



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

Peter M. Tolstoy

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Edem R. Chakalov

Иркутск, июль 2023

Non-covalent interactions laboratory

Staff and students



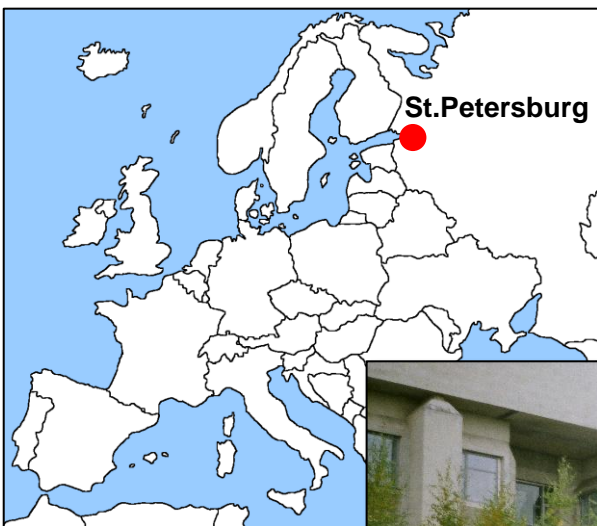
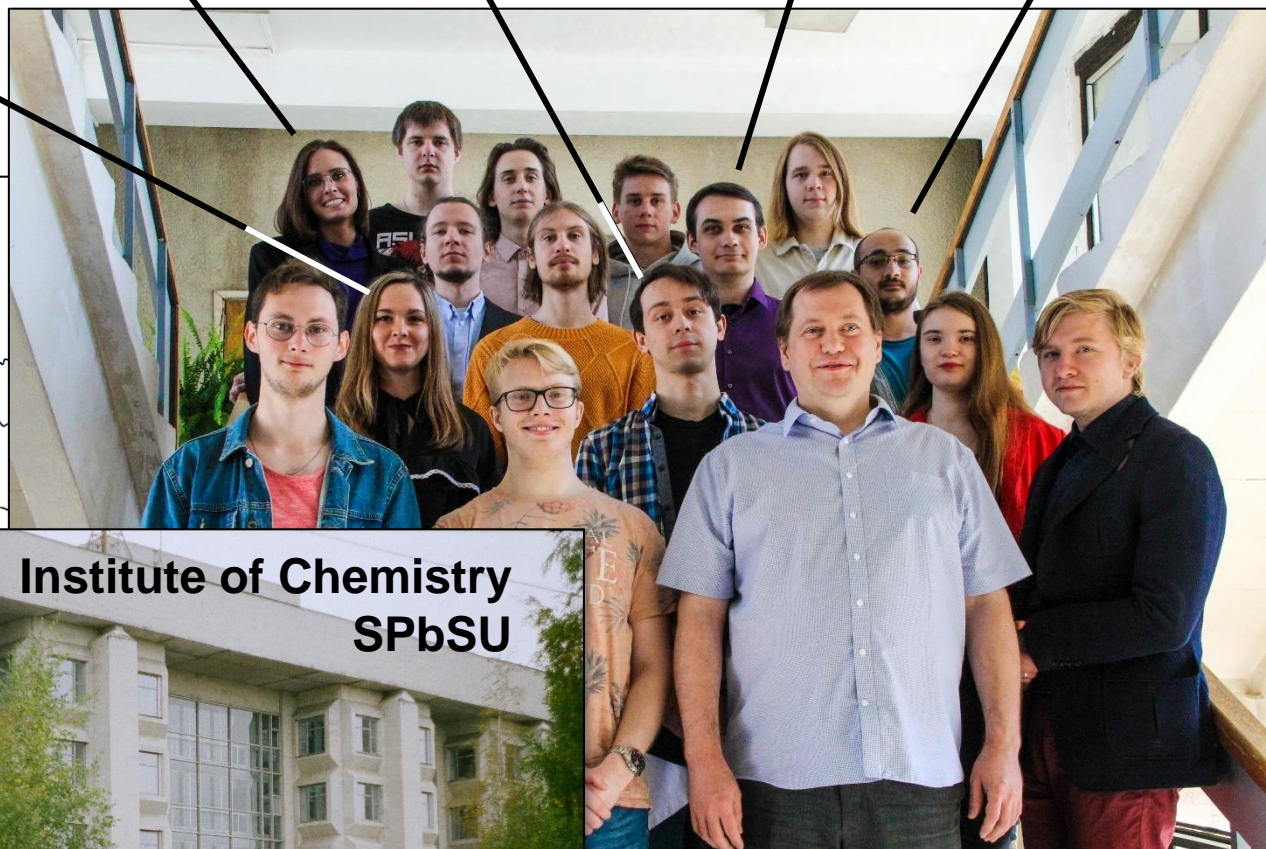
Dr. Mulloyarova

Dr. Tupikina

Chakalov

Kostin

Alkhuder



**Institute of Chemistry
SPbSU**

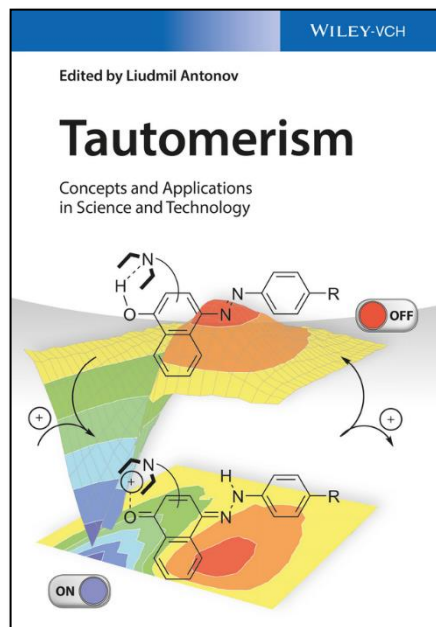
Book chapters

On which this presentation is based



3

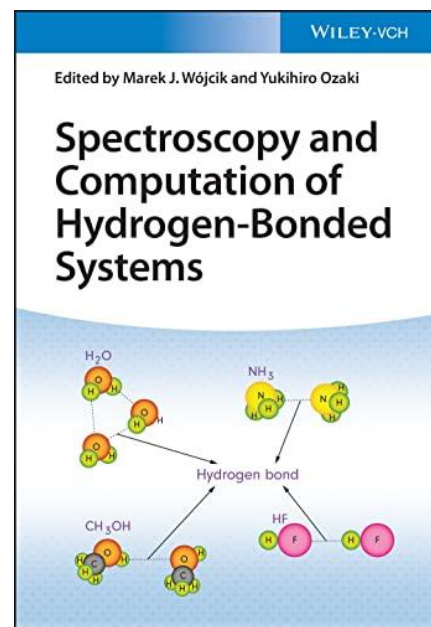
2016



*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

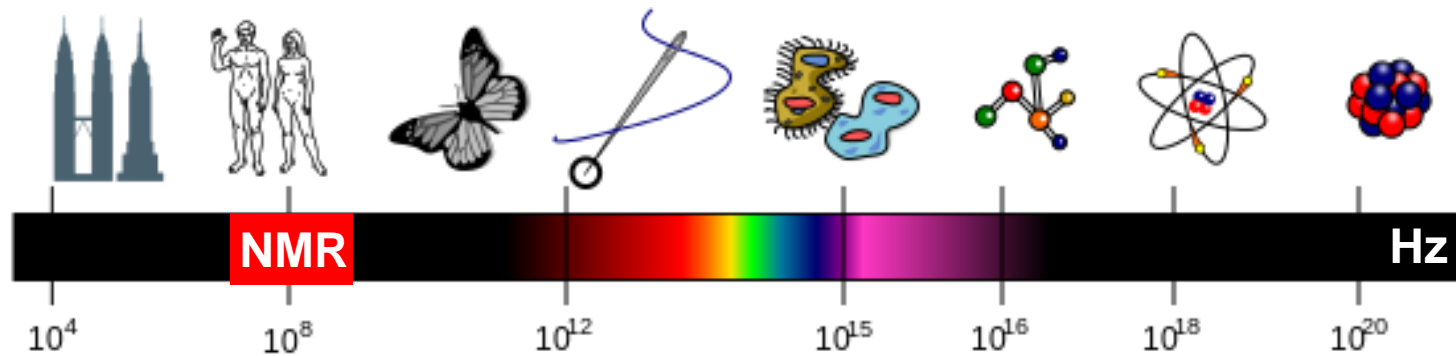


*P.M. Tolstoy
E.Yu. Tupikina*

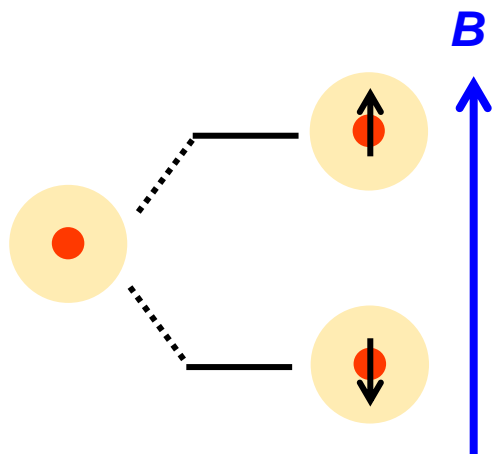
**Chapter 12: IR and NMR
Spectral Diagnostics
of Hydrogen Bond
Energy and Geometry**

NMR – main principles

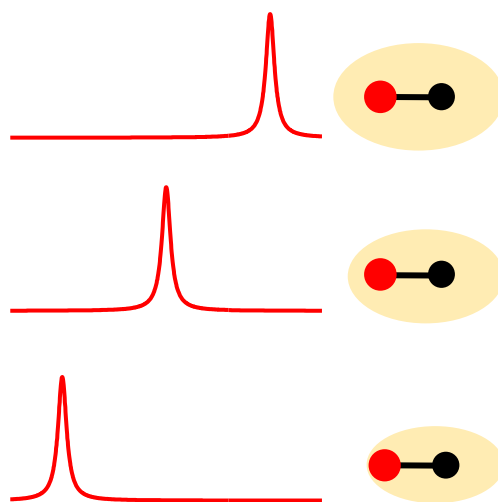
A reminder



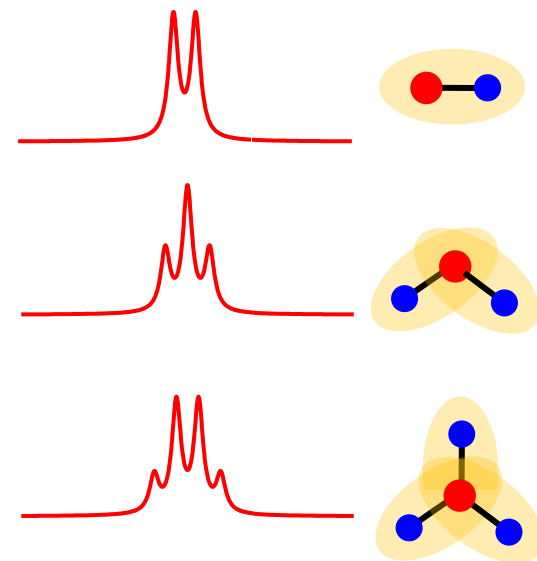
In magnetic field



Chemical shift



Spin-spin coupling



Non-covalent interaction

Different names for different elements



van der Waals forces

Hydrogen bond

Lithium bond

Berillium bond

dipole-dipole/charge-dipole etc...

