Universität Rostock Traditio et Innovatio

INSTITUT FÜR PHYSIK

Lecture Three: Dynamics and Spectroscopy of Hydrogen Bonds

Oliver Kühn

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Why Hydrogen Bonds ?

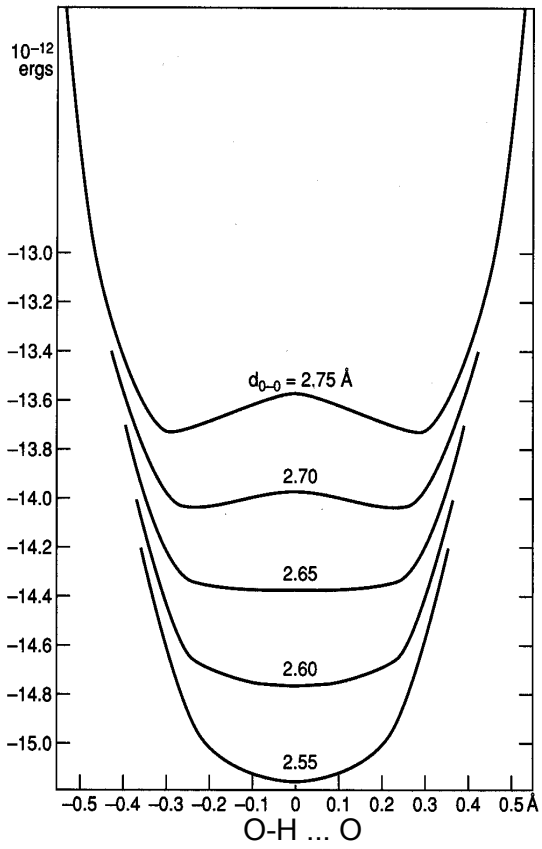
H-bonds & proton transfer → Physics, Chemistry, Biology

- the theoreticians answer:
  - H-bond: van der Waals → covalent
  - kinetic isotope effect (4 isotopes)
  - proton is quantum particle
  - tunneling even at room temperature
  - H-bond dynamics is multidimensional

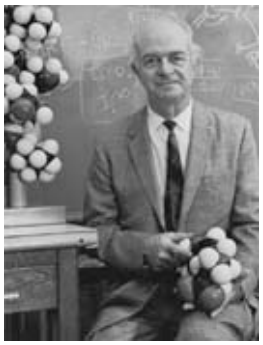
- M. L. Huggins (1936)

... hydrogen bridge theory will lead to a better understanding of the nature and behavior of complicated organic structures, such as proteins, starch, cellulose, sugar ....

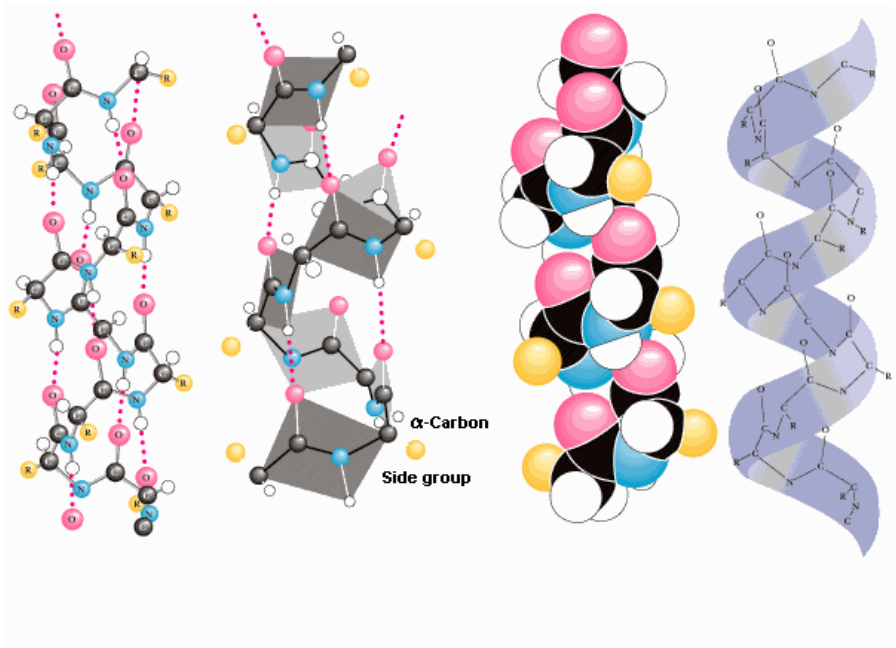
H^+ in H_2O



Alpha-Helix



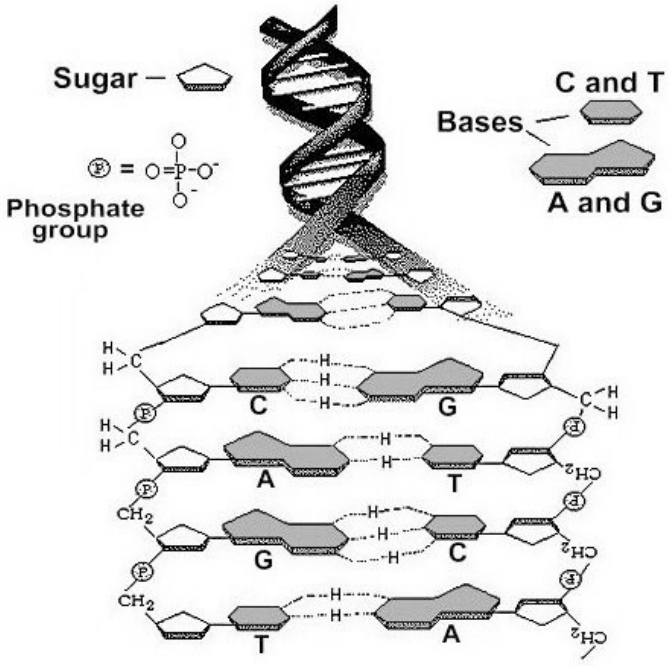
L. Pauling
(1951)



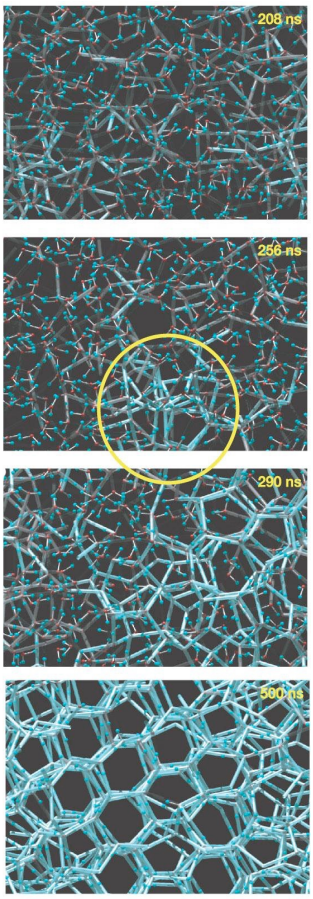
Biochemistry 2nd Ed. by Garrett and Grisham

DNA Structure

J. Watson, F. Crick
(1953)

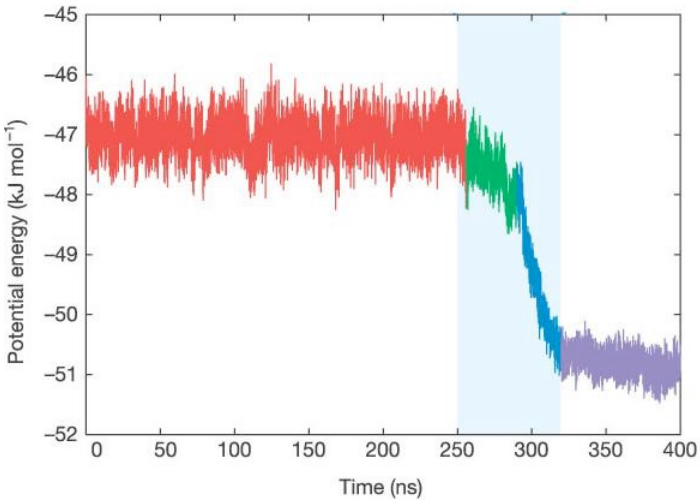


Freezing Of Water

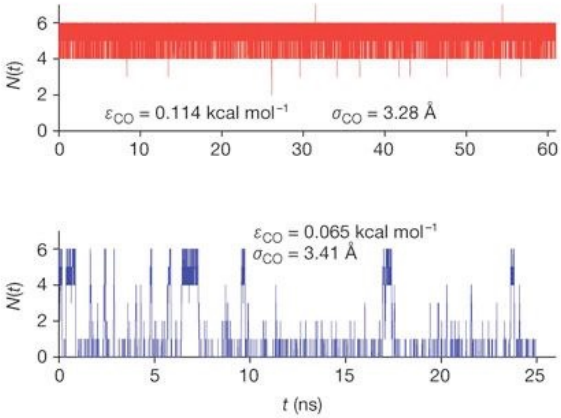


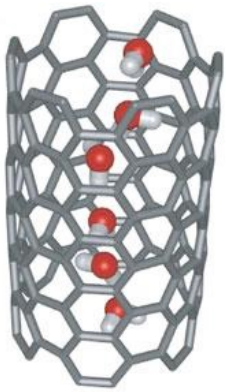
I. Ohmine et al. 2002

- fluctuating hydrogen bonded network
- spontaneous formation of polyhedral nucleus



Artificial Water Channels



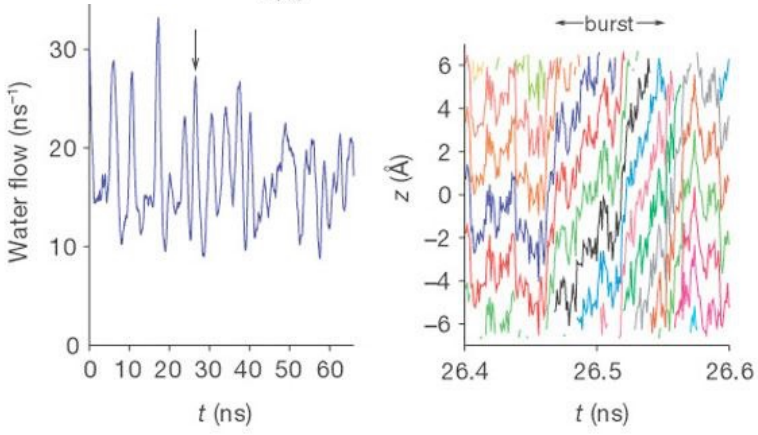


strong H-bonding + nonpolar environment

1D water wire

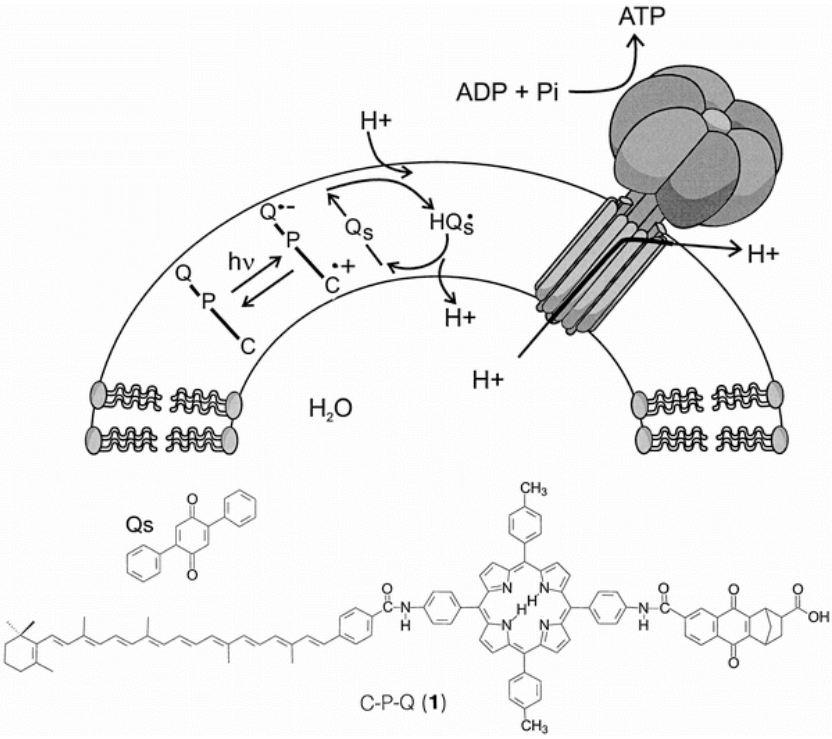
H-bonded network + fluctuations

concerted water flow (bursts)



