St Petersburg University
Institute of Chemistry
Non-Covalent Interactions Laboratory

Diagnostics of geometry of intermolecular complexes using the combination of advantages of optical and NMR spectroscopy

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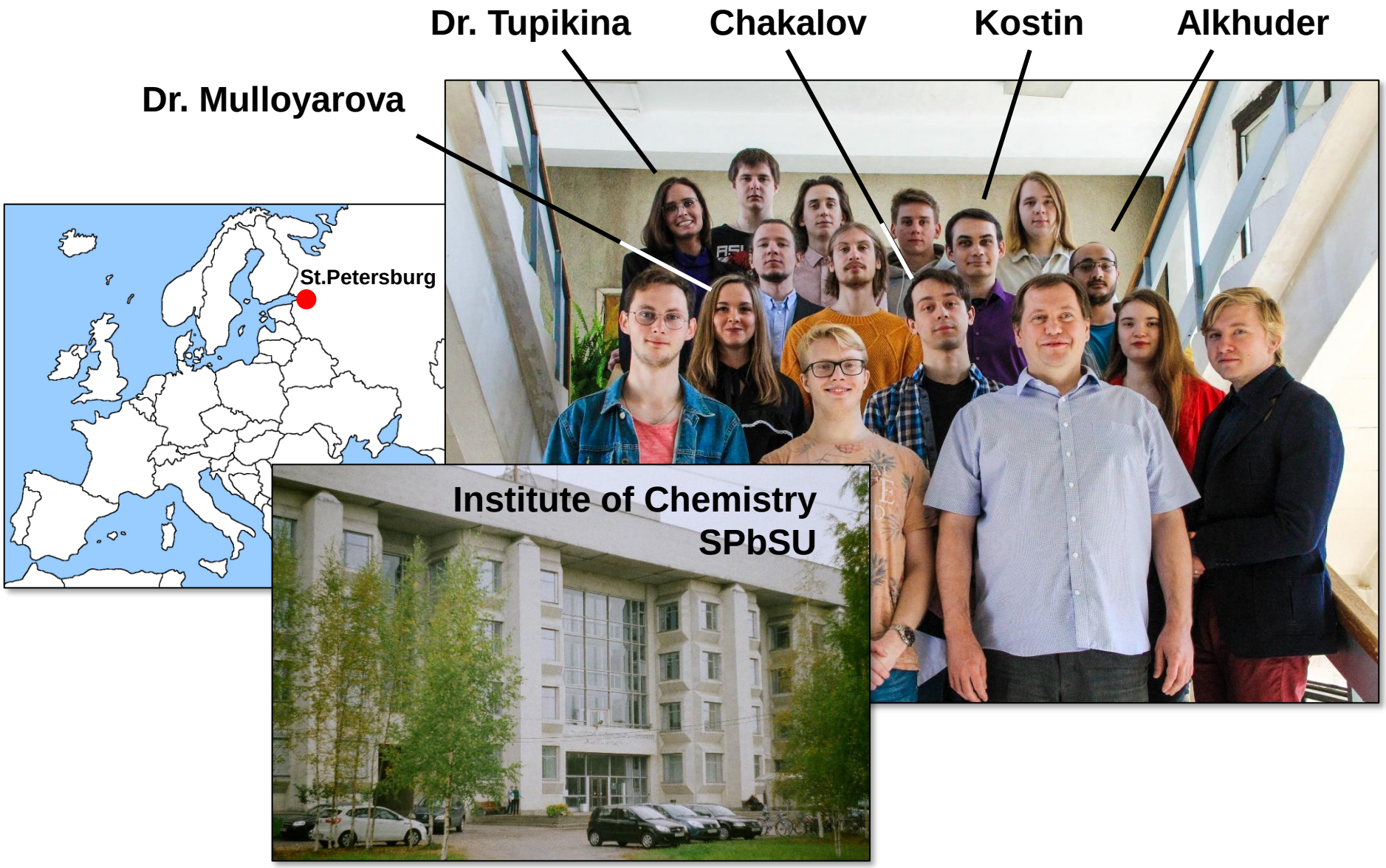
Иркутск, июль 2023

Non-covalent interactions laboratory

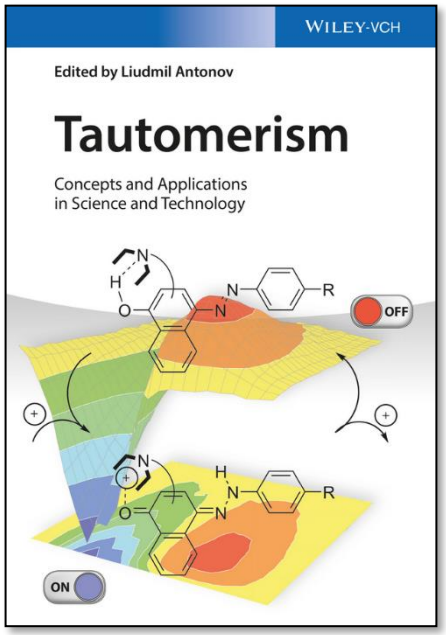
Staff and students



Book chapters

On which this presentation is based

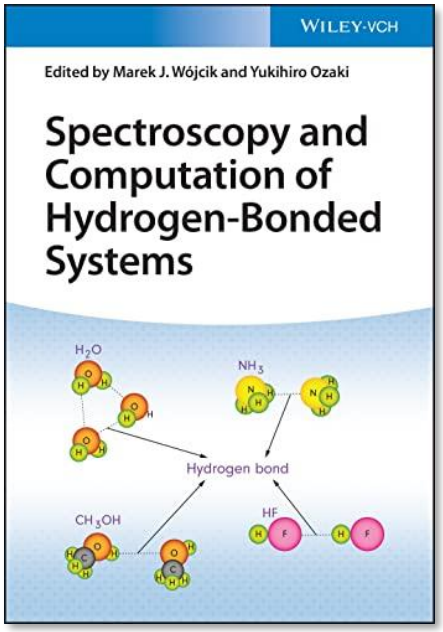
2016



H.-H. Limbach, G.S. Denisov, I.G. Shenderovich, P.M. Tolstoy

Chapter 14: Proton Tautomerism in Systems of Increasing Complexity: Examples from Organic Molecules to Enzymes

2023

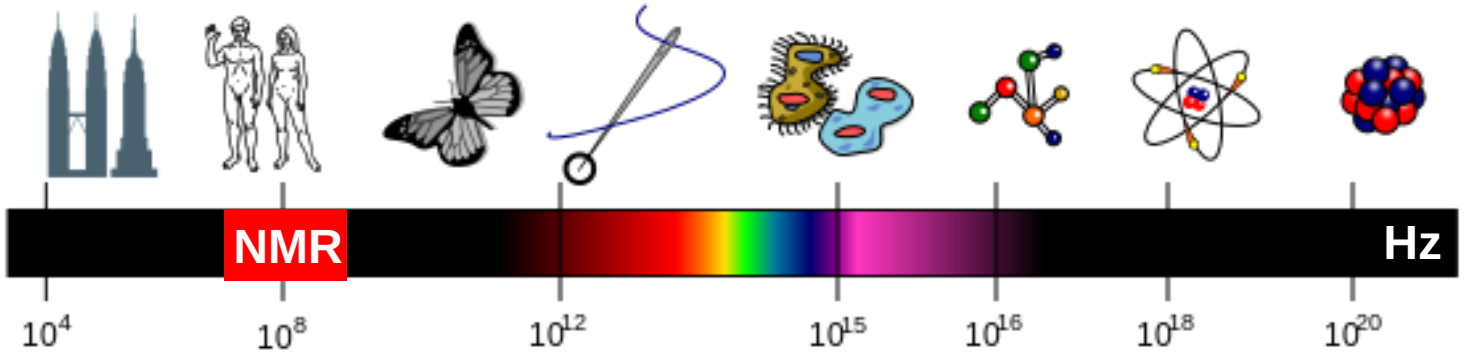


P.M. Tolstoy E.Yu. Tupikina

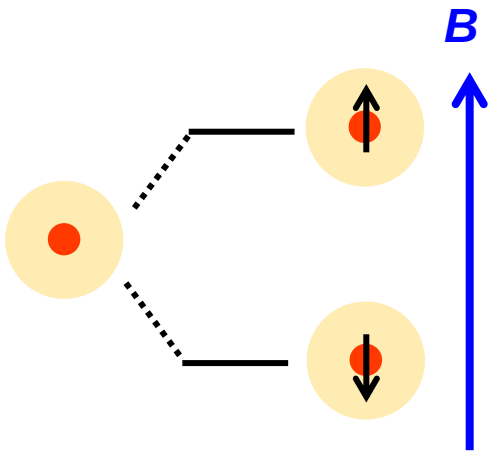
Chapter 12: IR and NMR Spectral Diagnostics of Hydrogen Bond Energy and Geometry