π - π stacking

metallophilic interaction

σ -hole interactions

Aerogen bond

Halogen bond

Chalcogen bond

Pnictogen bond

Tetrel bond

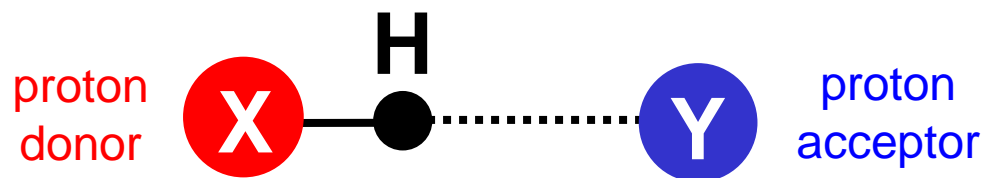
Icosagen bond

										<p>Hydrogen bond</p> <p>Lithium bond</p> <p>Berillium bond</p> <p>dipole-dipole/charge-dipole etc...</p> <p>π-π stacking</p> <p>metallophilic interaction</p>											
										<p>σ-hole interactions</p> <p>Aerogen bond</p> <p>Halogen bond</p> <p>Chalcogen bond</p> <p>Pnictogen bond</p> <p>Tetrel bond</p> <p>Icosagen bond</p>											
1 H	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne			
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar				
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr				
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe				
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn				
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og				
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				

Hydrogen bond

Modern definition

Definition of the hydrogen bond (IUPAC Recommendations 2011)*

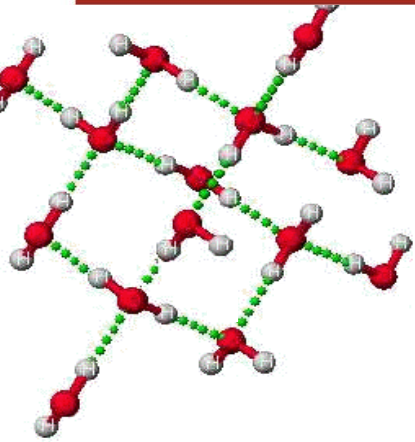


The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.

- | | |
|--------------------|--|
| 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, <i>J</i> -couplings across the X–H···Y bond |
| detectable | 6. The Gibbs energy should be greater than the thermal energy |

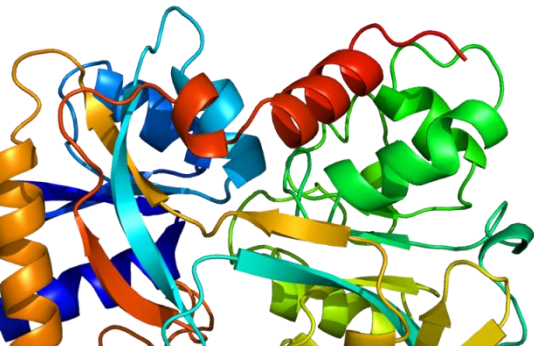
Hydrogen bond

A fairly well-working definition



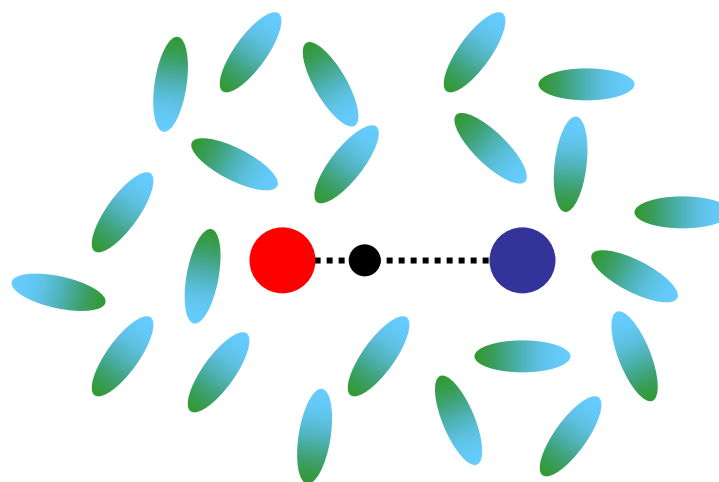
Hydrogen bond is like your spouse: immediately recognizable by the back of the hair in a crowd of a thousand people but you don't know how you did it.

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



Number of “protonation states”

In polar aprotic medium



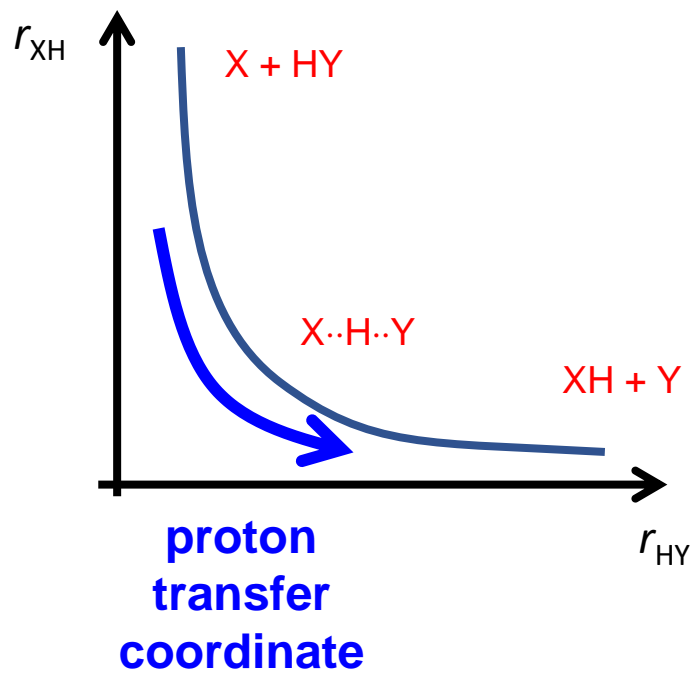
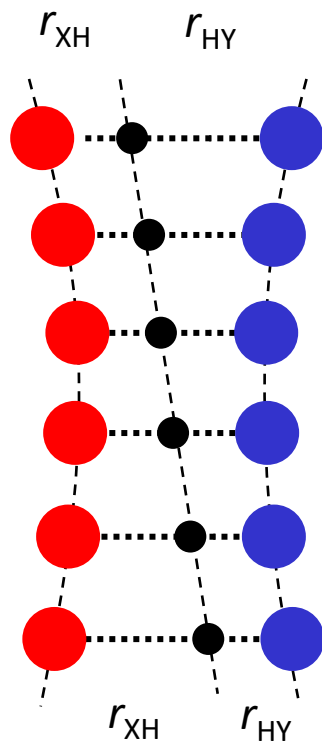
infinite number of protonation states

Gradual proton displacement

Interdependence of interatomic distances

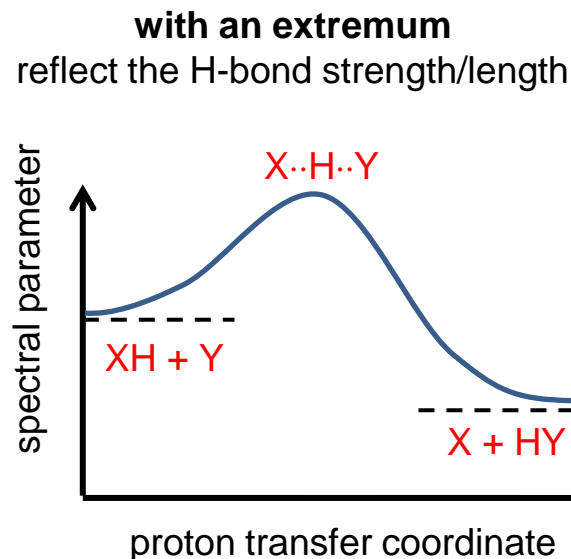
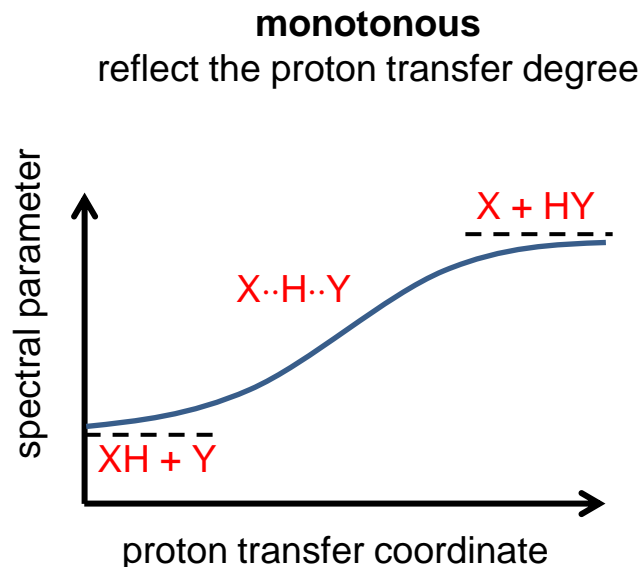


9

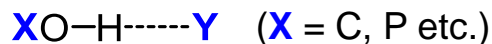


Hydrogen bond

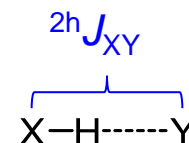
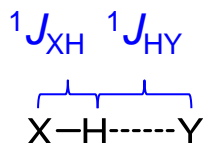
Spectral parameters change upon proton transfer



chemical shifts



coupling constants



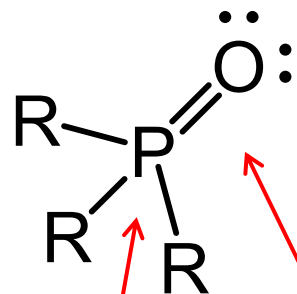
vibrational frequencies

$\nu(\text{CO}), (\text{PO})$ etc.

$\nu(\text{XH}) / \nu(\text{HY})$
 $\nu(\text{XY})$

Phosphine oxide as electron donor

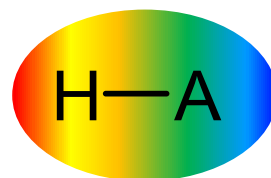
Lewis and Brønsted acids – distribution of electrostatic potential



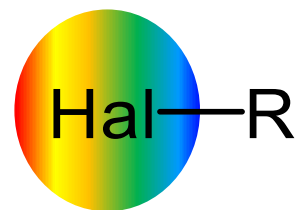
^{31}P NMR
chemical shift
 δP

PO
stretching
 ν_{PO}

Brønsted acid – proton donor (hydrogen bonds)



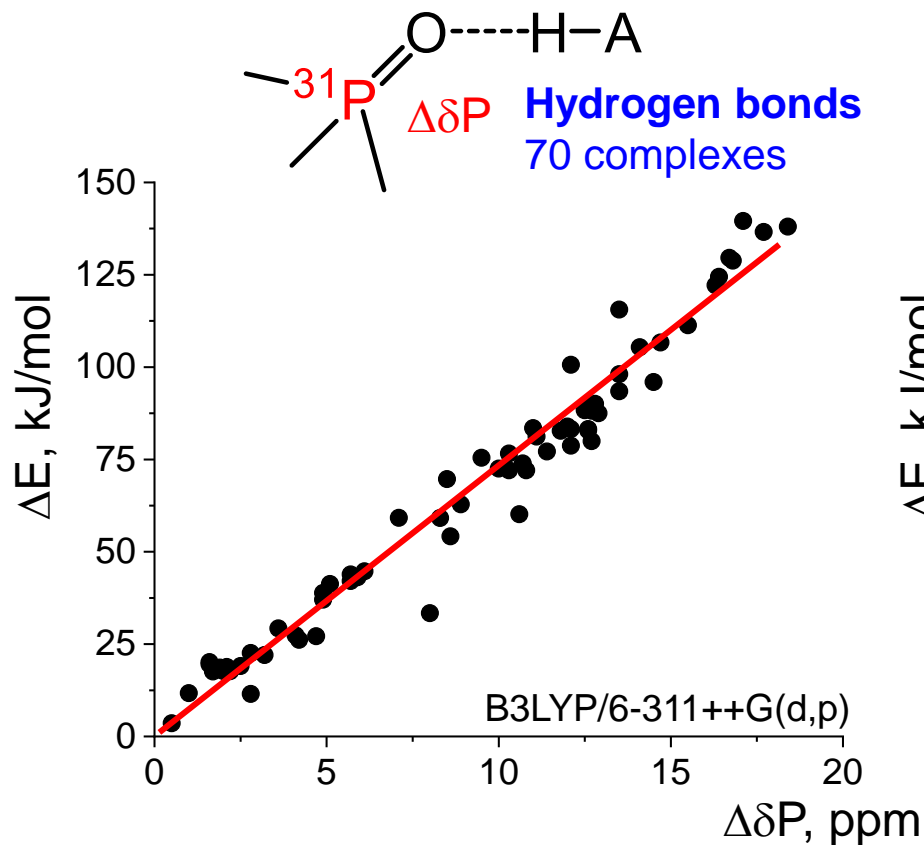
Lewis acid – electron acceptor (e.g. halogen bonds)



