



Joint Institute for Nuclear Research

Report of Summer Student Program
**Spectroscopic research of compounds with
hydrogen bonding**

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Contents

1. Description of the project	3
2. Hydrogen bonding	4
2.1. Definition.....	4
2.2. Parameters.....	6
2.3. Spectroscopic research.....	6
3. Neutron spectroscopy	8
3.1. Neutron properties.....	8
3.2. Neutron sources.....	9
3.3. Interaction with matter.....	11
3.4. Inelastic incoherent neutron scattering.....	13
3.5. Impact of isotopic effect on inelastic neutron scattering spectra.....	16
4. NERA Spectrometer	17
5. Neutron scattering spectra of compounds with hydrogen bonding	19
6. Experimental and computational data	20
7. Summary	24
8. Bibliography	25

1. Description of the project

I was the participant of Summer Student Program in Joint Institute for Nuclear Research (JINR) in Dubna for eight weeks. During the practice course, I studied opportunities of research in JINR. I visited the reactor and the following laboratories:

- Frank Laboratory of Neutron Physics – FLNP (where I was working),
- Van der Graaf Generator,
- Dzelepov Laboratory of Nuclear Problems – DLNP,
- Flerov Laboratory of Nuclear Reaction – FLNR,
- Veksler and Baldin Laboratory of High Energy Physics.

The purpose of my work here was the spectroscopic research of compounds with hydrogen bonding. Hydrogen bond is one of the important non-covalent interactions. It determines many chemical and physical properties of substances and determines the spatial structure of many organic compounds, such as DNA, proteins, medicines, making them biologically active.

NMR, IR and Raman spectroscopy are commonly used spectroscopic methods for investigation of the hydrogen bond. They complement each other. As for abovementioned methods, I have already known them. However, I studied the atypical inelastic incoherent neutron scattering method in JINR. Moreover, I prepared the IINS spectra and performed the quantum-mechanical calculations (Gaussian program) of vibrational modes of 3-nitrobenzene-1,2-dicarboxylic acid, 2-[(E)-(fenyloimino)metylo]fenol and its deuterated derivative 2-[(E)-(fenyloimino)metylo]fen[²H]ol. The IINS spectra were prepared with NuVis program. The IR and Raman spectra of the presented species were analysed. The conformational analysis of the studied compounds were also completed.

2. Hydrogen bonding

2.1. Definition

The hydrogen bond was discovered by Werner in 1902. It is a kind of non-covalent electrostatic interaction. Its energy is between 1 to 40 kcal/mole so it is stronger than a van der Waals interaction but weaker than covalent or ionic bonds. Nowadays the definition of hydrogen bonding given by the IUPAC says: *The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.* It takes place when the hydrogen atom bonds to a highly electronegative atom (also called “donor” – O, N, F). As a result the hydrogen atom has an excess of positive charge and it attracts to some other nearby highly electronegative atom (also called “acceptor”).

The hydrogen bond determines some chemical and physical properties of substances. By the first it changes the molecular weight by creating the dimers and another polymers. Afterwards it also increases the viscosity, the dipole moment, the melting and boiling point. It also changes the pK_a values of bases and acids. The hydrogen bond plays an important role in biologically active compounds. It determines the secondary and tertiary structures of proteins and nucleic acids. It is said that without hydrogen bonding there would be no life on our planet because it determines important properties of the most important compound in our life – water.

There are a few types of hydrogen bond shown in Figure 1:

- homonuclear and heteronuclear,
- homomolecular and heteromolecular,
- two-centre, three-centre, four-centre,
- double, triple,

and their combinations.

Hydrogen bonds are also divided into three types by the force of the bond:

- Strong hydrogen bonds,
- Moderate hydrogen bonds,
- Weak hydrogen bonds.

The physicochemical properties of each type of H-bond are presented in Table 1.

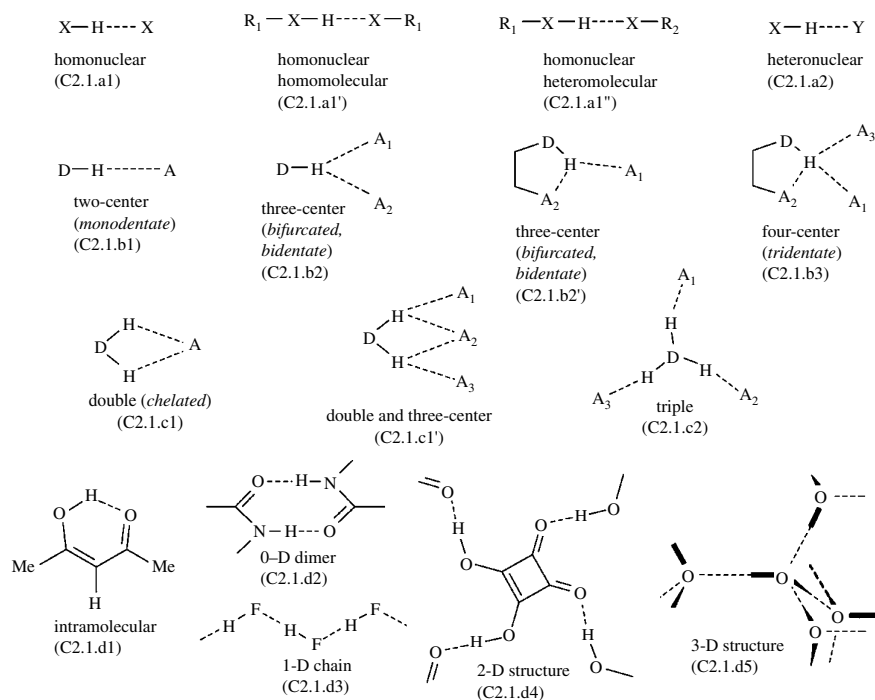


Fig. 1 Types of hydrogen bonding from: G. Gilli, P. Gilli, *The Nature of the Hydrogen Bond. Outline of a Comprehensive Hydrogen Bond Theory, International Union of Crystallography, Oxford Science Publication, Oxford University Press, 2009*

Table 1. Strong, moderate and weak hydrogen bonds and their properties

H - bond	Weak	Moderate	Strong
D - H ... A bond	Electrostatic	Electrostatic - covalent	Mostly covalent
Bond lengths	D - H << H... A	D - H < H... A	D - H ≈ H ... A
H ... A (Å)	3,2 - 2,2	2,2 - 1,5	1,5 - 2,2
D ... A (Å)	4,0 - 3,2	3,2 - 2,5	2,5 - 2,2
D - H - A angle (°)	90 - 150	130 - 180	165 - 180
Bond energy E_{HB} (kcal/mol)	1 - 4	4 - 15	15 - 45
Decrease of the IR $\nu(D-H)$ stretching (%)	<10	10 - 20	20 - 80
1H $\delta(D-H)$ chemical shift (ppm)	-	<14	14 - 22
Typical donors	C - H, P - H, S - H, Se - H	- O - H, = N - H	[= O - H] ⁺ [≡ N - H] ⁺
Typical acceptors	C - Hal, = S, = Se,	= O, ≡N, P = O	[Hal] ⁻ , [- O] ⁻ , [P - O] ⁻
Typical H - bonds	C - H ... O C - H ... N	- O - H ... O = - O - H ... N ≡ - N - H ... O = - N - H ... N ≡	R ₃ N ^{½+} ... H ⁺ ... ½-OOCR [F ... H ... F] ⁻ [O ₃ SO ... H ... OSO ₃] ⁻ [≡ N ... H ... N ≡] ⁺