NMR – main principles

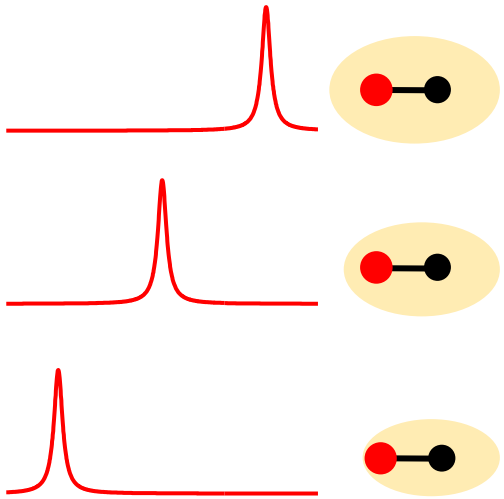
A reminder



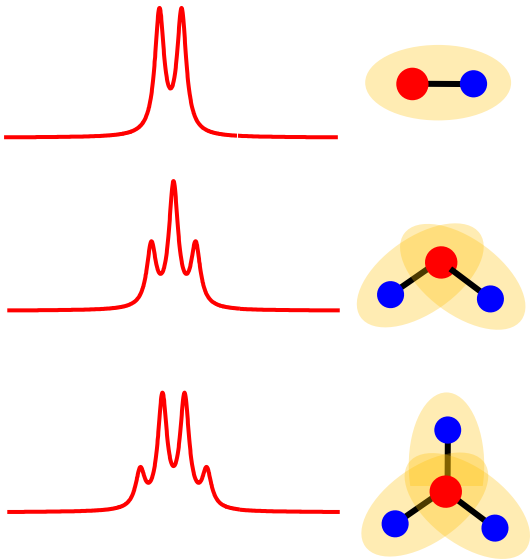
In magnetic field



Chemical shift

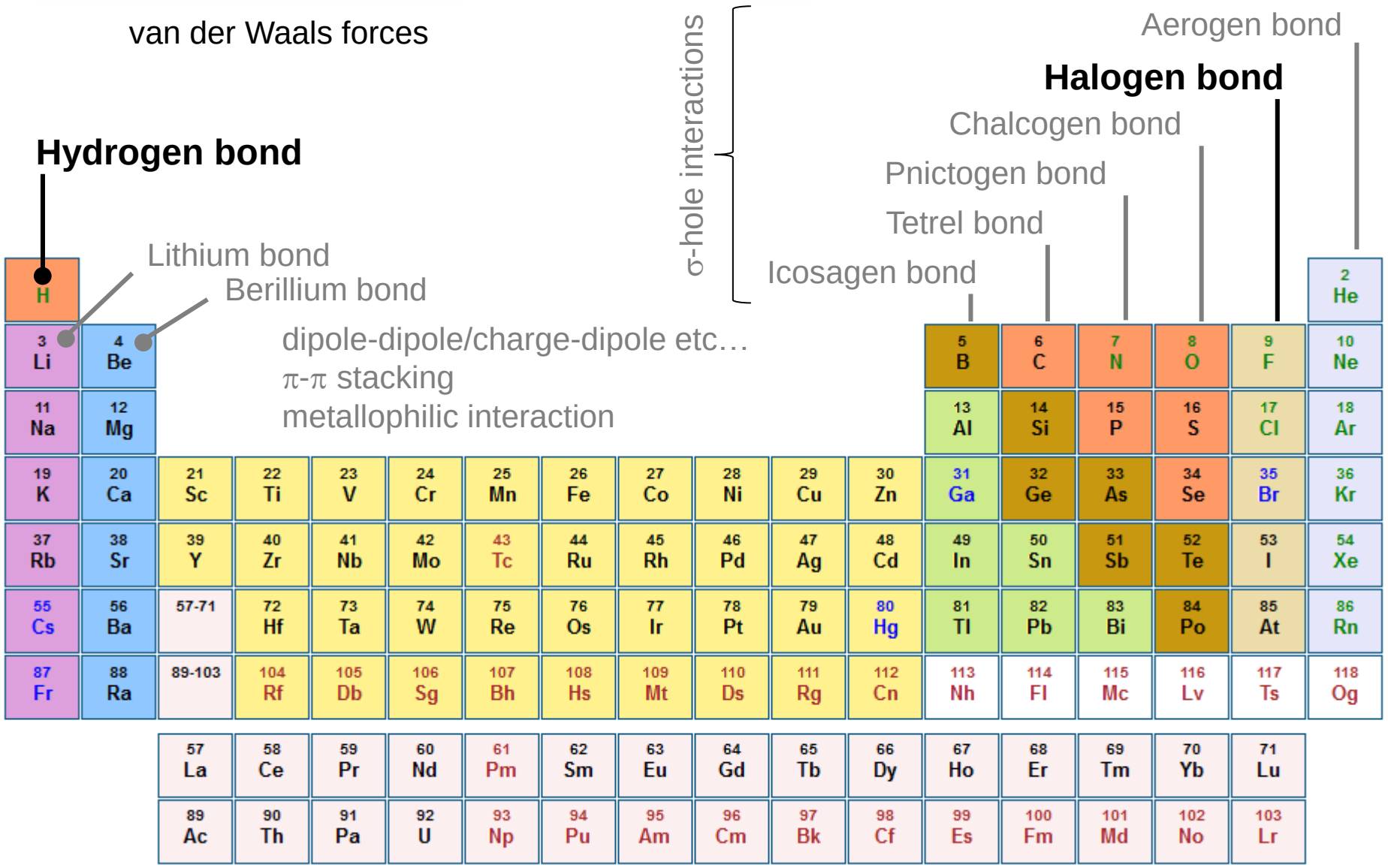


Spin-spin coupling



Non-covalent interaction

Different names for different elements

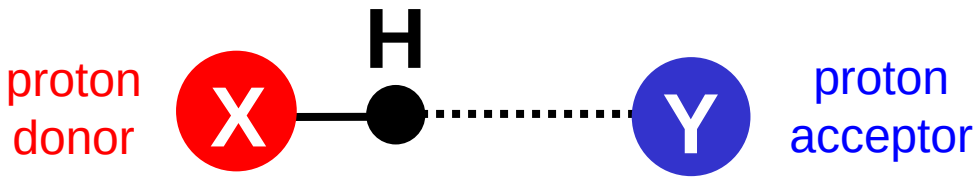


Hydrogen bond

Modern definition

Pure Appl. Chem., Vol. 83, No. 8, pp. 1637–1641, 2011.
doi:10.1351/PAC-REC-10-01-02

Definition of the hydrogen bond (IUPAC Recommendations 2011)*



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.

energy 1. Attractive forces: electrostatic, charge transfer, dispersion

el. struct. 2. X–H polarized, H···Y strength increases with electronegativity of X

geometry 3. X–H···Y is ~linear; the closer to 180°, the stronger it is, the shorter is H···Y; The longer X–H, the shorter is the H···Y

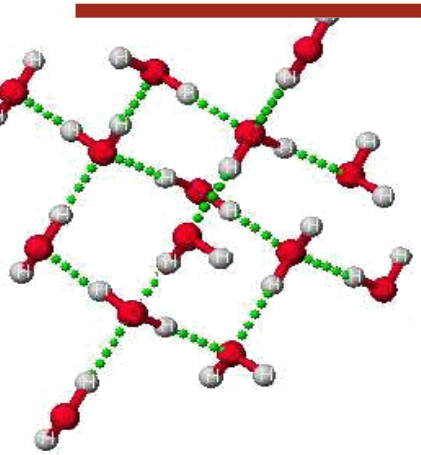
spectra 4. Red shift of X–H stretching, new low-frequency bands appear

5. H deshielding in NMR, *J*-couplings across the X–H···Y bond

detectable 6. The Gibbs energy should be greater than the thermal energy

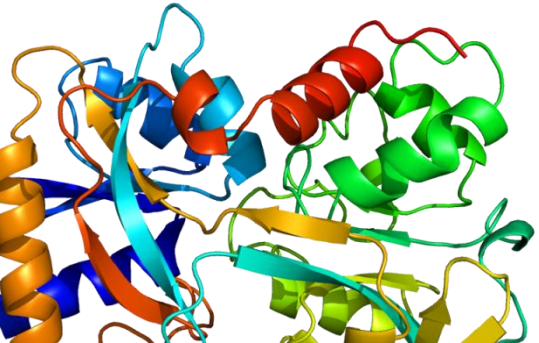
Hydrogen bond

A fairly well-working definition



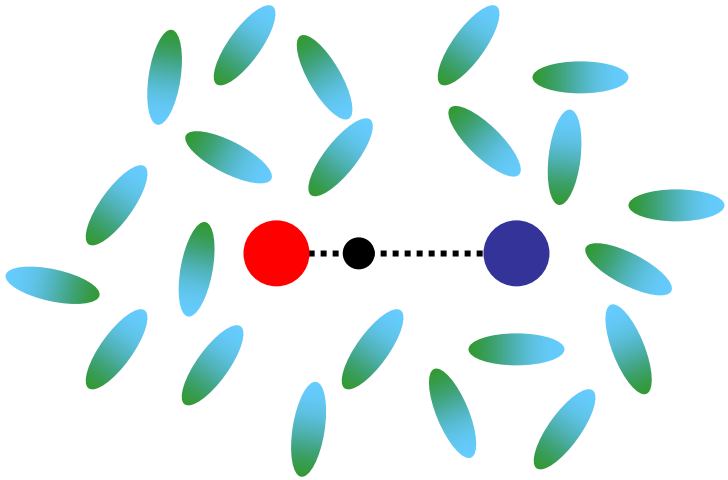
Hydrogen bond is like your spouse: immediately recognizable by the back of the hair in a crowd of a thousand people but you don't know how you did it.

— Prof. Piero Ugliengo speaking at XIV Horizons in Hydrogen Bond Research conference, Torino, 2003



Number of “protonation states”

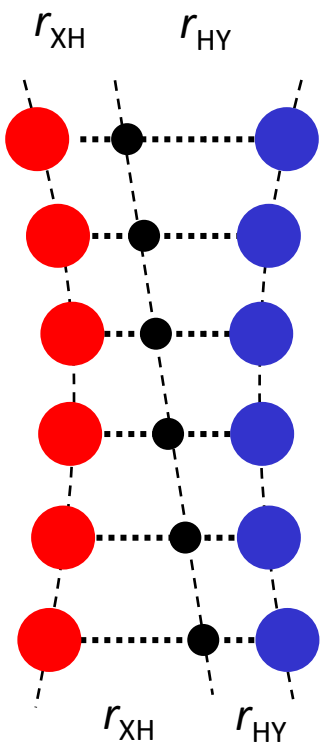
In polar aprotic medium

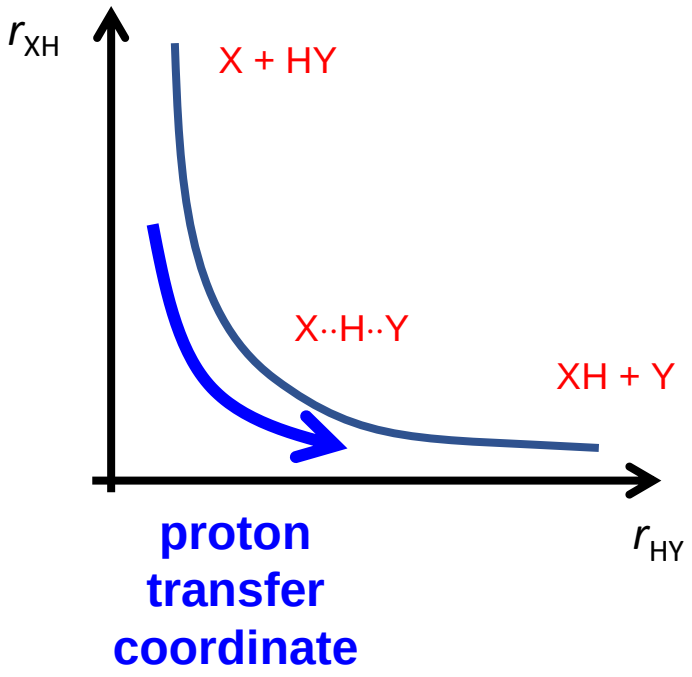


infinite number of protonation states

Gradual proton displacement

Interdependence of interactomic distances

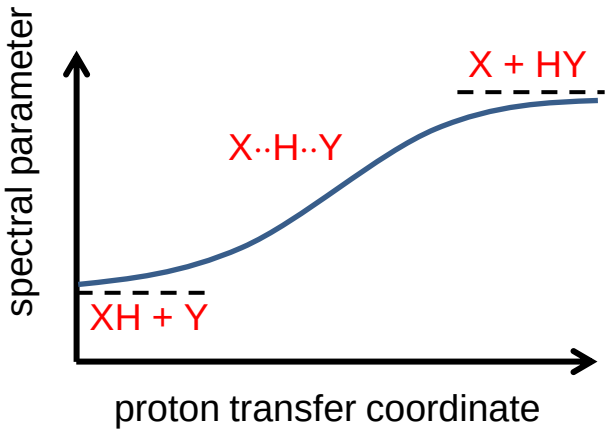




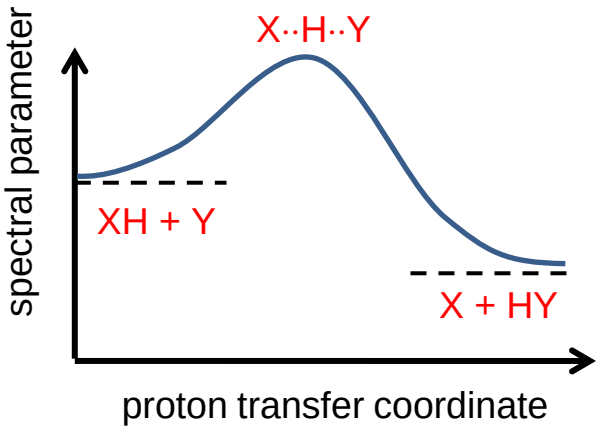
Hydrogen bond

Spectral parameters change upon proton transfer

monotonous
reflect the proton transfer degree



with an extremum
reflect the H-bond strength/length



chemical shifts

X–H------**Y** (**X**, **Y** = F, N, P etc.)

XO–H------**Y** (**X** = C, P etc.)

X–**H**------Y

coupling constants

$^{1}J_{XH}$ $^{1}J_{HY}$

X–H------Y

$^{2h}J_{XY}$

X–H------Y

vibrational frequencies

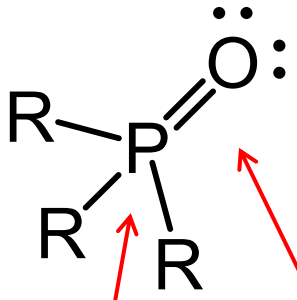
ν(CO), (PO) etc.