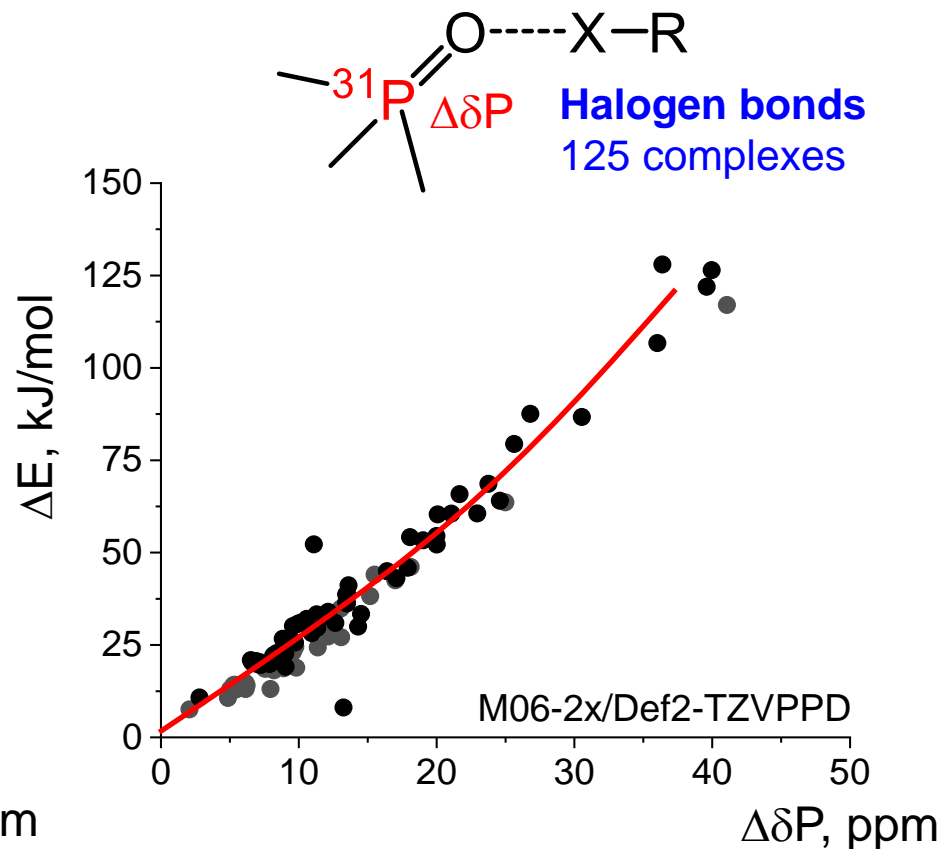
Testing Gutmann-Beckett method

Correlations with energy

^{31}P NMR chemical shift



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

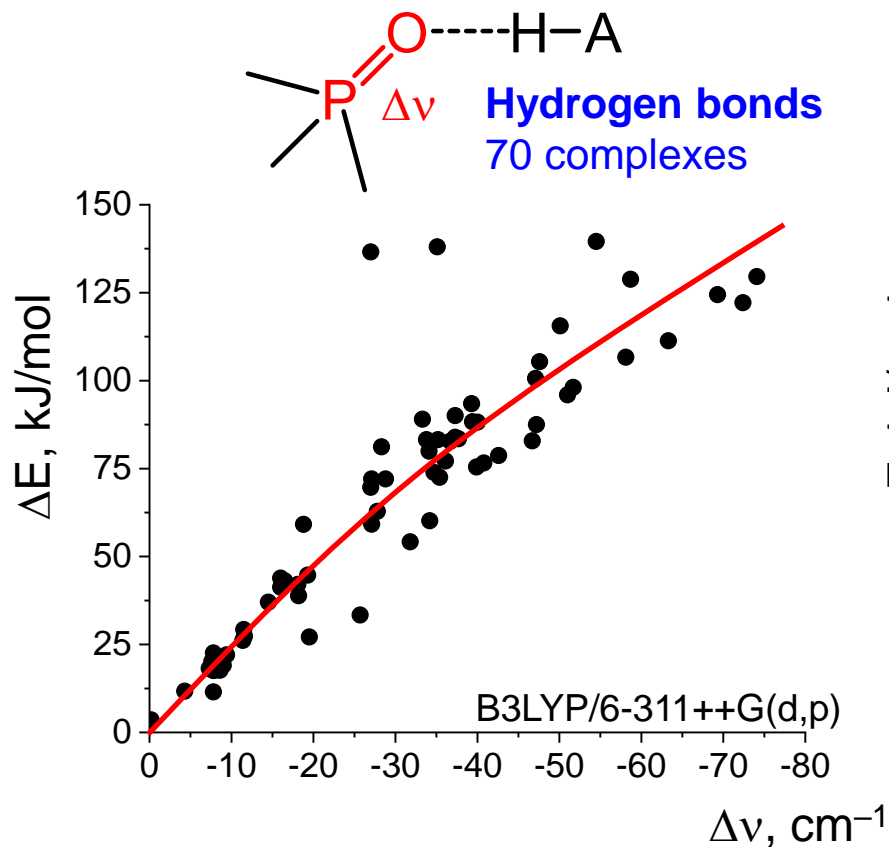


Ostras' et al.,
Molecules **2020**, 25, 1406

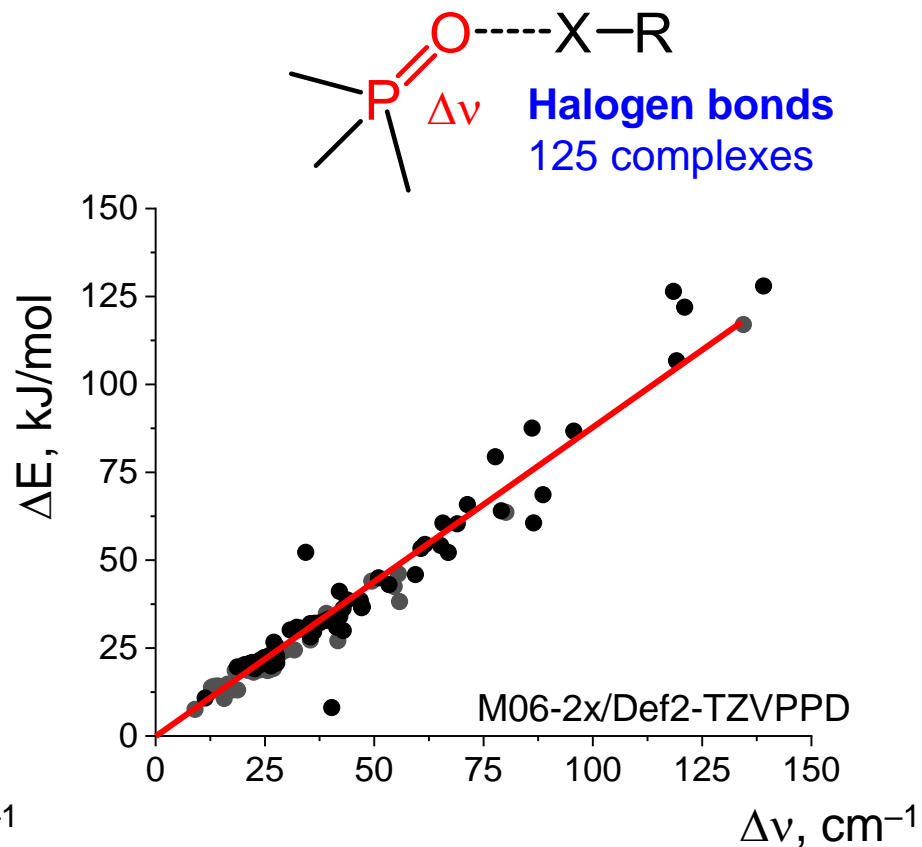
Testing Gutmann-Beckett method

Correlations with energy

P=O stretching frequency



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

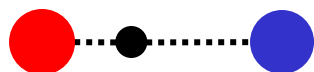


Ostras' et al.,
Molecules **2020**, 25, 1406

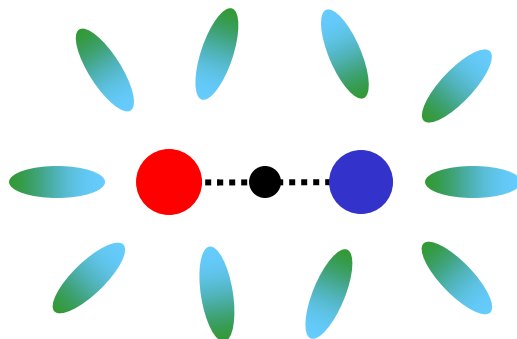
Averaging in NMR and optical spectra

Distribution of hydrogen bond geometries

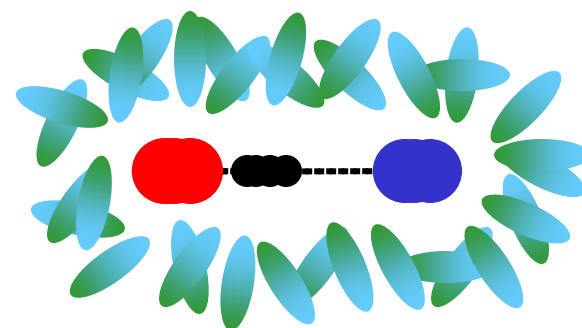
Gas phase



One solvent configuration

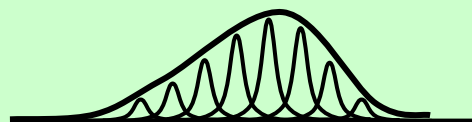


Many solvent configurations
(thermal fluctuations)

