

*Ab initio Molecular Dynamics Studies of
Anomalous Proton Transport Mechanisms
in Various Hydrogen-bonded Media*

Mark E. Tuckerman

Dept. of Chemistry

and Courant Institute of Mathematical Sciences

New York University, 100 Washington Sq. East

New York, NY 10003

Talk Outline

Proton transport in ammonium perchlorate crystal

Proton transport in water and acidic solutions

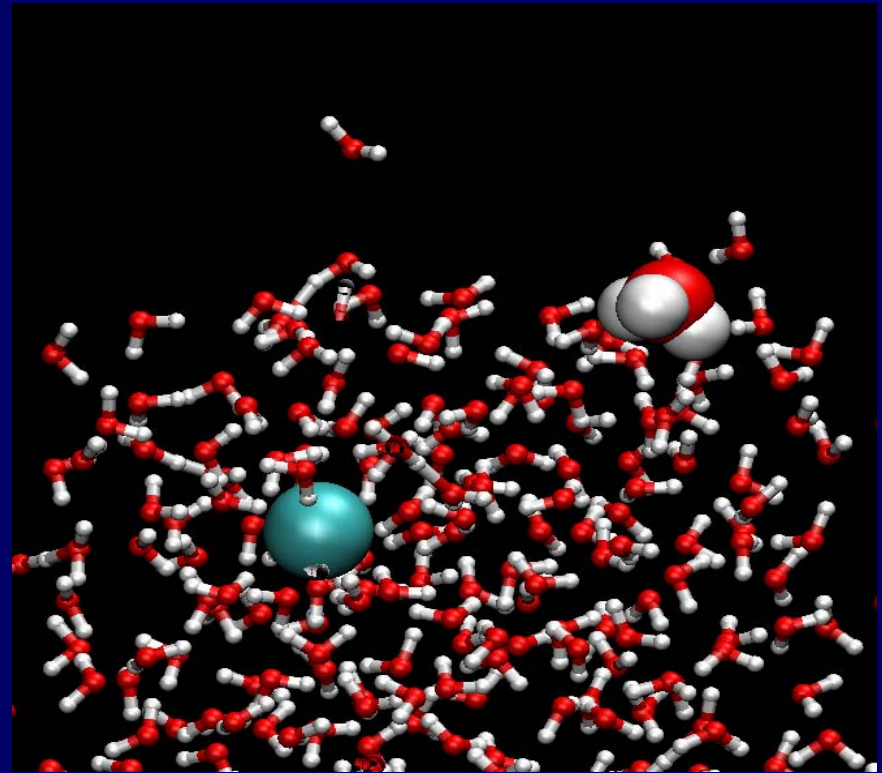
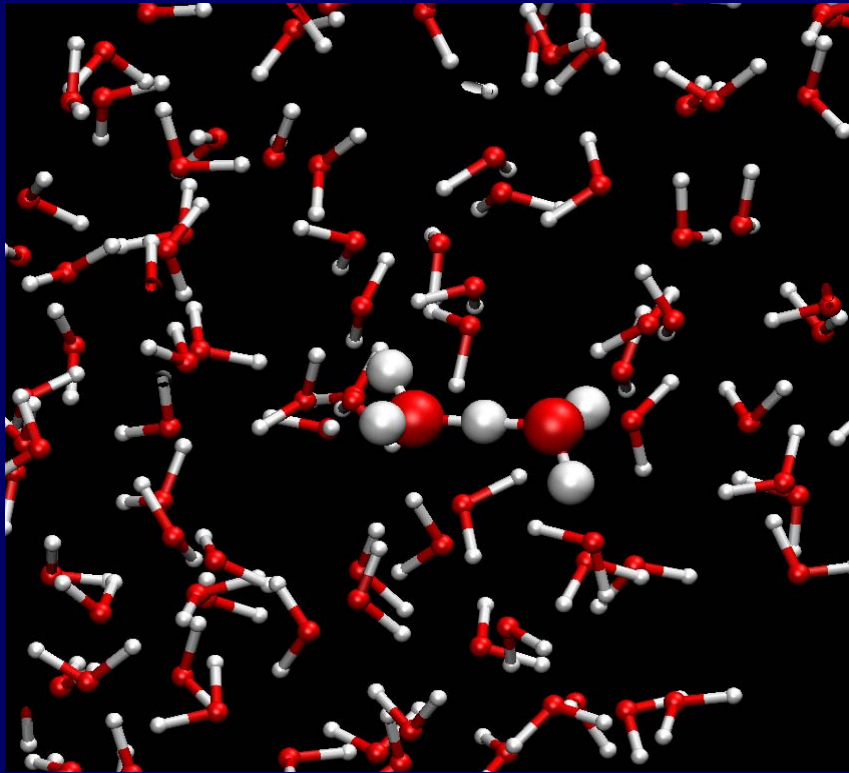
Proton transport in liquid methanol

