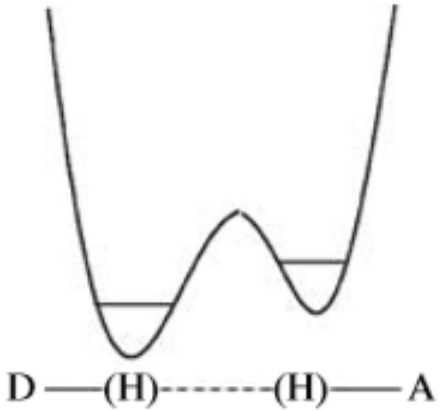


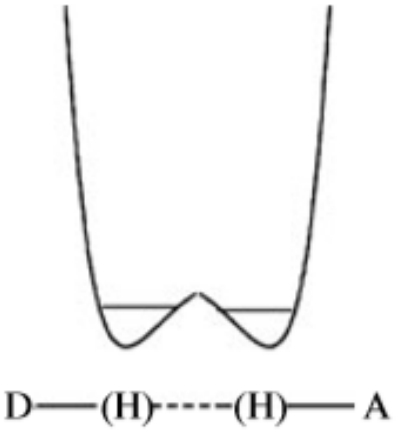
- hydrogen bonds form typically between polar or polarized X –H bonds and electronegative acceptor atoms