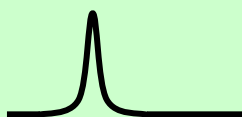


NMR spectra

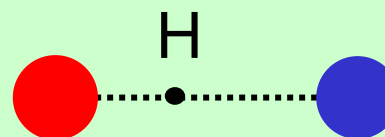
distribution of chem. shifts



averaged chem. shift



averaged geometry

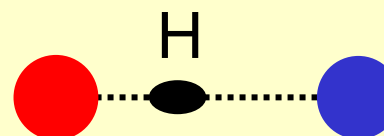


Optical spectra

distribution of absorption bands



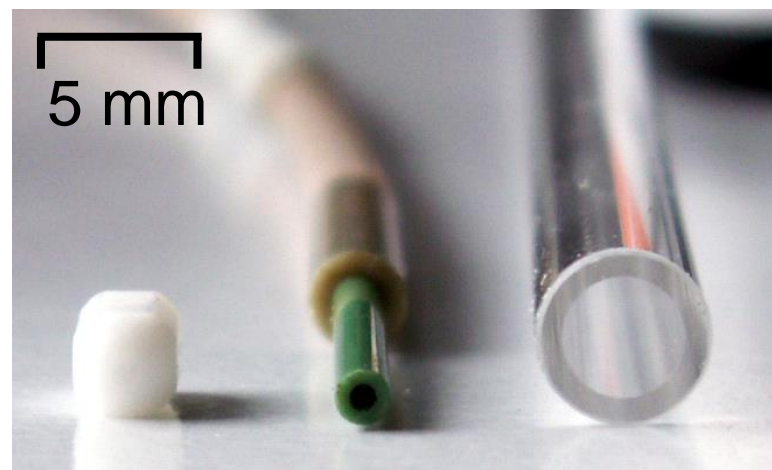
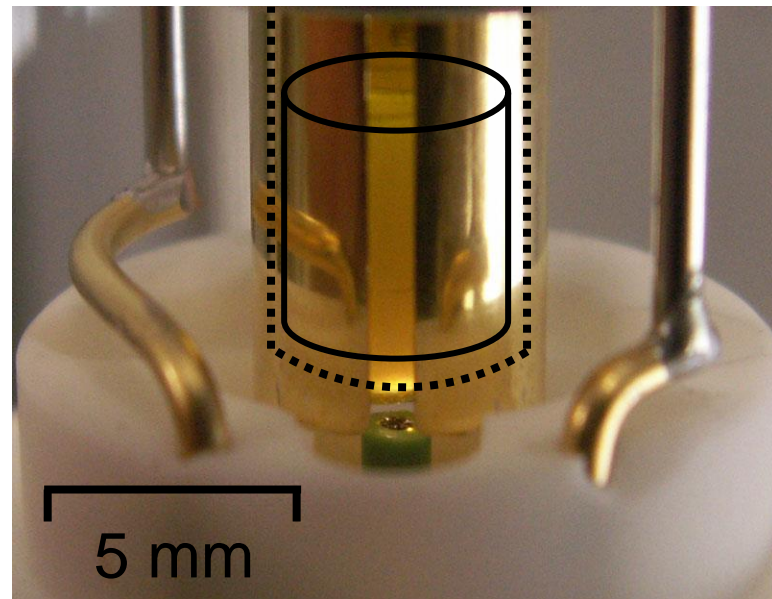
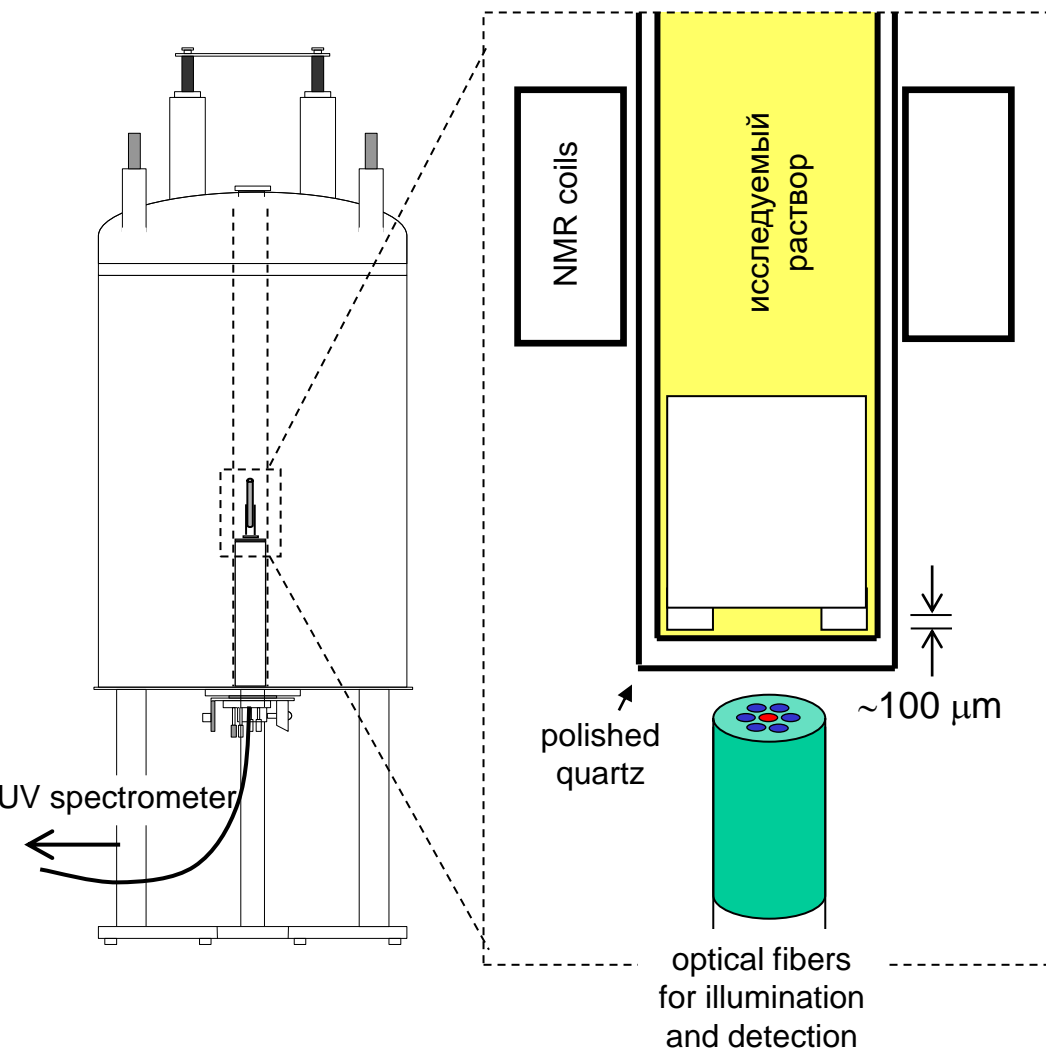
averaged geometry



+ information about the distribution of geometries

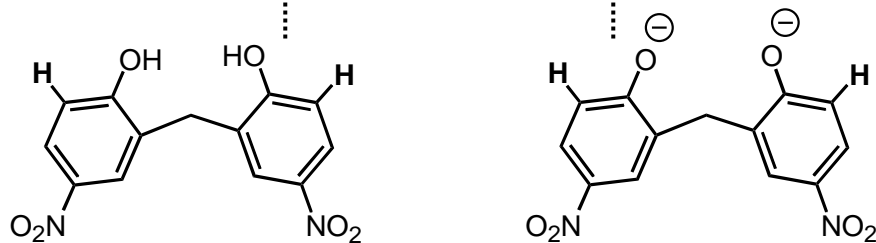
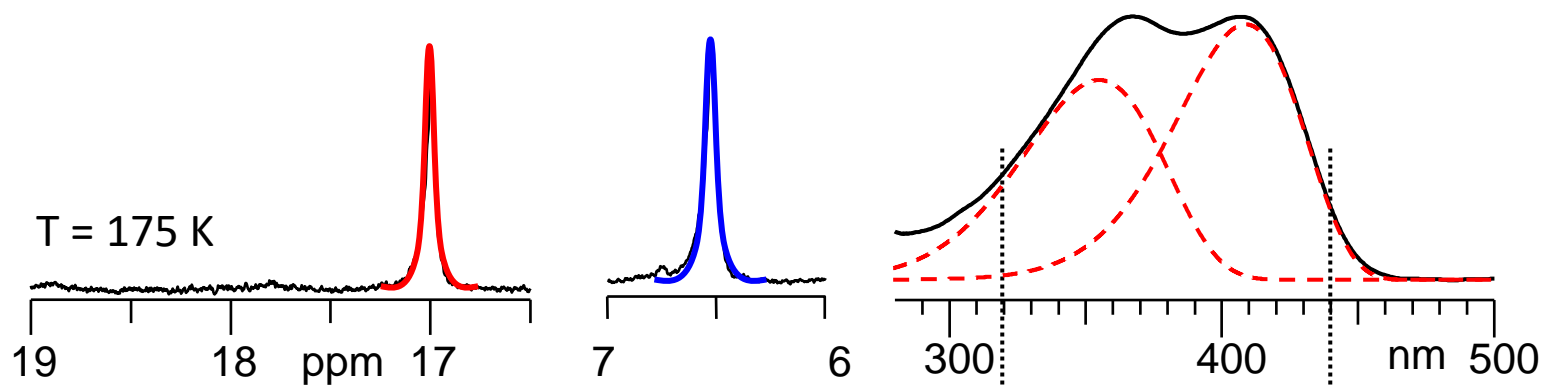
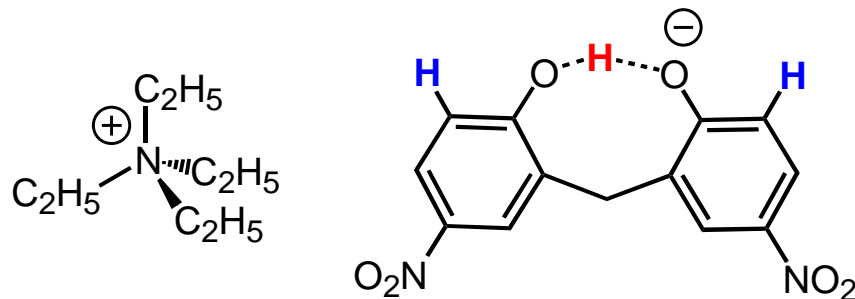
Setup for combined NMR/UV-vis measurements

UV-vis spectrometer inside NMR magnet



Proton jumps of central symmetry?

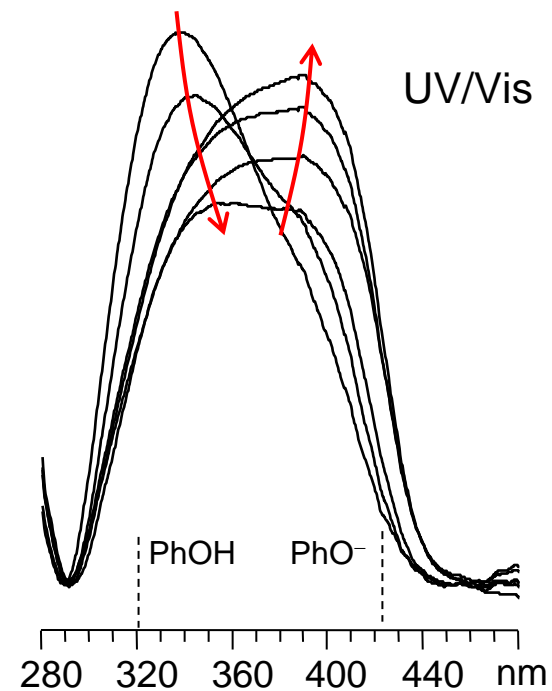
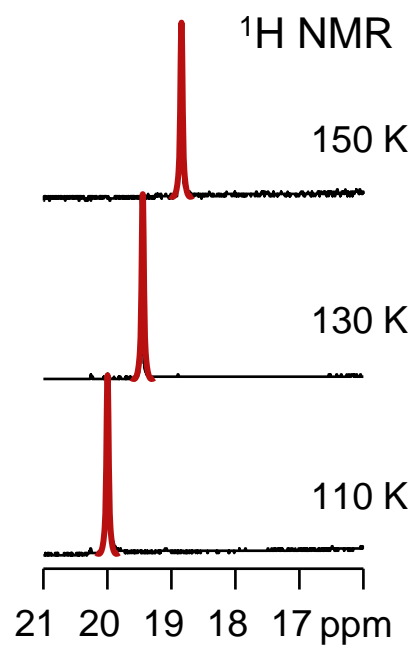
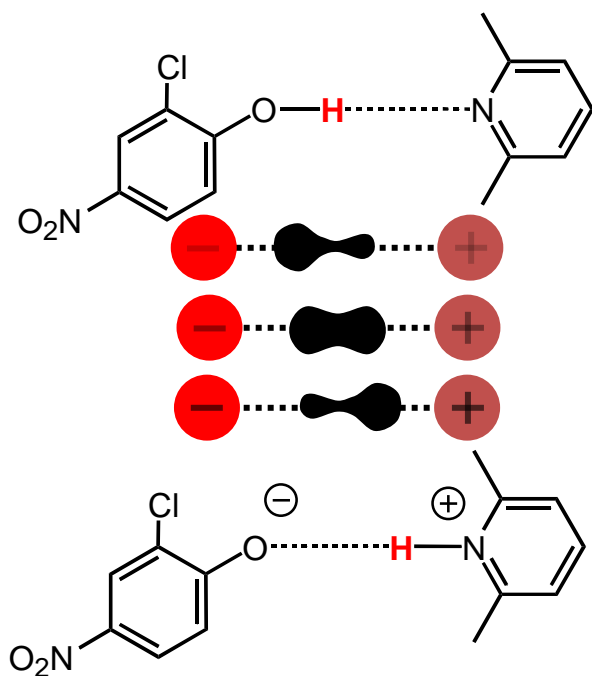
Advantages of combining NMR and optical spectroscopy