ν(XH) / ν(HY)

ν(XY)

Phosphine oxide as electron donor

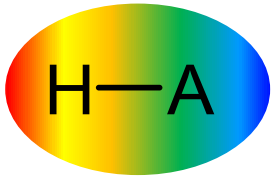
Lewis and Brønsted acids – distribution of electrostatic potential



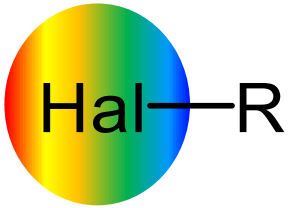
^{31}P NMR chemical shift δP

PO stretching ν_{PO}

Brønsted acid – proton donor (hydrogen bonds)



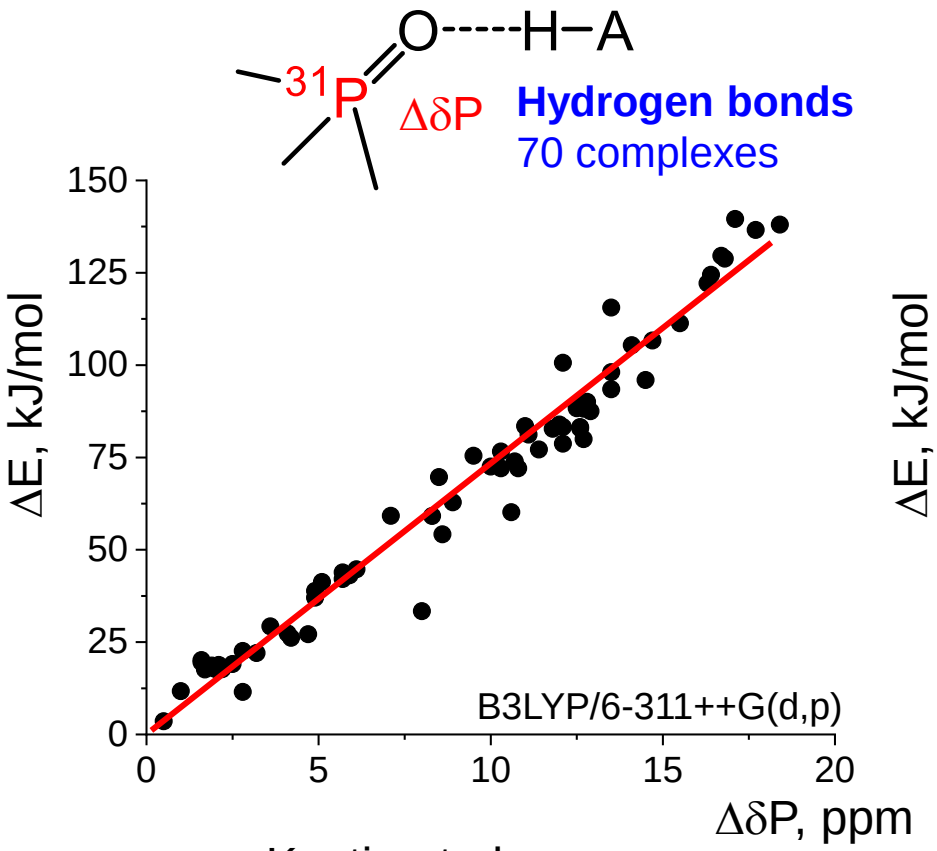
Lewis acid – electron acceptor (e.g. halogen bonds)



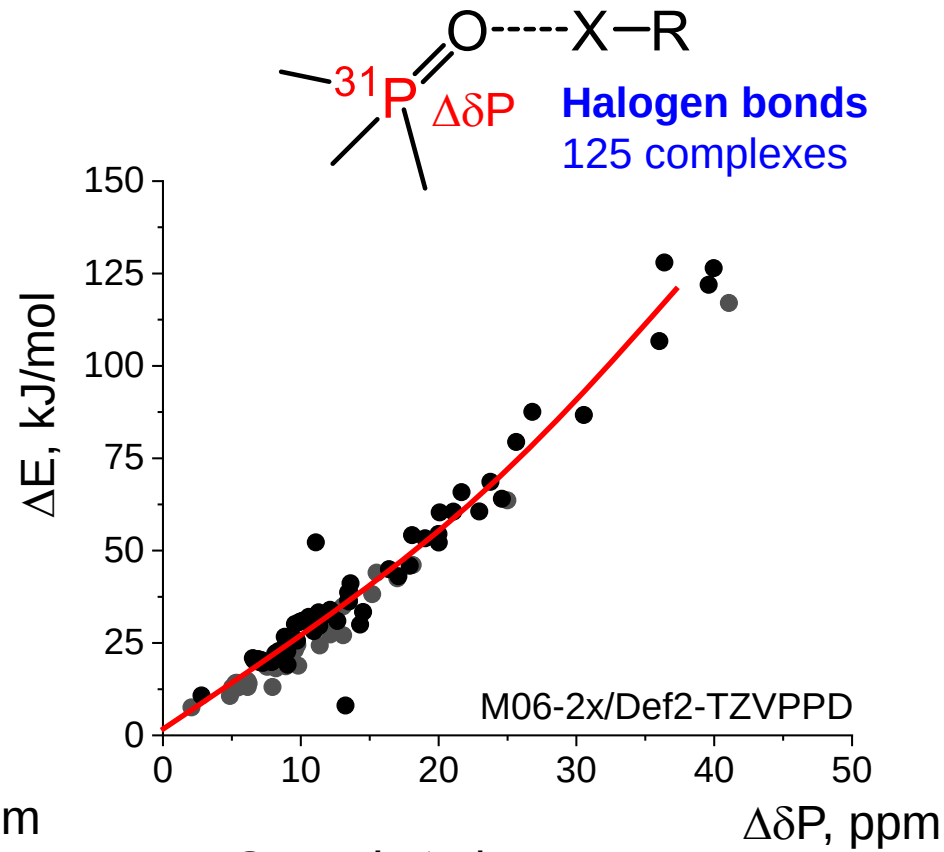
Testing Gutmann-Beckett method

Correlations with energy

^{31}P NMR chemical shift



Kostin et al.,
PCCP **2022**, *24*, 7121

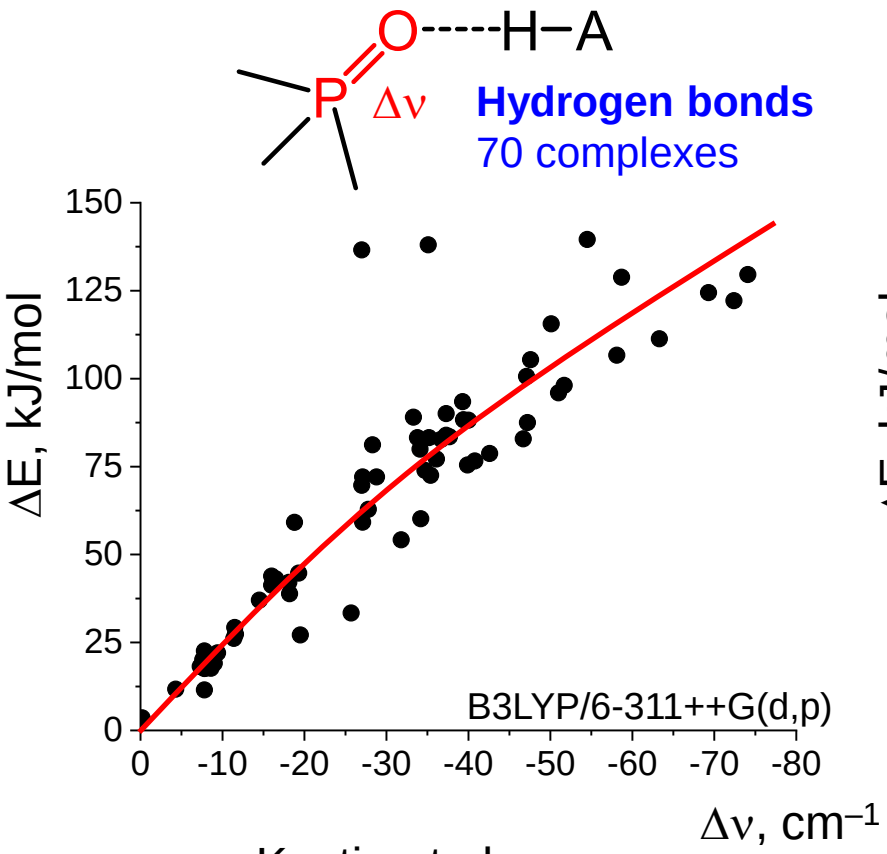


Ostras' et al.,
Molecules **2020**, *25*, 1406

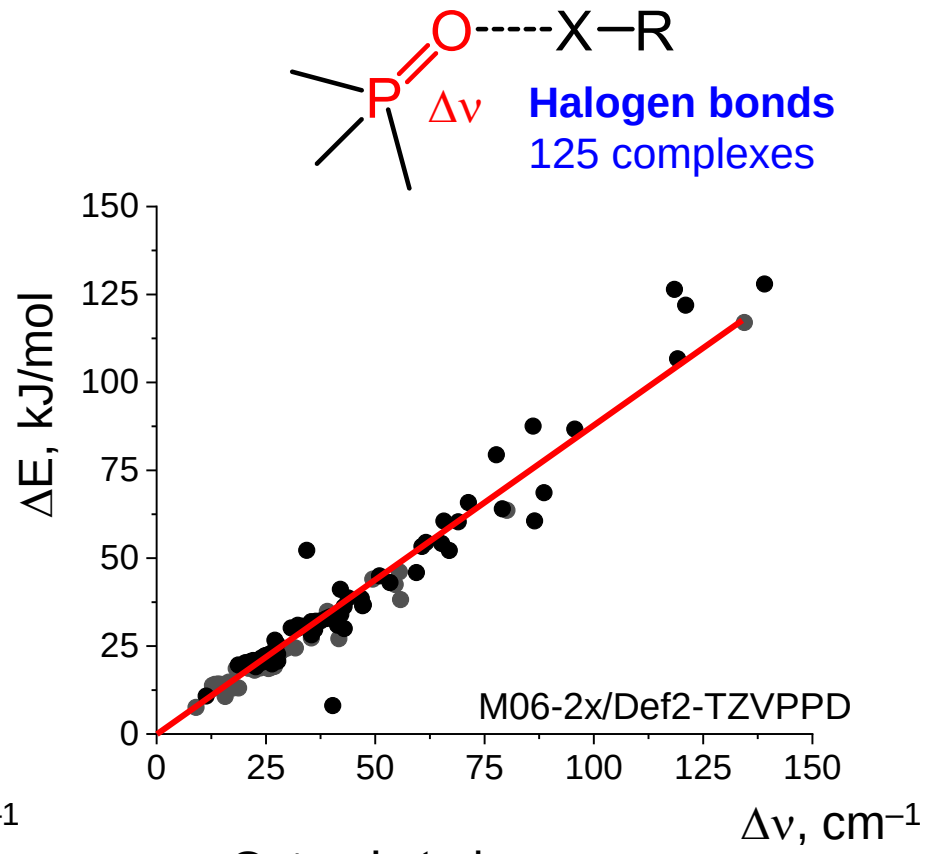
Testing Gutmann-Beckett method

Correlations with energy

P=O stretching frequency



Kostin et al.,
PCCP **2022**, *24*, 7121

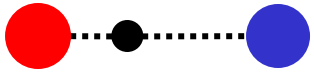


Ostras' et al.,
Molecules **2020**, *25*, 1406

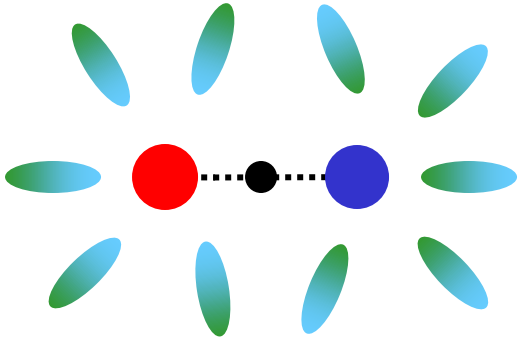
Averaging in NMR and optical spectra

Distribution of hydrogen bond geometries

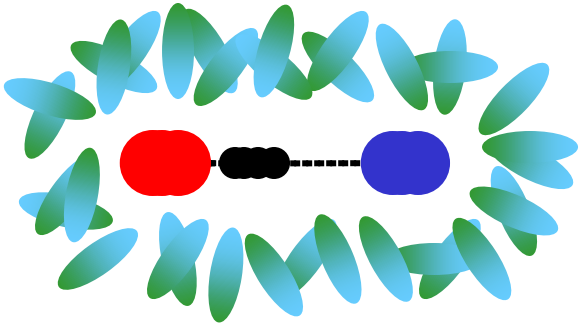
Gas phase



One solvent configuration

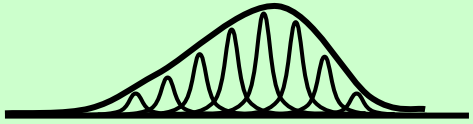


Many solvent configurations (thermal fluctuations)