- it possesses a significant electrostatic character

H-bond classification by physical properties







1

aSW-HB

2

aDW-MB

3

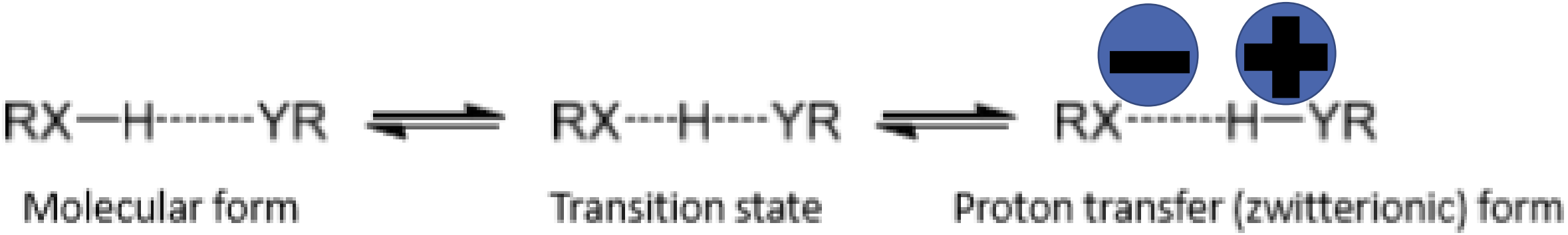
sDW-LB

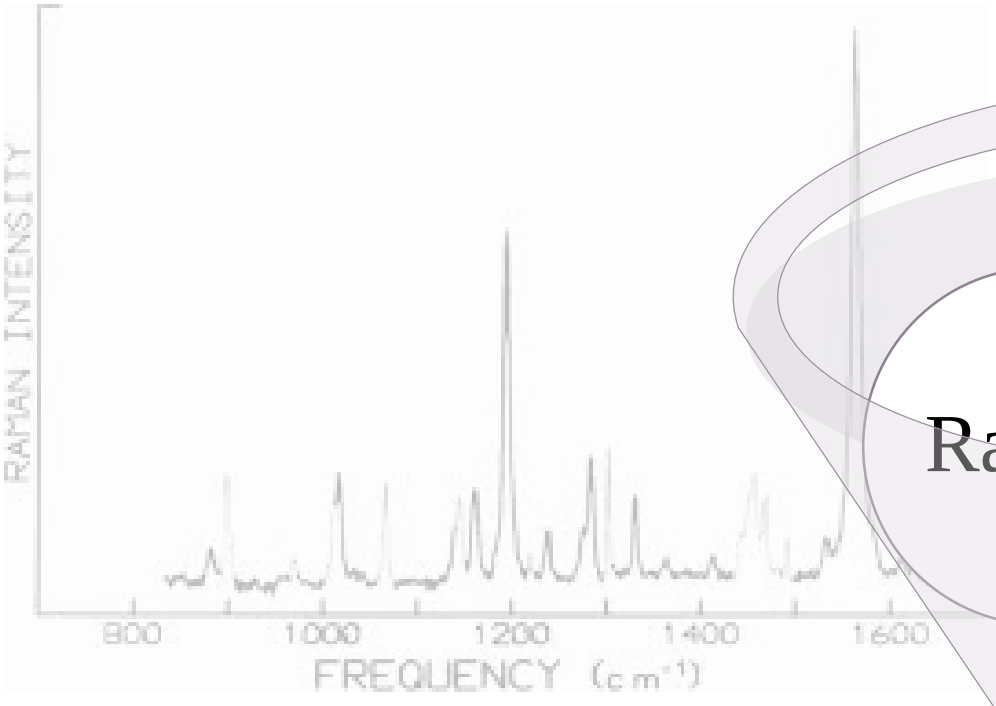
4

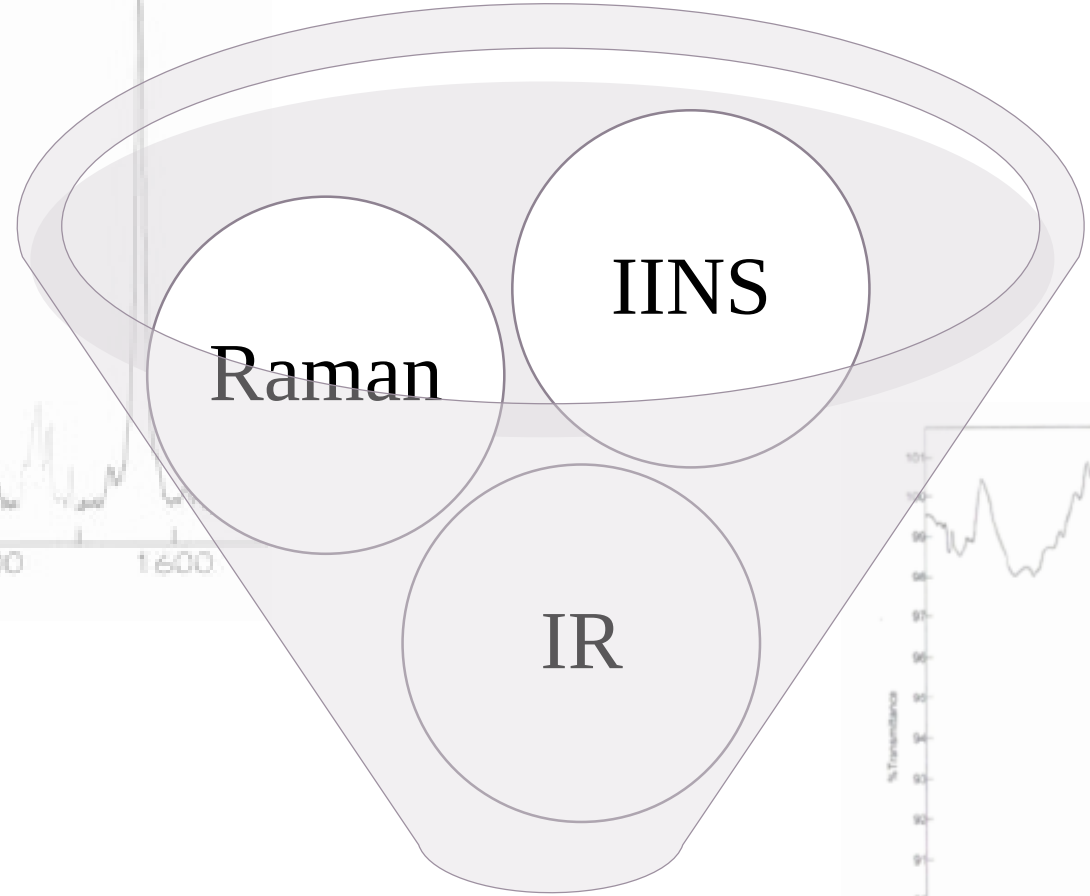
sSW-NB

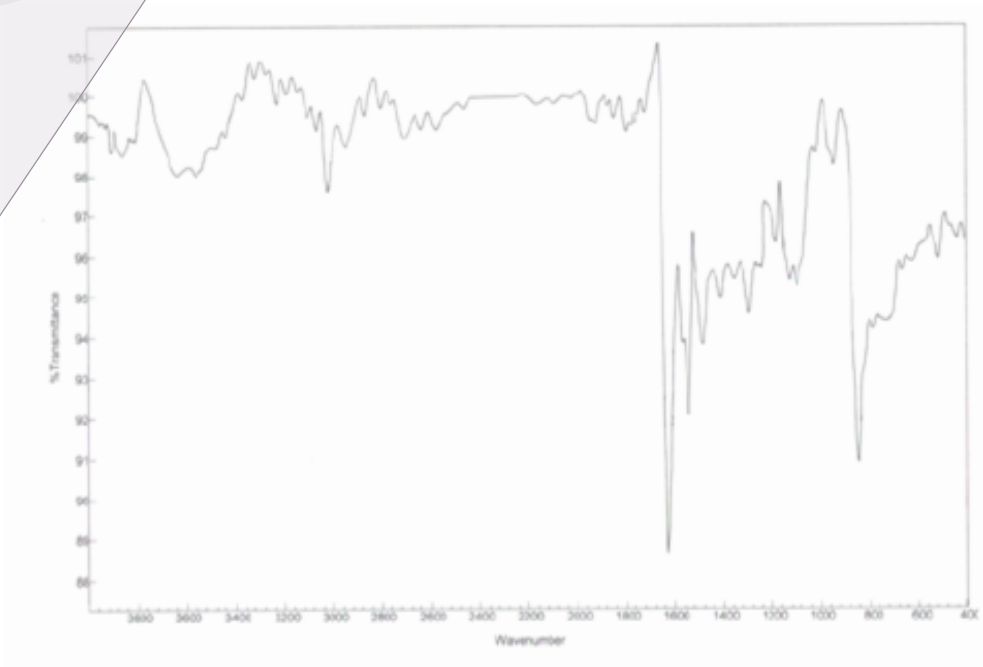
E

Tautomeric equilibrium









Spectroscopic research of compounds with hyndrogen bonds

RAMAN

- selection rules (complementary method to IR)
- reasearching energy levels of the molecule by observing the frequencies present in the radiation scattered by the molecule
- vibrations of molecules are active in the Raman spectrum if they are accompanied by a change in the polarization of the molecule
- solid, liquid, gaseous samples

IR

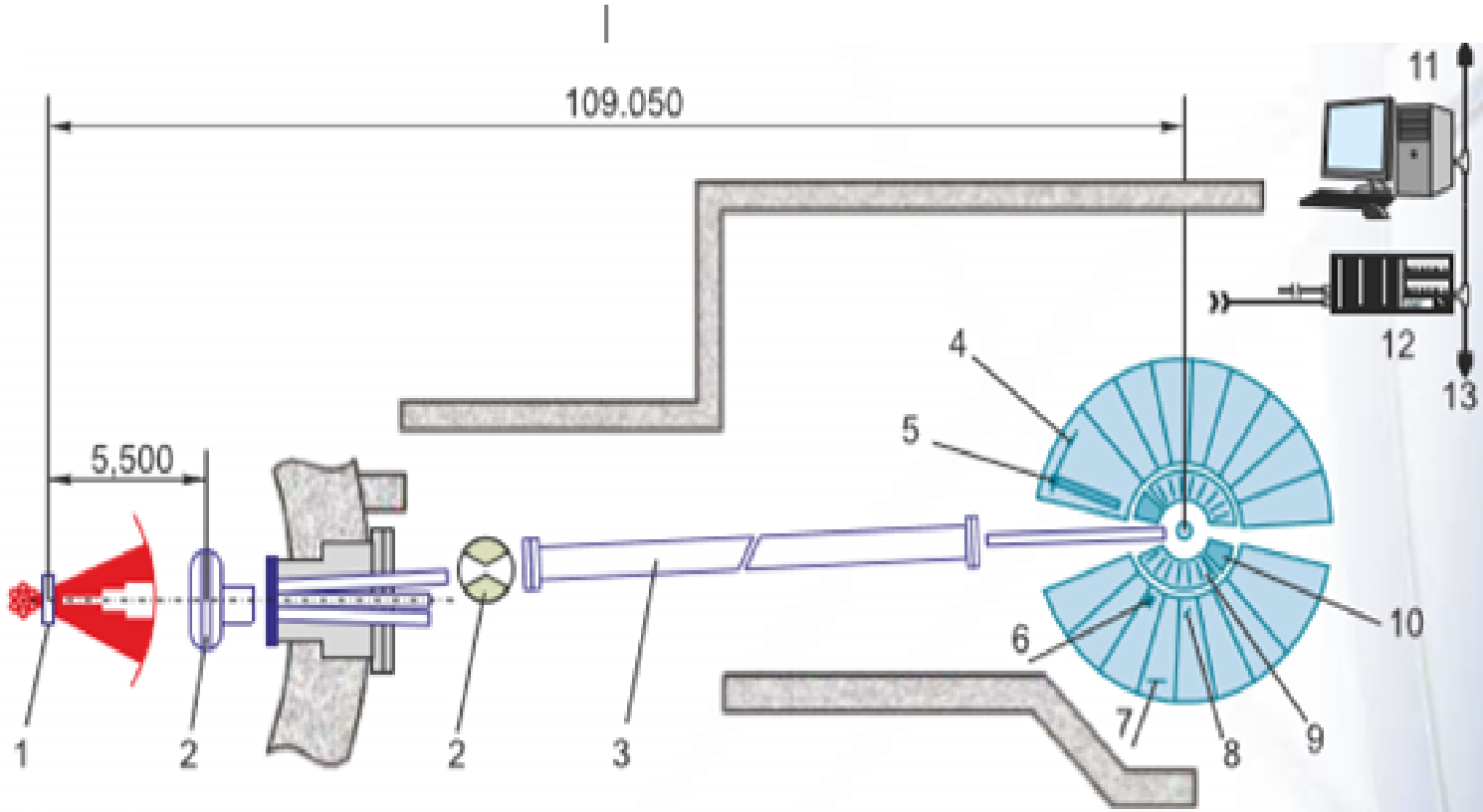
- selection rules
- the ability to register spectra in all states of matter in a wide range of temperatures
- oscillations determine the formation of different absorption bands
- the bands parallel to vibrations that cause changes in the dipole moment of the molecules
- low intensity for the low freq models
- solid, liquid, gaseous samples

IINS

- no selection rules connected with the symmetry of the molecule
- probability of the e.t. depends on the cross-section and on the amplitude of the vibration of an particular atom
- resolution does not exeed 2-3%
- solid state at low temperature – sample
- useful to the studies of molecular vibrations of low frequency internal modes