2.2. Parameters

In crystallography, the hydrogen bond is described by the following parameters shown in Figure 2:

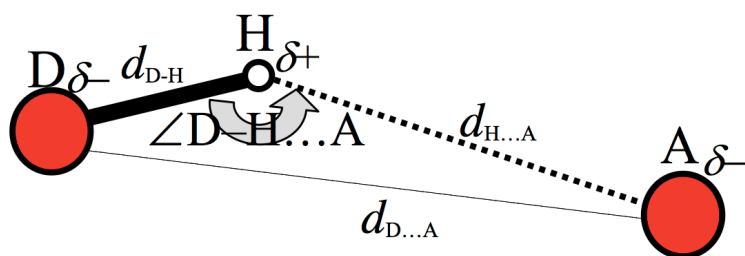


Fig. 2 The parameters of hydrogen bond:

D – the donor
H – the hydrogen atom
A – the acceptor
from L. Z. Ciunik,
Krystalochemia. Materiały uzupełniające dla studentów chemii, Wydział Chemii Uniwersytetu Wrocławskiego, Wrocław 2015

d_{D-H}	The donor – hydrogen distance
$d_{H...A}$	The hydrogen – acceptor distance
$d_{D...A}$	The donor – acceptor distance
$\angle D-H...A$	The donor – hydrogen ... acceptor angle

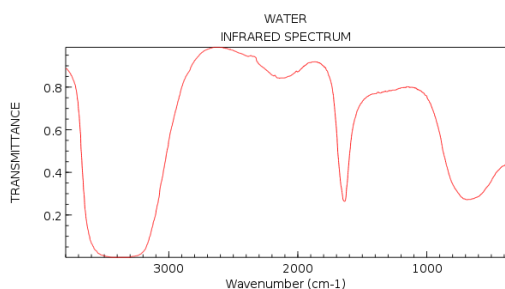
Usually we speak about hydrogen bond when the donor – hydrogen and donor – acceptor distance is smaller than the sum of their van der Waals radiuses and the angle between the donor, hydrogen and acceptor is bigger than 135°.

2.3. Spectroscopic research

There are many methods of detection and investigation of the hydrogen bond. Each has its limitations so it is useful to employ several methods at the same time. There are some commonly used spectroscopic methods like:

- IR spectroscopy
- Raman spectroscopy
- NMR
- INS spectroscopy

In infrared spectroscopy the D – H ... A bond formation provides the frequency shift $\Delta\nu = \nu^0 - \nu$ (the $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$) induced by the H – bond in the D – H stretching frequency. It also causes the broad band. IR became the primary method for H-bond detection in liquid, solid and gas phase. Because IR spectroscopy and Raman spectroscopy complement each other, the hydrogen bond is also investigated by the Raman spectroscopy. Figures 3 and 4 show the IR and Raman spectra of water, respectively.



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Fig. 3 The IR spectrum of water from <http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Type=IR-SPEC&Index=1>

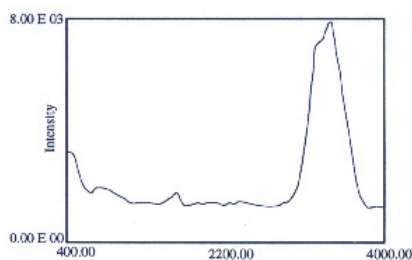


Fig. 4 The Raman spectrum of water from: <http://www.accessv.com/~yuan/yansci/yanwat.html>

Next, the ¹H NMR spectroscopy became also one of the most sensitive methods for detecting the presence of H-bonds in solution. The H-bonded protons provide that ¹H chemical shifts $\delta(\text{D-H})$ undergo much larger variations than the corresponding $\Delta\nu/\nu$ IR stretching frequency shifts. This method allows distinguishing the strong, moderate and weak H-bond because of different chemical shifts and its great resolution allows also detecting very small chemical shifts, like for C-H and S-H donors. The ¹H NMR spectra of water are shown in Figure 5. In the first one there is a mixture of 90 % H₂O in D₂O. As we can see there is a widening of the water signal. While there is 0,1 % of H₂O in D₂O we observe a clear signal.

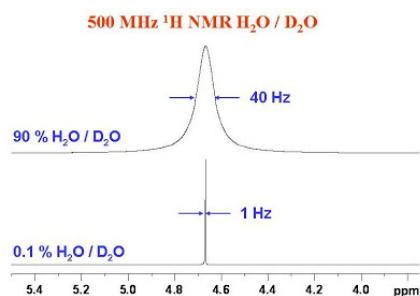


Fig. 5 The ¹H NMR spectrum of two mixtures of normal and high water in different proportions from: <http://u-of-o-nmr-facility.blogspot.ru/2007/10/width-of-your-water-line-radiation.html>

The inelastic neutron scattering (INS) or more precisely the incoherent inelastic neutron scattering (IINS) is commonly used to analyse the hydrogenated compounds and, hence, the compounds with hydrogen bond. During my work in Joint Institute for Nuclear Research in Dubna I learned that method and its impact on investigating the hydrogen bond.

3. Neutron spectroscopy

3.1. Neutron properties

The neutron is a particle without electric charge and with a mass about 1,0087 u ($1,675 \times 10^{-27}$ kg). Neutron consists of three quarks: two quarks d with the charge about $-\frac{1}{3}$ and the one u with a charge $+\frac{2}{3}$ (Figure 6). Neutron has a spin $s = \frac{1}{2}$.

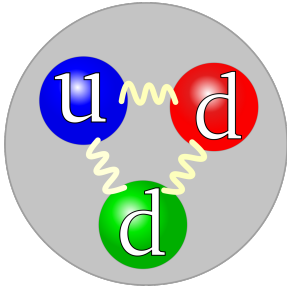


Fig. 6 The scheme of neutron from: https://upload.wikimedia.org/wikipedia/commons/thumb/8/81/Quark_structure_neutron.svg/2000px-Quark_structure_neutron.svg.png

Neutron was discovered by James Chadwick in 1932 (the Nobel prize in 1935). The α -particles beam was fired on beryllium nucleus, which gave neutron and the carbon nucleus:



The obtained neutrons collided with paraffin foil and ejected the protons from it. The protons were recorded by Geiger-Müller counter.

Neutrons are stable only in stable atomic nucleus. Free neutrons are labile and they decay with the mean lifetime $\tau = 889,1$ s into a proton (p), an electron (e) and an antineutrino ($\bar{\nu}_e$). This process is named β decay.



Neutron has the wave-particle properties. The de Broigle relation describes the neutron wavelengths:

$$\lambda_n = \frac{h}{m_n v_n} = \frac{h}{\sqrt{2m_n E_n}} \quad (1)$$

According to their energy there are different categories of neutrons (Figure 7):

- Epithermal neutrons
- Thermal neutrons
- Cold neutrons
- Ultracold neutrons

TABLE I. Characteristics of Neutrons at Selected Energies

Quantity	Unit	Definition	Ultracold	Cold	Thermal	Epithermal
Energy E	meV ^a		0.00025	1	25	1000
Temperature T	K	E/k_B	0.0029	12	290	12,000
Wavelength λ^b	Å	$h/(2mE)^{1/2}$	570	9.0	1.8	0.29
Wave vector k^c	Å ⁻¹	$(2mE)^{1/2}/h$	0.011	0.7	3.5	22
Velocity v^d	m/s	$(2E/m)^{1/2}$	6.9	440	2200	14,000

^a 1 meV = 1.6022 × 10⁻¹⁵ erg, the energy required to raise a proton up to a potential of 1 mV.