Proton displacement

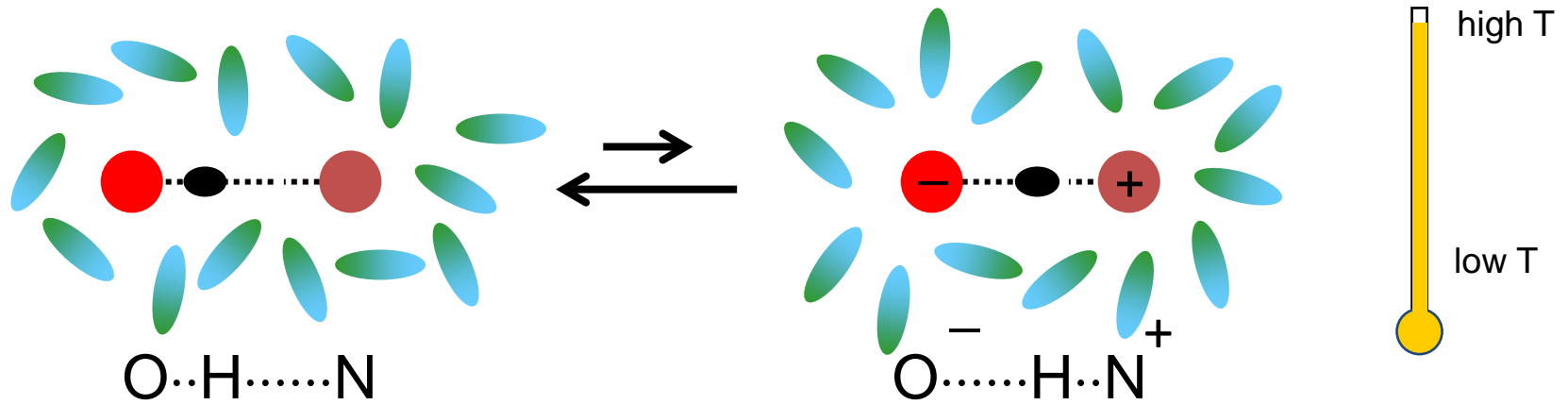
Advantages of combining NMR and optical spectroscopy

solvent: $\text{CDF}_3/\text{CDF}_2\text{Cl}$



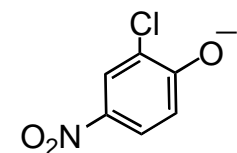
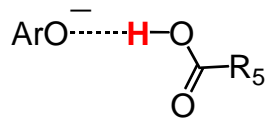
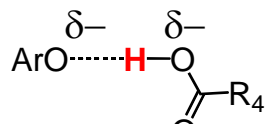
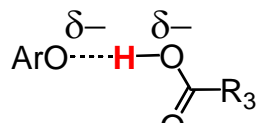
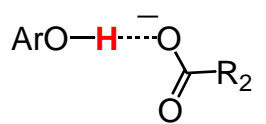
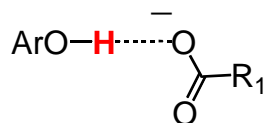
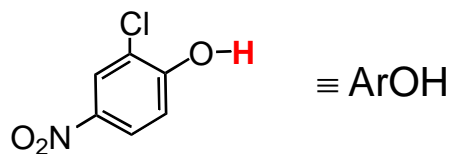
Proton displacement

Advantages of combining NMR and optical spectroscopy



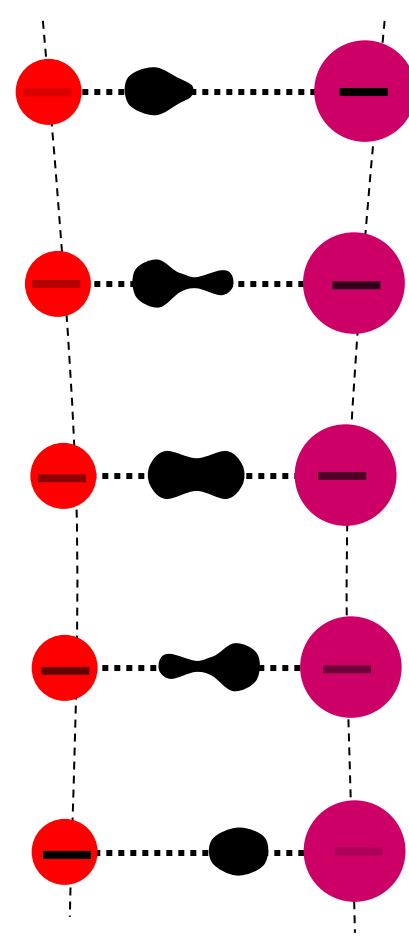
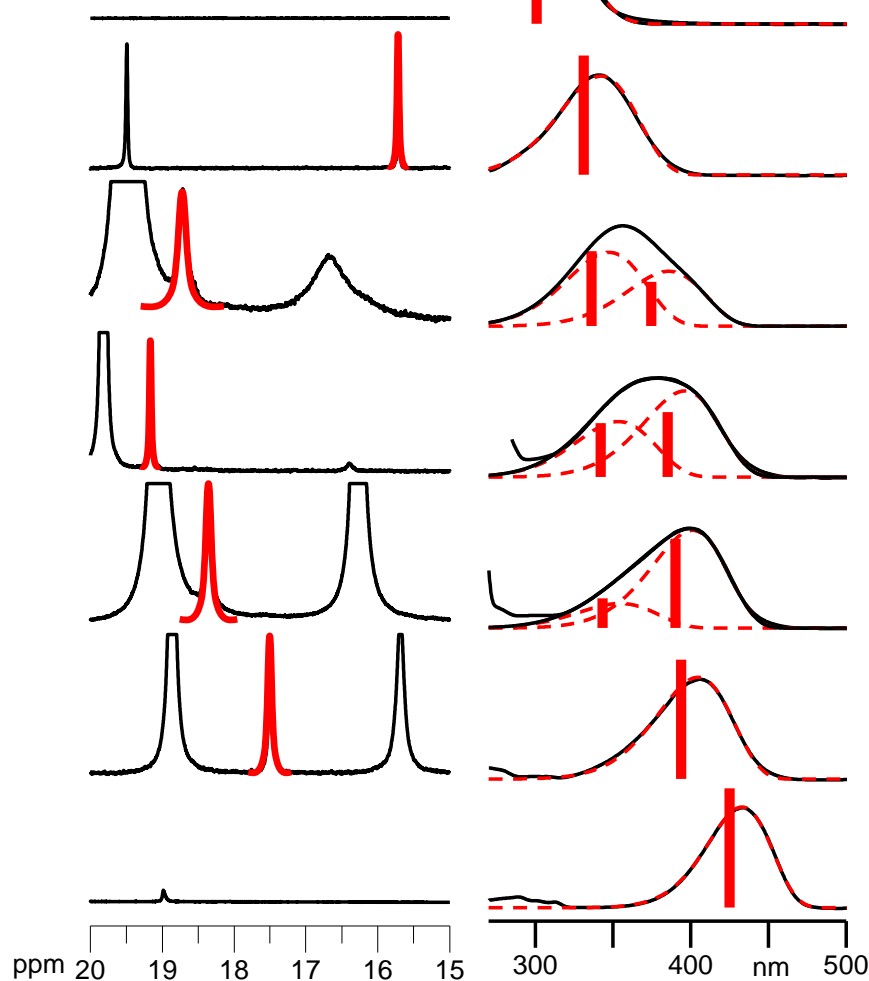
Proton displacement

Advantages of combining NMR and optical spectroscopy



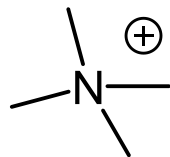
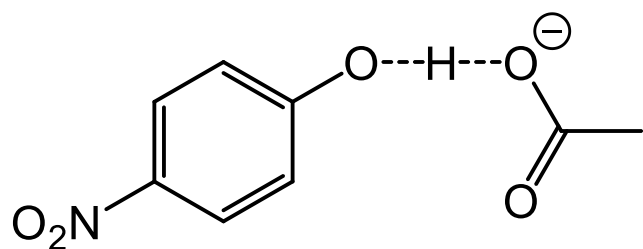
$^1\text{H NMR}$

UV-Vis



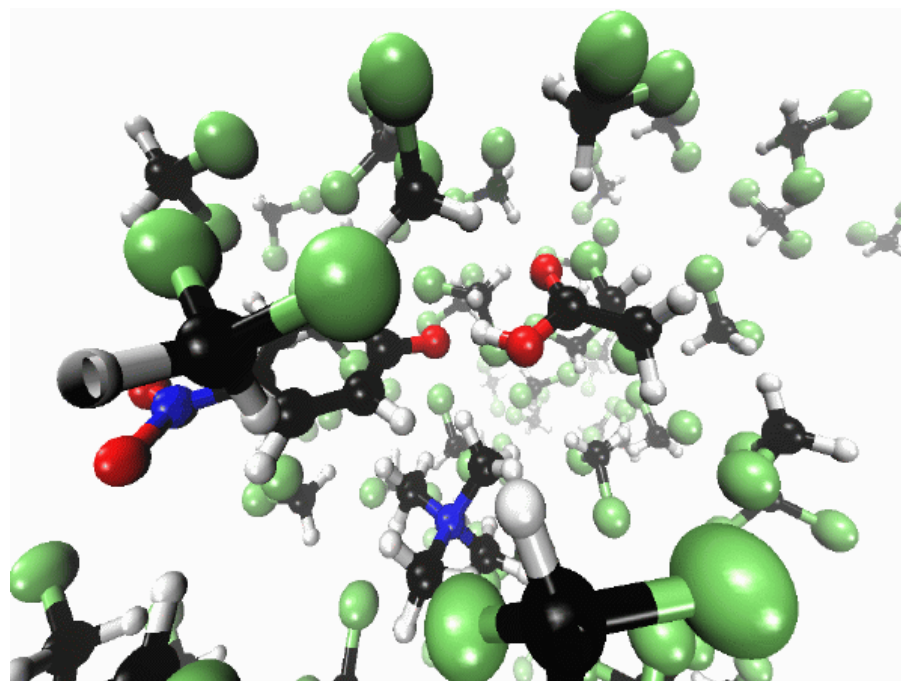
Solvent fluctuations

Molecular dynamics simulations



in CD₂Cl₂

ab initio MD simulation
(DFT MD using CP2K package)



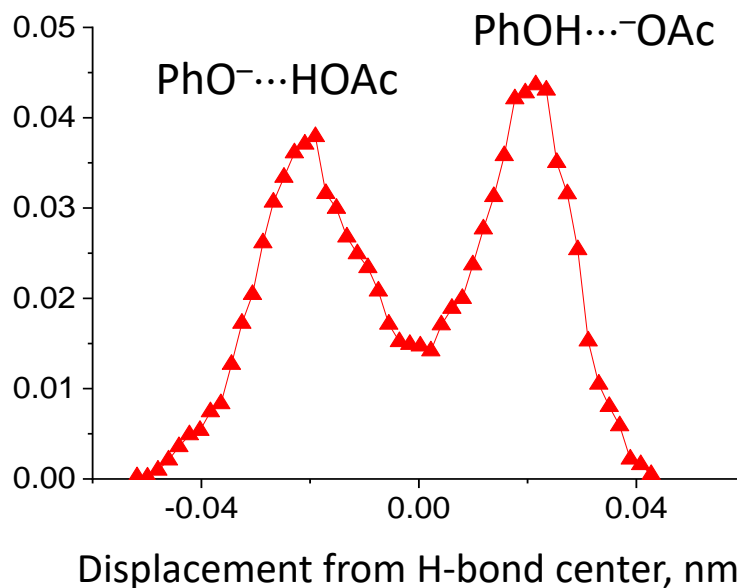
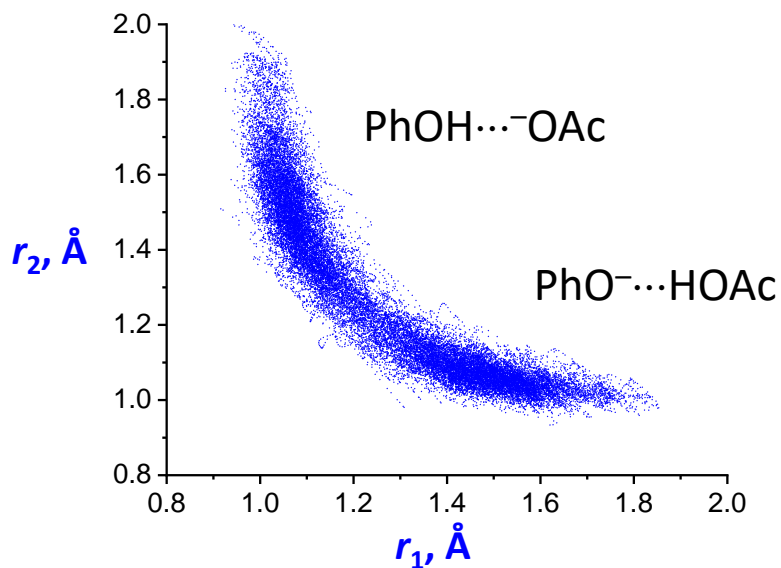
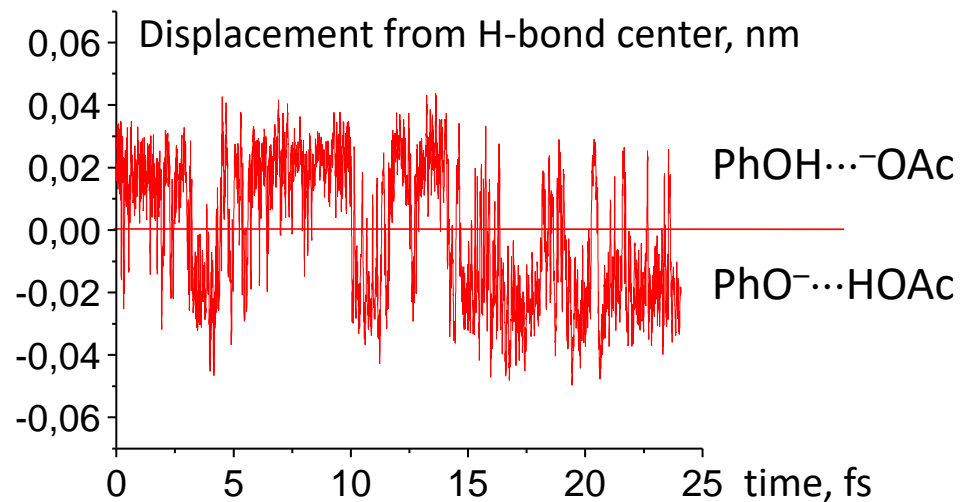
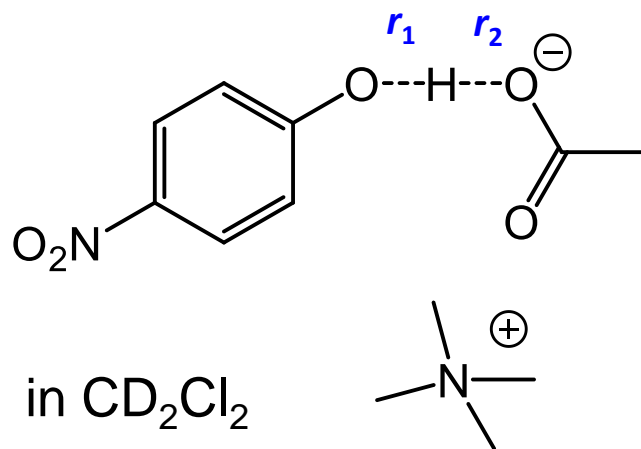
PCCP 2015, 17, 4634