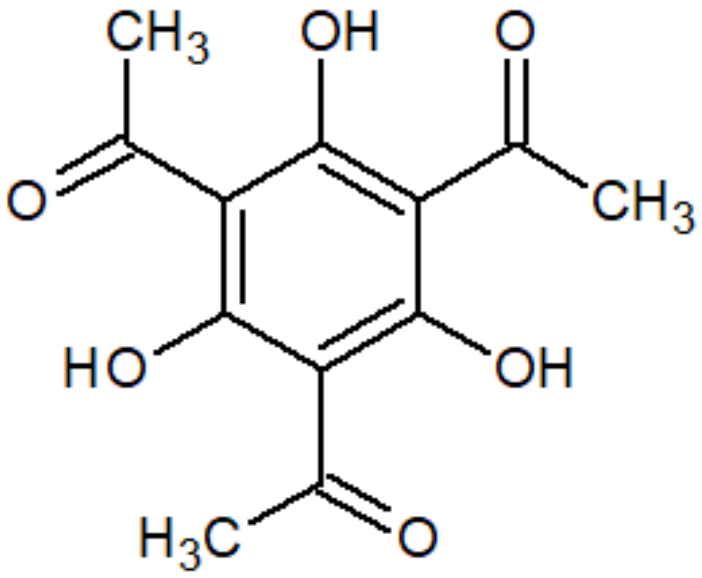
NERA

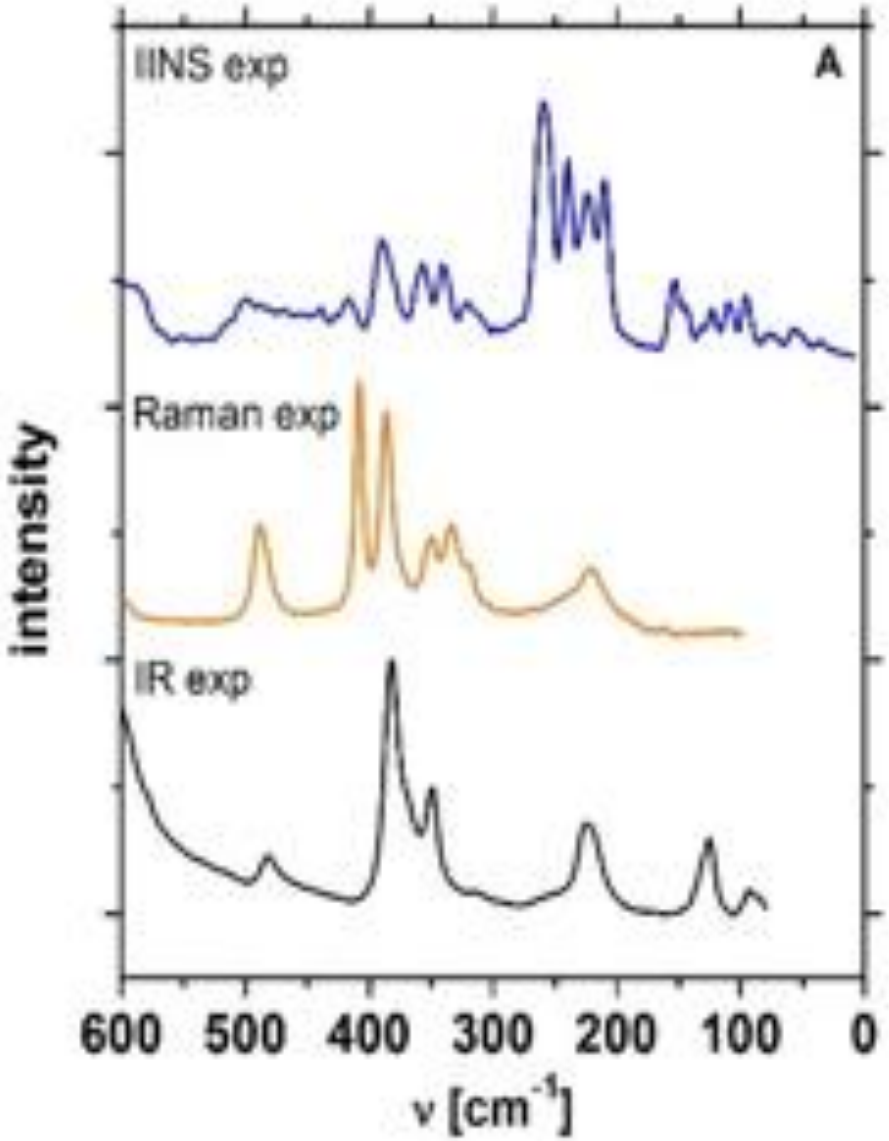
Neutron guide	Ni, mirror, vacuum
Guide aperture	50x160 mm^2
Thermal neutron flux at sample position	$4.6x10^6$ $n/cm^2/s$
Wavelength range	0.4 - 7.0 Å
Scattering angles range	10°-170°
Energy transfer range (INS)	ω=0-130 meV
Moderator - sample distance	109.5 m
Sample - detector distance	0.815 m (INS with Be-filter)
	1.015 m (INS with single crystal)
	1.415 m (neutron diffraction)
Resolution	
Inelastic scattering	Δω/ω=2-4%
Neutron diffraction	Δd/d=0.4% for λ >1Å



1 Moderator
2 Background Choppers
3 Ni Guide Tube
4 Detector for High Intensity Diffraction
5 Detector for High Resolution Diffraction
6 He^3 Detectors (INS and QNS)
7 Single Crystal QNS Analyzer
8 Pyrolytic Graphite INS Analyzer
9 Be-Filters
10 Collimators
11 VME control and operative visualization/analysis
12 VME Station (OS/9)Data Acquisition
13 EtherNet Data Transfer

Why we have to analyze three types of spectra ?

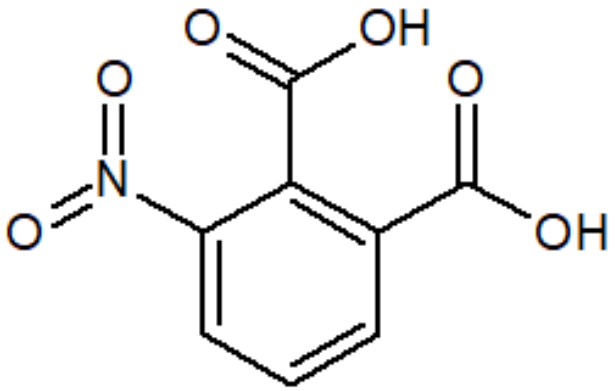




IINS (1100 – 50 cm^{-1}, T=10 K),
MIR i FIR (4000 – 50 cm^{-1}; 300 K < T 5 K),
Raman (T=300 K)