^b λ (Å) = 9.0446 [E (meV)]^{-1/2}.

^c k (Å⁻¹) = 0.69469 [E (meV)]^{1/2}.

^d v (m/s) = 437.39 [E (meV)]^{1/2}.

Source: "CRC Handbook of Chemistry and Physics" (R. C. Weast, M. J. Astle, and W. H. Beyer, eds.), 65th ed., CRC Press, Boca Raton, Florida, 1984.

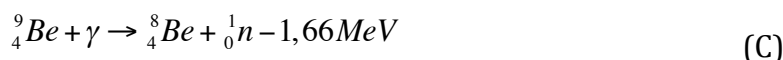
Fig. 7 Categories of neutrons and their description from R. Celotta, J. Levine, *Methods of Experimental Physics. Neutron Scattering*, Academic Press, INC, London 1986

3.2. Neutron sources

There are different types of neutron sources:

- Small neutron sources
- Nuclear fission
- Neutron sources based on particle accelerators

The γ radiation is used in *small neutron sources*. The γ quantum incident on a beryllium nucleus giving its isotope and neutron:



In *nuclear fission* an ²³⁵U absorbs a thermal neutron and decays into two smaller nuclei and gives on average 2,5 neutrons (Figure 8) with releasing 200 MeV of energy:

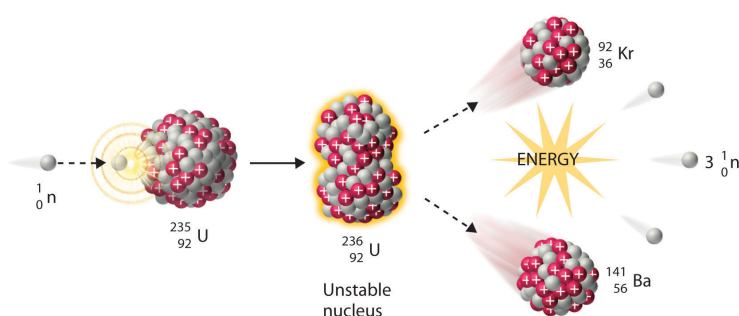


Fig. 8 An example of nuclear fission of ²³⁵U which decays into ¹⁴¹Ba and ⁹²Kr from http://www.nuclear-power.net/wp-content/uploads/2014/10/nuclear_fission.jpg?32b4fc

The obtained neutrons have the energies around 1 MeV.

This reaction chain proceeds in neutron reactors. There are two types of reactors: stationary and pulsed. In a stationary reactor from 2,5 neutrons 1 is needed to maintain the chain reactions, 0,5 is absorbed by the construction elements and there is one which can be used in research. The Figure 9 shows the scheme of a stationary reactor. The

nuclear uranium fuel is marked by 1. Between it there are regulating and emergency roots (2). The 3 is a cover and there is also a biological shield (4). The moderator (usually water) can also be used as a refrigerant (5). The obtained neutrons pass by neutron guide (6).

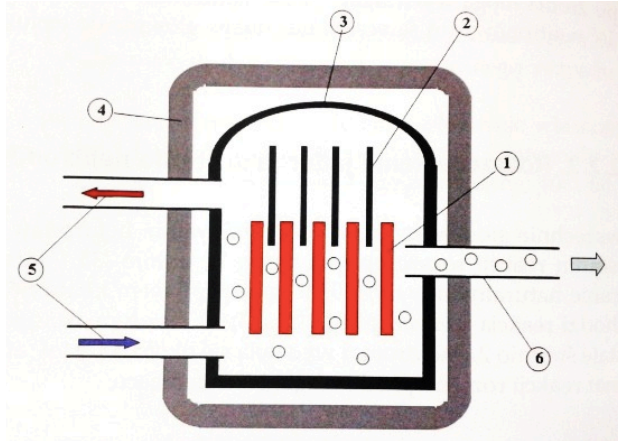


Fig. 9 The scheme of a stationary reactor. V. Belushkin, J. W. Wąsicki, *Wprowadzenie do neutronowych metod badania fazy skondensowanej materii*, Wydawnictwo Naukowe UAM, Poznań 2013

The second type of reactor is a pulsed reactor, which was built in 1960 in Joint Institute for Nuclear Research in Dubna (Figure 10) and named IBR-2. It is a fast reactor with a periodic action. Its core is made by 69 fuel assemblies filled by PuO_2 . Those assemblies are directly cooled by liquid sodium. The core is surrounded by 5 stationary reflectors and the sixth movable reflector. This movable reflector consists of: the main movable reflector and the auxiliary movable reflector. They rotate against each other with different rotating speed. While two reflectors are near the core the neutrons are reflexed to the core and it generates a power pulse. When the reflectors move away the power of reactor decreases. The whole reactor is also cooled by air and covered by two biological shields.

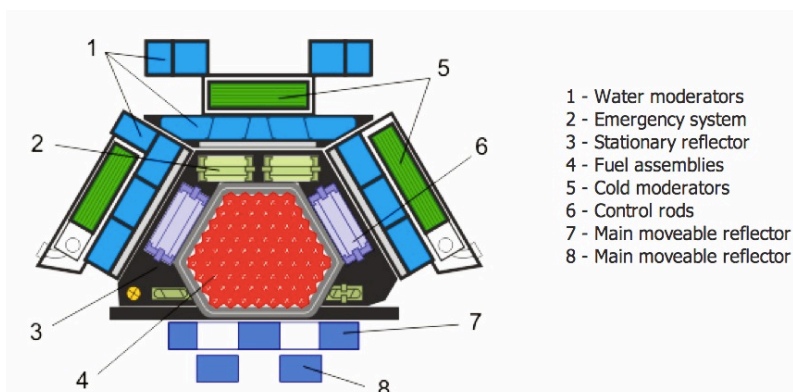
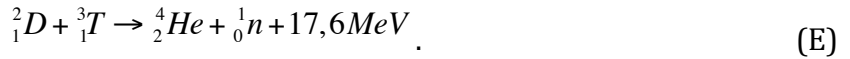


Fig. 10 The scheme of reactor core of IBR-2 and its description from : <http://flnp.jinr.ru/251/>

There are also *particle accelerators*, which can be neutron sources. A particle beam is fired on heavy nucleus. For example, deuterons are accelerated to the energy of 100 keV and they incident on a target of TiT_2 . In this process we obtain the nuclei of helium and neutrons:



When there is a target built from heavy chemical elements like Pb, W, Ta and very fast electron beam is fired on it, it provides a photonuclear reaction. Inhibitory electrons produce the γ quantum fluxes. This kind of radiation is called Bremsstrahlung. When these γ quants interact with the nuclei of a target, the neutrons are formed (γ, n). This source gives short and pulsed neutron beams. The accelerator, which uses that type of neutron source, is IREN in Dubna.