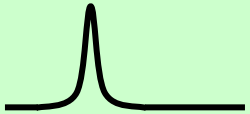


NMR spectra

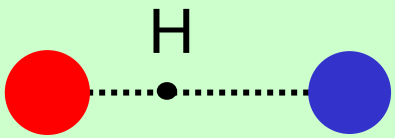
distribution of chem. shifts



averaged chem. shift

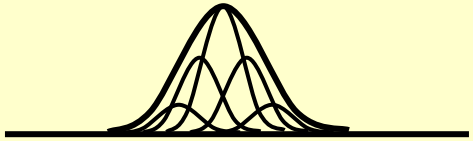


averaged geometry

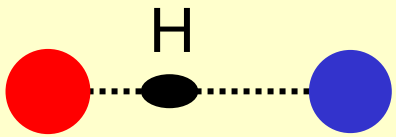


Optical spectra

distribution of absorbtion bands



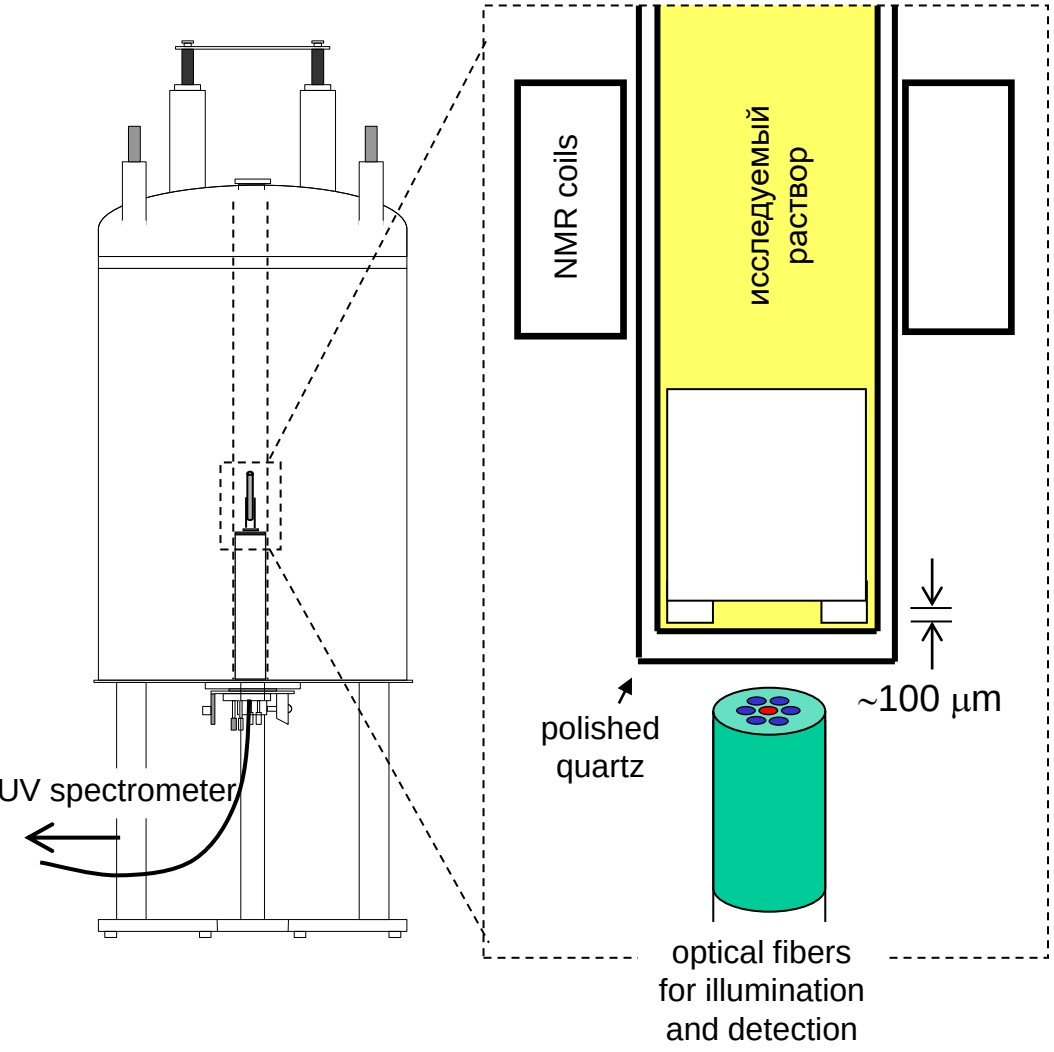
averaged geometry

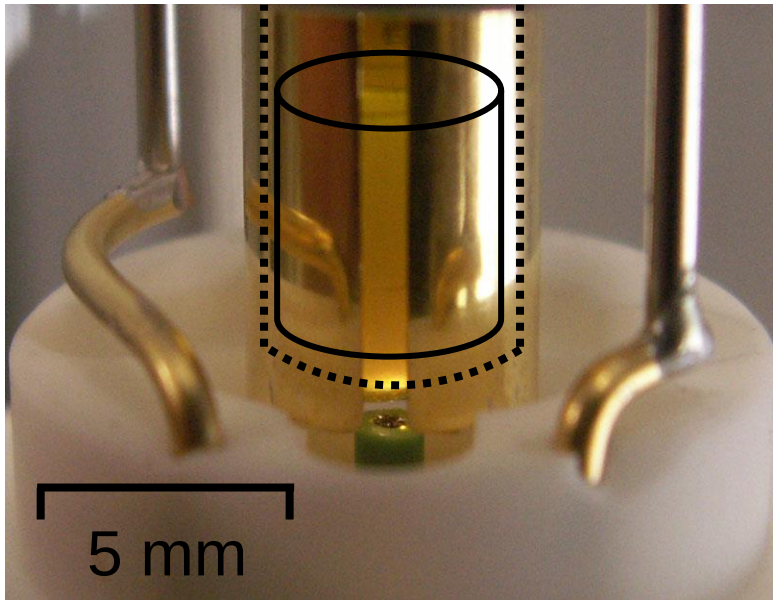


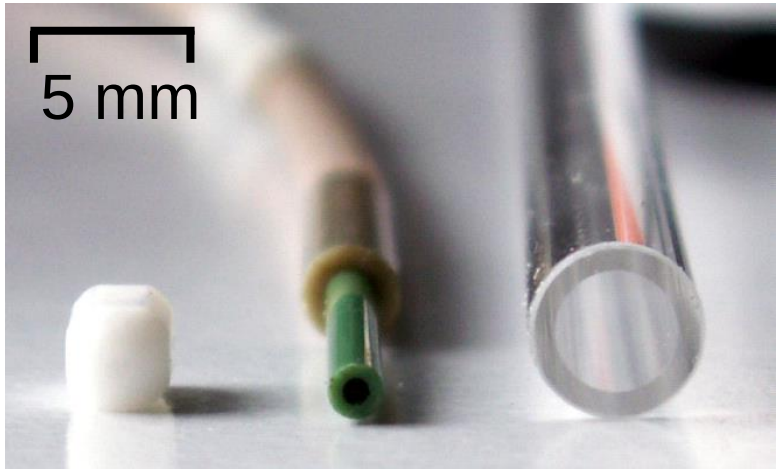
+ information about the distribution of geometries

Setup for combined NMR/UV-vis measurements

UV-vis spectrometer inside NMR magnet



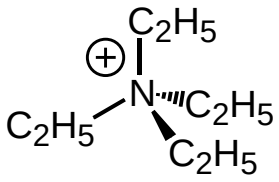


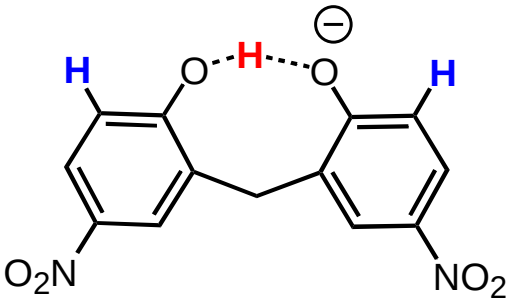


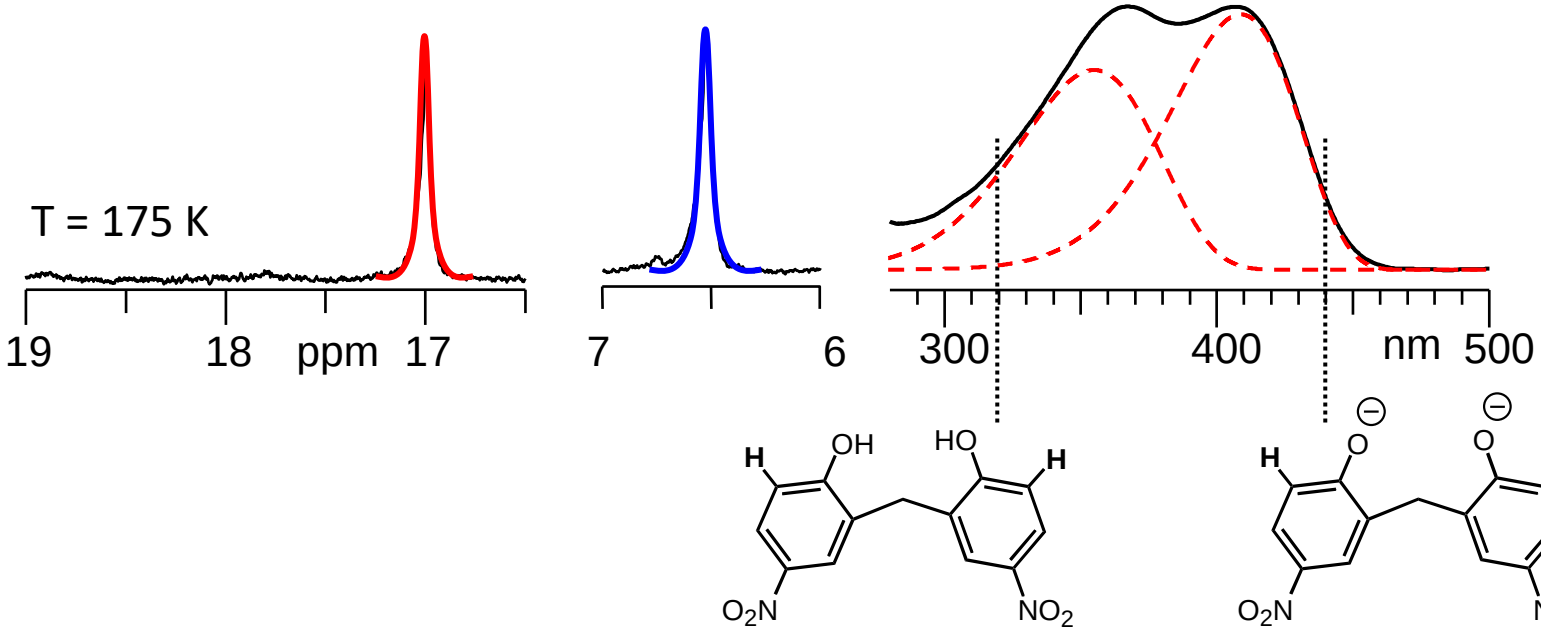
Angew. Chem. Int. Ed. **2009**, *48*, 5745

Proton jumps of central symmetry?