G. Hummer et al. 2001

Proton Pump



S. Steinberg-Yfrach et al. 1998

artificial photosynthesis

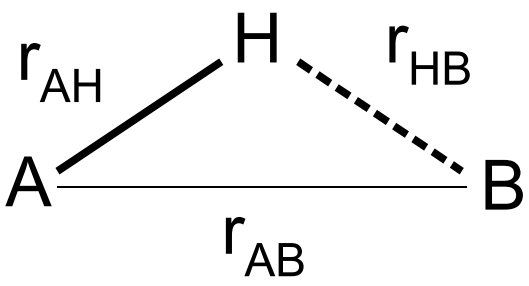
electron transfer

proton transfer

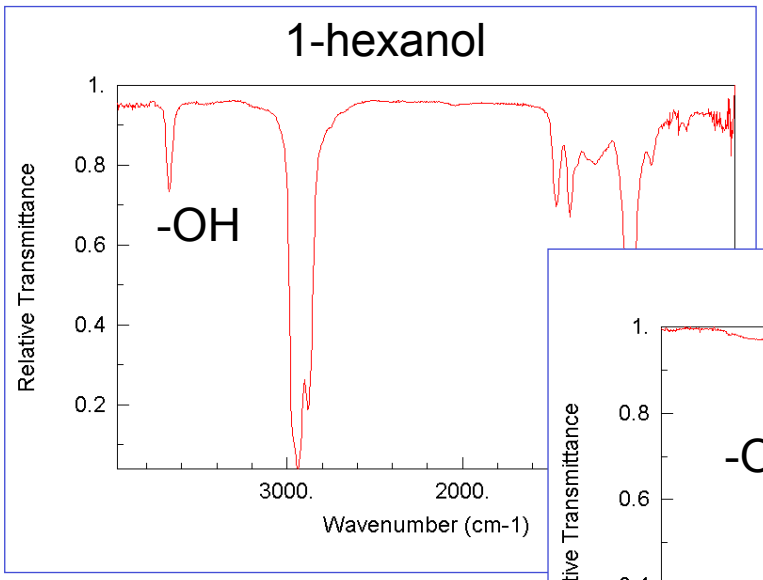
ATP production

Nature Of H-Bonds

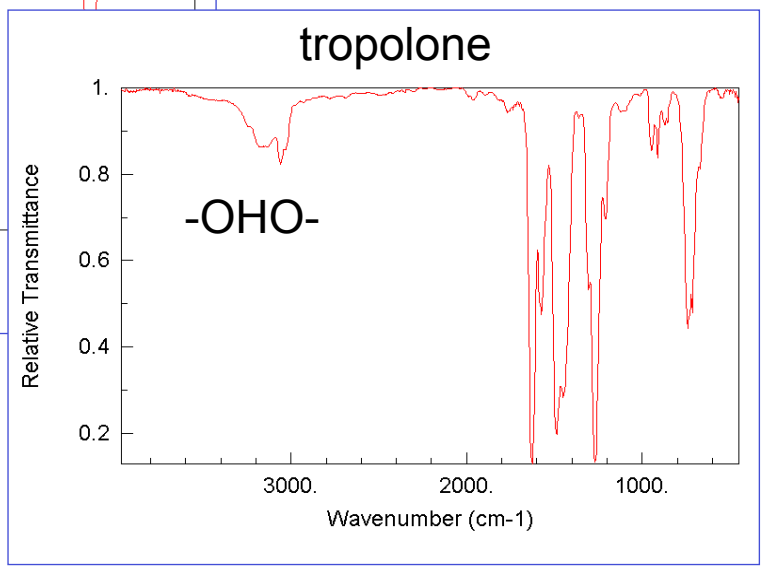
- donor-acceptor interaction involving hydrogen
- covalent A-H $\rightarrow$ $H^{+\delta}$ $\rightarrow$ interaction with B (lone pair or polarizable π electrons)
- H-bond interactions:
  - electrostatic (directionality)
  - charge transfer
  - dispersion
  - exchange repulsion
- H-bond geometry:



IR Spectra



➢ intramolecular H-bond



Weak H-Bonds

E_B = <4 kcal/mol

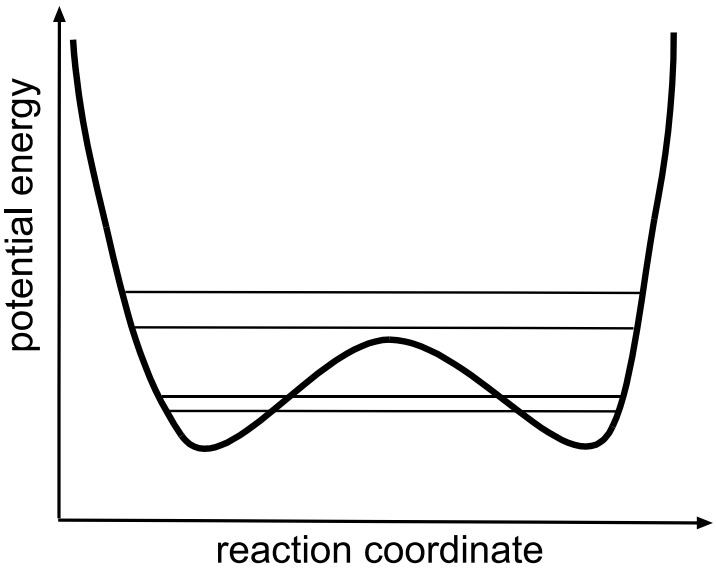
$\Delta\nu$ = <10%

r_{AB}=3.2-4.2 Å

r_{BH}=2.2-3.2 Å

➢ directionality

➢ tunneling



• HCl...benzene (T-form), C-H...B in crystals, forced contacts

Moderate H-Bonds

E_B = 4-15 kcal/mol

$\Delta\nu$ = 10-25%

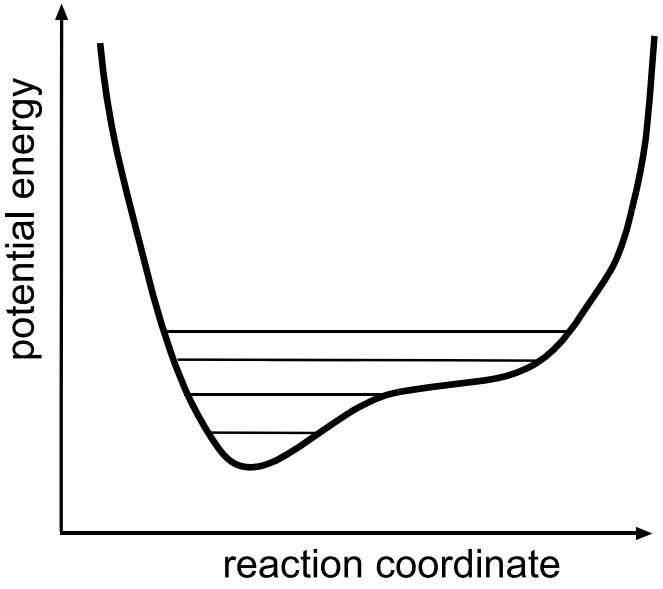
r_{AB}=2.5-3.2 Å

r_{BH}=1.5-2.2 Å

• neutral D/A:

➢ O-H...O

• intramolecular H-bonds



• biological systems:

➢ packing, solvation, conformation

Strong H-Bonds

E_B = 14-40 kcal/mol

$\Delta\nu$ = 25%

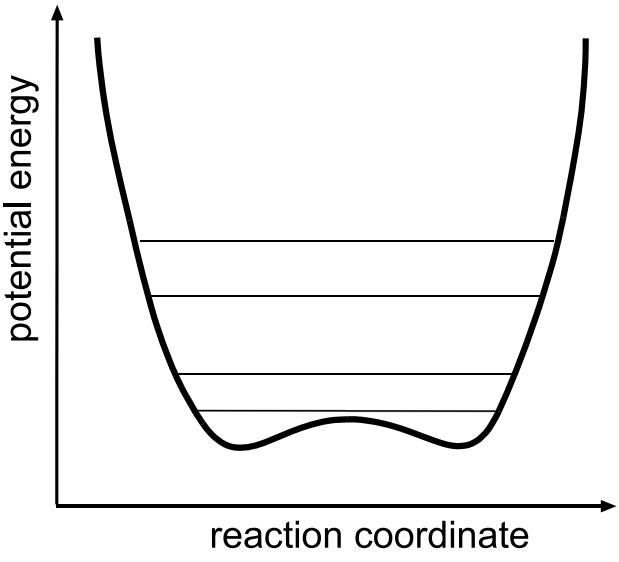
r_{AB}=2.2-2.5 Å

r_{BH}=1.2-1.5 Å

• low/vanishing barrier

➢ delocalized wave function

➢ sensitive to environment

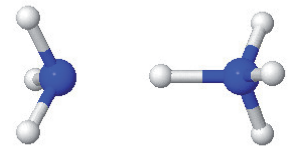


• $[FHF]^-$,O-H...O^-, N-H...N^-, enzymes (?), forced contacts

IR Spectroscopy of Strong H-Bonds in Gas Phase

Protonated Ammonia Clusters $NH_4^+(NH_3)_n$

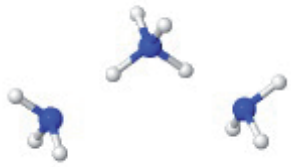
n=1



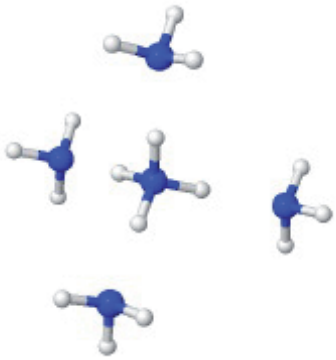
n=3

- N...H...N HBs
- NH_3 channels
- proton wires

n=2

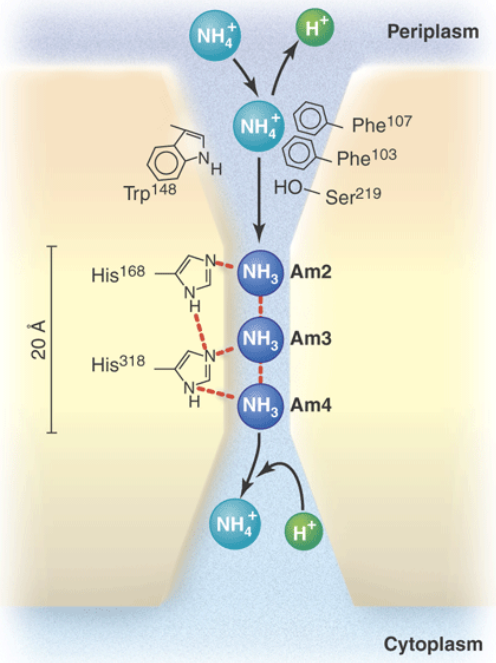


n=4

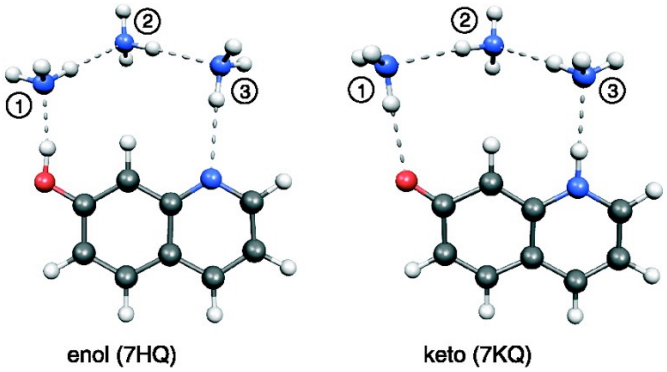


NH_3-Networks

AmtB NH_3 channel (E. coli)