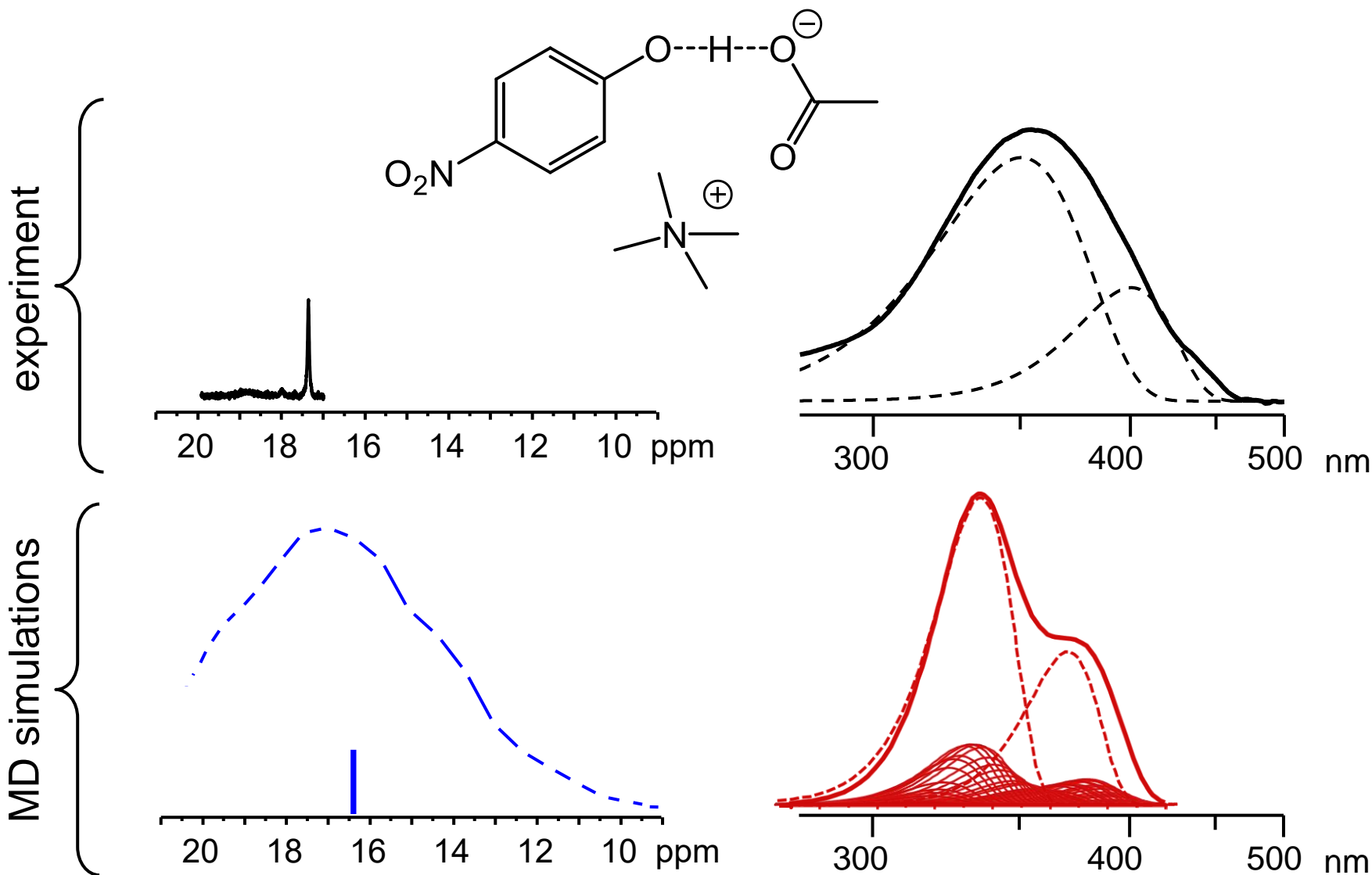
Solvent fluctuations

Molecular dynamics simulations

PCCP 2015, 17, 4634

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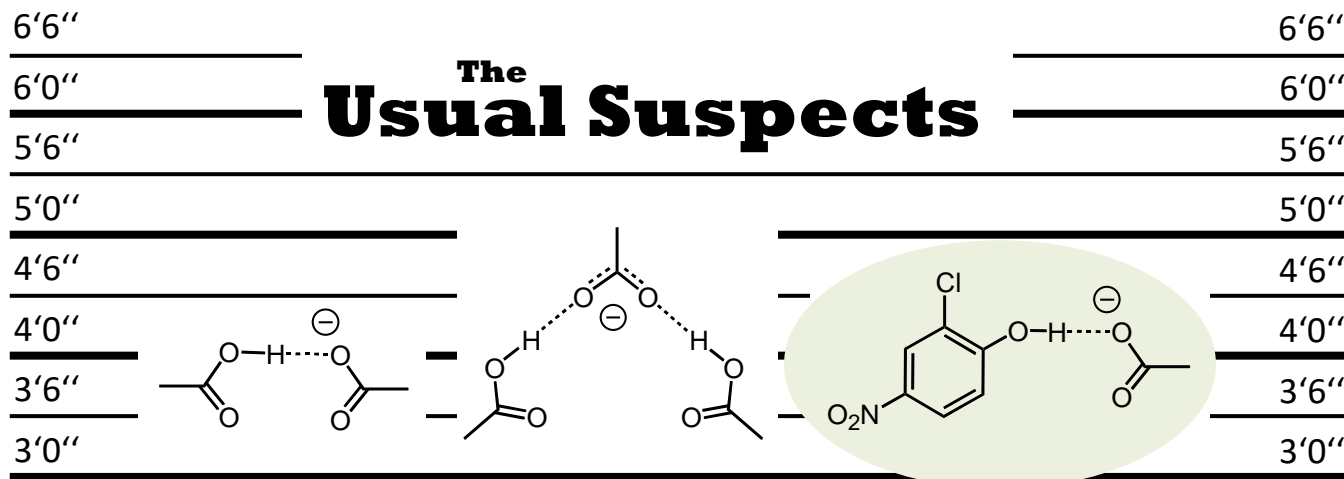
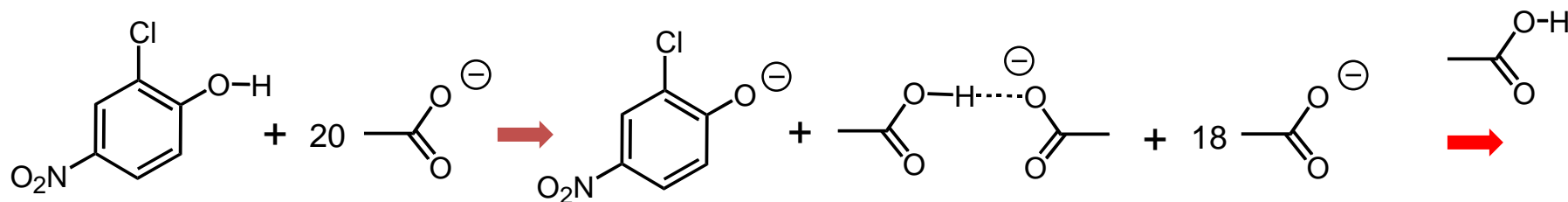


2D NMR – UV-vis spectroscopy

Example of the problem

JPCL 2011, 2, 1106

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acid homo-conjugates

hetero-conjugate

2D NMR – UV-vis spectroscopy

Example of the problem

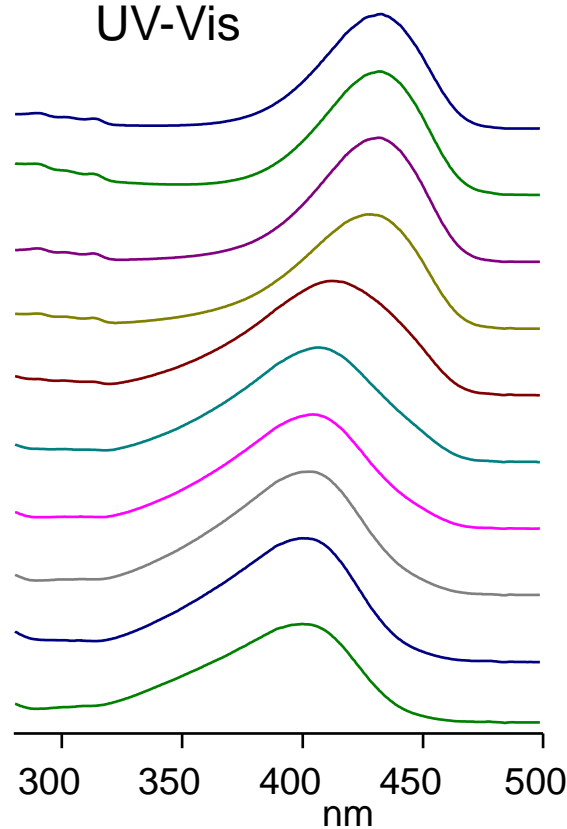
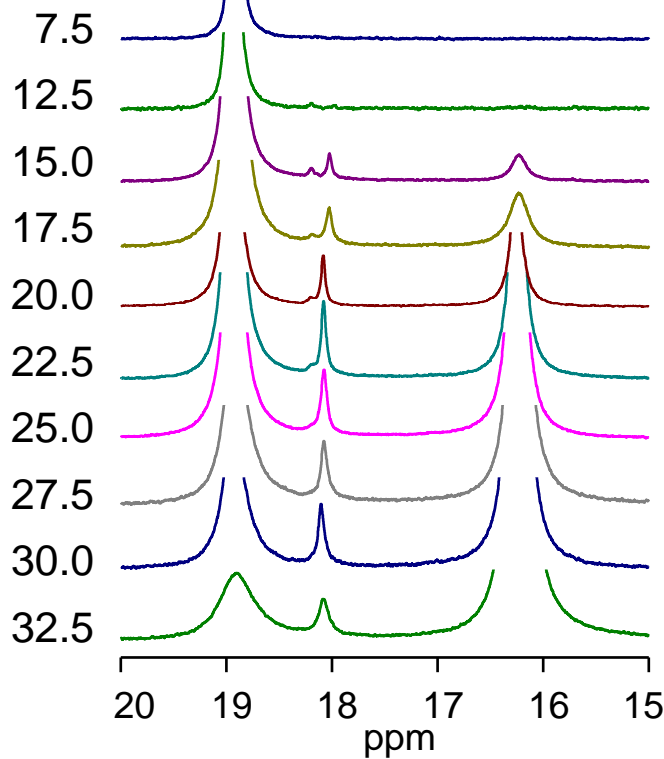
JPCL 2011, 2, 1106