Advantages of combining NMR and optical spectroscopy



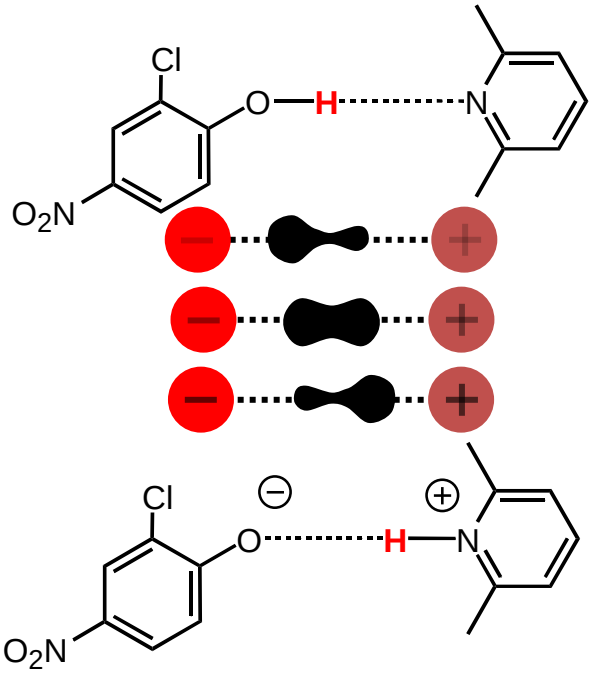


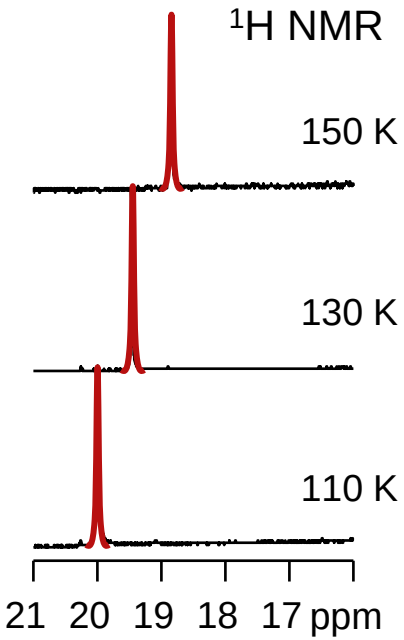


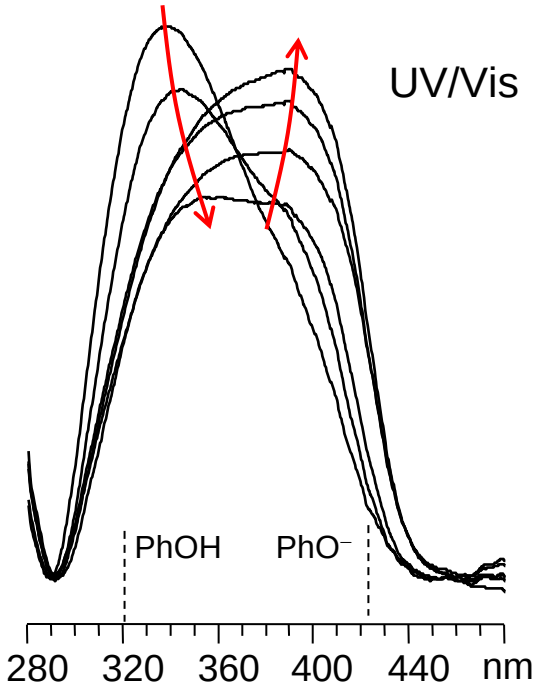
Proton displacement

Advantages of combining NMR and optical spectroscopy

solvent: CDF_3/CDF_2Cl

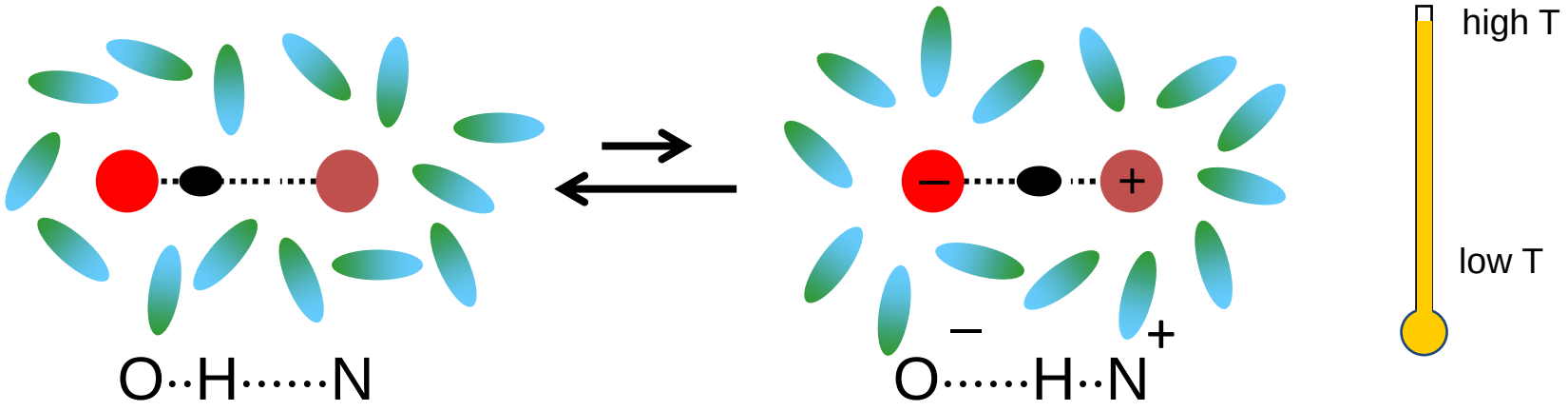






Proton displacement

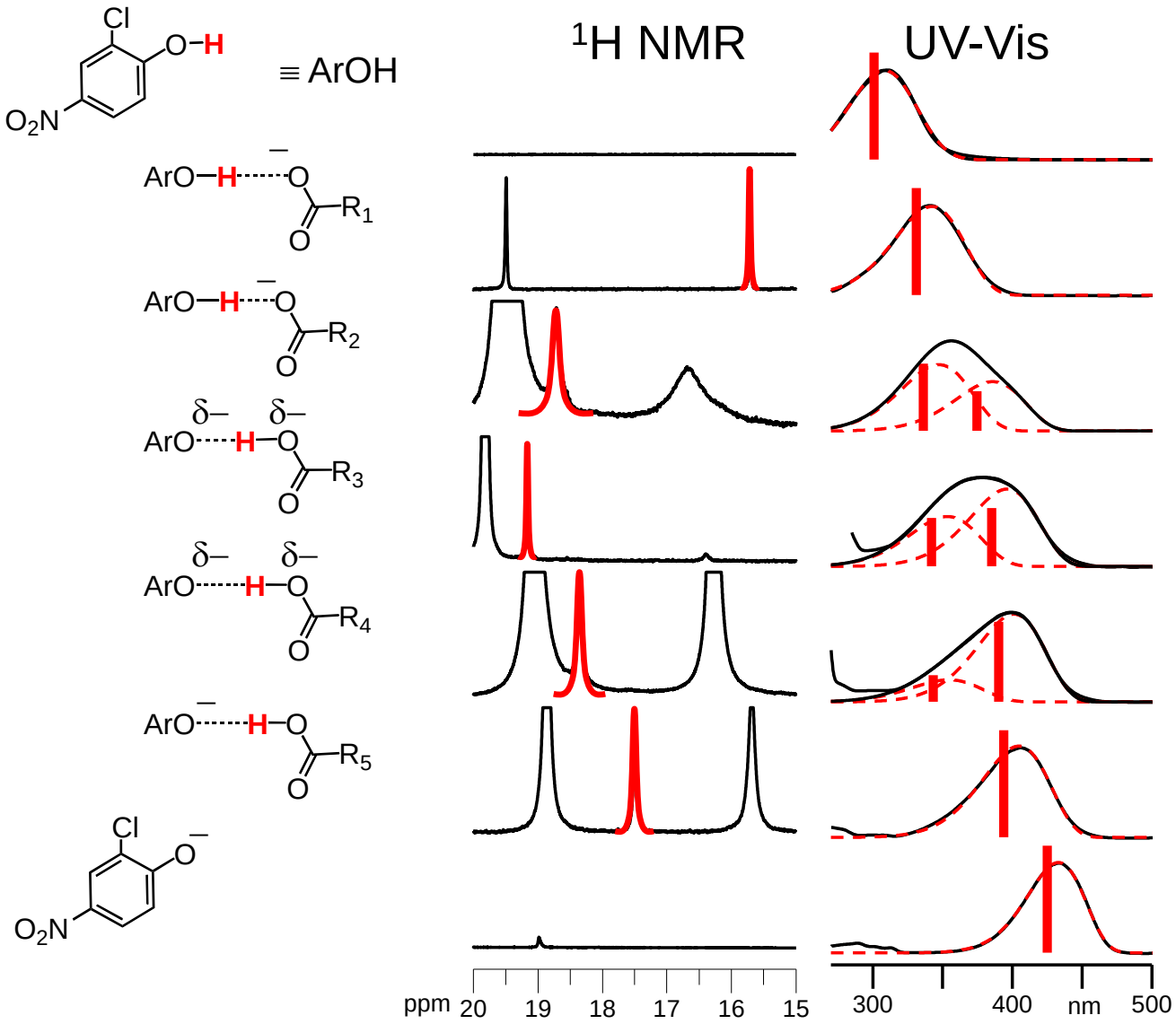
Advantages of combining NMR and optical spectroscopy

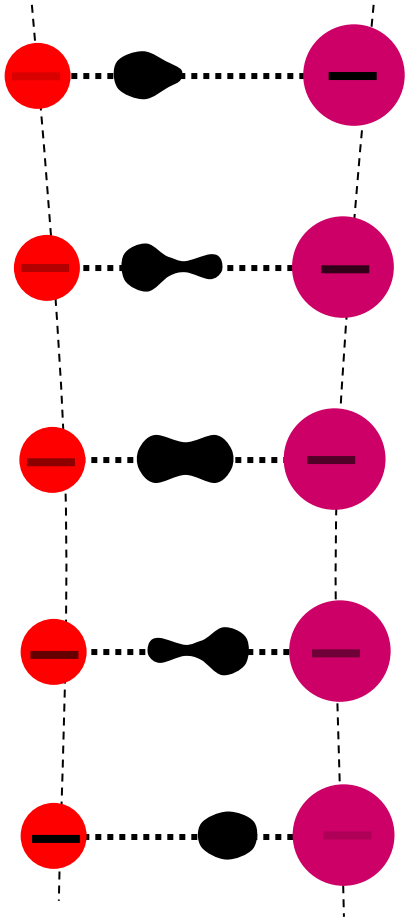


JACS **2011**, *133*, 7897

Proton displacement

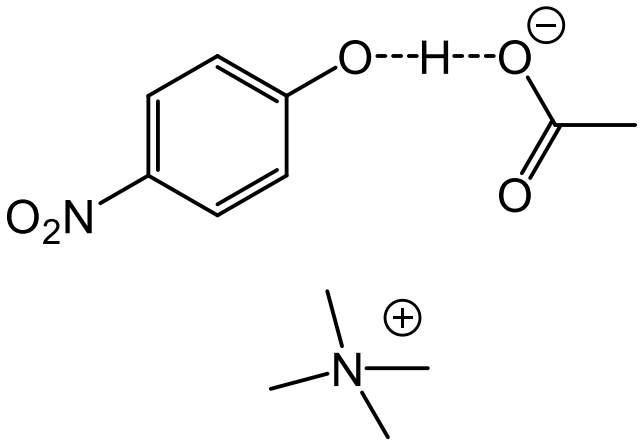
Advantages of combining NMR and optical spectroscopy





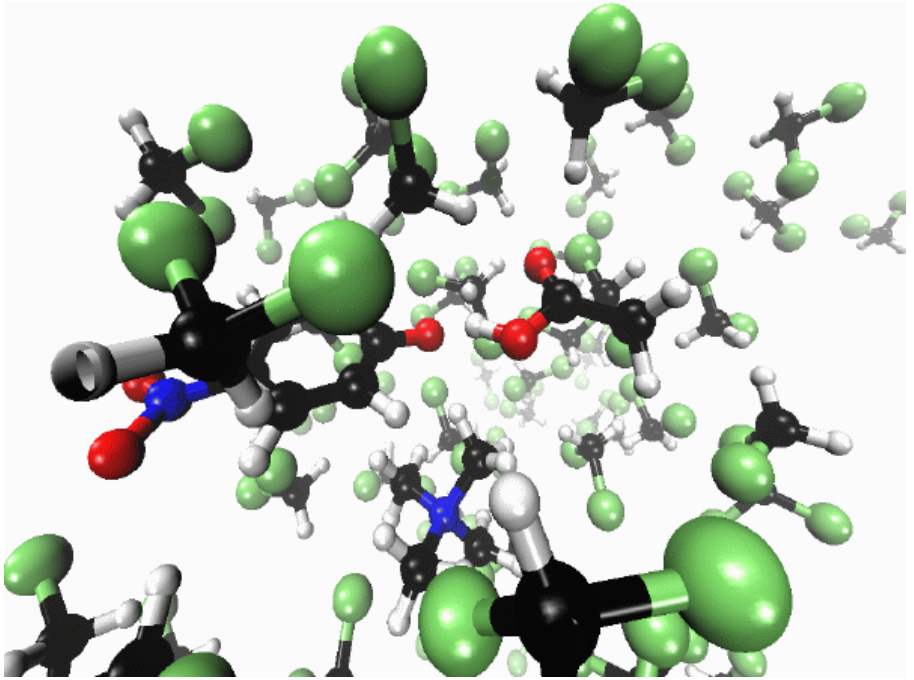
Solvent fluctuations

Molecular dynamics simulations



in CD_2Cl_2

ab initio MD simulation
(DFT MD using CP2K package)