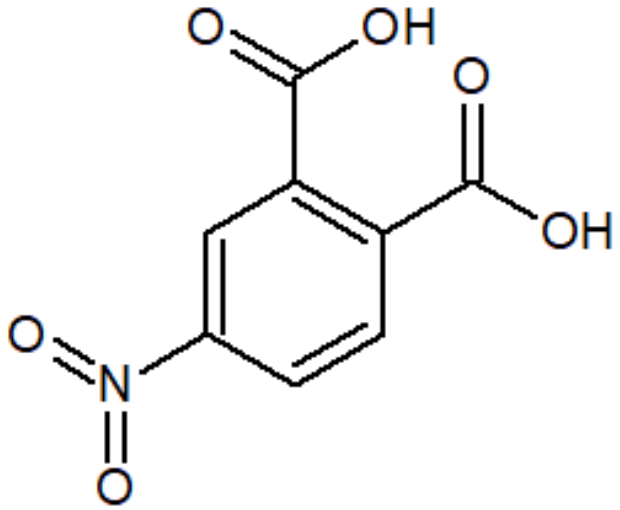
Experimental and computational

Analyzed chemical compounds

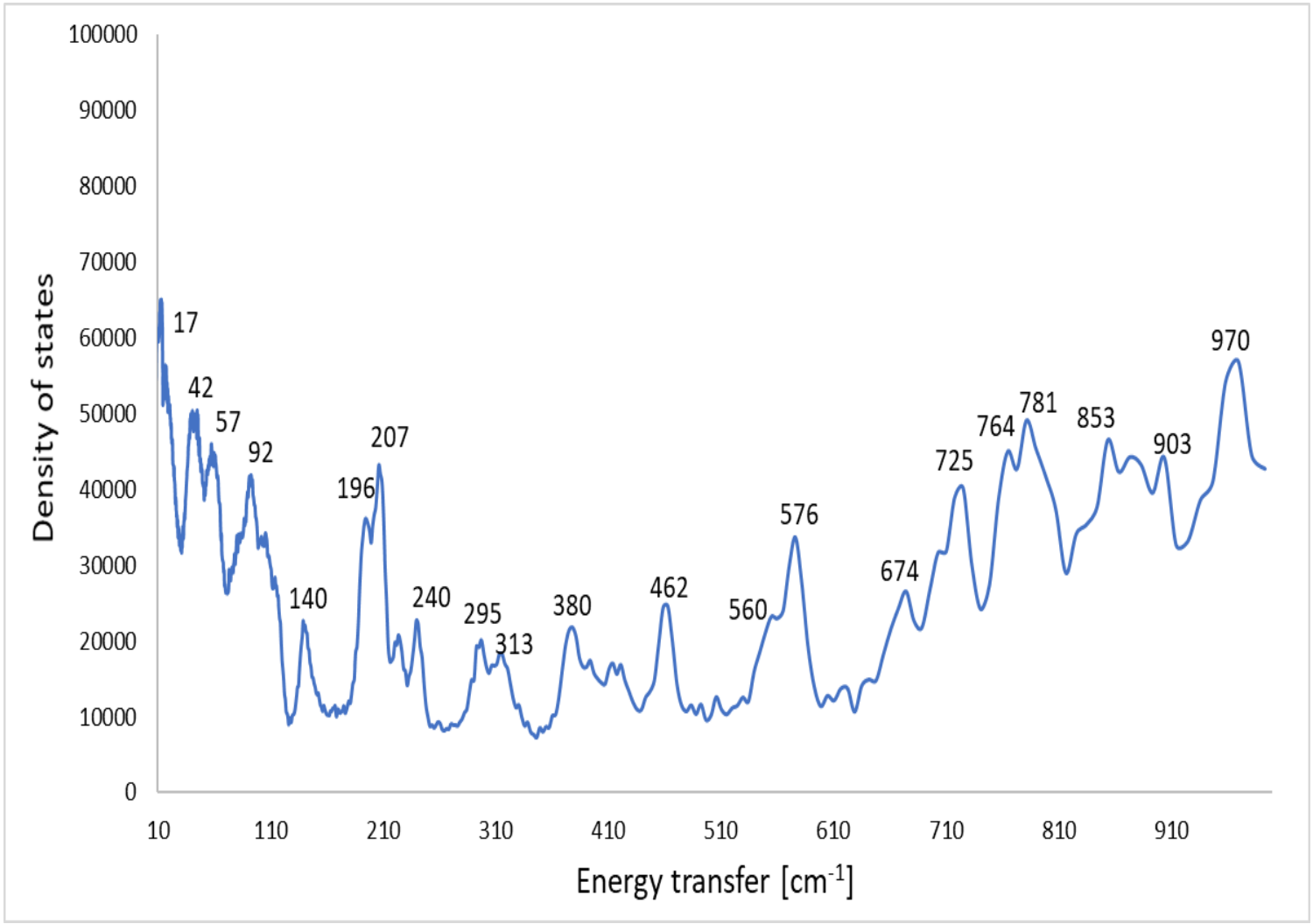


3-nitrobenzene-1,2-dicarboxylic acid
(3-nitrophthalic acid)

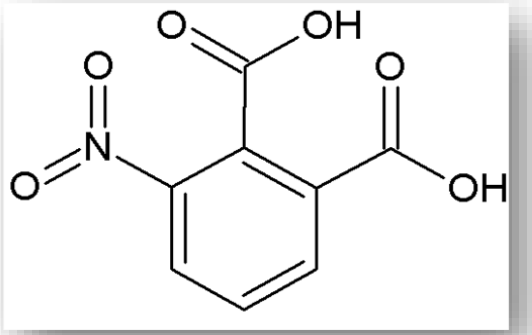
4-nitrobenzene-1,2-dicarboxylic acid
(4-nitrophthalic acid)