NH_3-wires

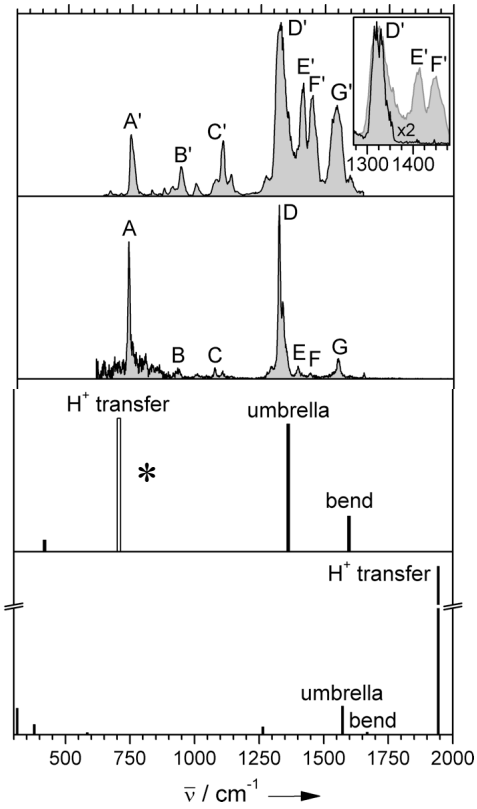


7-hydroxyquinoline·$(NH_3)_3$

S. Khademi et al. Science 305, 1587 (2004)

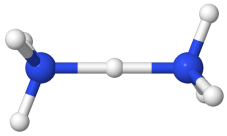
C. Tanner et al. Science 302, 1736 (2003)

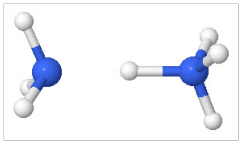
IR Spectrum of $N_2H_7^+$

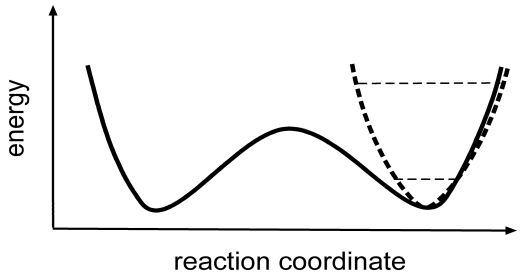


IRMPD (Asmis)

IRVPD (Johnson)





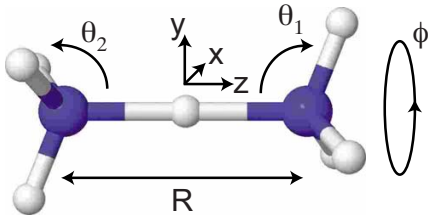


* T. Asada et al., JPCA ('01)

$N_2H_7^+$: 6D Model

- kinetic energy for non-Cartesian coordinates
- assumptions:
  - use constraints to restrict motions to model coordinates
  - no kinetic coupling between proton and NH_3 fragments
  - torsion decoupled from vibrations

model coordinates



$$T = -\frac{\hbar^2}{2\mu_p}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2}$$
$$-\frac{\hbar^2}{2I_0}\sum_{i=1,2}\frac{\partial}{\partial u_i}g(u_i)\frac{\partial}{\partial u_i},$$

$$g(u) = (1-u^2)(3m_{\mathrm{H}}+m_{\mathrm{N}})/(3m_{\mathrm{H}}u^2+m_{\mathrm{N}})$$

$$u_i = \cos\theta_i \qquad I_0 = 3m_{\mathrm{H}}R_{\mathrm{NH}}^2$$

$$\mu_p = \frac{2m_{\mathrm{H}}(3m_{\mathrm{H}}+m_{\mathrm{N}})}{7m_{\mathrm{H}}+2m_{\mathrm{N}}} \qquad \mu_R = \tfrac{1}{2}(3m_{\mathrm{H}}+m_{\mathrm{N}})$$

Y. Yang, O.K., Mol. Phys. 106, 2445 (2008)

- potential energy and dipole moment surfaces
  - n-mode correlation expansion

$$V(\mathbf{Q}) = \sum_i V^{(1)}(Q_i) + \sum_{i<j} V^{(2)}(Q_i, Q_j) + \sum_{i<j<k} V^{(3)}(Q_i, Q_j, Q_k) + \dots$$

$$V^{(2)}(Q_i, Q_j) = V(\mathbf{Q}) - \sum_i V^{(1)}(Q_i)$$

$$\mu(\mathbf{Q}) = \sum_i \mu^{(1)}(Q_i) + \sum_{i<j} \mu^{(2)}(Q_i, Q_j)$$

  - recall MCTDH

$$i\hbar \dot{A}_J = \sum_K H_{JK} A_K$$

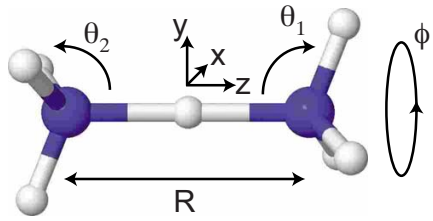
$$H_{JK} = \int d\mathbf{Q}\, \phi^{(1)}_{j_1}(Q_1) \dots \phi^{(f)}_{j_f}(Q_f) H \phi^{(1)}_{k_1}(Q_1) \dots \phi^{(f)}_{k_f}(Q_f)$$

  - preferential: sum of products form

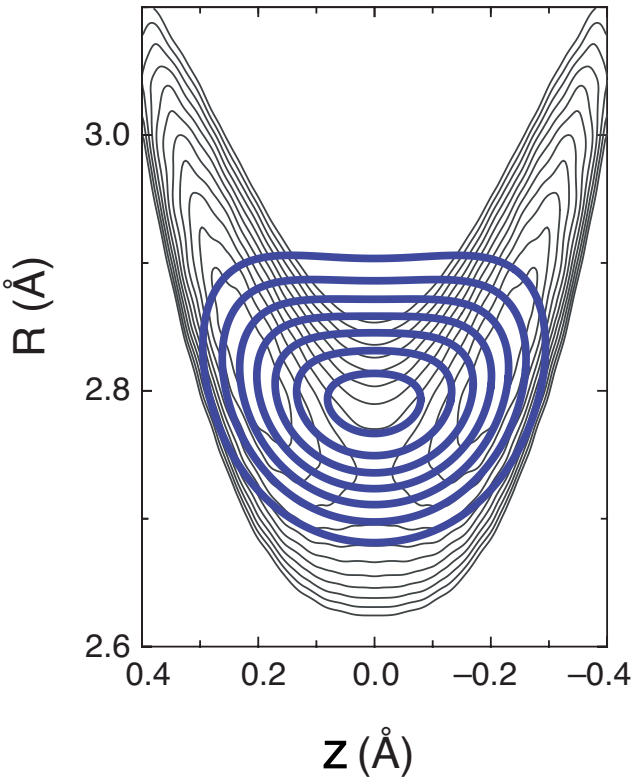
$$H = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{f} h^{(\kappa)}_r \quad \rightarrow \quad H_{JK} = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{f} \langle \phi^{(\kappa)}_{j_\kappa} | h^{(\kappa)}_r | \phi^{(\kappa)}_{k_\kappa} \rangle$$

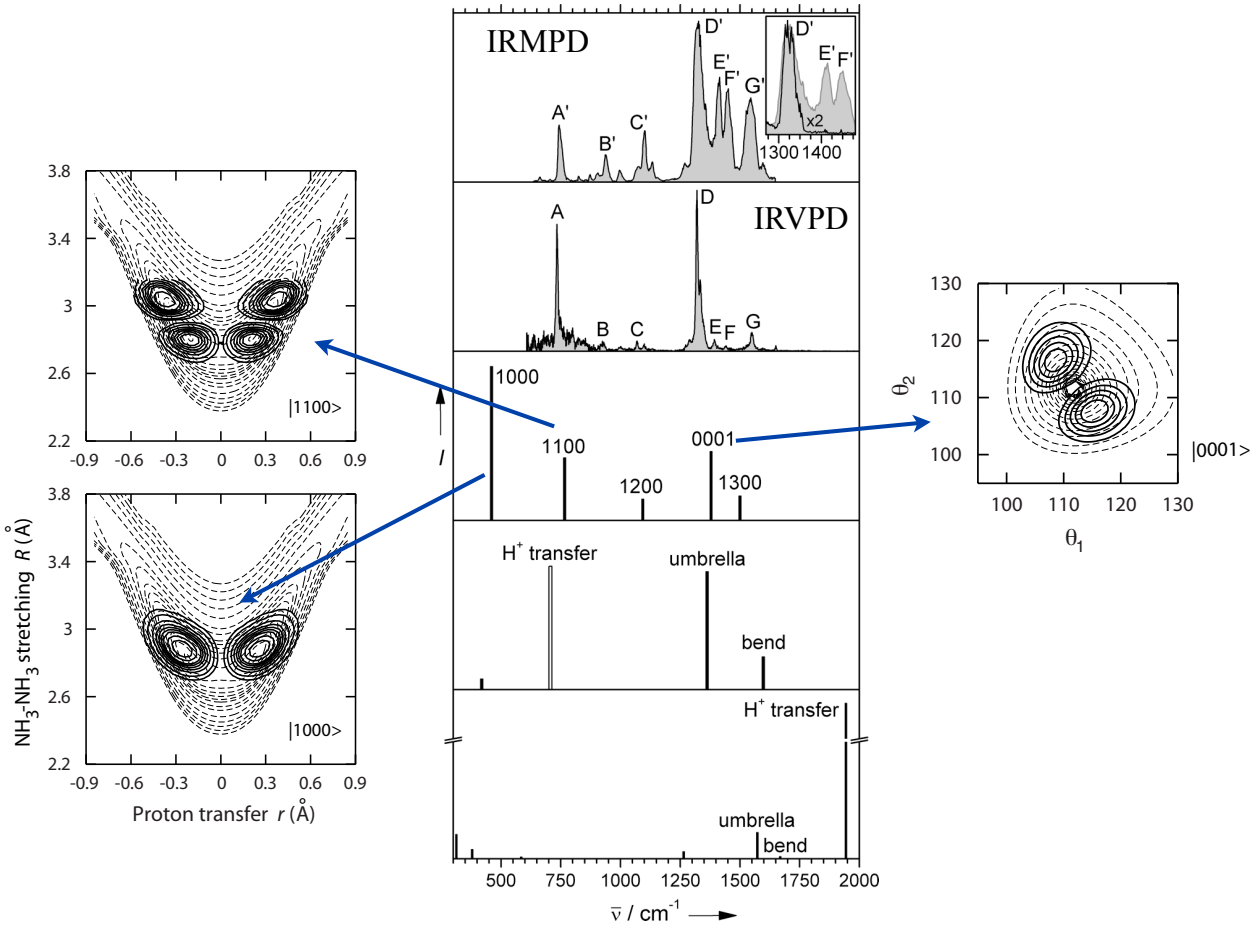
$N_2H_7^+$: ZPE Effect

- model coordinates



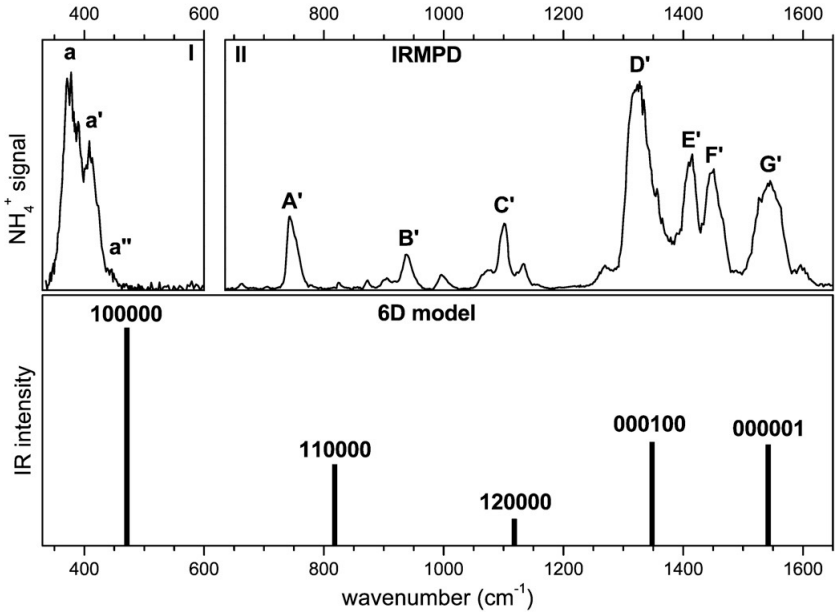
- reaction barrier: ~350 cm^{-1} (>kT at RT)
- structure determined by ZPE effect