And the last example of neutron source based on a particle accelerator is the *spallation process*. It takes place in the nuclear reaction between the high-energy particles and heavy elements. Firstly the intense beam of protons is focused onto a target (e.g. uranium). The nucleus of the target becomes excited and there are multiple intranuclear reactions taking place. As a result nucleus produces the very high-energy neutrons. Finally, the nucleus throws out neutrons, protons, deuterons, α particles, photons and neutrinos. So in those reactions one proton and one heavy nucleus create many neutrons.

To sum up it is important to use the neutron source, which produces many neutrons but also does not release much energy so that it is needed to optimize the neutron production.

3.3. Interaction with matter

When a neutron is near the nucleus it could be:

- Absorbed by nucleus and excite it. After that nucleus could: emit γ quantum, undergo fission or throw away α particles, protons etc.
- Scattered by the nucleus that changes its energy and direction movement.

When the sample is under neutron beam ϕ_0 and I_s is the number of scattering acts and I_a is the number of absorbing acts, the cross section for scattering σ_s and absorption σ_a are given by equations:

$$I_s = \phi_0 \sigma_s, \quad (2)$$

$$I_a = \phi_0 \sigma_a. \quad (3)$$

The σ_s and σ_a are measured in barns (1 barn = 10^{-28} square meter).

The differential cross section for neutron scattering $\frac{d\sigma}{d\Omega}$ describes the probability that the scattered neutron can be detected at a given angle Ω and will be found in the solid

angle $d\Omega$. A double differential cross section describes the probability that the neutron will leave the sample at a given angle Ω and will be found in the solid angle $d\Omega$ and its energy will be changed from $\hbar\omega$ to $\hbar(\omega + d\omega)$. That gives an equation:

$$\sigma_s = \int d\Omega \frac{d\sigma}{d\Omega} = \int d\omega \int d\Omega \frac{d^2\sigma}{d\Omega d\omega} . \quad (4)$$

Neutrons interact with nuclei by nuclear and magnetic forces. For nuclear forces the potential impact between neutron and nucleus is given by the Fermi pseudo potential, which is given by the equation:

$$V(\vec{r}) = \frac{2\pi\hbar^2}{m} \sum_i b_i \delta(\vec{r} - \vec{R}_i) , \quad (5)$$

where b_i is the scattering length, \vec{R}_i is the position of nucleus i in a sample and \vec{r} is the position of a neutron. The mass of a neutron is given by m and δ is the Dirac delta. This is summed over every nuclei taking part in scattering. The scattering length is the base parameter, which describes the interaction between neutron and nucleus and it depends on the isotope and the relative spin orientation of each other. The average value of $\langle b_i \rangle$ for every isotopes and spin orientations is named coherent scattering length $b_i^{coh} = \langle b_i \rangle$. The average square variation of b_i is the incoherent scattering length: $b_i^{inc} = \sqrt{\langle b_i^2 \rangle - \langle b_i \rangle^2}$.

The scattering lengths for chosen elements and their isotopes are shown in Figure 11. Opposite to x ray scattering, the length scattering for neutrons depends irregularly to the Z number of an element and it depends of its isotopes. However, in the sample there is a mixture of isotopes, it means that it has both coherent and incoherent scattering length. The cross sections for the coherent and incoherent scattering will be:

$$\sigma_{coh} = 4\pi \langle b \rangle^2 , \quad (6)$$

$$\sigma_{inc} = 4\pi \left(\langle b^2 \rangle - \langle b \rangle^2 \right) , \quad (7)$$

relatively and the total cross section will be the sum of the coherent and incoherent cross sections:

$$\sigma = \sigma_{coh} + \sigma_{inc} . \quad (8)$$

The coherent and incoherent cross sections for neutron scattering allow recognizing various properties of condensed matter. Coherent scattering gives the information about the equilibrium structure, crystal structure excitation or magnetic

subnet excitation. Incoherent scattering describes single atoms or molecules, for example its diffusion in the crystal.

We consider the hydrogen atom as an example. Its nucleus has the spin $s=1/2$ and it is built only by one proton. The experimental scattering lengths are: $b^+=1,08 \times 10^{-12}$ cm for triplet and $b^-=-4,74 \times 10^{-12}$ cm for singlet and the average value of b : $\langle b_i \rangle = -0,38 \times 10^{-12}$ cm. Thus the coherent and incoherent value of cross section will be: $\sigma_{coh}(H)=1,8 b$ and $\sigma_{inc}(H)=79,8 b$. This value is the largest incoherent cross section of all isotopes and makes the hydrogen atom the prime incoherent scatterer, which can be exploited for hydrogen containing materials. And for the atom of deuter, which nucleus consists of one proton and one neutron and has a spin $s=1$, the values of cross sections are: $\sigma_{coh}(D)=5,6 b$, $\sigma_{inc}(D)=2,0 b$.

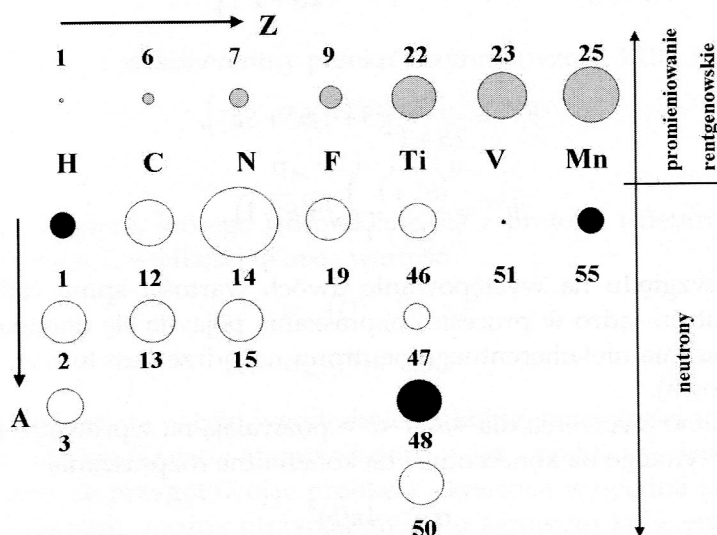


Fig. 11 The comparison of the scattering lengths proportional to the diameter of circles for x rays (promieniowanie rentgenowskie) and neutrons (neutrony). The black circle means the negative scattering lengths, from: V. Belushkin, J. W. Wąsicki, *Wprowadzenie do neutronowych metod badania fazy skondensowanej materii*, Wydawnictwo Naukowe UAM, Poznań 2013

3.4. Inelastic incoherent neutron scattering

The investigating method being used in the scientific team in which I was working is *inelastic incoherent neutron scattering*. To study this method it is indispensable to know about different kinds of neutron scattering.

The first one is *elastic neutron scattering*. It is when a neutron beam incident on a fixed, point scatterer like nucleus and there is no change in the energy of the incident neutron. Although the direction of the wave vector of the neutron changes, its magnitude does not. The example of this kind of scattering is *diffraction*.

When neutrons are scattered by matter, the scattering from each of the individual nuclei are added. Nuclei are not fixed because atoms in matter undergo atomic vibrations. Nuclei can also recoil during a collision with a neutron. As nuclei are moving

they can impart or absorb energy of neutrons. This kind of neutron scattering is named *inelastic neutron scattering* and in this process the direction and the magnitude of the neutron wave vector change.

These two types of neutron scattering provide different scattering effects. So we are talking about *coherent neutron scattering* when the neutron wave interacts with the whole sample as a unit and then the scattered waves from different nuclei interfere with each other. As this type of neutron scattering depends on the relative distances between the constituent atoms, it gives the information about the structure of materials.