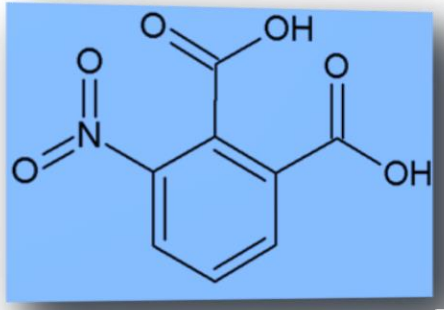


Spectrum prepared in NuVis

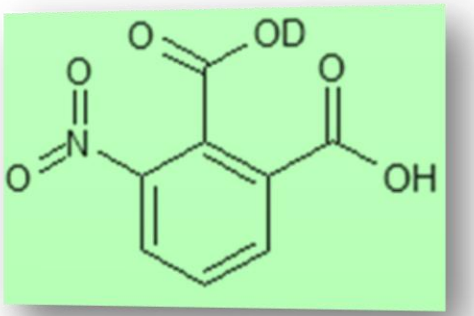


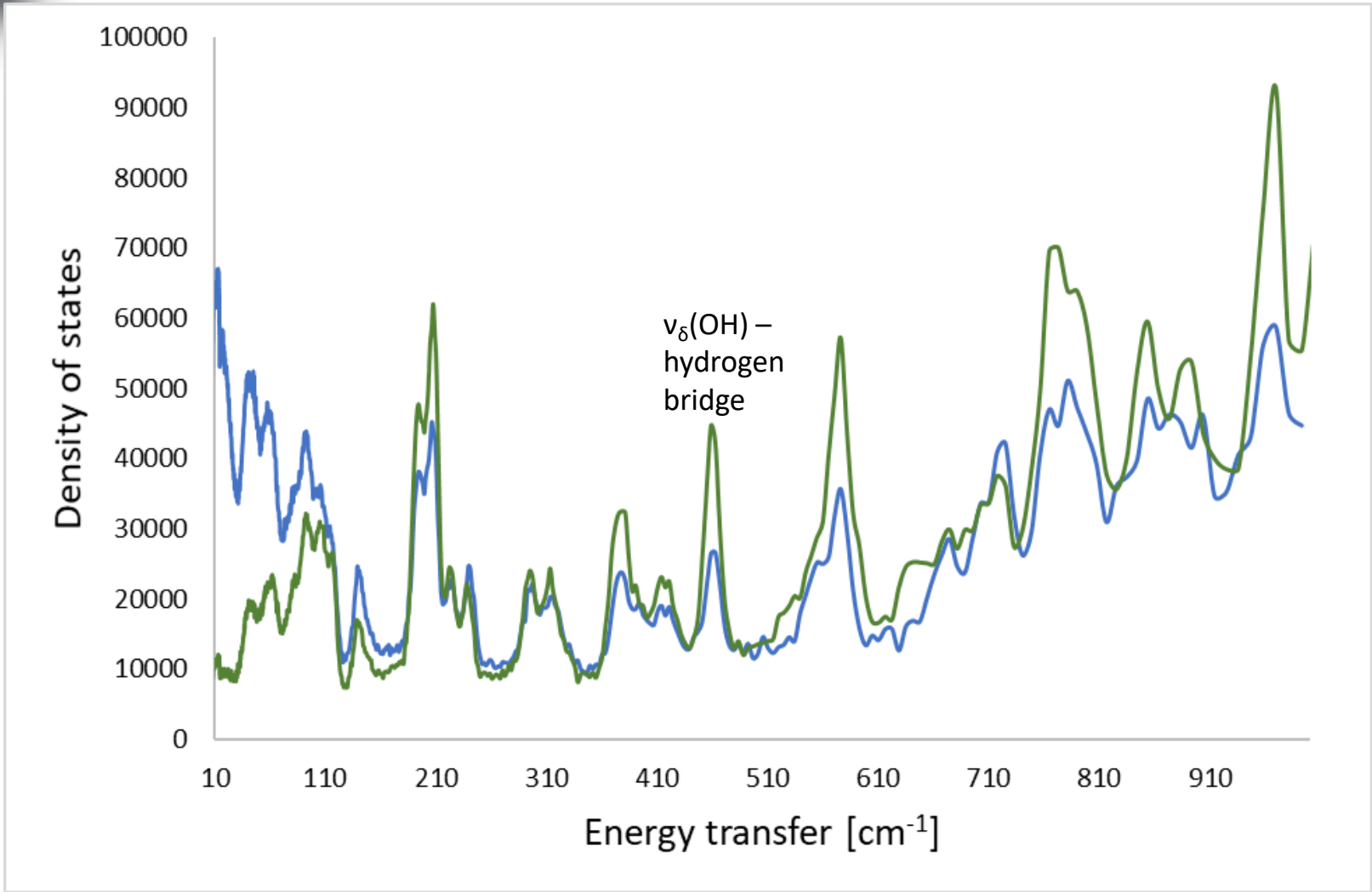
5 K

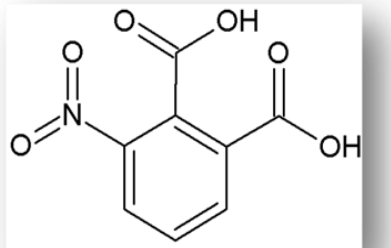




Spectrum prepared in NuVis, 5K



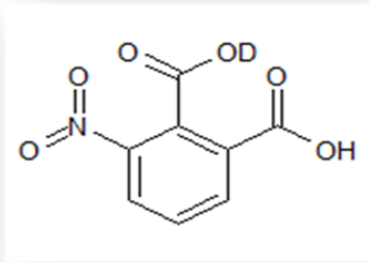


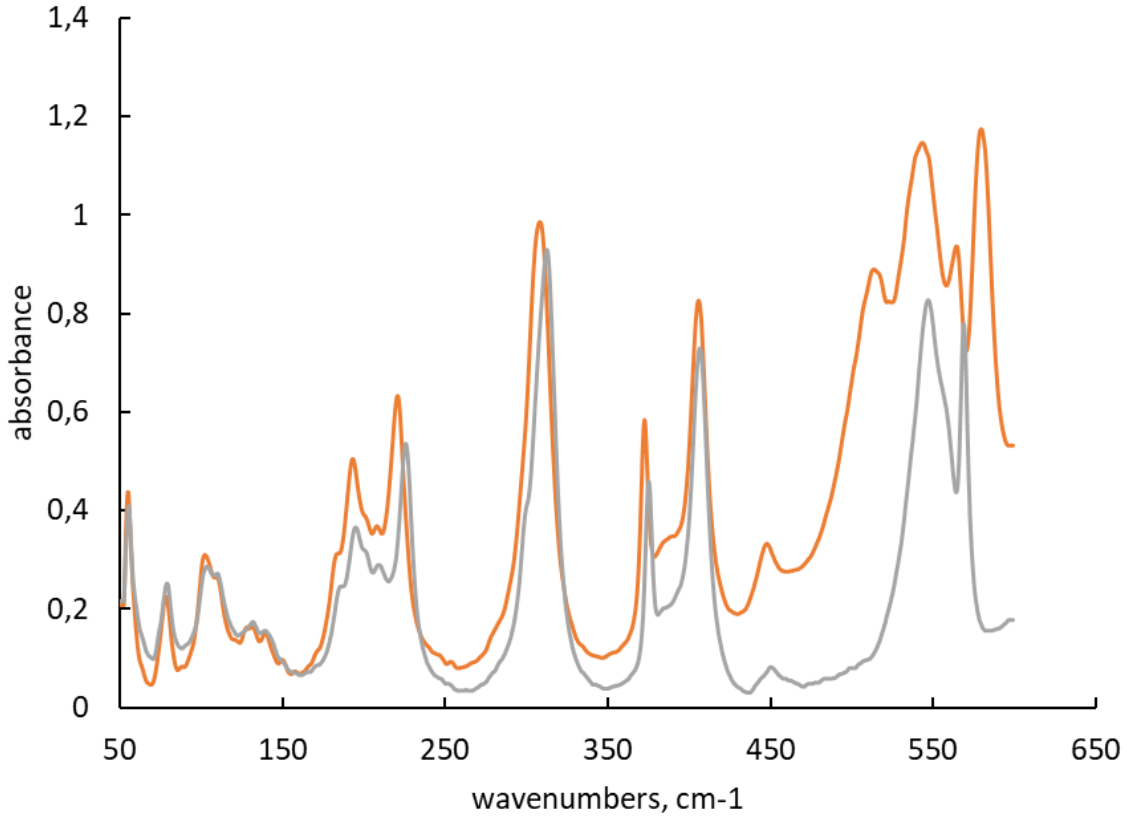


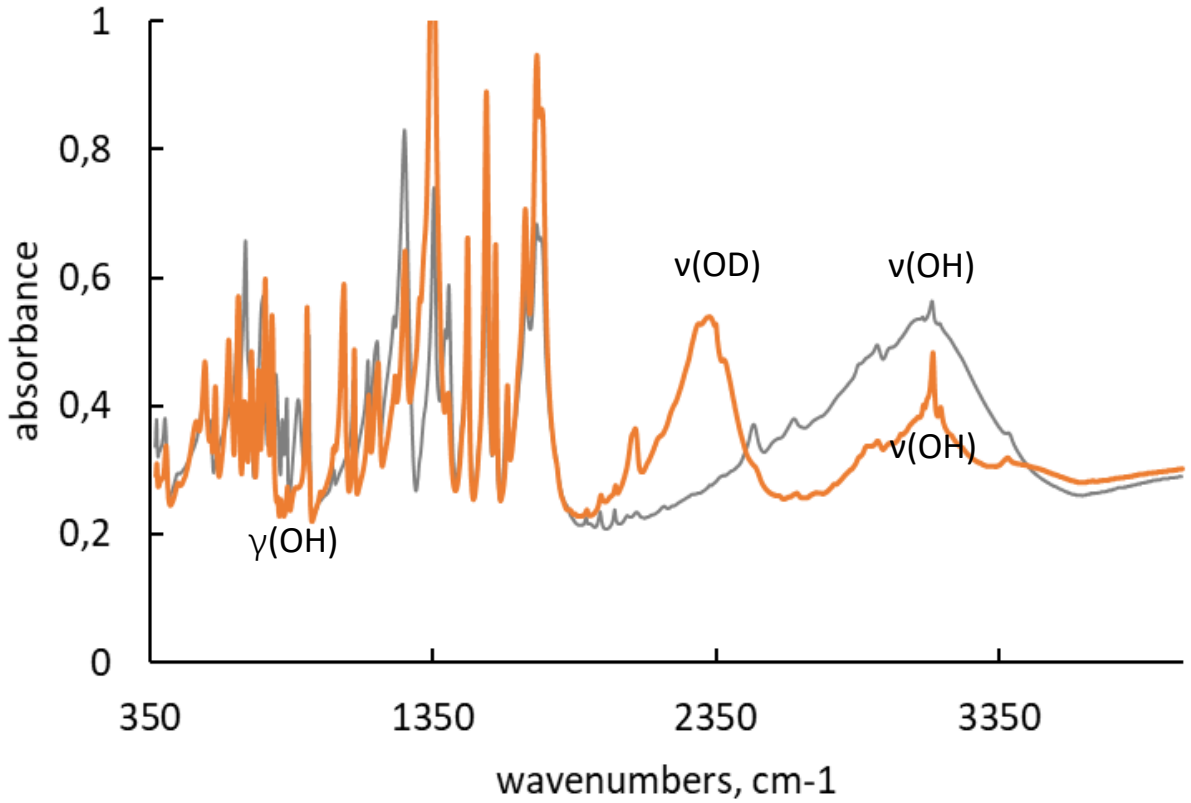
IR

FIR

MIR





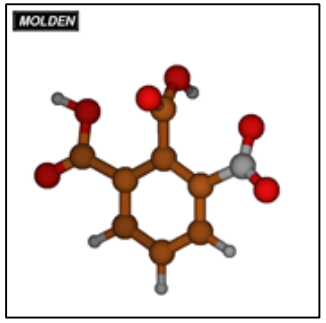


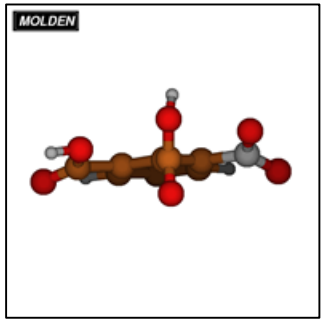
OD

OH

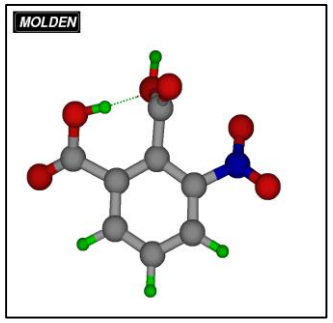
3-nitrophthalic acid conformers