K. Asmis, M. Johnson, O.K. et al., Angew. Chem. 46, 8691 ('07)

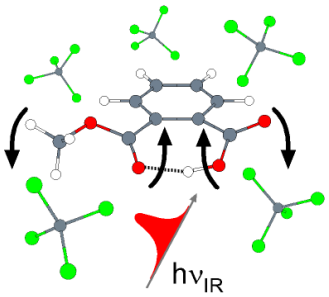
NH-Stretching Mode

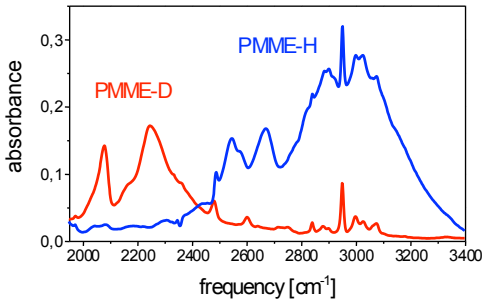


- extreme red-shift due to strong H-bond

Y. Yang, O.K., K. Asmis et al., J. Chem. Phys. 129, 224302 ('08)

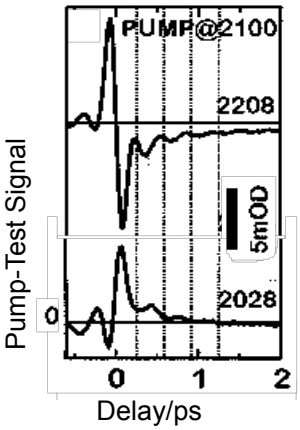
Dissipative H-Bond Wave Packets





- oscillations in IR pump-probe spectra

Stenger et al., 2002

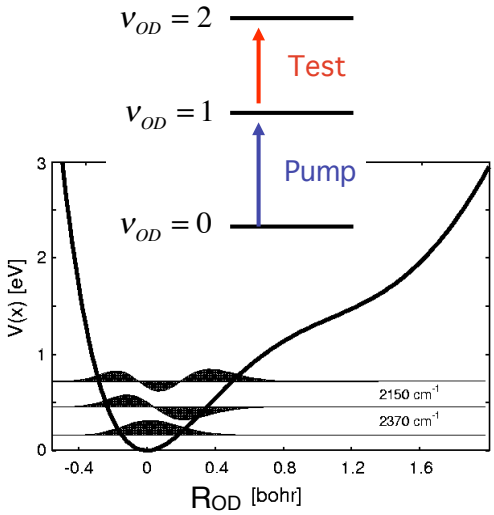


Experiment

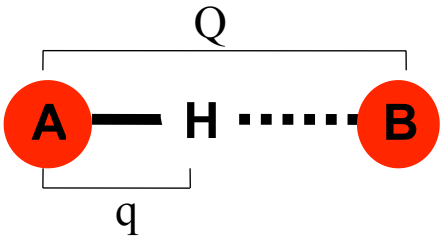
$T_1(v_{OD})$ ~200 fs

T_{cool} ~ 20 ps

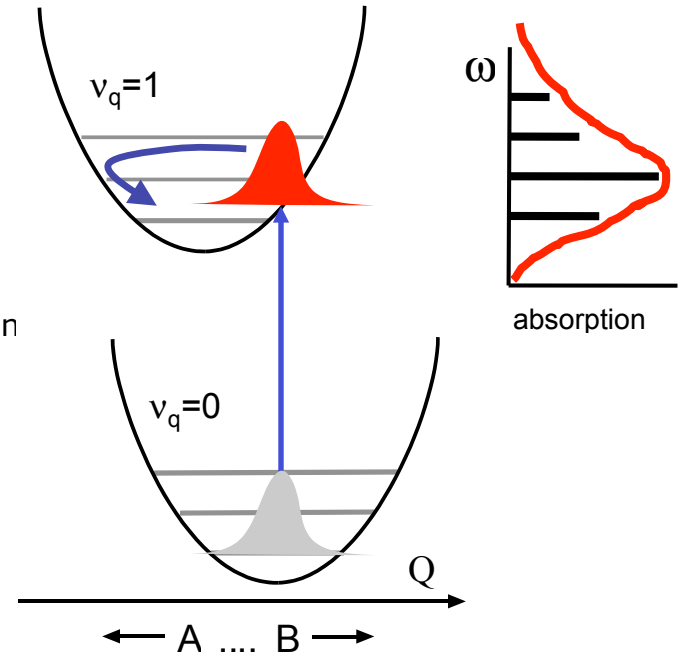
V_{osz} ~ 100 cm^{-1}



A Simple Model

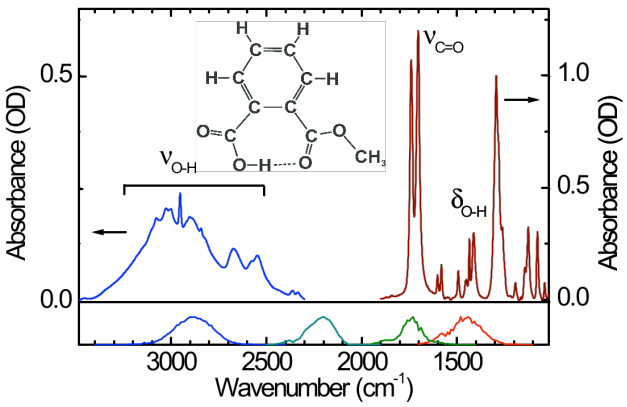


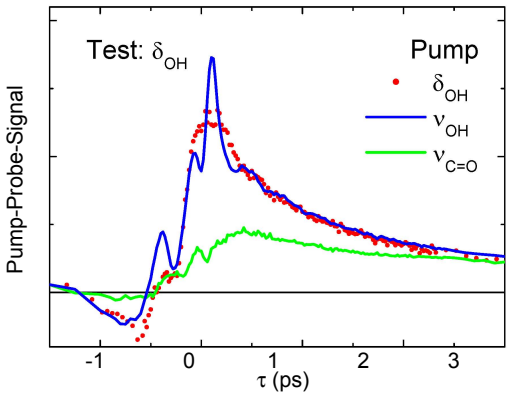
- adiabatic separation of high- and low-frequency modes
- Franck-Condon like progression
- excitation of wave packets possible
- theoretically reproduced with reaction surface model

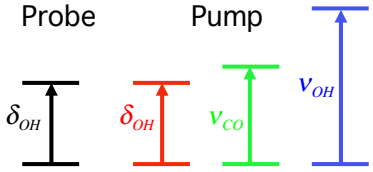


Vibrational Energy Relaxation

- two-color pump-probe spectroscopy





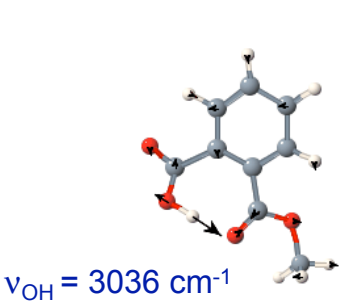


$T_1(\nu_{OH})$=200fs, $T_1(\delta_{OH})$=800fs
relaxation via δ_{OH}=1 (>30%)
T_{cool} ~ 20 ps

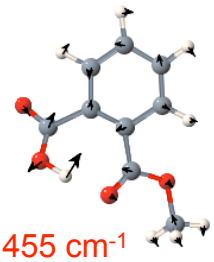
K. Heyne et al. JPCA 108, 6083 (2004)

5D Dissipative Model

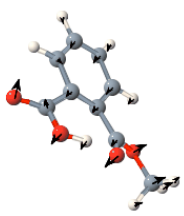
4-mode correlation potential - B3LYP/6-31+G(d,p)



ν_{OH} = 3036 cm^{-1}

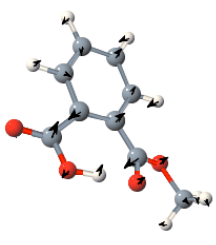


δ_{OH} = 1455 cm^{-1}

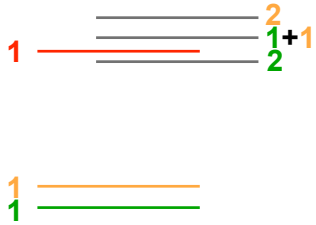


ν_{HB} = 63 cm^{-1}

γ_1 = 792 cm^{-1}



γ_2 = 690 cm^{-1}



labeling of states $\longrightarrow (v_\nu, v_\delta, v_{\gamma_1}, v_{\gamma_2})$

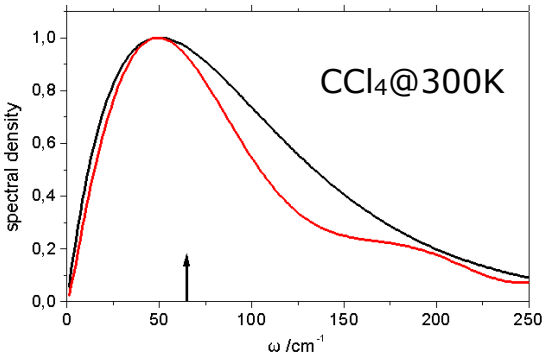
- system-bath model
  - low-frequency H-bond mode

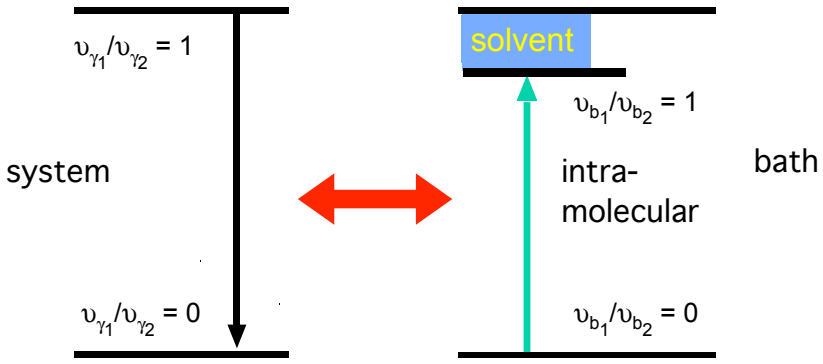
$$H_{\mathrm{S-R}}^{(\mathrm{HB})} = Q_{\mathrm{HB}} \sum_{\xi} c_{\xi} x_{\xi}$$

  - out-of-plane deformation

$$H_{\mathrm{S-R}}^{(\gamma)} = Q_{\gamma} \sum_{i,\xi} g_{\gamma,i,\xi}\, q_i\, x_{\xi}$$