Proton transport in methanol/water mixtures

SEE POSTER:

Proton transfer in water and at the liquid-vapor interface: a combined *ab initio* and polarizable multi-state EVB molecular dynamics approach

G. Brancato, H. -S. Lee and MET



Ab initio molecular dynamics

R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

Given a system of N nuclei with positions

$$\mathbf{R}_1, \dots, \mathbf{R}_N \equiv \mathbf{R}$$

Classical evolution:

$$\begin{aligned} M_I \ddot{\mathbf{R}}_I &= \mathbf{F}_I(\mathbf{R}) \\ &= -\langle \Psi_0(\mathbf{R}) | \nabla_I H_{\text{elec}}(\mathbf{R}) | \Psi_0(\mathbf{R}) \rangle - \nabla_I U(\mathbf{R}) \end{aligned}$$

Kohn-Sham Density Functional Theory:

$$\begin{aligned} E[\{\psi_i\}, \{\mathbf{R}\}] &= -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &+ E_{\text{xc}}[n] + \sum_{I=1}^N \int d\mathbf{r} n(\mathbf{r}) V_{\text{ext}}(|\mathbf{r} - \mathbf{R}_I|) + U(\mathbf{R}) \end{aligned}$$

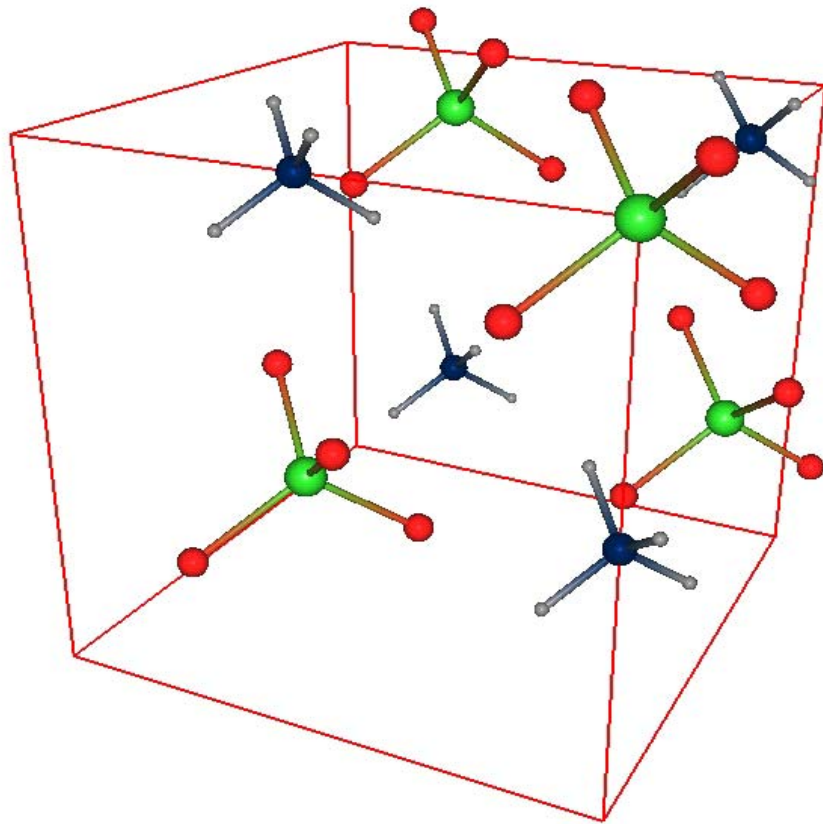
$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

