Analysis of spectroscopic and theoretical results of compounds with intermolecular hydrogen bonding

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SUMMER STUDENT PRACTICE
JINR 2014
The hydrogen bonding definition:

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**.


\[ X–H \cdots A \]

Figure 1. Schematic representation of a typical hydrogen bond potential.[8] A hydrogen bond length differing from \(d_0\) implies a force towards a geometry of lower energy, that is, by attraction if \(d > d_0\) and repulsion if \(d < d_0\). Note that the interaction can at the same time be “stabilizing” (or “bonding”) and “repulsive”! The distortions from \(d_0\) occurring in practice are limited by the energy penalties that have to be paid, and in crystals, only a few hydrogen bonds have energies differing by more than 1 kcal mol\(^{-1}\) from optimum.
Hydrogen bonding: the experimental evidence

\[ X-H \cdots A \]

IR spectra: Left: 2,4,6-tri-Cl-phenol (no hydrogen bond); right: 2,4,6-tri-Cl-phenol + N-benzylidenomethylamine (hydrogen bonding occurrence). Asterix: stretching mode of the X-H bonding.

Upon generation of a hydrogen bond a wide maximum corresponding to the stretching mode of hydrogen bond occurs.
HYDROGEN BOND: EXPERIMENTAL INVESTIGATION

VIBRATIONAL SPECTROSCOPY:
• IR and Raman
• INS
Hydrogen bonding investigation: IR and Raman

Selection rules:

• Rule of mutual exclusion
  In general, molecular vibrations symmetric with regard to the centre of symmetry are forbidden in the infrared spectrum, whereas molecular vibrations which are antisymmetric to the centre of symmetry are forbidden in the Raman spectrum. This is known as the rule of mutual exclusion.
Hydrogen bonding investigation: IR and Raman

Selection rules:

- **Infrared absorption** can be detected if the dipole momentum $\mu$ in a molecule is changed during the normal vibration. The intensity of an infrared absorption band $I_{IR}$ depends on the change of the dipole moment $\mu$ during this vibration

\[
I_{IR} \propto \left( \frac{\partial \mu}{\partial q} \right)_0^2
\]

where $q$ is the normal coordinate.
Hydrogen bonding investigation: IR and Raman

Example

Selection rules:

- A Raman active vibration can be detected if the polarizability $a$ in a molecule is changed during the normal vibration. The intensity of a Raman active band $I_{Raman}$ depends on the change of polarizability $a$ during this vibration:

$$I_{Raman} \propto \left( \frac{\partial a}{\partial q} \right)_0^2$$

where $q$ is the normal coordinate.
**IINS (Inelastic Incoherent Neutron Scattering): Theoretical aspects**

The main contribution to the incoherent neutron scattering comes from the interaction of the atom and neutron spins and from the random isotope distribution in the sample.

- **Momentum transfer:**
  \[ Q = k_i - k_f \]

- **Energy transfer:**
  \[ E_T = E_i - E_f = \frac{\hbar^2}{8 \pi^2 m_n} (k_i^2 - k_f^2) \]

Cross sections \([b]\): coherent | incoherent
---|---
Hydrogen | 1.758 | 79.7
Deuterium | 5.597 | 2.04
Carbon | 5.6 | 0.001
Nitrogen | 11.0 | 0.49
Oxygen | 4.23 | 0.000
Fluorine | 4.017 | 0.0008
Chlorine | 11.531 | 5.2
Iron | 11.4 | 0.22

\( E_i, E_f \) – energy of the incident and scattered neutrons
\( k_p, k_i \) – wave vectors of the incident and scattered neutrons

In inelastic scattering, exchange of energy and momentum between the incident neutron and the sample causes both the direction and the magnitude of the neutron’s wave vector to change.

In incoherent scattering, the incident neutron wave interacts independently with each nucleus in the sample; that is, the scattered waves from different nuclei have random or indeterminate relative phases and thus cannot produce constructive interference.
IINS (Inelastic Incoherent Neutron Scattering): Theoretical aspects

Double differential crosssection: \( \left( \frac{d^2 \sigma}{d \Omega d \omega} \right) \) describes the density of the probability, that the incident neutron with energy: \( \frac{h}{2 \pi} \omega \) is scattered by an angle: \( \theta \), within the solid angle element: \( d\Omega = 2\sin \pi \theta d\theta \), and into the energy range: from \( h\omega' \) to \( h(\omega'+d\omega') \).

\[
\left( \frac{d^2 \sigma}{d \Omega d \omega} \right)_{\text{inc}} = \frac{\sigma_{\text{inc}}}{4 \pi} \frac{k_f}{k_i} S_{\text{inc}}(Q, \omega) \\
\left( \frac{d^2 \sigma}{d \Omega d \omega} \right)_{\text{coh}} = b_{\text{coh}}^2 \frac{k_f}{k_i} S_{\text{coh}}(Q, \omega)
\]

Fourier transform of the correlation function of the nuclei pairs and describes the collective motion of atoms and molecules.

Fourier transform of the autocorrelation function of atomic nuclei and describes individual atomic and molecular movements.
The $S(Q,\omega)$ function is named the **scattering law**. It depends only on structural and dynamical properties of a system.

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

Where:

$$Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos \theta$$

**Mean square displacement:**

$$U^2 = \frac{\hbar}{2m\omega} = \frac{16.759}{\mu \nu}$$
IINS (Inelastic Incoherent Neutron Scattering): Experimental approach

Inverted geometry time-of-flight spectrometer NERA at the IBR-2 high flux pulsed reactor in Dubna

Fig. 1. Scheme of the inverted geometry NERA-PR INS spectrometer (Dubna, Russia)

IINS (Inelastic Incoherent Neutron Scattering):
Experimental approach

Energy of the unscattered neutron beam \( E_i \)

\[
t_i = t - \frac{(L_{f1} + L_{f2})}{\nu_f}
\]

\[
\nu_f = \sqrt{\frac{2E_f}{m}}
\]

\[
E_i = \frac{mv_i^2}{2} = \frac{m}{2} \left( \frac{L_i}{t - \frac{(L_{f1} + L_{f2})}{\nu_f}} \right)^2
\]

Change of the neutron energy upon inelastic scattering

\[
\frac{h}{2\pi} \omega = E_f - E_i
\]
IINS (Inelastic Incoherent Neutron Scattering): Experimental approach

Change of the momentum upon inelastic scattering

\[ Q = \frac{8m \pi^2}{h^2} (E_i + E_f - 2 \sqrt{E_i E_f} \cos (\varphi)) \]
**INS**

- **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 exceed 2-3%
- **samples**: solid state at low temperature
- **useful for the studies of molecular vibrations of low frequency internal modes**

**IR and Raman**

- **selection rules**
- **low intensity** for the low freq modes (hydrogen bonding dynamics)
- **solid, liquid, gaseous samples**
Experimental results

IR and QM

IR SPECTRA (GAZ)

MP2/6-31G(d,p)

B3LYP/6-31G(d,p)

IR SPECTRA (GAZ)

IINS

Why hydrogen bonding investigation is important?

Antigen – antibody recognition
DNA structure
Protein structure

All backbone amide hydrogens are hydrogen bonded, either intramolecularly or to solvent.
References


- J.M. Janik, Fizyka Chemiczna, PWN 1989
Thank you for your attention!