adding acetic acid

^1H NMR

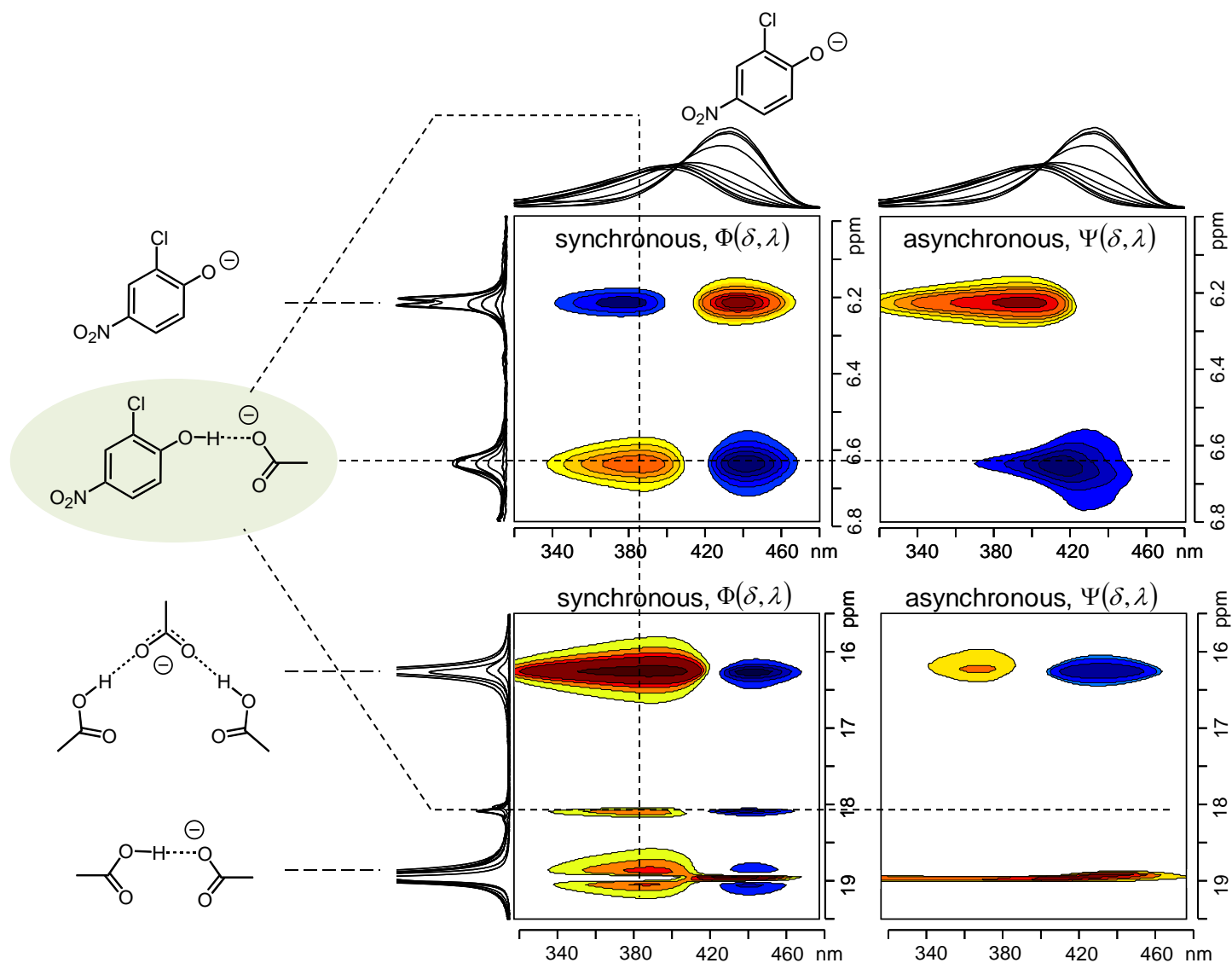
UV-Vis



2D NMR – UV-vis spectroscopy

Example of the problem

JPCL 2011, 2, 1106



CD₂Cl₂
170 K

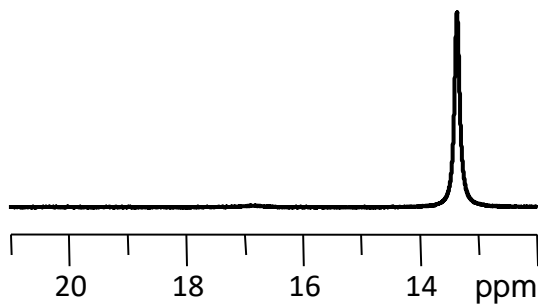
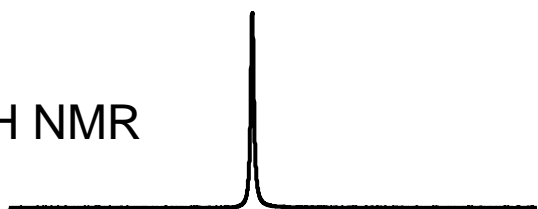
NMR – IR combination

Proton tautomerism in OHN hydrogen bonds

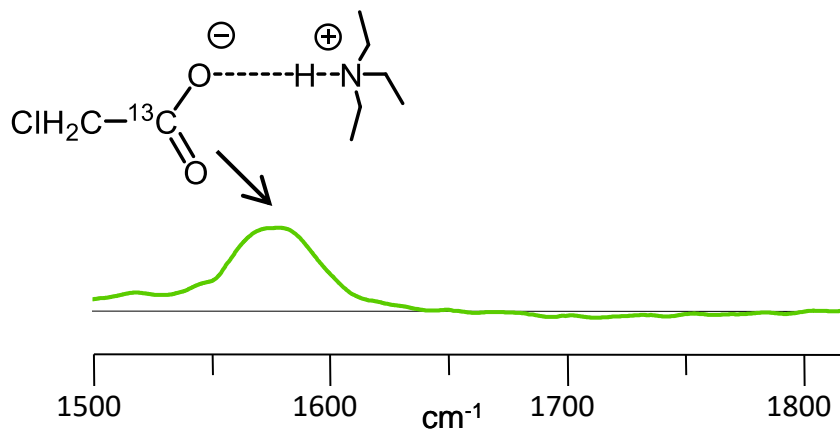
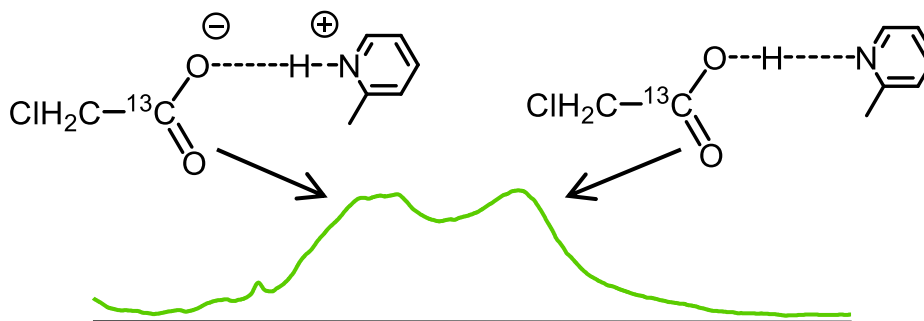
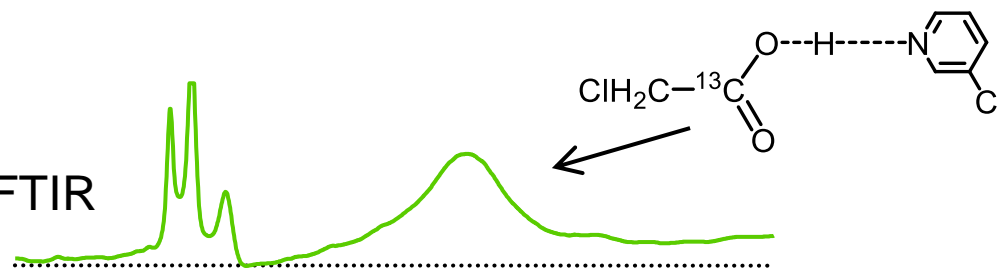
PCCP 2017, 19, 1010

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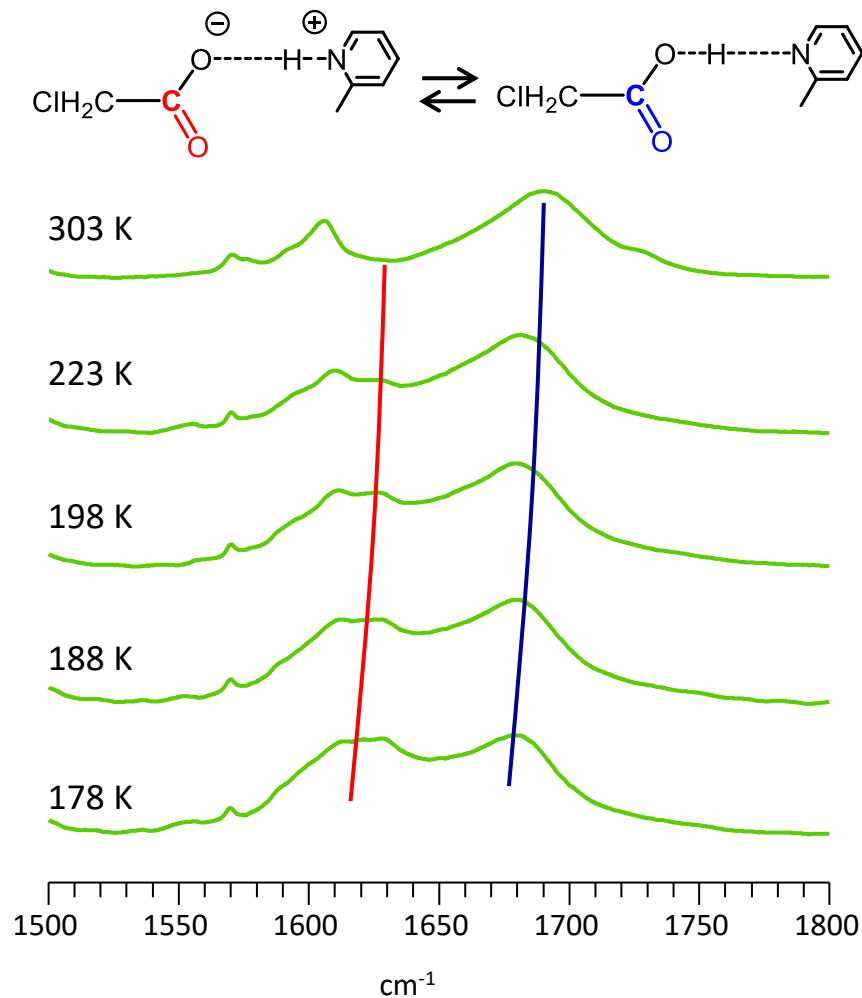
^1H NMR