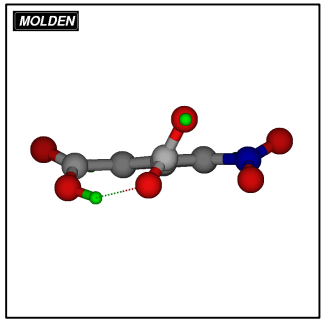
E(I)=0 kcal/mol



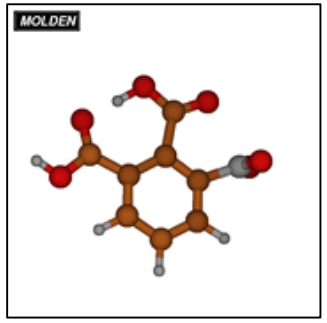


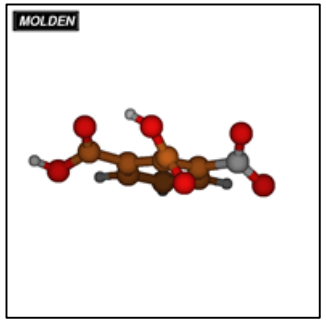
E(II)=2,35 kcal/mol



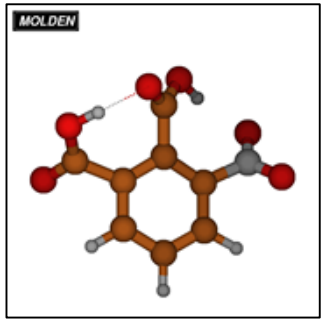


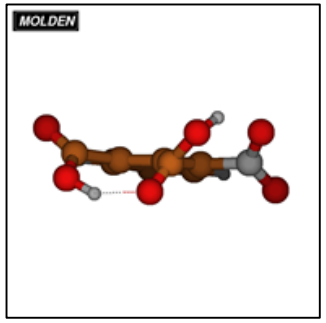
E(III)=3,93 kcal/mol



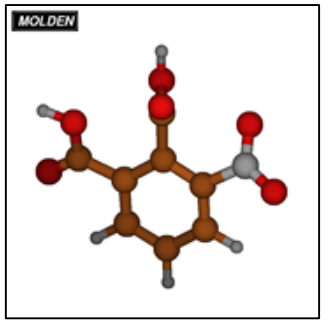


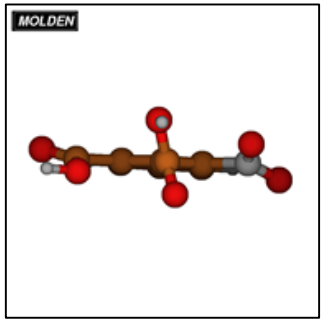
E(IV)=4,67 kcal/mol

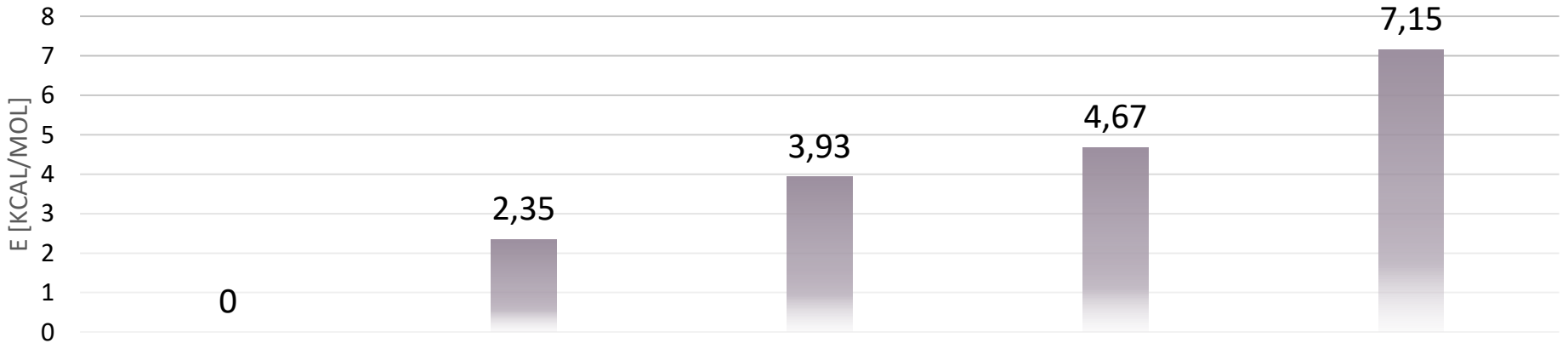




E(V)=7,15 kcal/mol

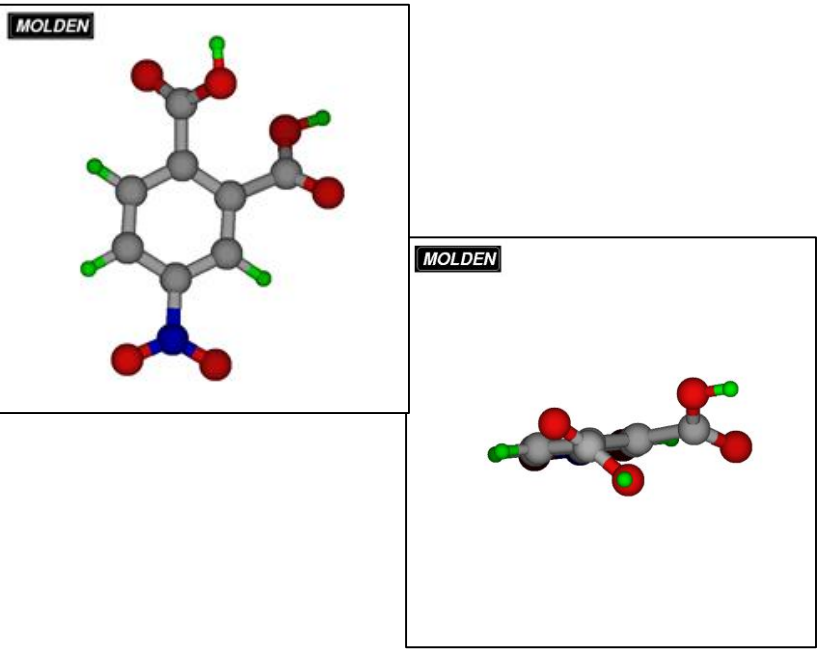




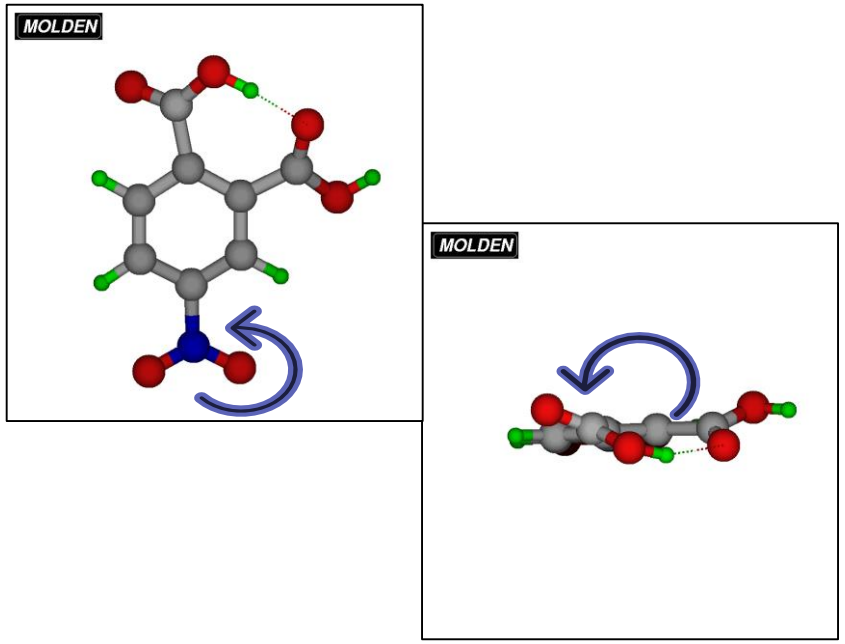


4-nitrophthalic acid conformers