In *incoherent neutron scattering* an incident neutron wave interacts independently with each nucleus so that the scattered waves have indeterminate relative phases and they do not interfere with each other. However, the intensities from each nucleus add up.

The combination of these kinds of neutron scattering gives four methods and its applications is presented in Table 2.

Table 2. Types of neutron scattering.

type of neutron scattering	elastic	inelastic
coherent	equilibrium structure, crystal structure	collective motions of the atoms which produce vibrational waves in crystalline lattice
incoherent	(quasielastic): fast stochastic motions of molecules and molecules groups	single atoms/molecules as atomic diffusion in crystalline lattice

To investigate the neutron scattering it is indispensable to get to know about the *phonons*, and *magnons*. As we know, in reality atoms are not frozen in fixed positions in a crystal. As they have thermal energy, they oscillate about their lattice site and move around inside a small volume with the lattice site at its centre. We can name this position in the centre the official position. As atoms are connected with each other by the binding forces, when one atom oscillate, neighbouring atoms also start to oscillate with different frequencies and wavelength travelling in different directions. In effect they form the wave, which starts passing up and down. There are many waves like that

which are formed by these thermal motions of atoms. We can describe the superposition of these waves moving through the lattice. These fundamental vibrational waves in a crystal in which nuclei oscillate in a coordinated manner are named *phonons*. The energy of phonons is quantized and has a ν that is the frequency of atomic motion associated with the phonon.

Besides the neutron interaction with atomic nuclei, there is also an interaction between a neutron and the magnetic field from the fact that a neutron has a magnetic moment. The neutron experiences this magnetic force, when it passes near the electron. As most electrons in atoms are paired, they do not have the magnetic moment, but in some other atoms there are no paired electrons from the valence shell. So neutrons could be also scattered by the resulting magnetic moments. It happens for example in ferromagnetic and antiferromagnetic materials, which have aligned magnetic moments of their electrons (in ferromagnetic they are pointed in the same direction and in antiferromagnetic in opposite directions). In the neutron scattering only the component of the sample's magnetization that is perpendicular to the scattering vector, is effective. As in magnetized materials the directions of the atomic moments can oscillate, they form a wave of magnetic oscillation that passes through the sample. These magnetic excitations are called *magnons*. Thus, they are magnetic analogues of the phonons and can be measured by the inelastic neutron scattering.

Returning to the inelastic incoherent neutron scattering the double differential cross section for incoherent neutron scattering will be:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_1}{k_0} \sum_i (b_i^{inc})^2 S^{inc}(\vec{Q}, \omega), \quad (9)$$

where the k_0 and k_1 are the wave vector of incident and scattered (relatively) neutron wave and $S^{inc}(\vec{Q}, \omega)$ is the incoherent scattering law. Mathematically it is a spatial and time Fourier transformation of autocorrelation function, which describes the probability that the atom being at one point in time $t=0$ will be found at a second definite point in time t . Thus, this method allows investigating monoparticles dynamics effects like:

- local and quasilocal vibrations of admixtures,
- crystal field splitting,
- intramolecular vibrations,
- phonons and magnons density of states.

In spectroscopic studies of intramolecular vibrations of molecules containing hydrogen atoms we can say that in the scattering law there are only the vibrations of hydrogen. It is because for hydrogen there is a big value of a scattering length. It gives an equation for the scattering law:

$$S(Q, n\omega) = \frac{1}{n!} (Q^2 \langle U^2 \rangle)^n \exp(-Q^2 \langle U^2 \rangle), \quad (10)$$

where $\langle U^2 \rangle$ is an average value of a square vibration amplitude and n is the principal quantum number. For $n=0$ this equation describes the dependence of the intensity of neutron scattering from Q . For $n=1$ it describes the first excited state of oscillator. The neutron scattering is analogic to the optical spectroscopy. But there are the differences, which make this method an important complement for optical spectroscopy. Firstly there are no selection rules. Secondly, the signal intensity is proportional to U meanwhile for optic spectroscopy it is not. Furthermore, the large amplitude of hydrogen vibrations and the anomaly large cross section for neutron scattering makes the neutron spectroscopy an unusually sensitive method for investigating the samples containing hydrogen atoms. As we know, deuter does not have that large cross-section, so by changing the hydrogen atom for deuter, we can define the type of vibrations that corresponds to the signals in neutron spectrum. Finally, these materials, which are not transparent for visible and infrared spectrum, are transparent for neutrons (e.g. metals).

The inelastic incoherent neutron scattering is also used in the studies of phonons density of states – $g(\omega)$. This function characterises the probability that the vibrational waves with the frequency ω will exist in a crystal. For compounds containing hydrogen atoms the cross section for incoherent scattering will be described by:

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{inc} = \frac{k_1}{k_0} N \frac{|Q^2|}{4\omega M} (b_H^{inc})^2 e^{-2W} G_H(\omega) \left(\cosh \frac{\hbar\omega}{2kT} \pm 1 \right), \quad (11)$$

where M is the mass of crystal unit cell, and $G_H(\omega)$ is the phonons density of states for hydrogen.

3.5. Impact of isotopic effect on inelastic neutron scattering spectra

An isotopic effect occurs when there are the differences of chemical and physical properties for different isotopes of the same chemical element. It also provides the differences of chemical compounds properties built from different isotopes of the same element.

The most common examples of compounds consisting of two isotopes are water and heavy water. They have different molecular weights, densities, melting and boiling points or permittivity. They also have different biological activities.

The difference of isotopes mass causes also differences in chemical activity because it changes the velocity of reactions. This effect is called kinetic isotopic effect.

Isotopic effect is clearly visible and, hence, useful in spectroscopic research. For example, in NMR technique as hydrogen nucleus has the spin $s=1/2$ and deuterium nucleus has $s=1$, it provides that in ^1H NMR spectrum we will not see any signals of deuterium. This effect can be used for example to detect another signal, which was covered by the one of hydrogen. Hydrogen-deuterium exchange provides the change of vibration frequency. For IR spectroscopy it will be the shift about 1,35 towards smaller wave numbers. So, recording two spectra – for hydrogenated and deuterated samples and comparing them – we can detect the signals of changed hydrogen atoms.

Finally, in neutron spectroscopy there is a huge difference between the cross sections of the hydrogenated and deuterated molecules. As the incoherent inelastic neutron scattering cross section is anomaly large for hydrogen, this technique is very sensitive for this isotope but it is not for deuterium. These modes with deuterium appear only weakly in the spectrum. Often the bands seem to disappear altogether from the spectrum. The advantage over the optical technique is that the spectrum is less congested.

The hydrogen-deuterium exchange also gives another important opportunity: it allows studying individual hydrogen atoms free from the interference of other hydrogen vibrations. This is why neutron spectroscopy is a unique method for the study of hydrogen bonds.