FTIR



solvent:
 $\text{CH}_2\text{Cl}_2 / \text{CD}_2\text{Cl}_2$
 $T = 175 \text{ K}$

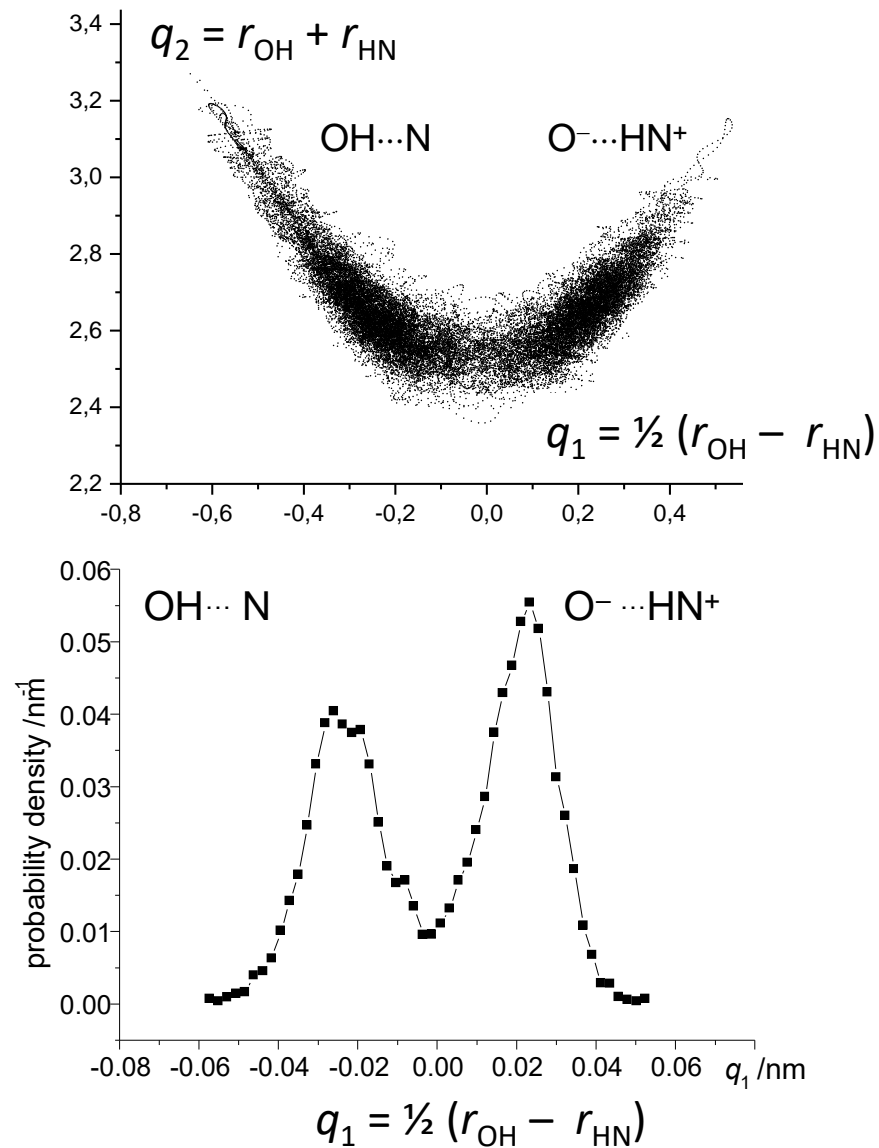
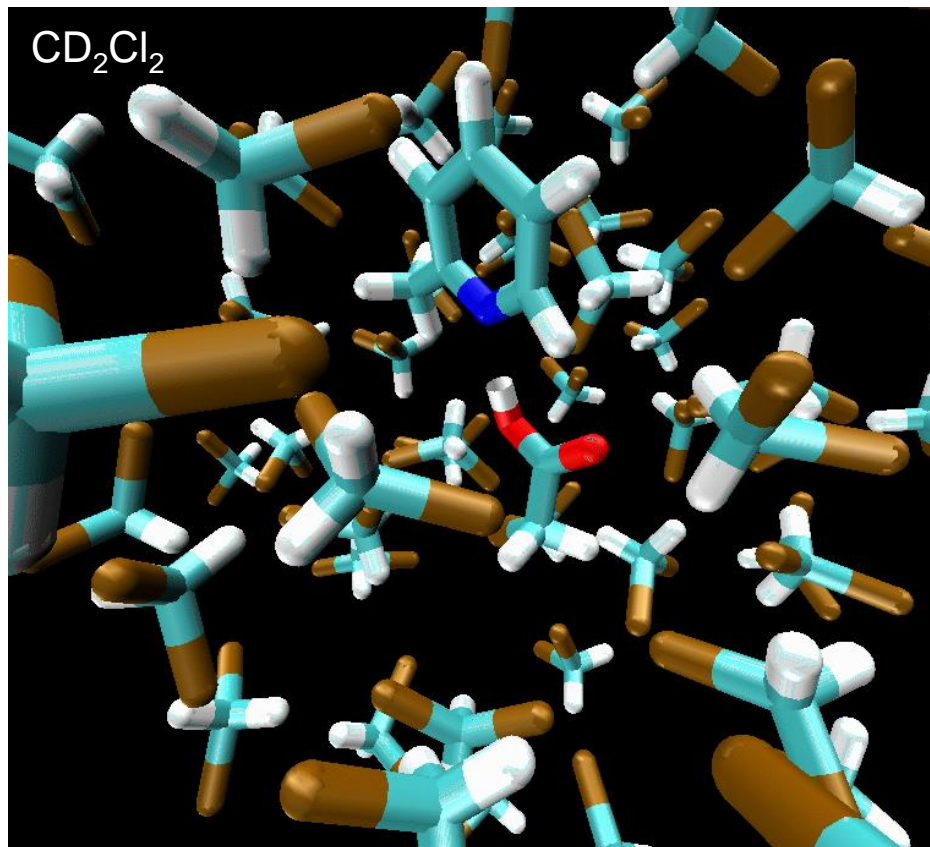
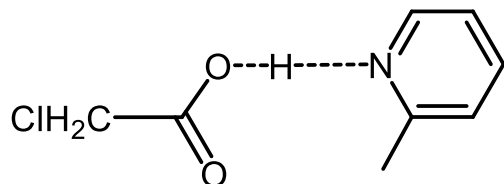


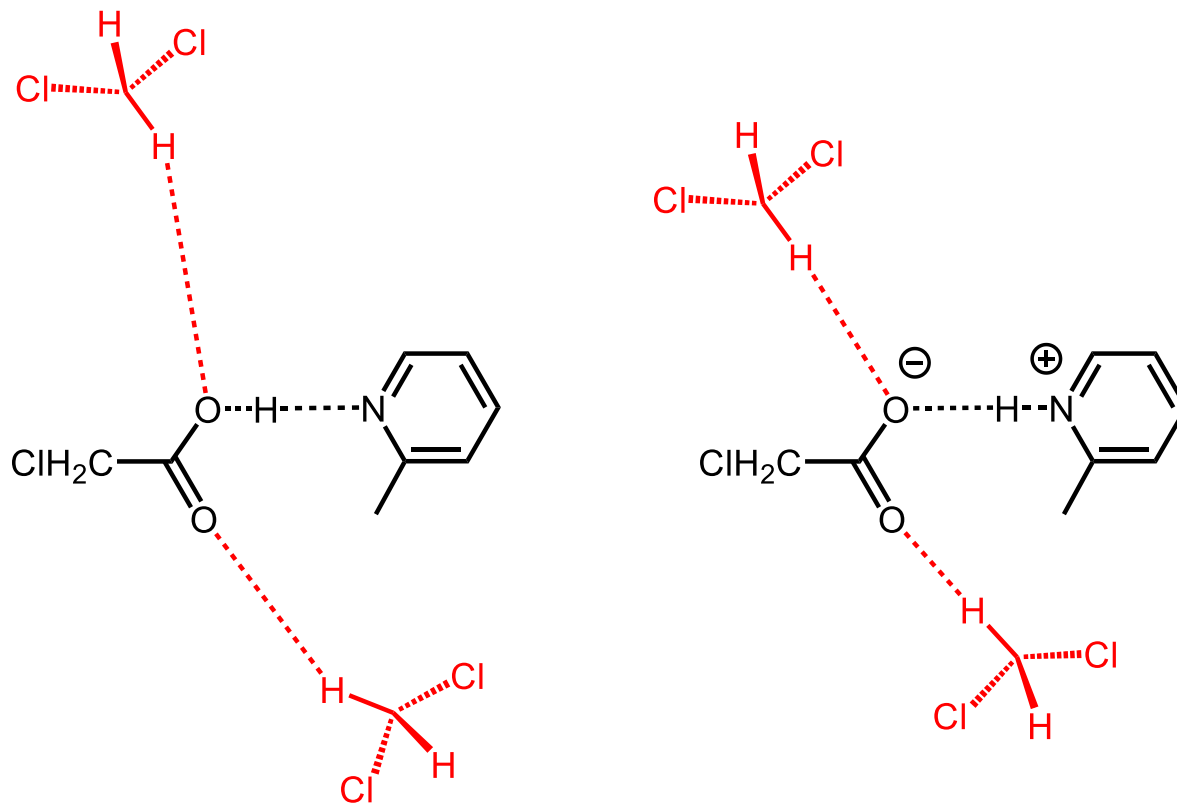
NMR – IR combination

Proton tautomerism in OHN hydrogen bonds

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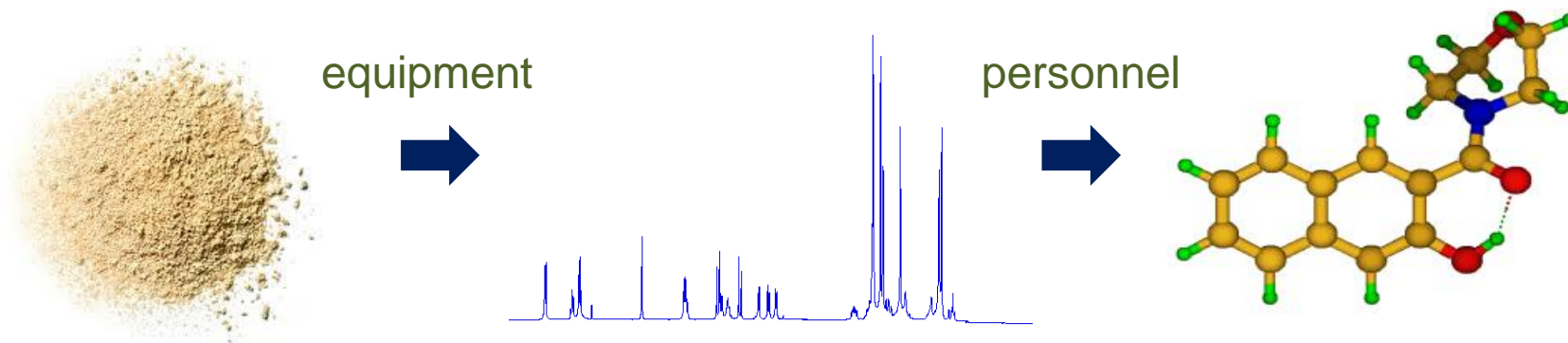




Formation/breaking of CH...O=C hydrogen bonds correlates well with proton transfer in OHN bond

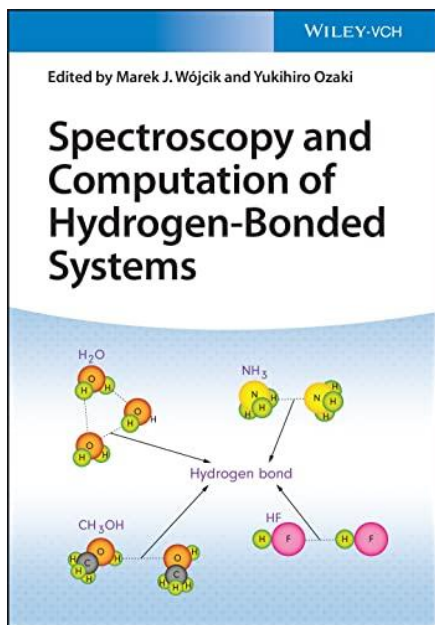
Summary and outlook

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



*P.M. Tolstoy
E.Yu. Tupikina*

63 pages in print

- I. Introduction**
 - I.1. Solving the reverse spectroscopic problem**
 - I.2. Spectral markers for proton transfer and H-bond length**

- II. Spectral characterization of hydrogen bond geometry**
 - II.1. Description of hydrogen bond geometry**
 - II.2. Averaging of NMR parameters and proton tautomerism**
 - II.3. NMR hydrogen bond correlations**
 - II.3.1. OHO bonds – ^1H NMR chemical shifts
 - II.3.2. OHO bonds – ^{13}C and ^{31}P NMR chemical shifts
 - II.3.3. OHN bonds
 - II.3.4. NHN bonds
 - II.3.5. FHF, FHN and FHO bonds
 - II.3.6. Vicinal H/D isotope effects for H-bonded complexes
 - II.4. IR hydrogen bond correlations**
 - II.4.1. Proton donor stretching vibration
 - II.4.2. Proton donor deformational vibrations
 - II.4.3. Carbonyl stretching vibration

- III. Spectral markers for hydrogen bond energy**
 - III.1. Defining hydrogen bond energy**
 - III.2. NMR characterization of H-bond energy**
 - III.3. IR characterization of H-bond energy**
 - III.3.1. Proton donor stretching band shift
 - III.3.2. Proton donor stretching band intensity
 - III.3.3. Proton donor deformational vibrations
 - III.3.4. Low-frequency hydrogen bond stretching frequency
 - III.3.5. Stretching vibrations' force constants
 - III.3.6. Carbonyl stretching vibration