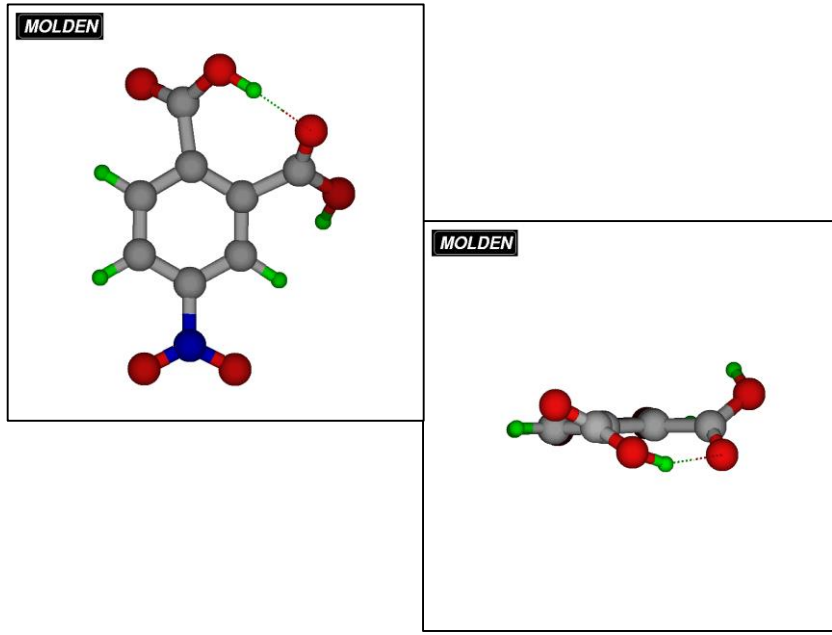
E(I)=0 kcal/mol

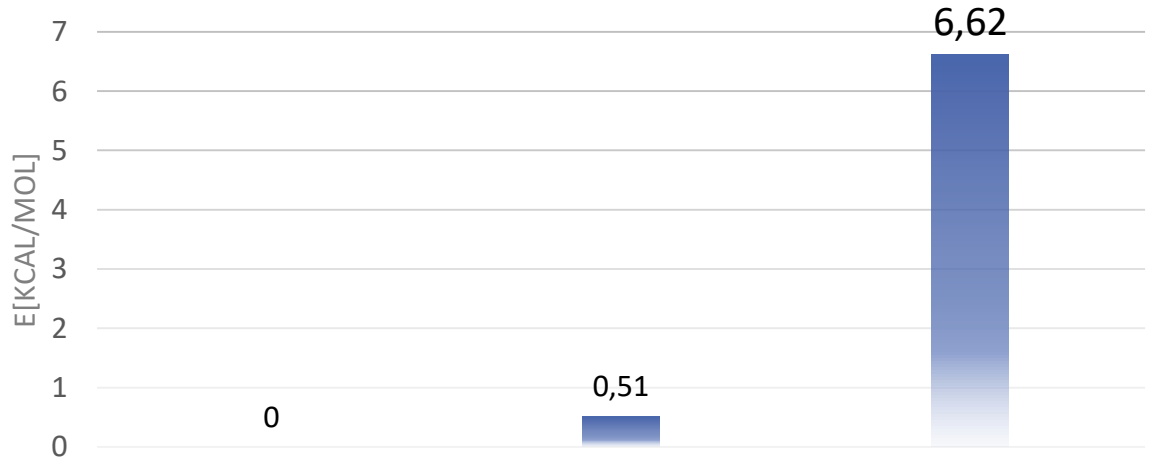


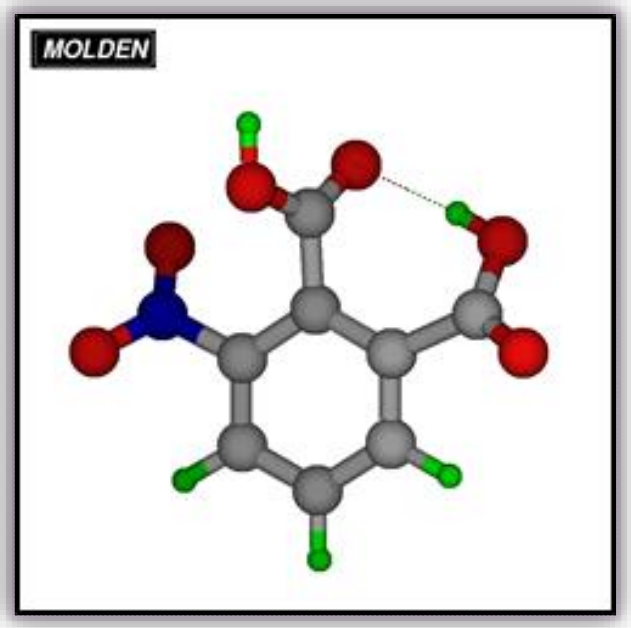
E(II,III)=0,51 kcal/mol

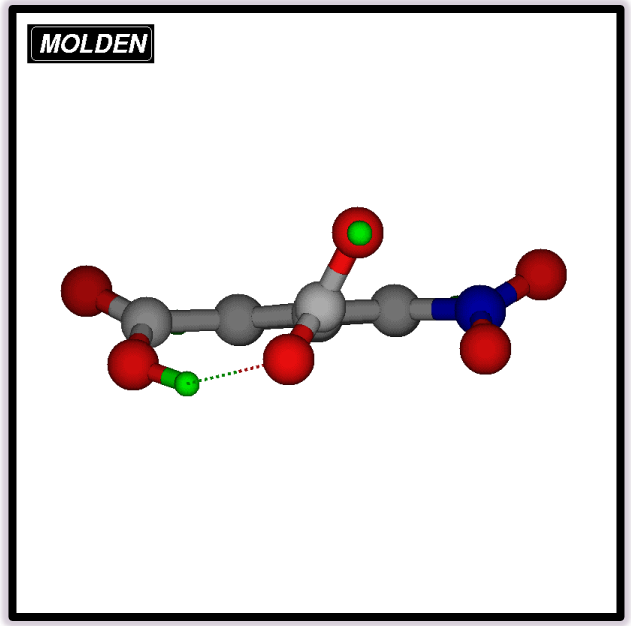


E(IV)=6,52 kcal/mol

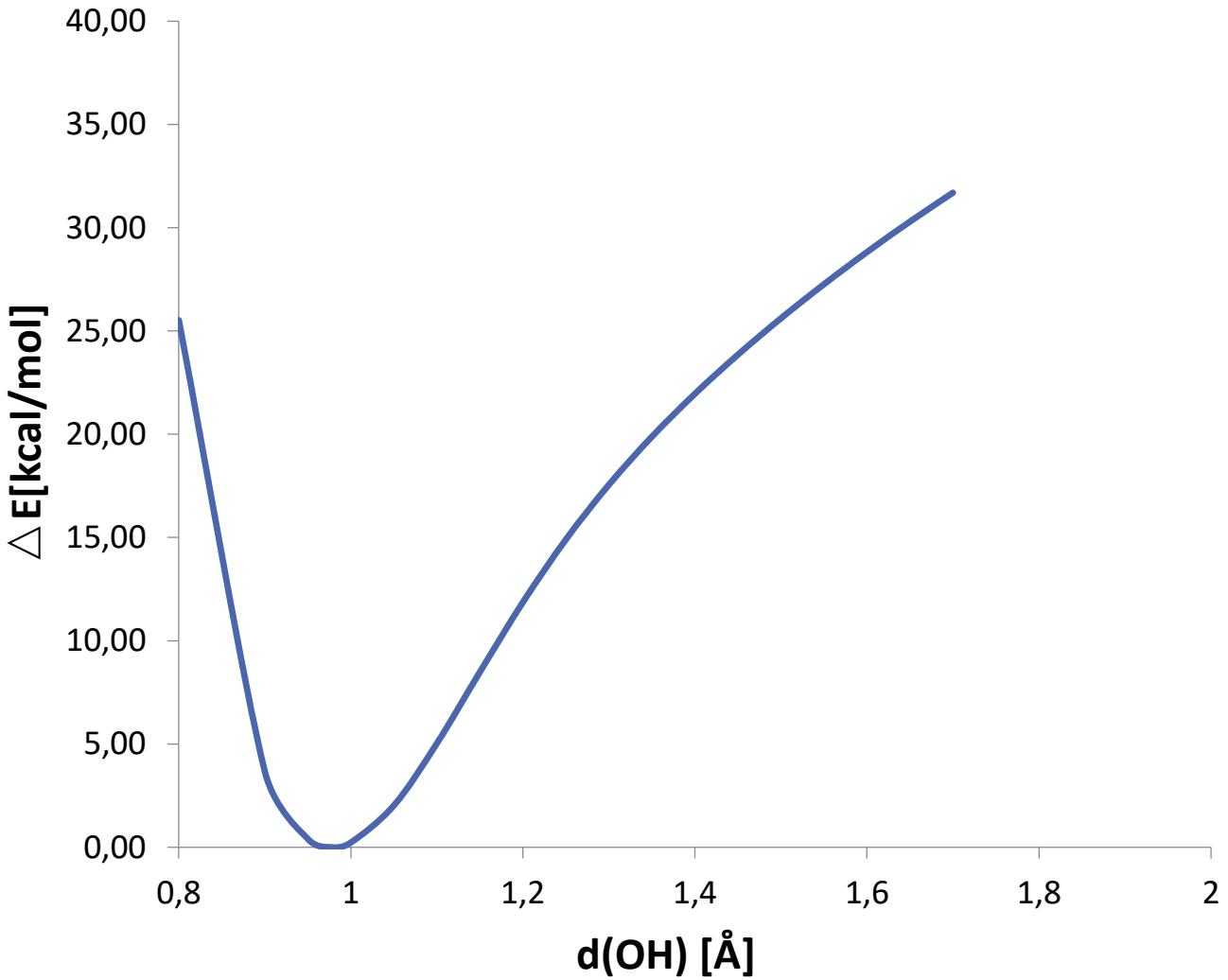




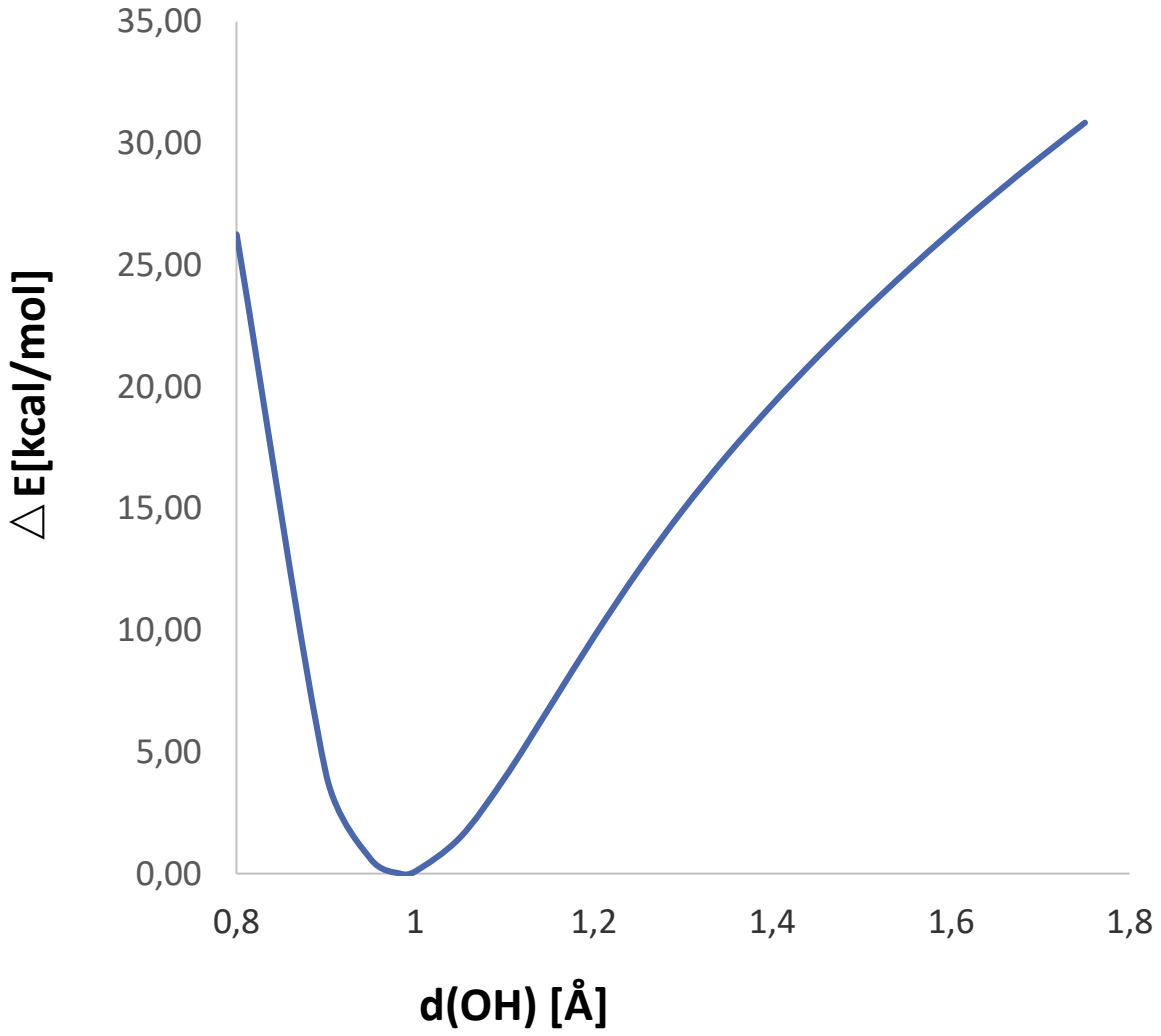


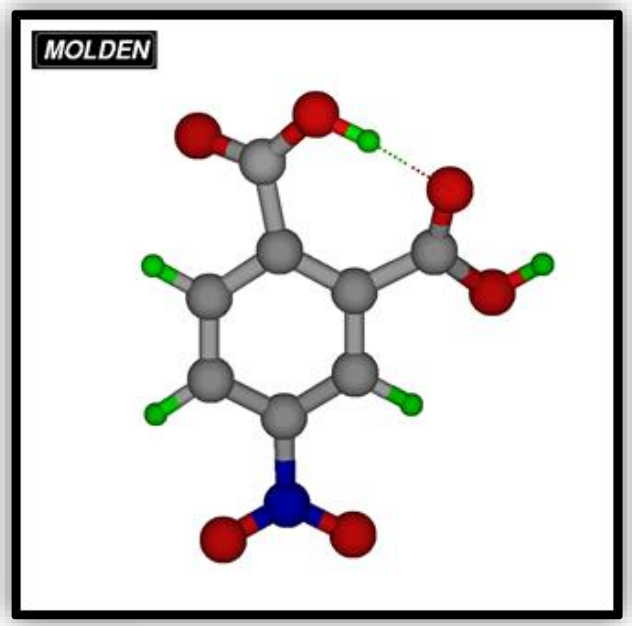


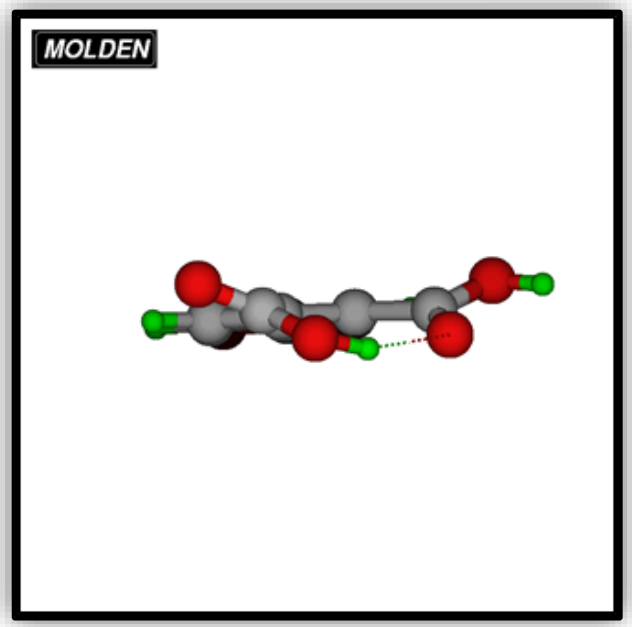
Elongation of the hydrogen bond 3-nitrophthalic acid



Elongation of the hydrogen bond 4-nitrophthalic acid







Conclusions

- Hydrogen bond is so important electrostatic interactions for the science, people, their health and all the world
- To receive full of the information about the chemical compound with hydrogen bonding it is necessary to use three experimental methods IR, Raman, IINS
- Quantum computations allow you to get a lot of information about the structure and interactions
- By changing the positioning of substituents or individual atoms we get seemingly the same compounds but with different interesting properties

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Thank you for your attention