    - 3rd order model

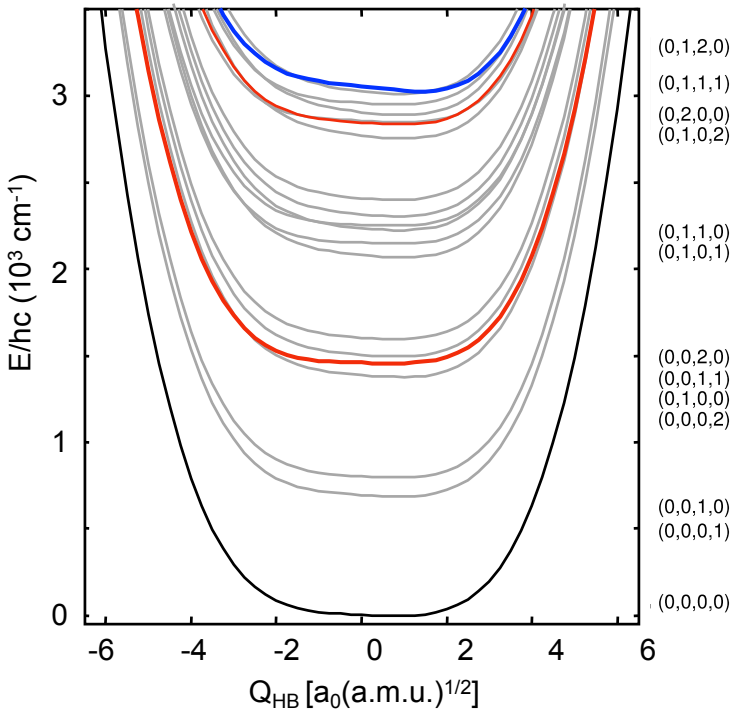


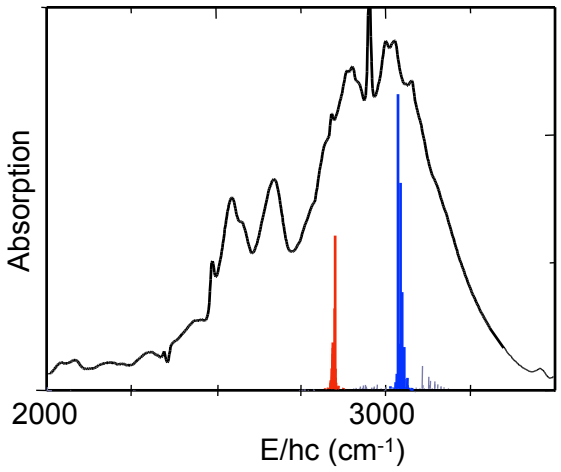


H. Naundorf, O.K. PCCP 5, 79 (2003)

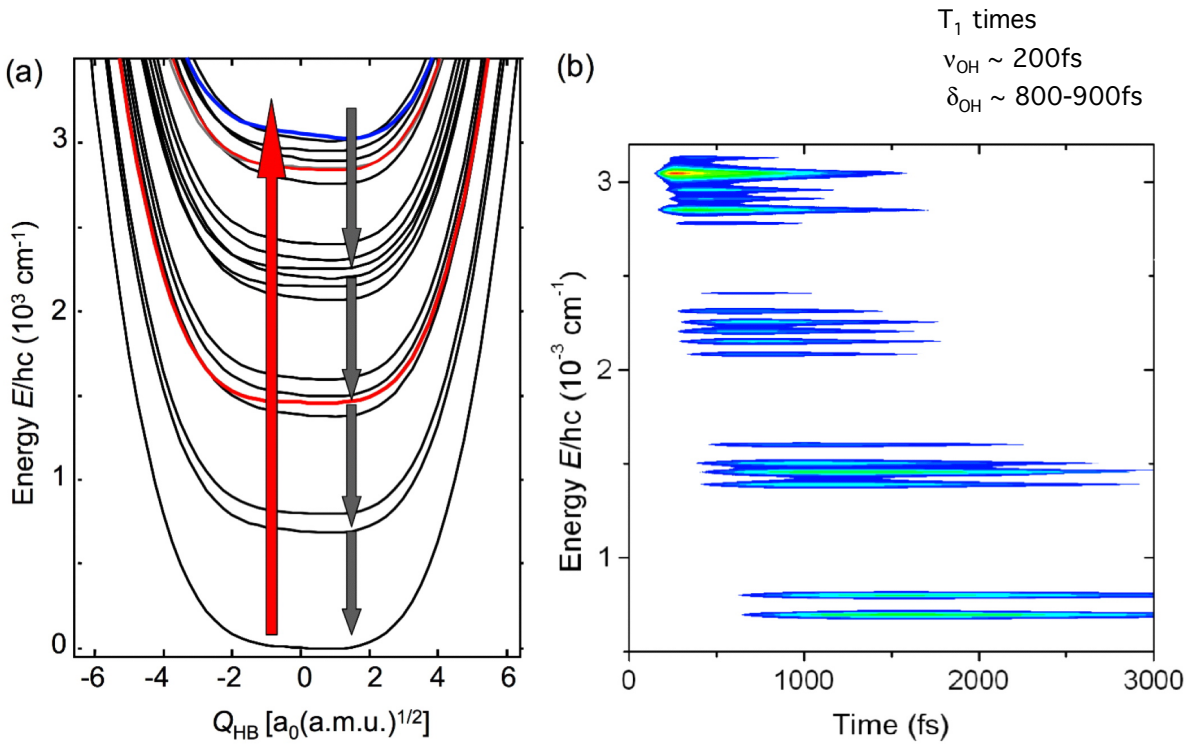
- potential energy curves and IR spectrum

$$(\mathrm{v}_{\nu}, \mathrm{v}_{\delta}, \mathrm{v}_{\gamma_1}, \mathrm{v}_{\gamma_2})$$



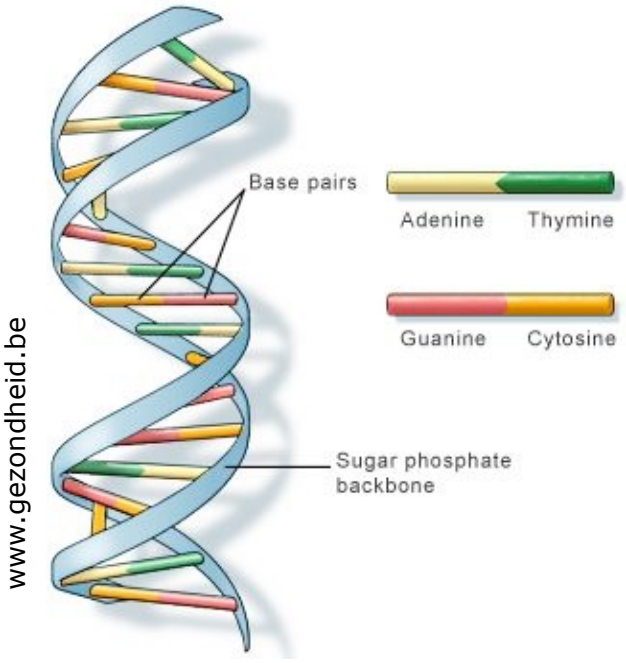


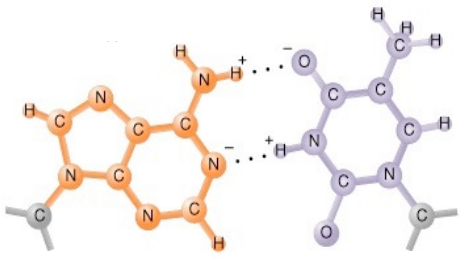
- cascaded energy relaxation

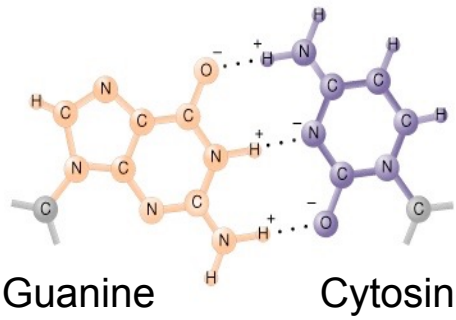


K. Heyne et al. JPCA 108, 6083 (2004)

Hydrogen Bonds in DNA

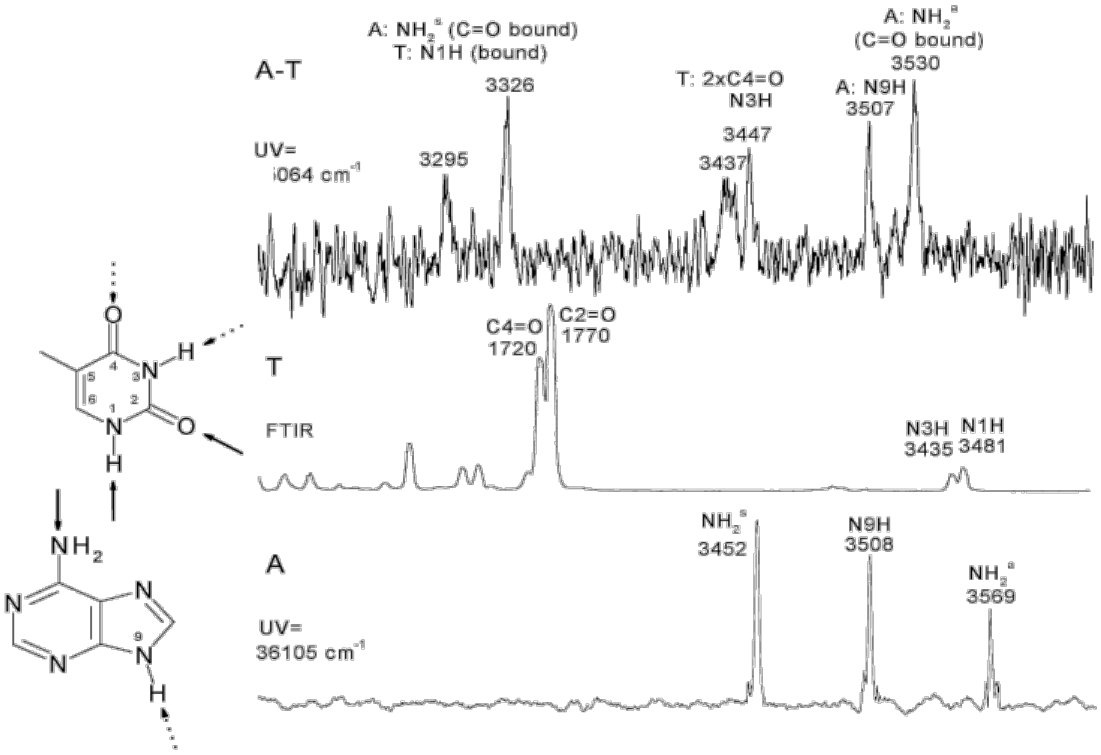






Base Pairs in Gas Phase: The Quest for the Structure

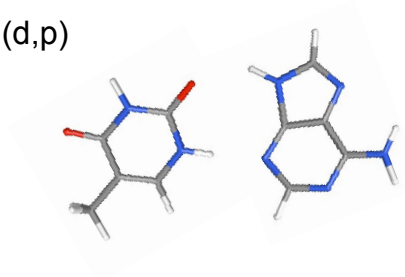
- IR-UV Double Resonance Spectra



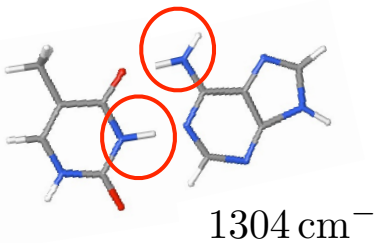
Kleinermanns et al., ChemPhysChem, 4, 838 (2003)

A-T Isomers

HF/6-31G(d,p)

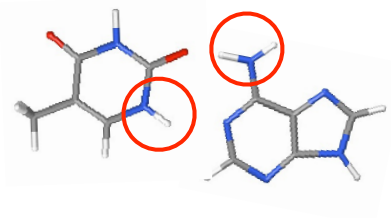


WC



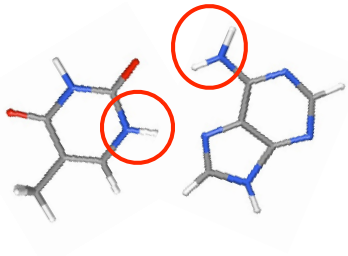
$1304\ \mathrm{cm}^{-1}$

A



$1038\ \mathrm{cm}^{-1}$

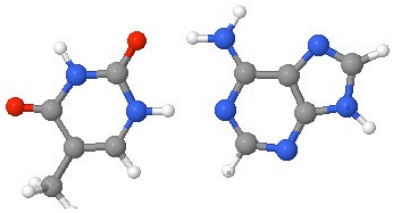
B



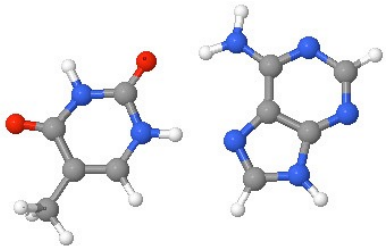
$1433\ \mathrm{cm}^{-1}$

Optimized Structures

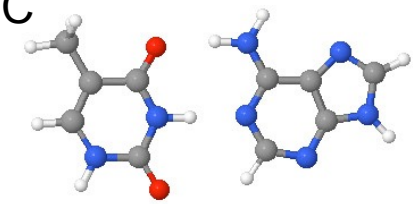
A



B

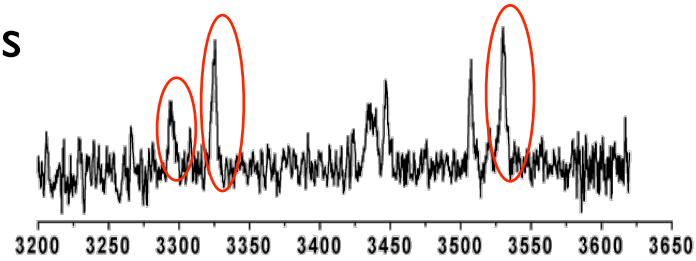


WC



HF 6-31G(d,p)	DFT/B3LYP 6-31+ +G(d,p)	MP2 TZP
0 cm^{-1}	0 cm^{-1}	0 cm^{-1}
395 cm^{-1}	364 cm^{-1}	406 cm^{-1}
266 cm^{-1}	466 cm^{-1}	420 cm^{-1}