4. NERA Spectrometer

The spectrometer which I studied during my work in JINR is NERA spectrometer. This is an inverse geometry time-of-flight spectrometer. In this type of spectrometer a pulsed neutron source produces the polychromatic neutron beams with the period T . They have continuous energy spectrum and their energy E_i is appointed from the time of flight measured between a source and a sample. The energy of scattered neutrons is monochromated by a monochromator placed after the sample. The detectors are placed

at different angles that provides recording of spectra for different values of scattering vector \vec{Q} and for the same value of ω . The time-of-flight will be given by the equation below:

$$t_i = t - \frac{(L_{f1} + L_{f2})}{v_f}, \quad (12)$$

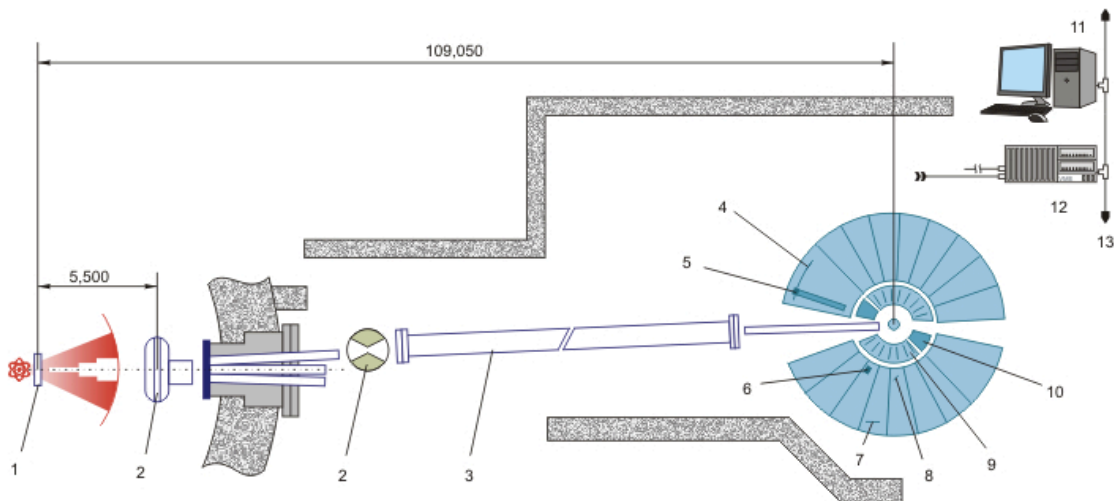
where t is unrestricted time from the neutron beam generation, L_{f1} and L_{f2} are the distances between a sample and a monochromator and a monochromator and a detector

relatively, $v_f = \sqrt{\frac{2E_f}{m}}$ is the velocity of scattered neutrons determined by crystal. Thus, the neutron energy will be:

$$E_i = \frac{m}{2} \left(\frac{L_i}{t - \frac{L_{f1} + L_{f2}}{v_f}} \right)^2, \quad (13)$$

where L_i is the neutron time-of-flight from the source to the sample.

The spectrometer and its description is presented in Figure 12.



- 1 - Moderator
- 2 - Background Choppers
- 3 - Ni Guide Tube
- 4 - Detector for High Intensity Diffraction
- 5 - Detector for High Resolution Diffraction
- 6 - He³ 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

Fig. 12 The scheme of NERA spectrometer in Joint Institute for Nuclear Research in Dubna from <http://flnp.jinr.ru/134/>

The produced neutron beam is slowed in the moderator (1) and background choppers (2) remove the background. After that, the neutron beam goes through the neutron guide (3). The neutron beam is incident on the sample (11). A spectrometer has 2 parts, each with 8 sections for measuring the inelastic scattering and one for the elastic scattering. The 4 and 5 are the diffraction detectors and (7) is a single crystal quasielastic neutron scattering analyser. For the inelastic incoherent neutron scattering the devices are used: ^3He Detectors (6) Pyrolytic Graphite INS Analyser (8), Be-filters (9) and collimators (10). At the same time 16 IINS spectra are registered at angles from 20° to 160° . Be-filters are cooled in liquid nitrogen.

5. Neutron scattering spectra of compounds with hydrogen bonding

The dynamics of the hydrogen atom in a hydrogen bond is controlled by the potential surface between the two electronegative atoms, which participate in the hydrogen bond. Because of the high cross section of the hydrogen atoms the dynamics can be thoroughly examined by inelastic incoherent neutron scattering. As the hydrogen bond causes the geometric and energetic distinctions, it changes also bond lengths. It provides some spectroscopic consequences.

Usually we describe the vibrations of the hydrogen atom in hydrogen bonds by relating them to the vibrations that existed before the bond was formed. The most known examples of compounds with hydrogen bond occur in oxygen-oxygen systems (O-H...O). The presence of the hydrogen bond causes the in-plane and out-of-plane deformations. The example of that deformation is presented in Figure 13:

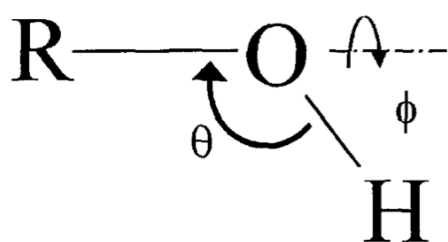


Figure. 13 The internal deformations of an alcohol group described by:
 Θ – the in-plane deformation
 ϕ – the libration, which become out-of-plane deformation, from: PCH. Mitchell, SF. Parker, AJ. Ramirez-Cuesta, J. Tomkinson, *Vibrational Spectroscopy with Neutrons With Applications in Chemistry, Biology, Material Science and Catalysis, Series on Neutron Techniques and Applications – Vol. 3, World Scientific, Singapore, 2005*

In this example of system the $\nu(\text{H}\dots\text{O})$ stretch appears with the value of 200 cm^{-1} . The θ deformation which is expected to be about 500 cm^{-1} , stiffens and becomes the in-plane deformation $\delta(\text{O-H}\dots\text{O})$ with the vibration from 900 cm^{-1} to 1500 cm^{-1} for weak and strong hydrogen bonds, respectively. And the twist ϕ becomes the out-of-plane

deformation – $\gamma(\text{O-H}\dots\text{O})$ and occurs from 600 cm^{-1} to 1200 cm^{-1} for weak and strong hydrogen bonds, respectively. The band of this vibration is usually easy to identify in INS because in this vibration the hydrogen atom performs most movements. There is the relationship between $\gamma(\text{O-H}\dots\text{O})$ and the oxygen-oxygen distance – $R(\text{OO})$ given by the following equation:

$$R(\text{OO}) = 3,01 - 0,00044(\gamma) \quad (14)$$

For the $\nu(\text{O-H})$ stretch the vibration falls from 3200 cm^{-1} to 2900 cm^{-1} upon weak hydrogen bond formation. This value changes most because of the lengthening and weakening of the original O-H bond.

6. Experimental and computational data

Three samples measured on NERA spectrometer shown in Figure 14:

- 1) 3-nitrobenzene-1,2-dicarboxylic acid
- 2) 2-[(E)-(fenyloimino)metylo]fenol and isotopically labelled
- 3) 2-[(E)-(fenyloimino)metylo]fen[^2H]ol

Their chemical structures are presented below:

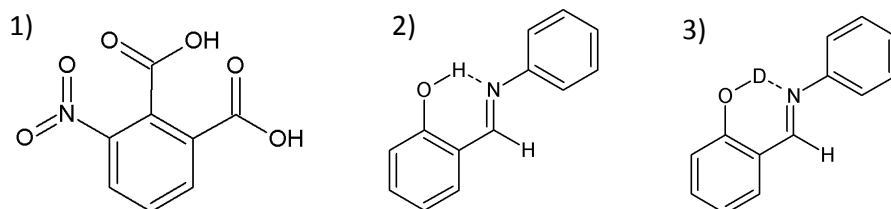


Fig. 14 Measured samples, description in the text.