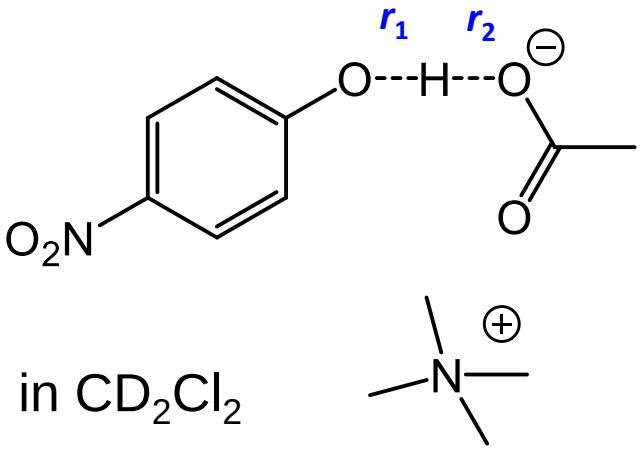


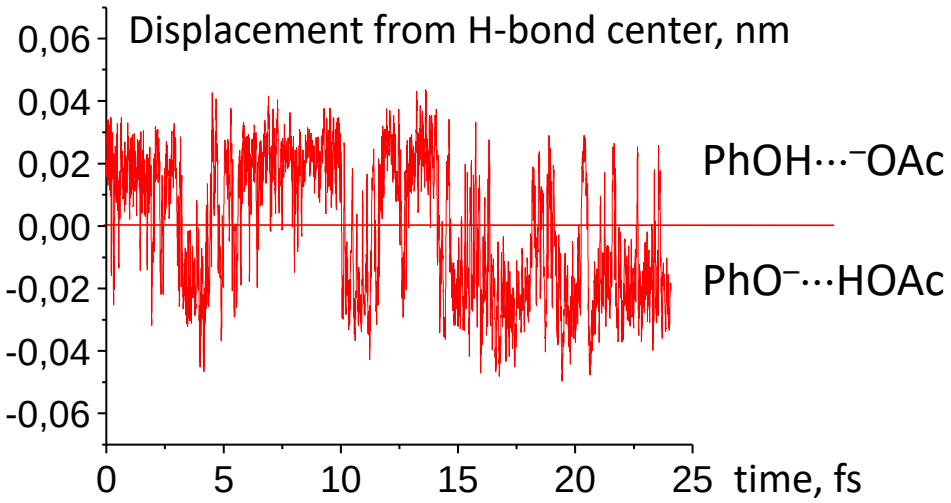
PCCP **2015**, *17*, 4634

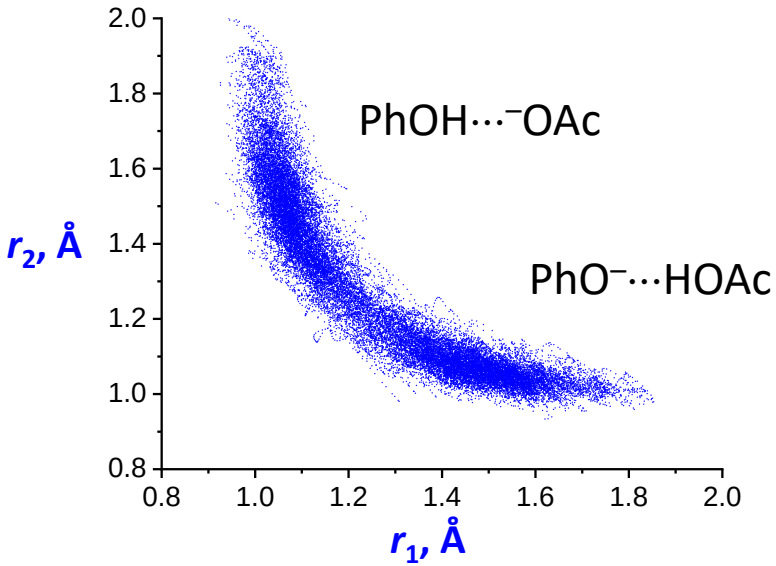
Solvent fluctuations

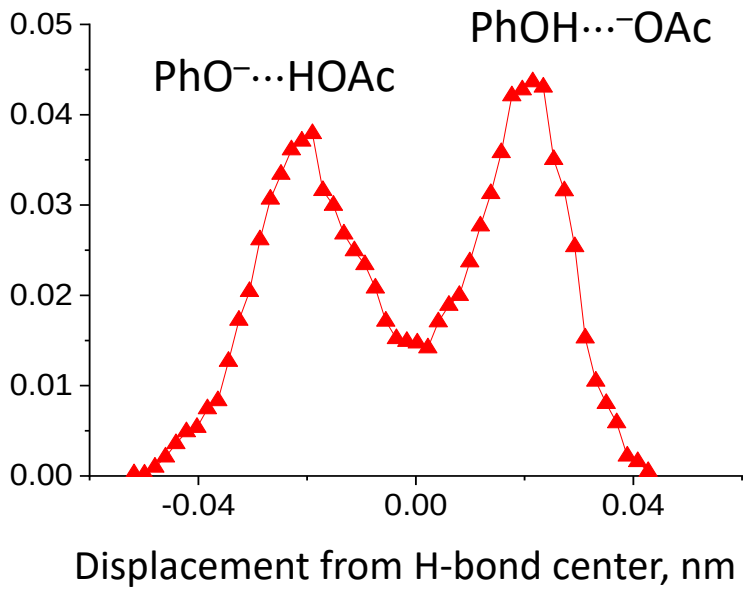
Molecular dynamics simulations

PCCP **2015**, *17*, 4634





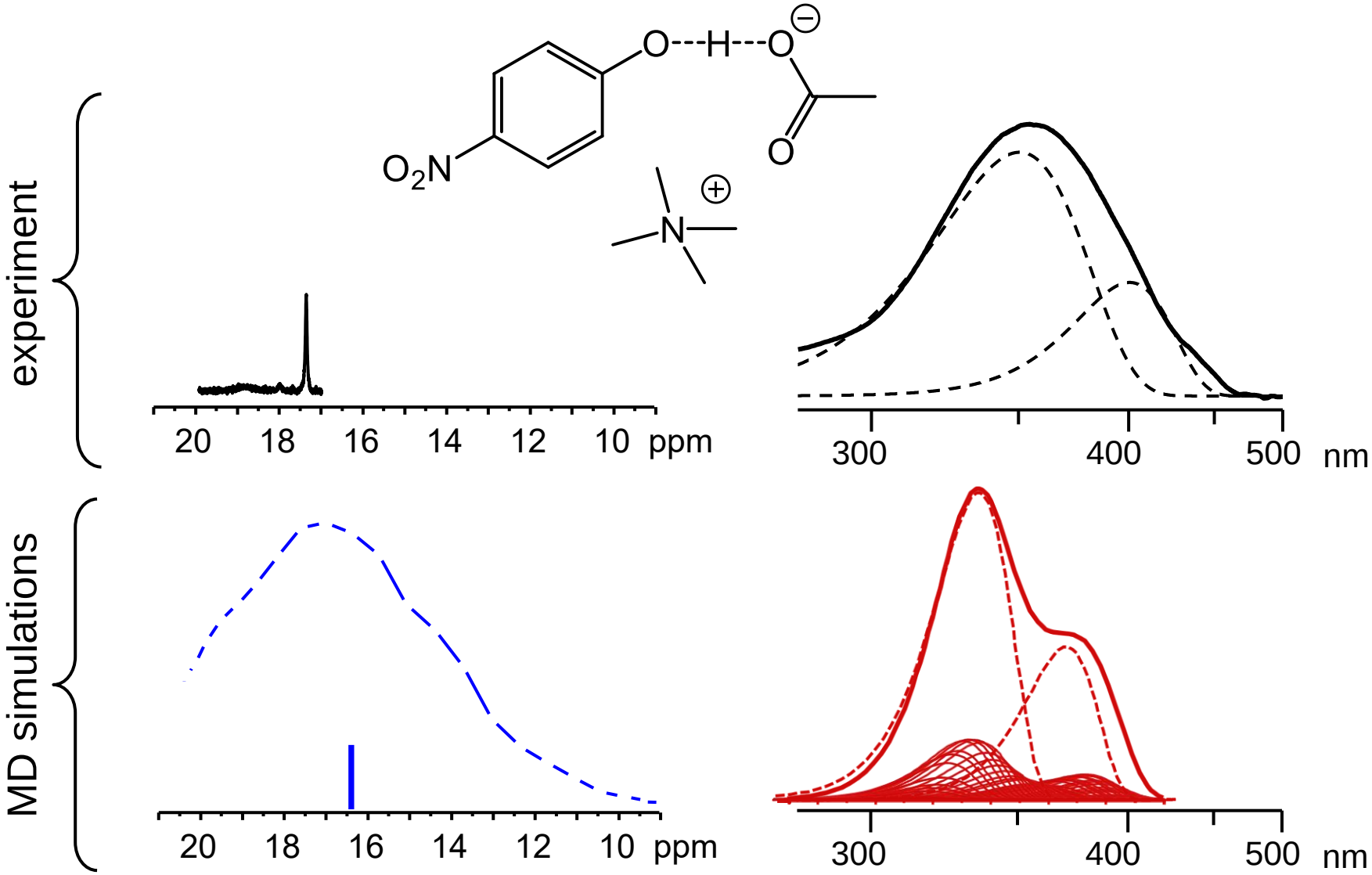




Solvent fluctuations

Molecular dynamics simulations

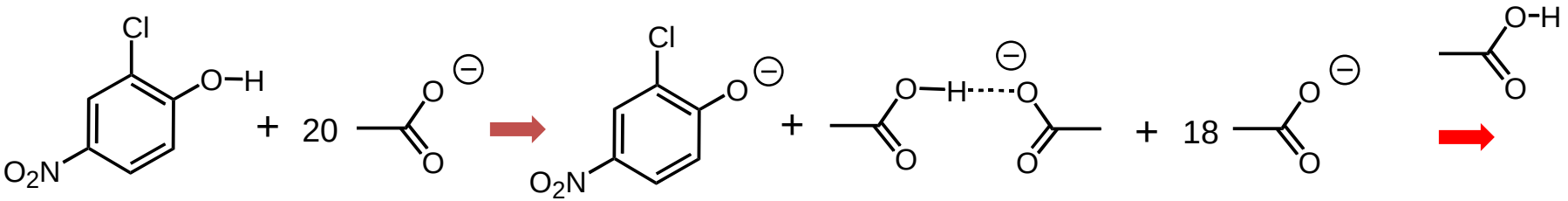
PCCP **2015**, *17*, 4634

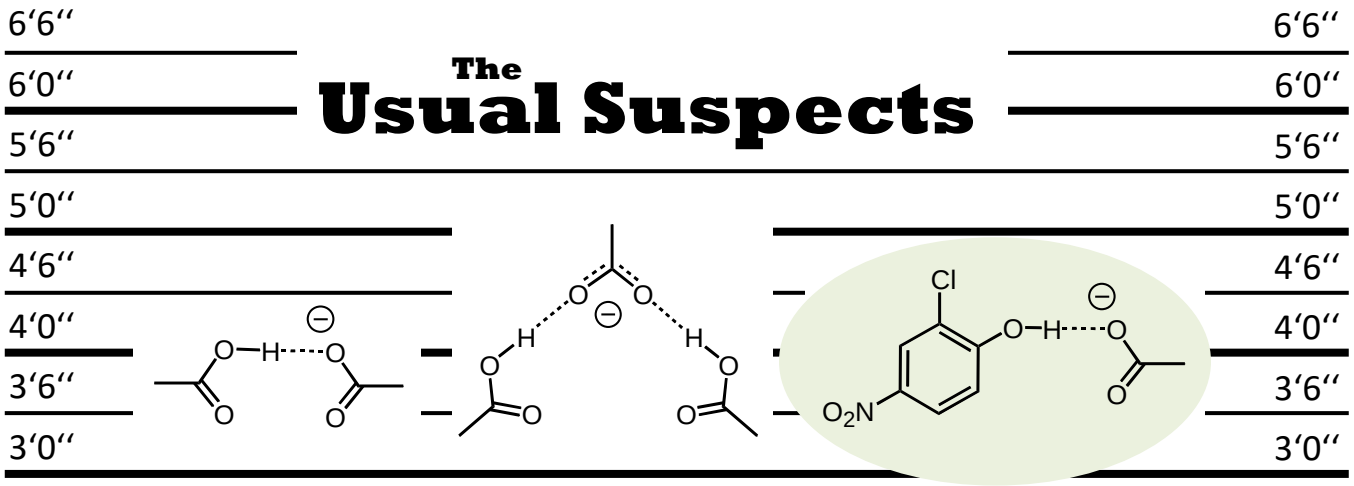


2D NMR – UV-vis spectroscopy

Example of the problem

JPCL **2011**, 2, 1106





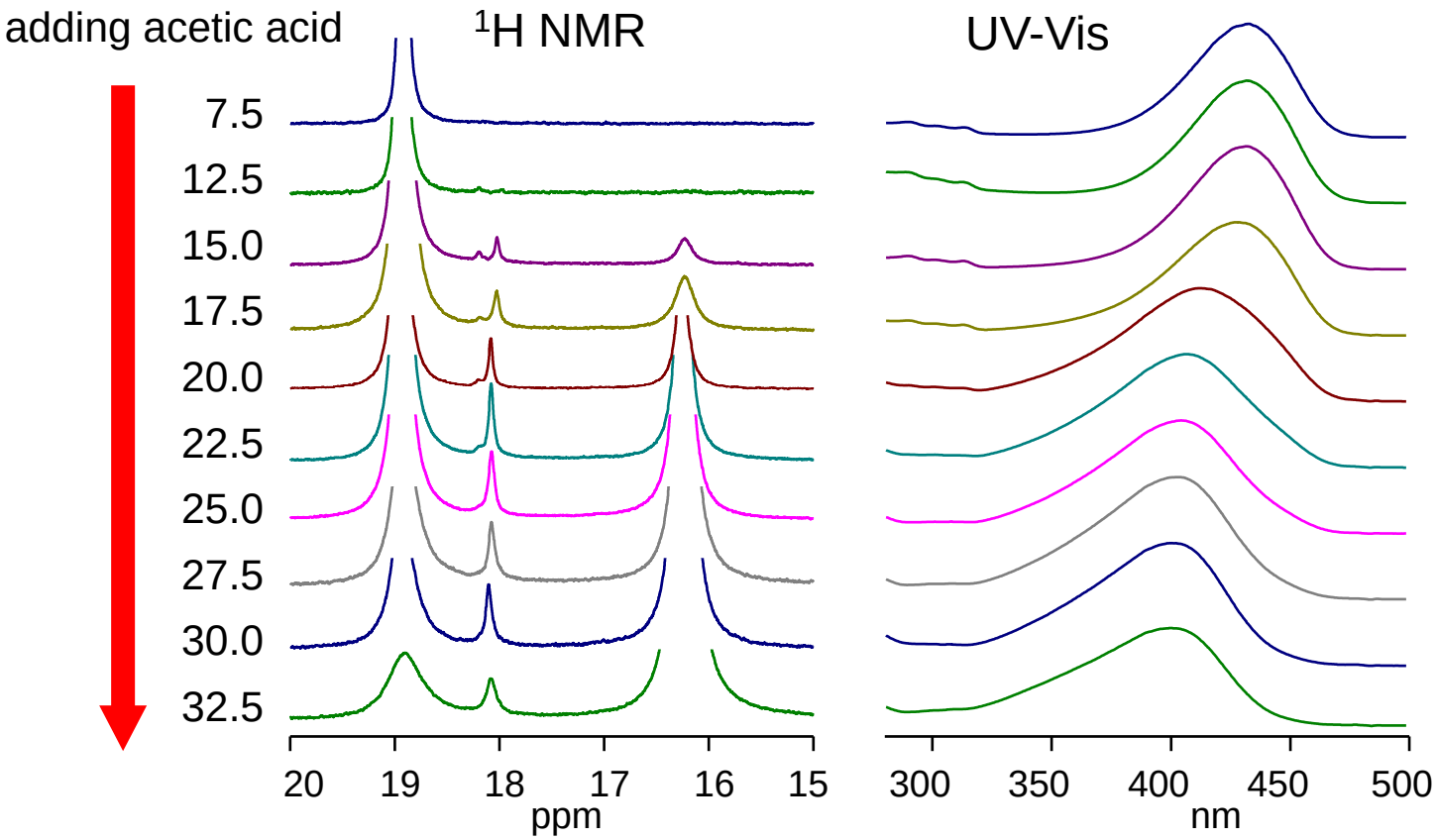
acid homo-conjugates

hetero-conjugate

2D NMR – UV-vis spectroscopy

Example of the problem

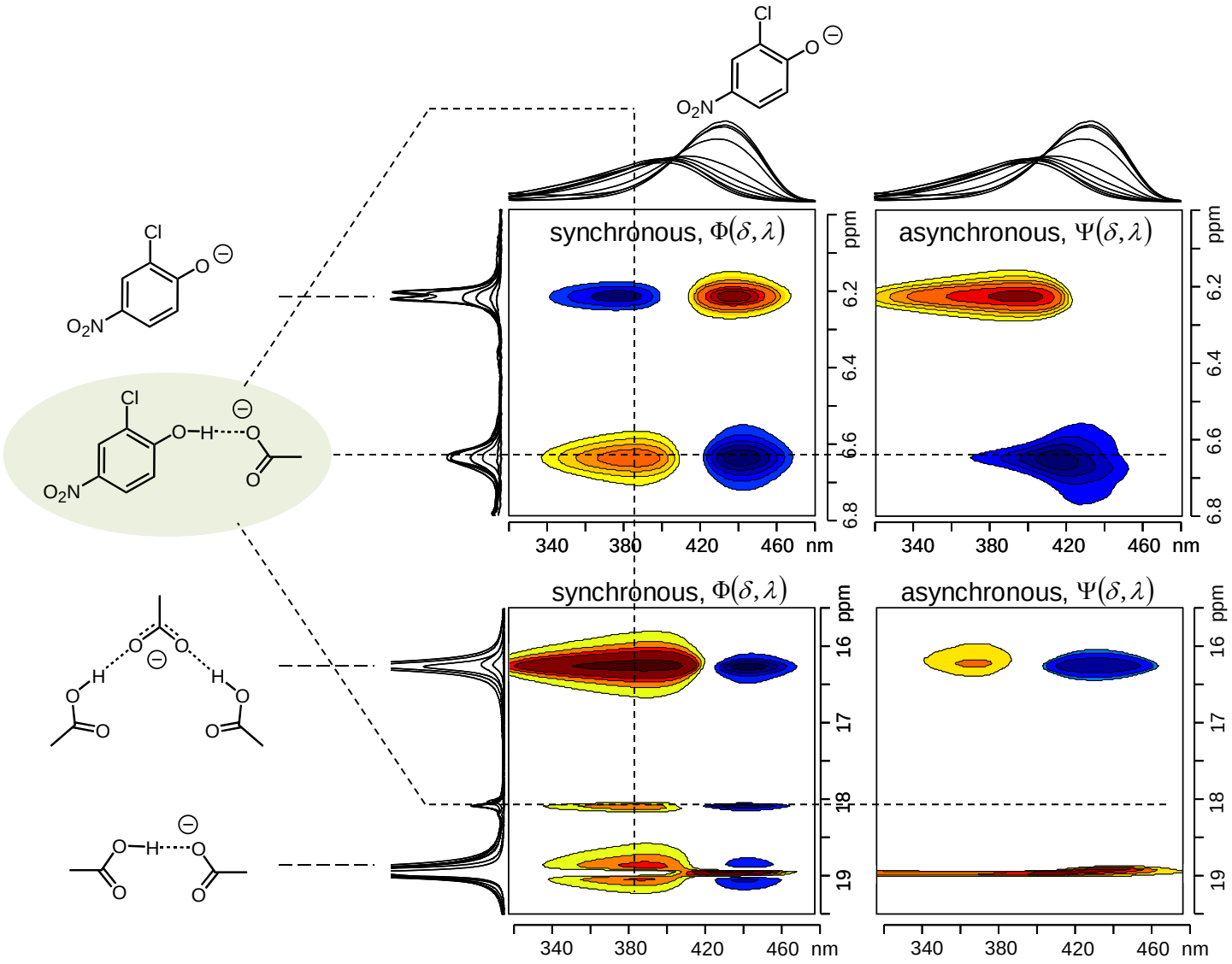
JPCL **2011**, 2, 1106