Target Modes



ν_{as}= 3530 cm^{-1}

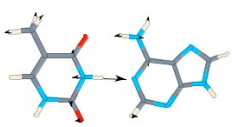
ν_{sy}= 3326 cm^{-1}

ν_{NH}= 3295 cm^{-1}

WC

ν_{as}= 3698 cm^{-1}

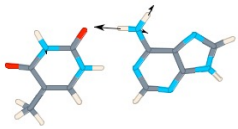
ν_{sy}= 3411 cm^{-1}



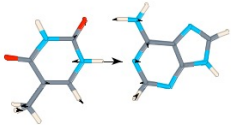
ν_{NH}= 2981 cm^{-1}

A

ν_{as}= 3689 cm^{-1}

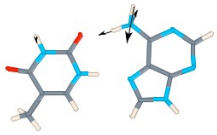


ν_{sy}= 3386 cm^{-1}



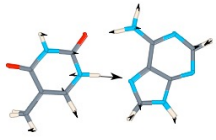
ν_{NH}= 3098 cm^{-1}

B



ν_{as}= 3683 cm^{-1}

ν_{sy}= 3442 cm^{-1}



ν_{NH}= 3284 cm^{-1}

Potential Energy Surfaces

- expand PES in normal mode coordinates $\mathbf{Q} = \{Q_{as}, Q_{sy}, Q_{NH}\}$
- use (exact) 3-mode expansion

$$V(\mathbf{Q}) = \sum_i V^{(1)}(Q_i) + \sum_{i<j} V^{(2)}(Q_i, Q_j) + \sum_{i<j<k} V^{(3)}(Q_i, Q_j, Q_k)$$

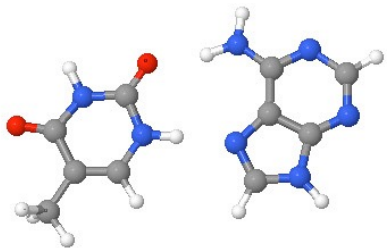
$V^{(1)}$: MP2 energies on numerical grid

$V^{(2)} + V^{(3)}$: DFT up to 4th order derivative

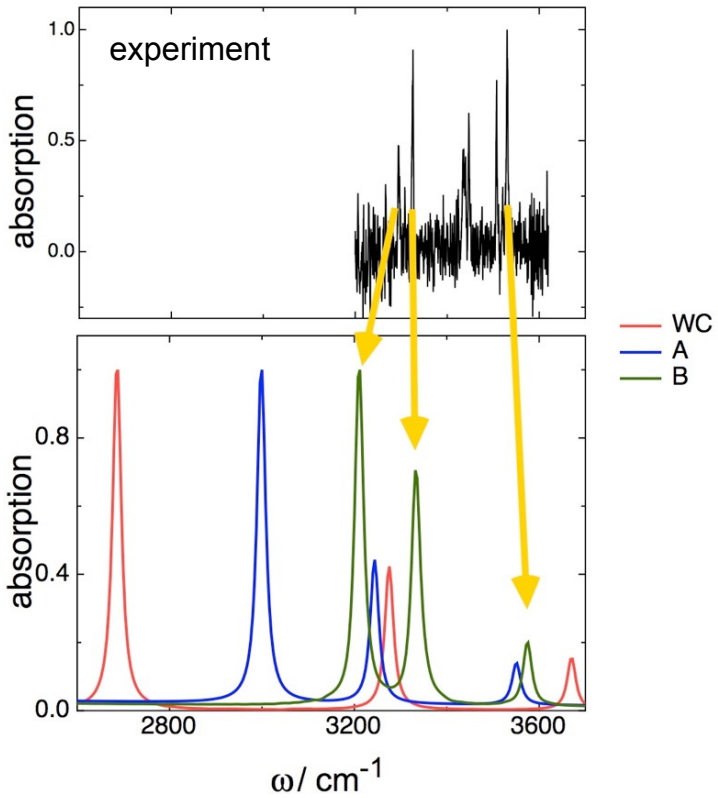
- 1-mode dipole moment

$$\mu(\mathbf{Q}) \approx \sum_i \mu^{(1)}(Q_i)$$

Structure vs. IR Absorption

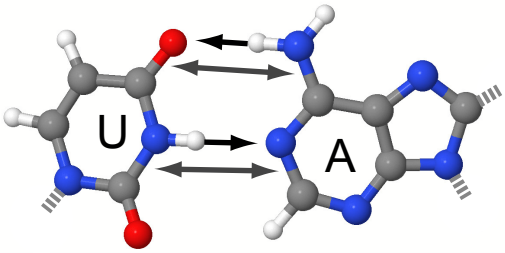


isomer B

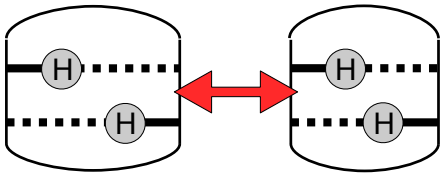


G. K. Krishnan, O.K., CPL 435, 132 (2007)

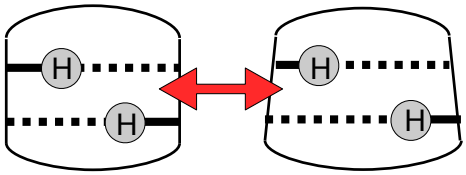
Dynamics of DNA Base Pairs in Solution



correlated dynamics



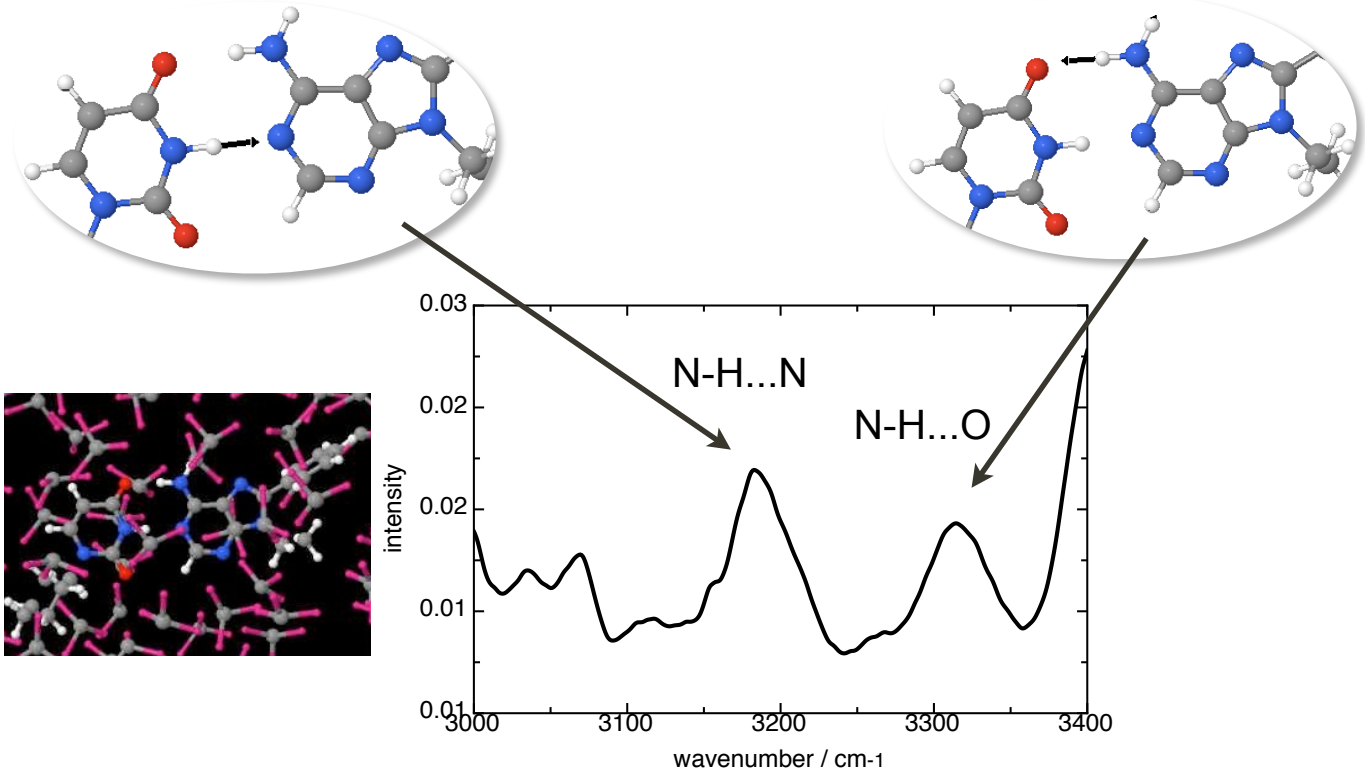
anticorrelated dynamics



- H-Bond dynamics / correlations
- vibrational energy flow
- environmental effects

⟶ IR spectrosopy

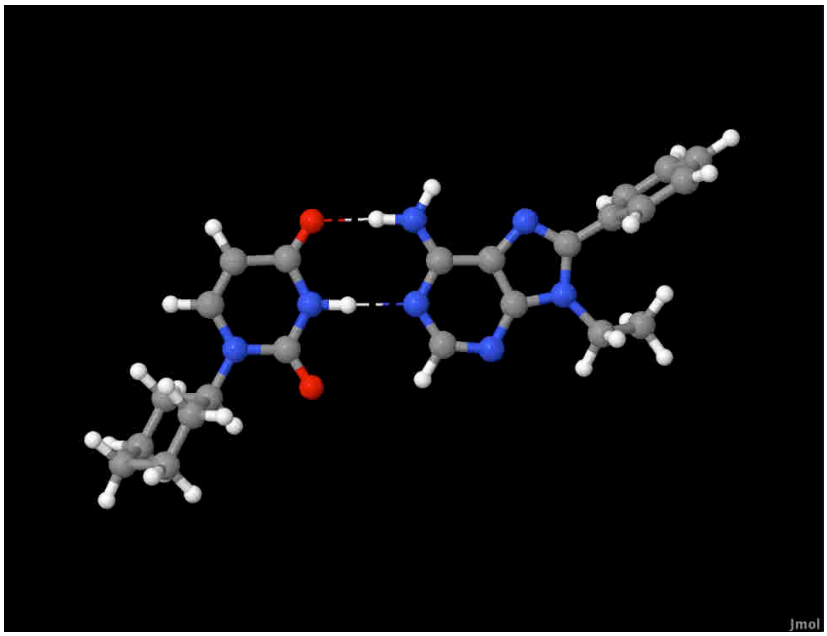
Solvated Base Pairs



S. Woutersen et al., JCP 121, 5381 (2004)

QM/MM Trajectory

- 9-ethyl-8-phenyladenine : 1-cyclohexyluracil in 100 $CDCl_3$ at 298K

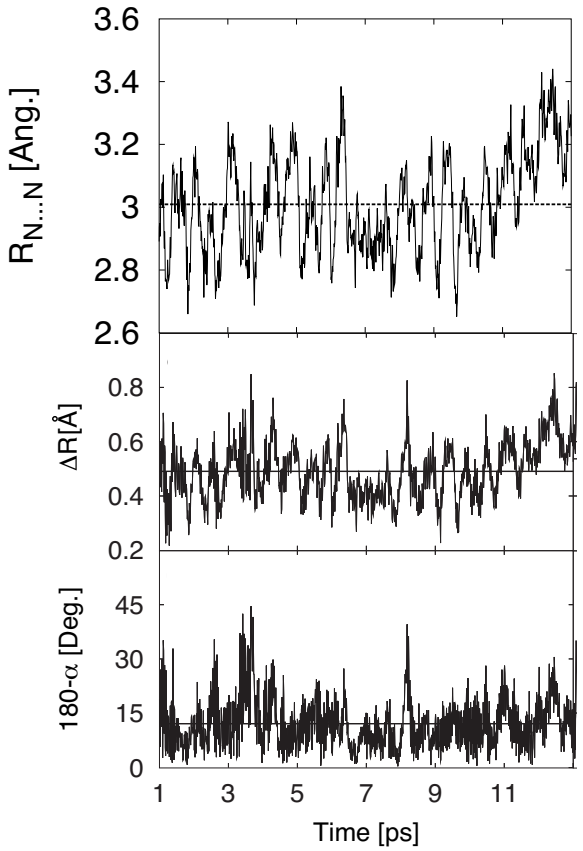


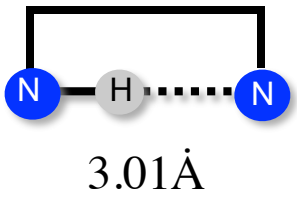
CPMD/GROMOS

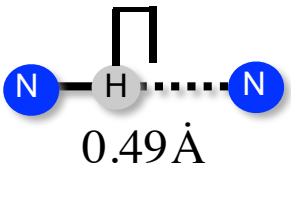
QM(BLYP, TM-PP, 70Ry)/MM (Gromos96)