The spatial structures of the first compound were optimised in Gaussian program. It was calculated for the gas phase. The obtained conformers are presented in Figure 15 with the calculated IR spectra of the first one:

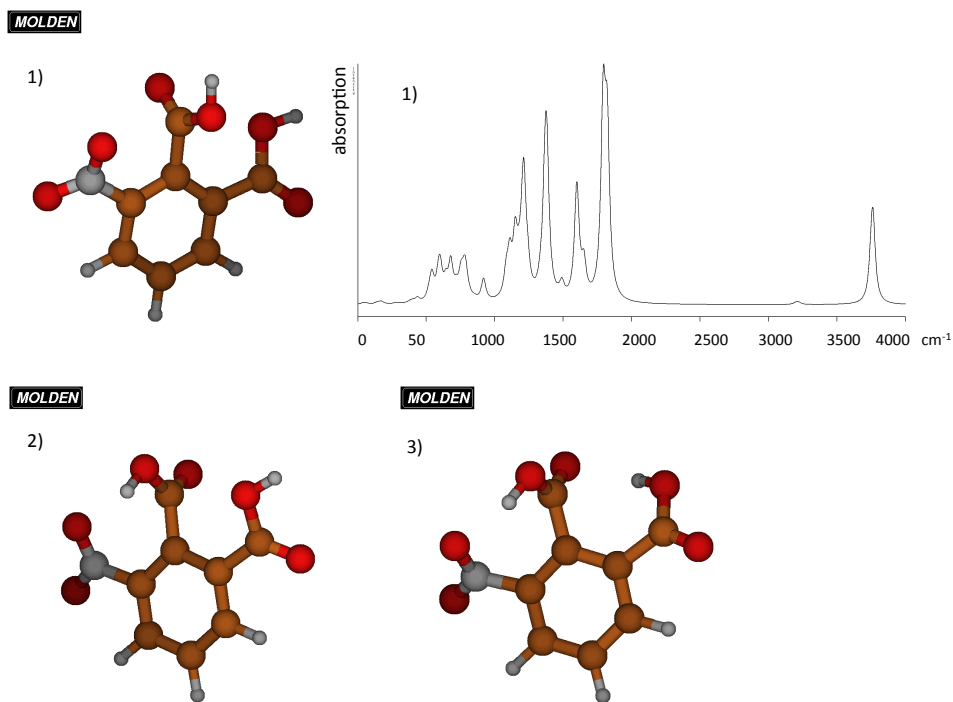


Fig. 15 Calculated conformers for 3-nitrobenzene-1,2-dicarboxylic acid and the calculated IR spectrum of the first one.

As we can see there are three conformers. The first one has the smallest energy. The second has a higher value and the difference between energy of the first and the second conformer equals 4,67 kcal/mol as well as between the first and for the third one is 7,15 kcal/mol. The energy difference is not big, it means that the conformers are observed in the gas phase and they can transform into each other.

The obtained IINS spectrum of 3-nitrobenzene-1,2-dicarboxylic acid is presented in Figure 16.

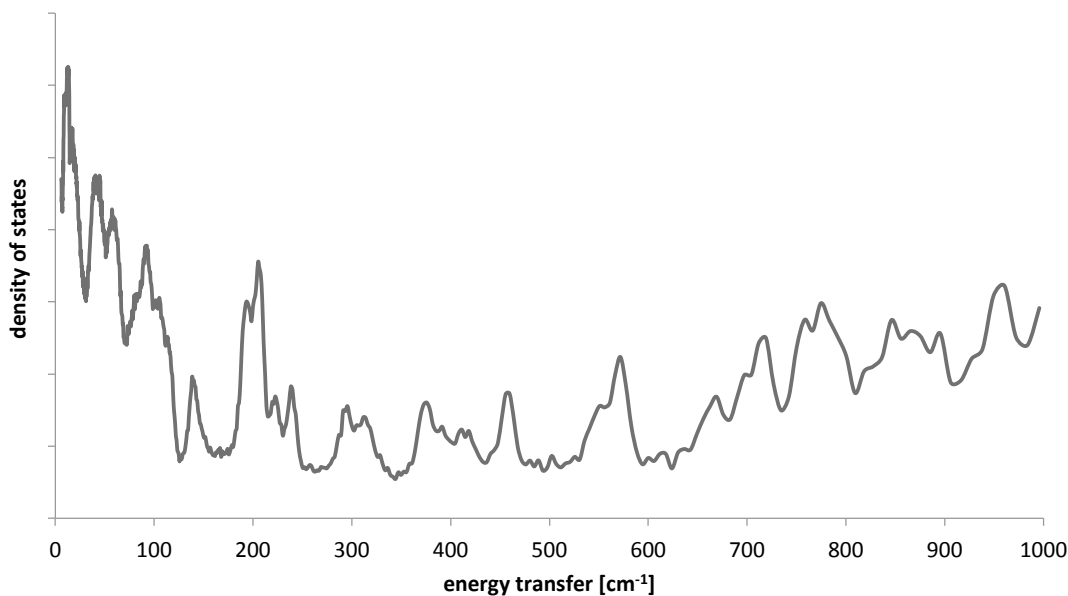


Fig. 16 The IINS spectrum of 3-nitrobenzene-1,2-dicarboxylic acid prepared with the NuVis program

For next compounds, which are ortho-hydroxyaryl Schiff bases, we completed the calculations with the Gaussian program and there we found two conformers (Figure 17).

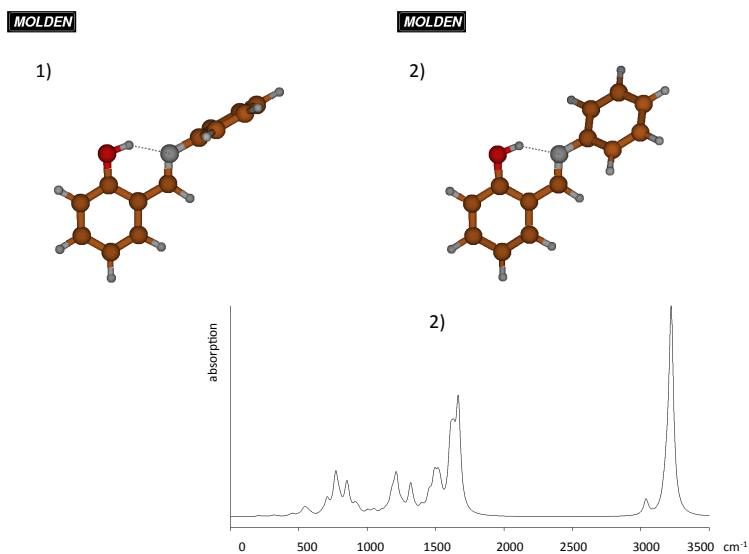


Fig. 17 Calculated conformers for 2-[(E)-(fenyloimino)metylo]fenol and the calculated IR spectrum of the second conformer

The second one has the smallest value of energy and the IR spectrum was calculated with Gaussian program (Figure 17). As we can see there is an intramolecular hydrogen bond between the hydroxyl group and the nitrogen from the imine group.

The obtained IINS spectra of the ortho-hydroxyaryl Schiff base and its deuterated analogue are presented in Figure 18.