2D NMR – UV-vis spectroscopy

Example of the problem

JPCL **2011**, 2, 1106

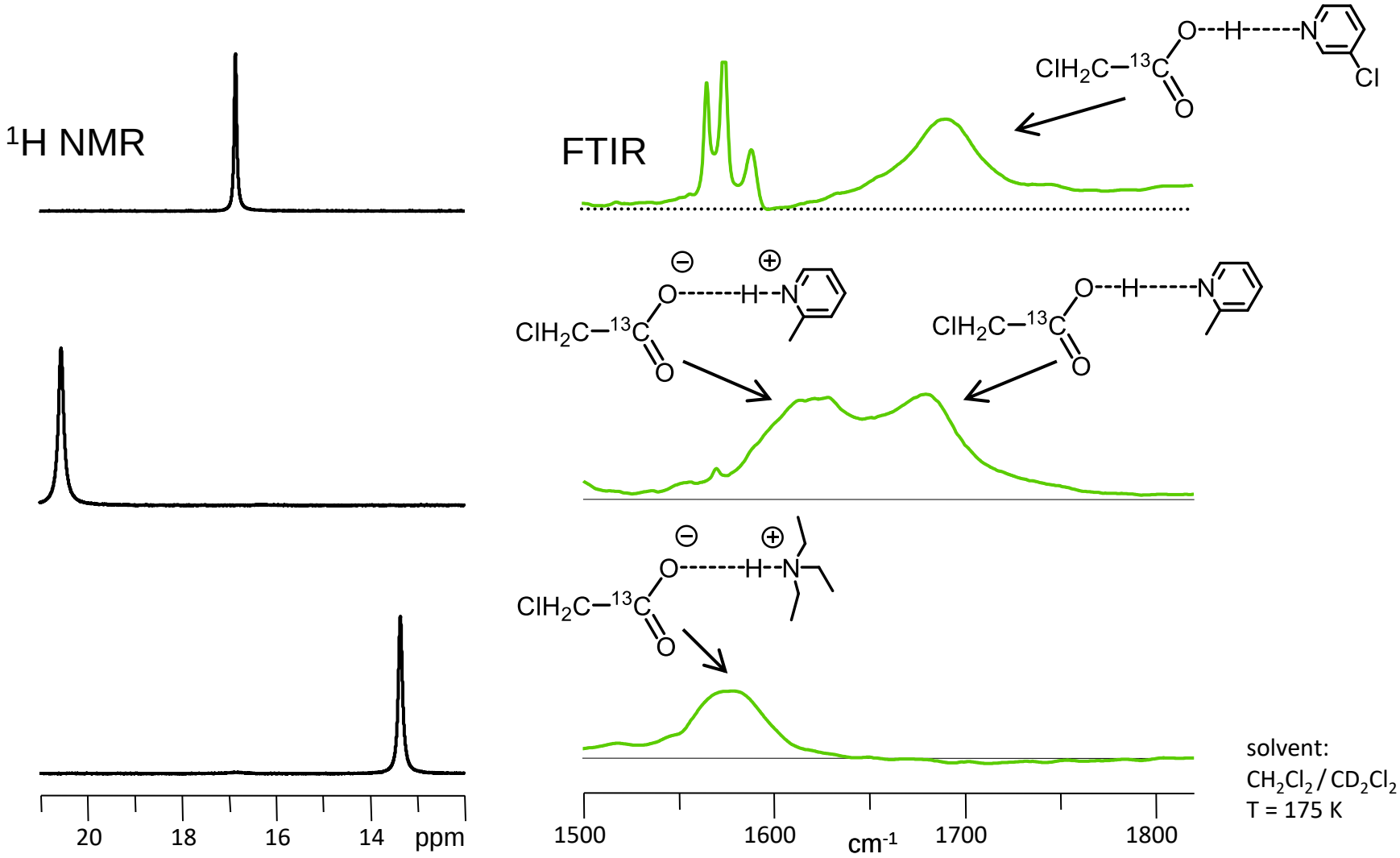


CD_2Cl_2
170 K

NMR – IR combination

Proton tautomerism in OHN hydrogen bonds

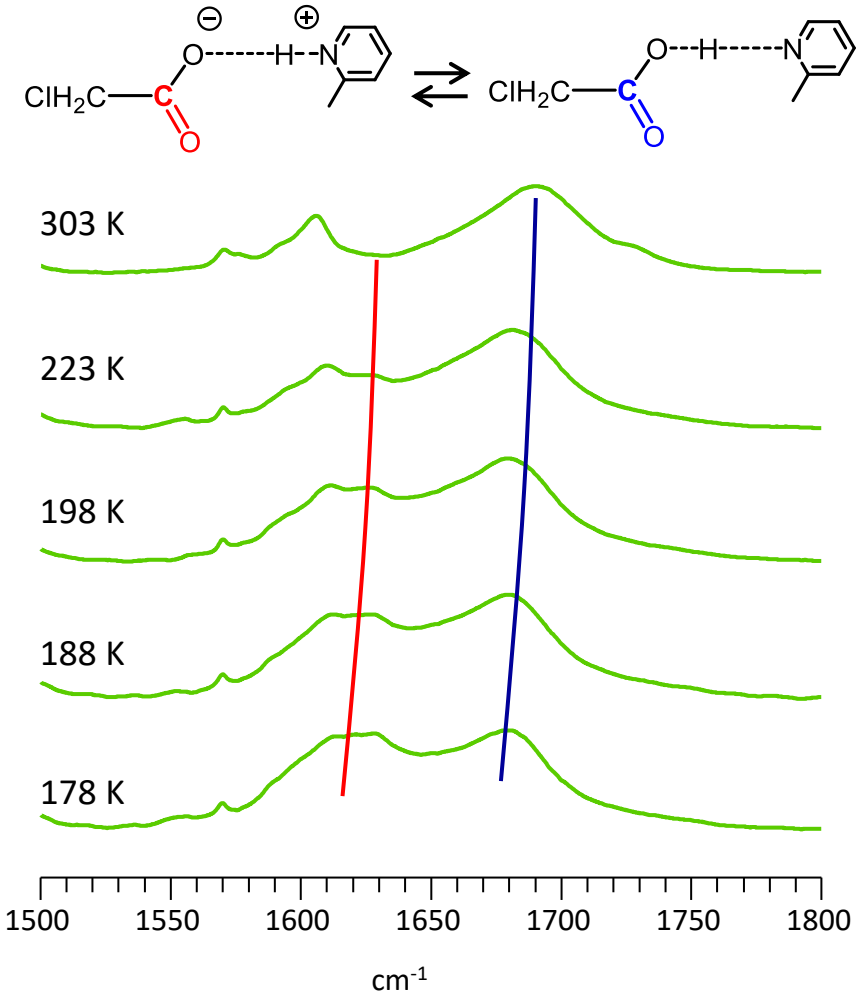
PCCP **2017**, *19*, 1010



NMR – IR combination

Proton tautomerism in OHN hydrogen bonds

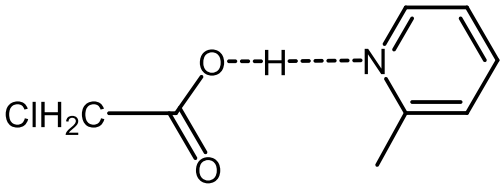
PCCP **2017**, *19*, 1010

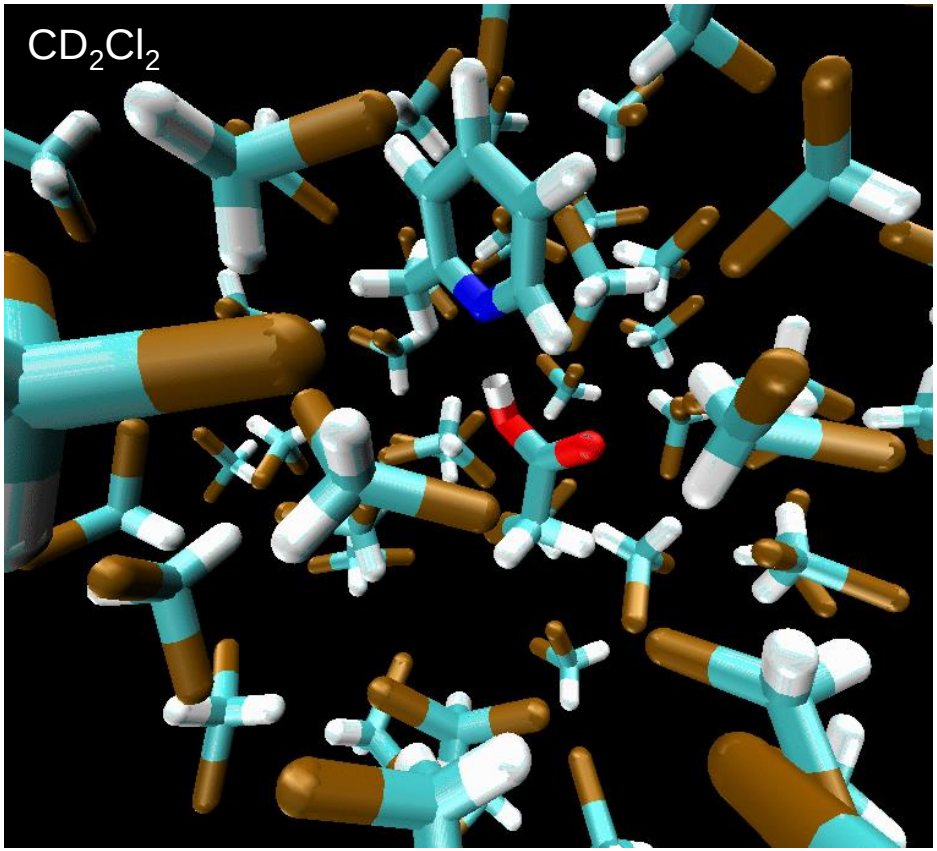


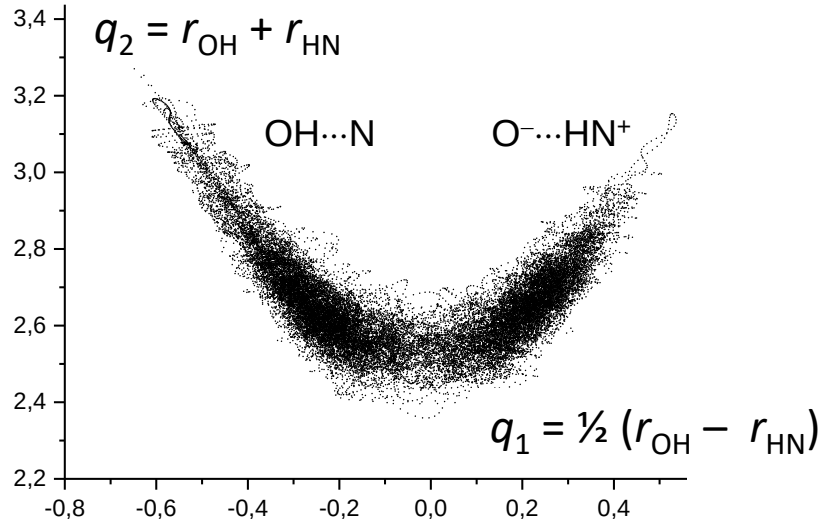
NMR – IR combination

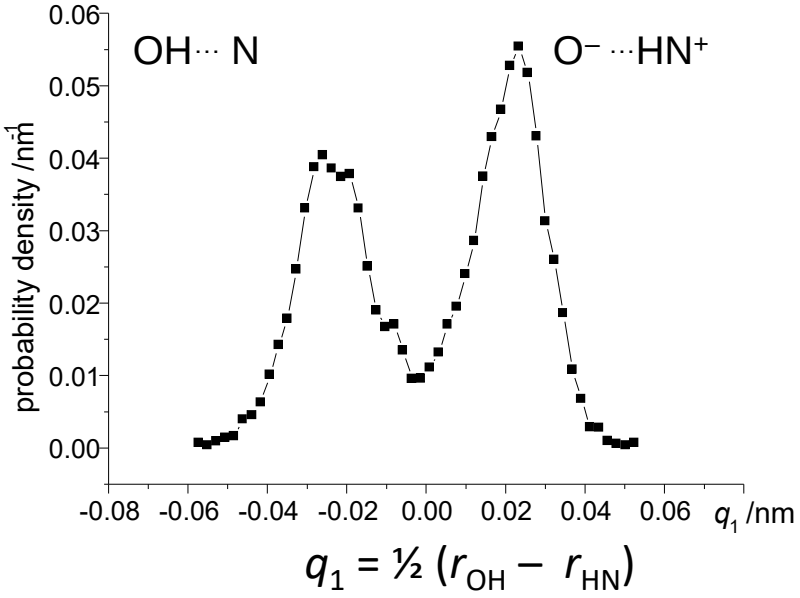
Proton tautomerism in OHN hydrogen bonds

PCCP **2017**, *19*, 1010





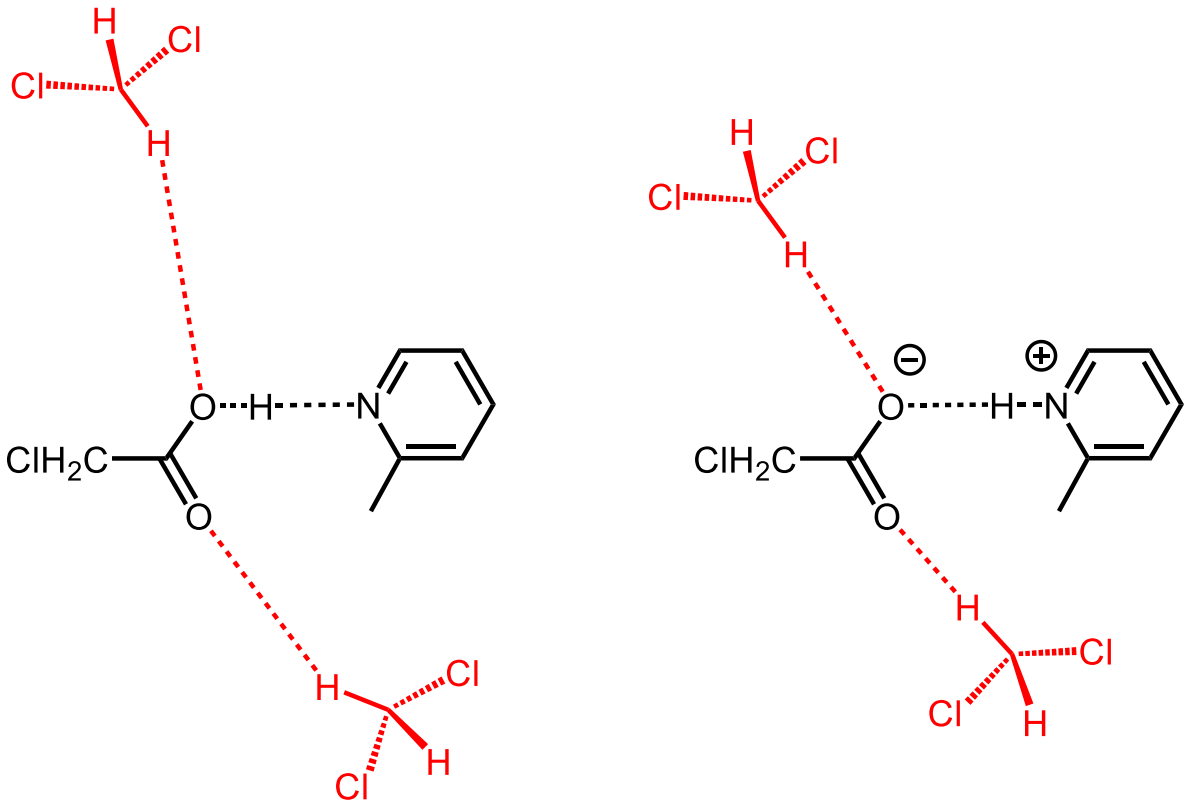




NMR – IR combination

Proton tautomerism in OHN hydrogen bonds

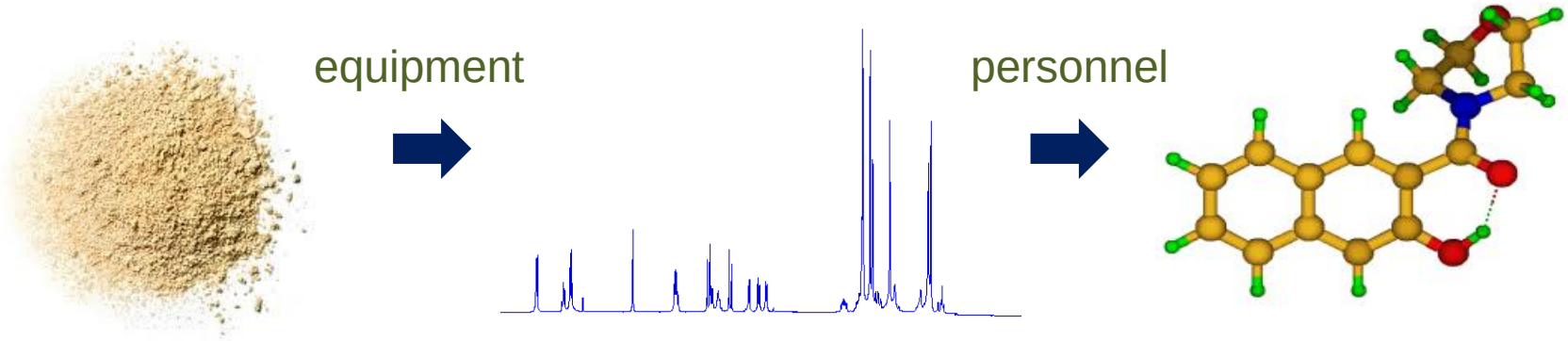
PCCP **2017**, *19*, 1010