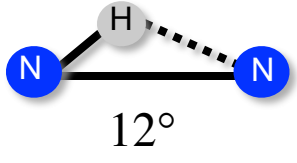
T~13ps

N-H...N HB Geometry

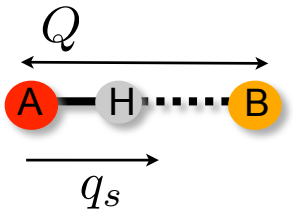








Lineshape Model



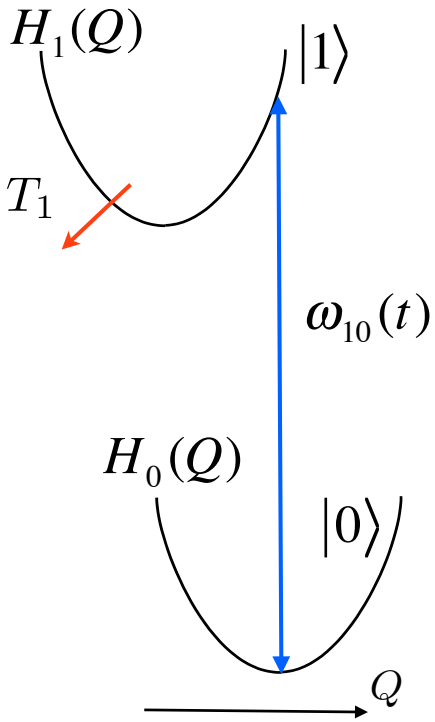
- IR absorption spectrum

$$\sigma(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, \exp\{i(\omega - \langle\omega_{10}\rangle)t - t/2T_1\}\, J(t)$$

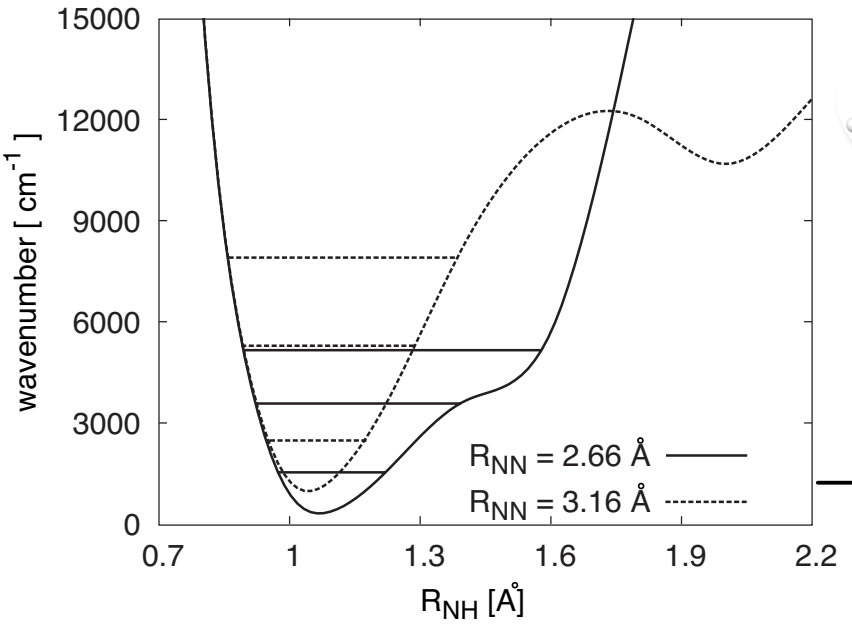
- phenomenological decay (non-adiabatic transitions)
- cumulant approximation

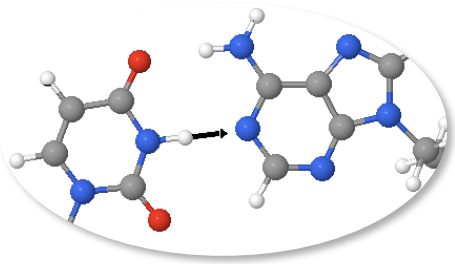
$$J(t) \simeq \exp\{-g_{10}(t)\}$$

$$g_{10}(t) \equiv \int_0^t d\tau \int_0^\tau d\tau' \,\langle \delta\omega_{10}(\tau')\delta\omega_{10}(0)\rangle_{\mathrm{eq}}$$



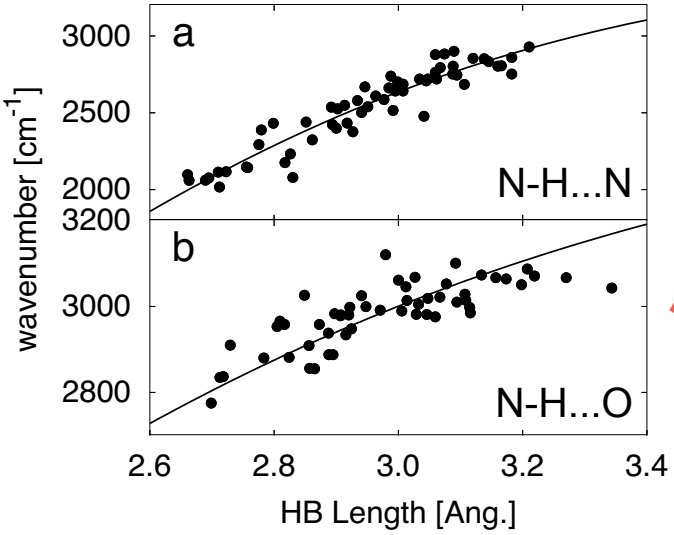
On-The-Fly Potentials

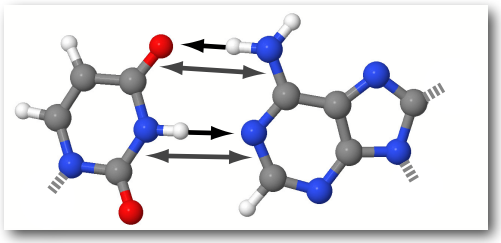


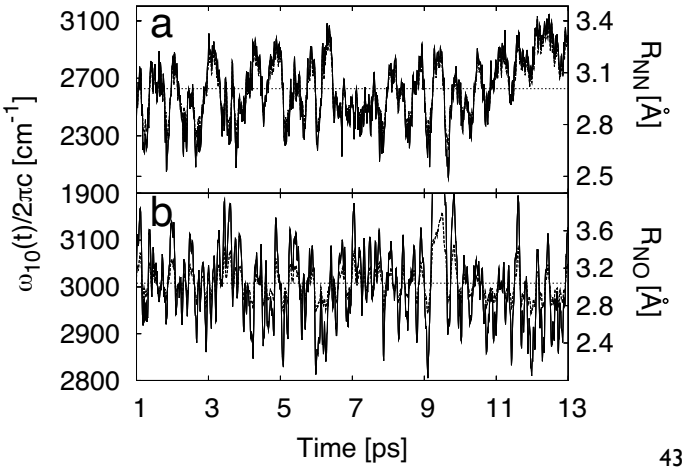


excitation frequencies
transition dipole moments

On-the-Fly Correlations







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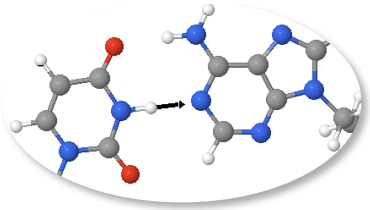
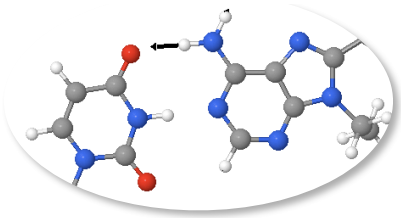


IR Spectrum



N-H...N

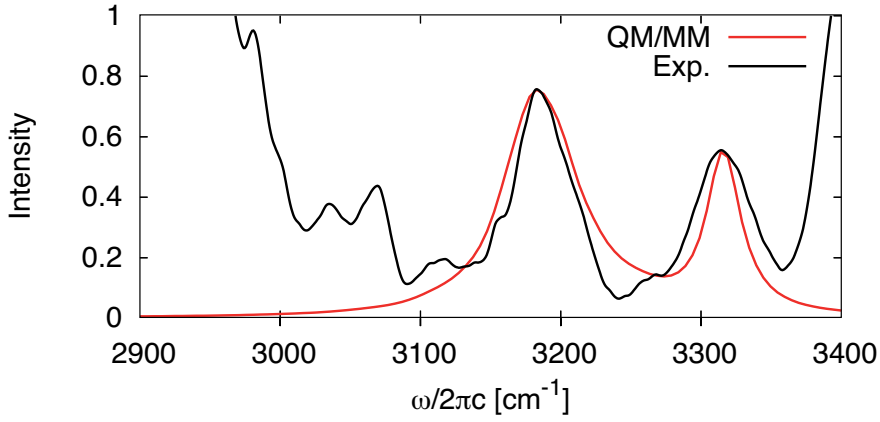
$\Gamma_{FWHM} = 56\ (36)\,cm^{-1}$

$\Gamma^{exp}_{FWHM} = 53\,cm^{-1}$

N-H...O

$\Gamma_{FWHM} = 27\ (23)\,cm^{-1}$

$\Gamma^{exp}_{FWHM} = 41\,cm^{-1}$



Y. Yan, O.K., PCCP (2010)

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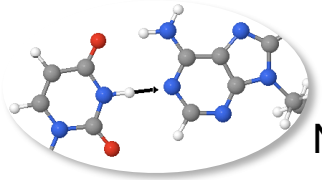
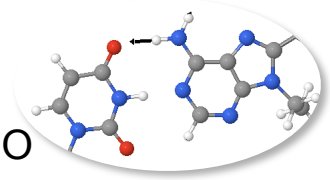
2nd Order Cumulant Approximation