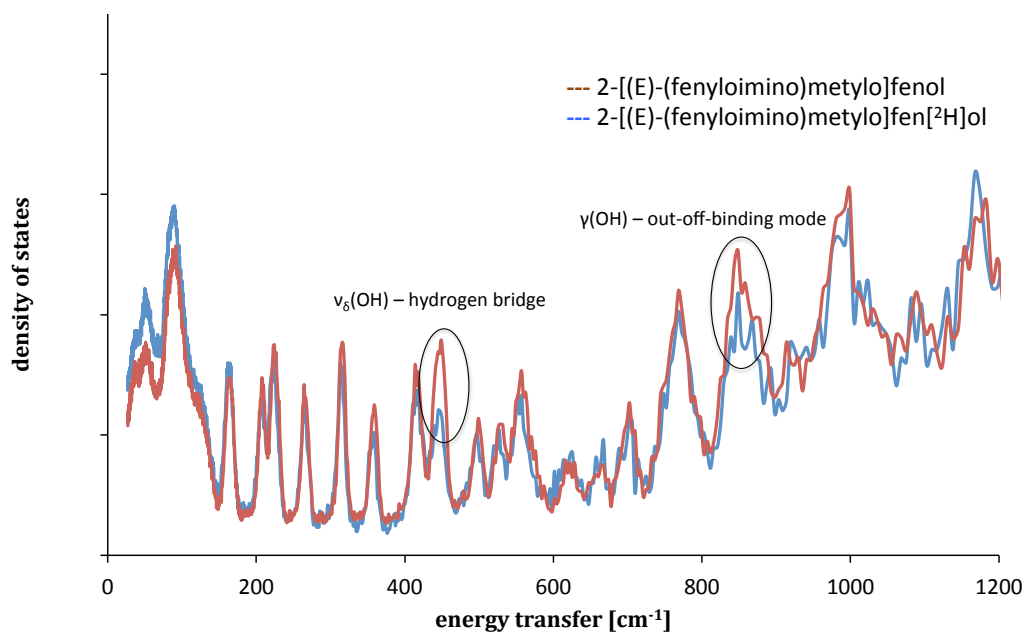


Fig. 18 The IINS spectra of 2-[(E)-(fenyloimino)metylo]fenol (orange line) and 2-[(E)-(fenyloimino)metylo]fen[²H]ol (blue line) prepared with the NuVis program

The assignments of two bands in the spectra were made. The bands correspond to:

- $\nu_s(\text{OH})$ – hydrogen bridge
- $\gamma(\text{OH})$ – out-of-binding mode

IR and Raman spectra were also recorded, which are presented in Figures 19 and 20.

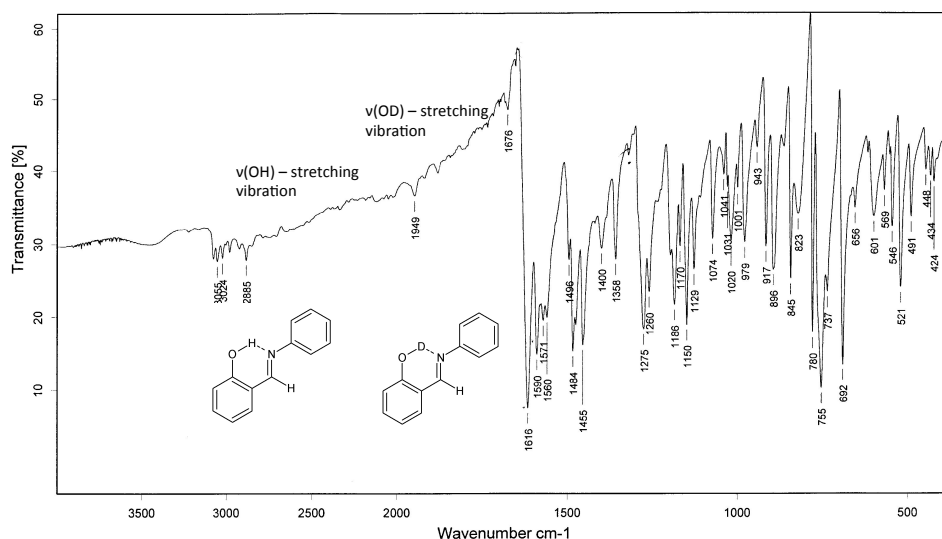


Figure 19 The IR spectrum of partly deuterated 2-[(E)-(fenyloimino)metylo]fenol in the solid state

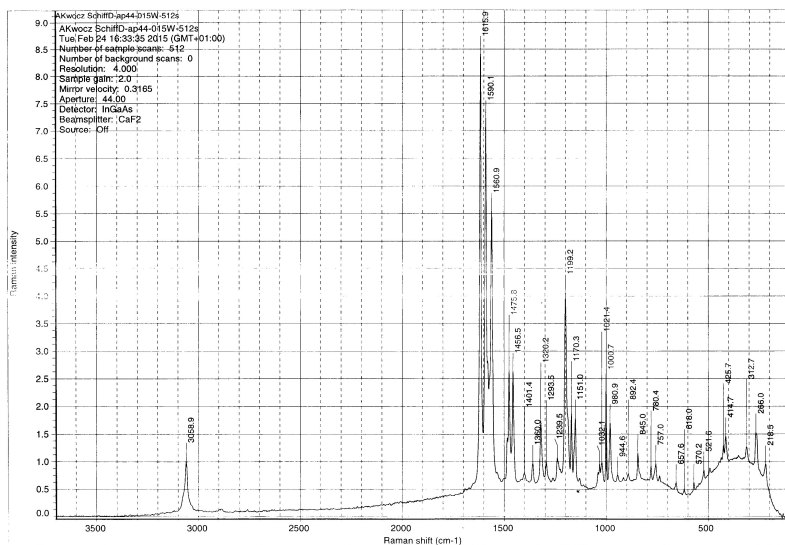


Fig. 20 The Raman spectrum of partly deuterated 2-[(E)-(fenyloimino)metylo]fenol in the solid state

The presence of hydrogen bonding causes the widening of the stretching vibrational band in IR spectra. Furthermore, two very broad bands corresponding to hydrogenated and deuterated derivatives are observed. Hydrogen-deuterium exchange causes the shift of vibrations frequency towards smaller wave numbers. Therefore, two broad bands in the IR spectrum are assigned to the $\nu(\text{OH})$ stretching vibration and the $\nu(\text{OD})$ stretching vibration.

Thus, those frequencies, which we can detect using neutron spectroscopy, are not visible in IR or Raman spectra. So, it means that these three kinds of spectroscopy complement each other.

7. Summary

I have learned much during my practice in Joint Institute for Nuclear Research and I have broadened my scientific horizons.

I found out that the neutron spectroscopy is a very useful research method of physico-chemical properties of condensed matter. This method gives many opportunities. It is an important complement to the other spectroscopic methods like IR, Raman or NMR. The incoherent inelastic neutron scattering is an irreplaceable method to investigate the hydrogen bond because it is anomaly sensitive for hydrogen atoms.

Although IINS allows precise examining the hydrogenated compounds, it gives many opportunities especially in research of organic compounds. They are commonly hydrogenated, where hydrogen bonds exist. This kind of bond is a very common and important electrostatic interaction without which there will not be life on our planet and it is the reason why we should investigate hydrogen bond especially in organic compounds.

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