Formation/breaking of CH···O=C hydrogen bonds
correlates well with proton transfer in OHN bond

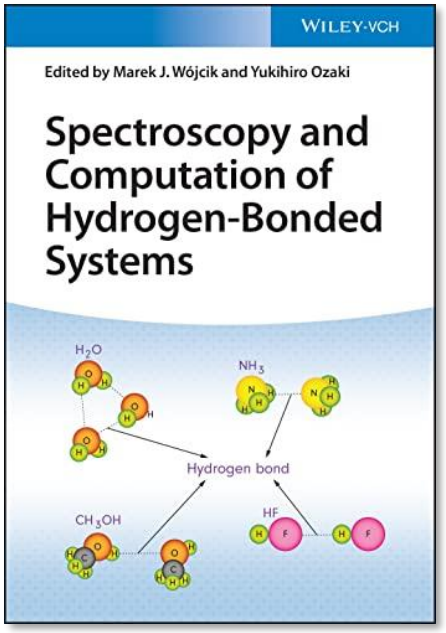
Summary and outlook

Combining the advantages of optical and NMR spectroscopy



- **Essentially 1D problem of H-bond geometry allows one to construct correlations with spectral parameters**
- **Correlations are possible in NMR and optical spectroscopy alike**
- **Main differences are due to different characteristic times of methods**
- **Obtained data are often complementary to each other, which facilitates spectral assignments and interpretation**

IR and NMR Spectral Diagnostics
of Hydrogen Bond Energy and Geometry



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E.Yu. Tupikina

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