- quantum-classical approximation

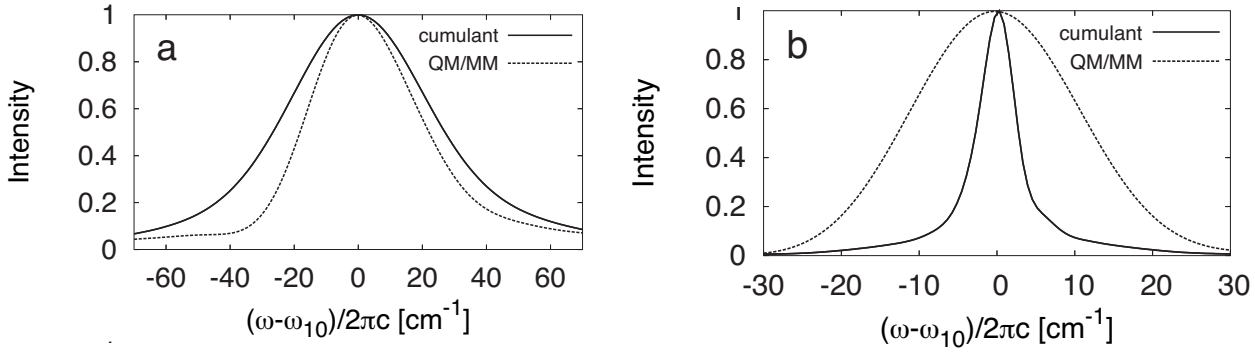


$$J(t) = \left\langle \exp\left[i \int_0^t d\tau\, \delta\omega_{10}(\tau) \right] \right\rangle_{\mathrm{eq}}$$

N-H...N



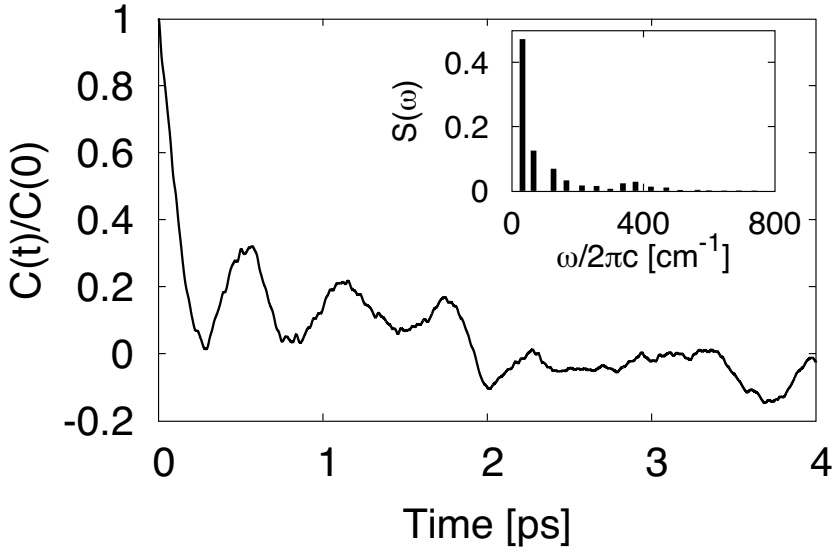
N-H...O



- non-Gaussian statistics of fluctuations for N-H...O hydrogen bond

Gap-Autocorrelation N-H...N

$$C(t) = \sum_j S_j \omega_j^2 [\coth(\hbar\omega_j/2kT)\cos\omega_j t + i \sin\omega_j t]$$



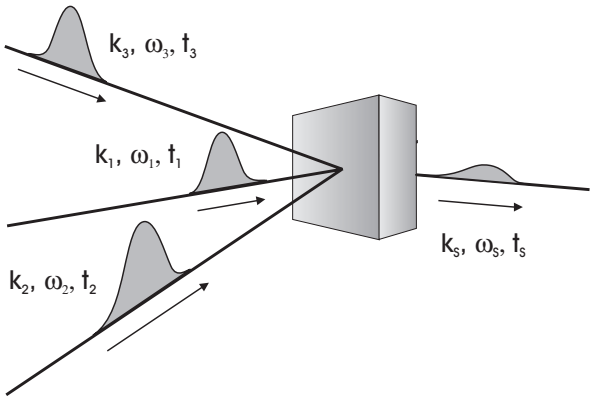
- reconstruction of spectral density

Nonlinear Spectroscopy of Base Pairs

- open questions
  - role of population relaxation $\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$

pump-probe spectroscopy:

$\mathbf{k}_1 = \mathbf{k}_2 = \mathrm{k}_{\mathrm{pump}} \quad \mathbf{k}_s = \mathbf{k}_3 = \mathbf{k}_{\mathrm{probe}}$



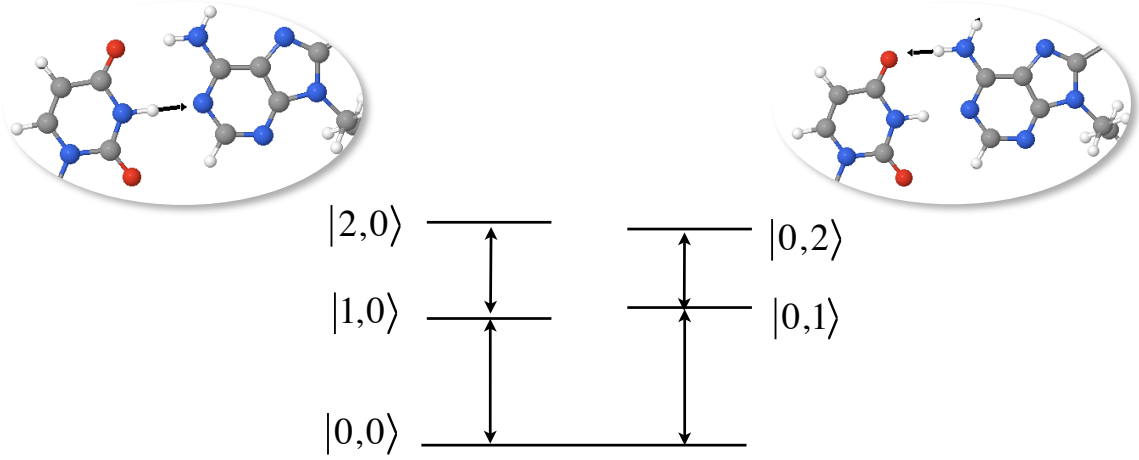
  - correlated motion

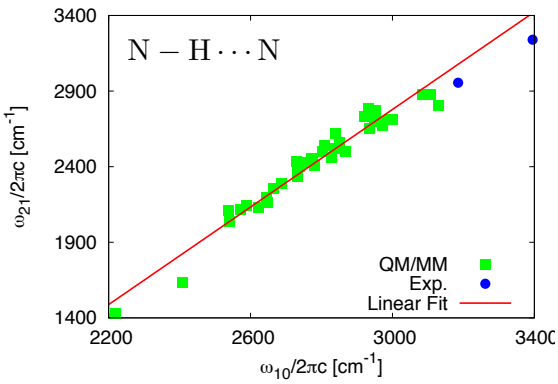
2D spectroscopy:

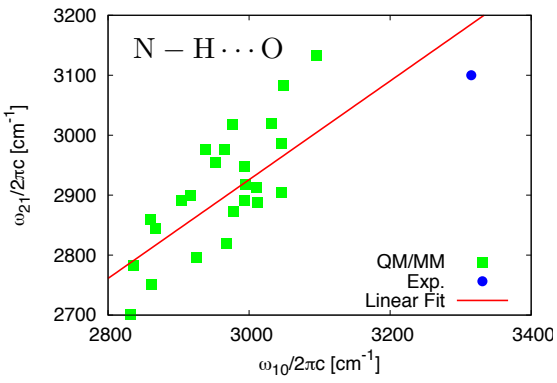
$\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$

$\longrightarrow$ model for excited state absorption needed

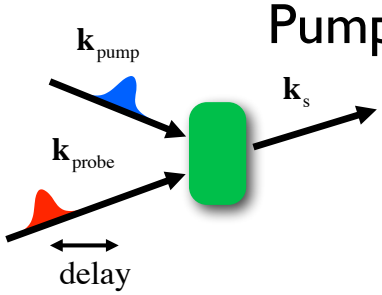
Overtone Excitations

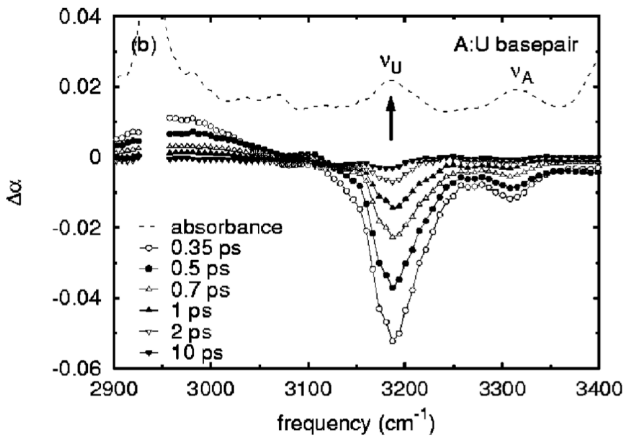


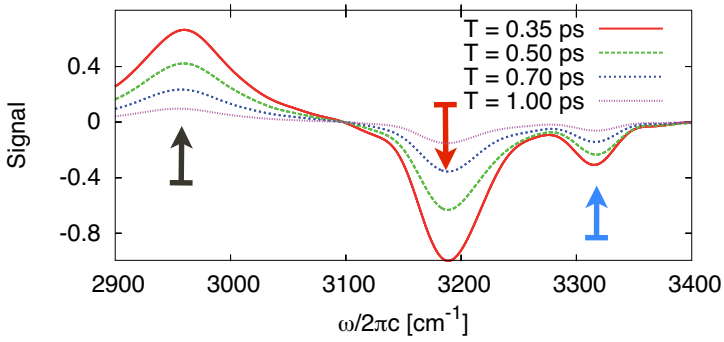


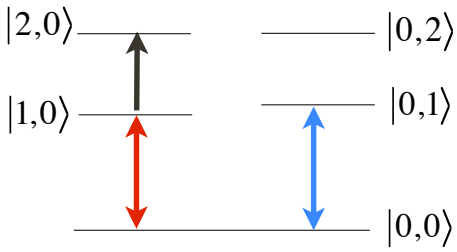


Pump-Probe Spectroscopy





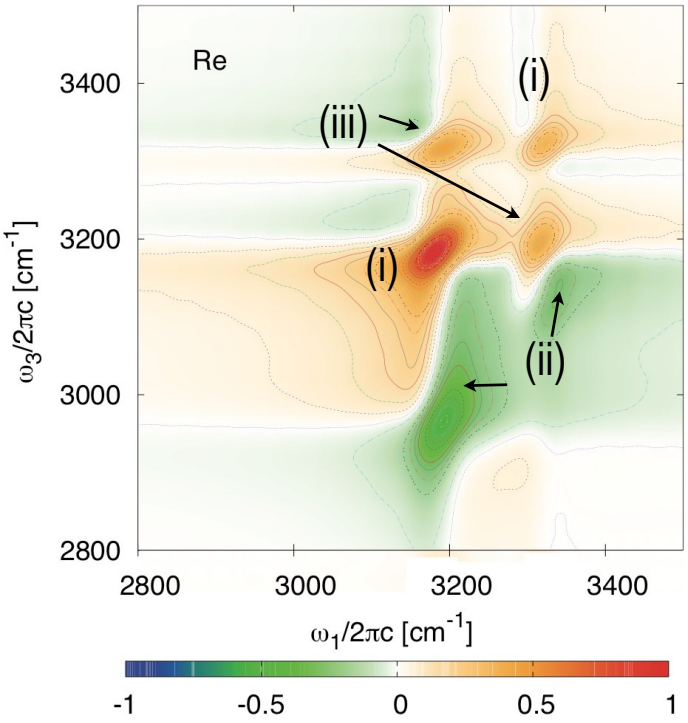




$T_1^{(\mathrm{NHN})} = 340$ fs $\quad T_1^{(\mathrm{NHO})} = 430$ fs

S. Woutersen et al., JCP 121, 5381 (2004) Y. Yan, O.K., JPCB 111, 5254 (2011)

2D IR Spectroscopy

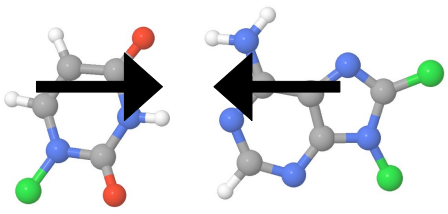


(i) ground state bleaching/ stimulated emission

(ii) excited state absorption

(iii) cross peak absorption

- correlated dynamics



Y. Yan, O.K., JPCB 111, 5254 (2011)