Car-Parrinello dynamics:

$$\begin{aligned} \mu |\ddot{\psi}_i\rangle &= -\frac{\partial E}{\partial \langle \psi_i |} + \sum_{i,j} \Lambda_{ij} |\psi_j\rangle \\ M_I \ddot{\mathbf{R}}_I &= -\nabla_I E \end{aligned}$$

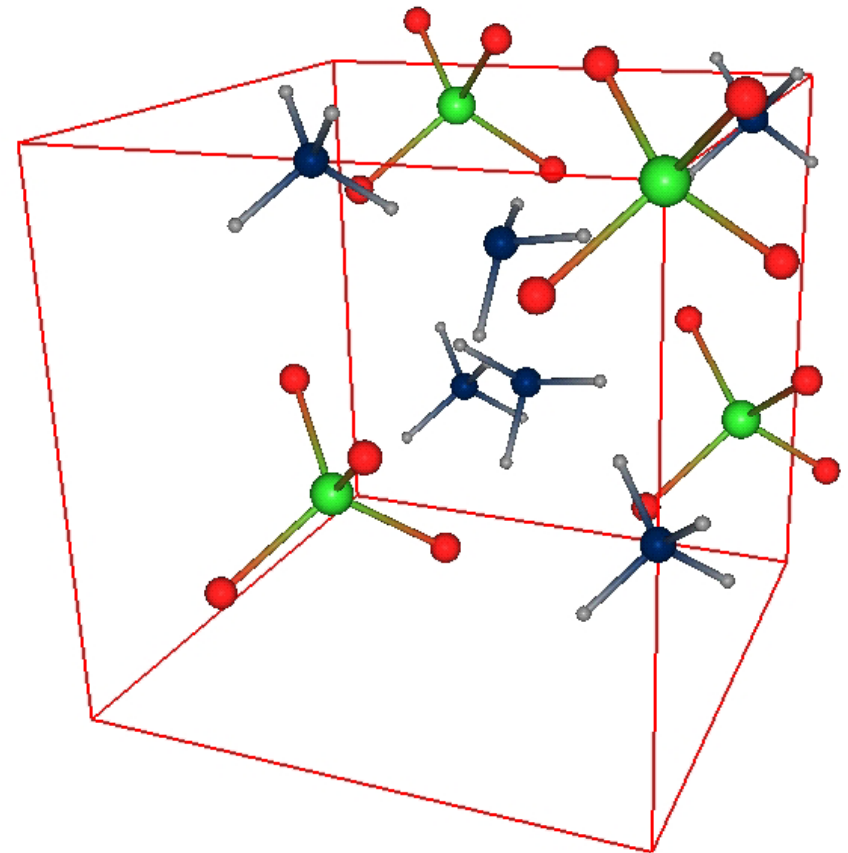
Ammonium perchlorate crystal

- Thermally labile materials used as an oxidizer in rocket fuels.
- Undergoes an orthorhombic \rightarrow cubic structural phase transition at $T = 513$ K.
- In the cubic phase, experiments find proton conductivity increases by factor of 5 upon doping with neutral ammonia.
- Thought that rotational dynamics of the ions plays a role in the conduction mechanism.



Pure Cubic AP Crystal

Cubic AP crystal + ammonia



Simulation specifics

L. Rosso and MET, *Solid State Ionics* **161**, 219 (2003)

- **Temperature:** Orthorhombic 300 K, Cubic 530 K
- **Cubic:** 15.26 x 15.26 x 7.63 Å
- **Ortho:** 9.2 x 11.6 x 7.63 Å
- **Simulation Lengths:** Pure: 15 ps, Doped 30 ps
- **BLYP functional**
- **Martins-Troullier pseudopotentials**

Calculation of infrared spectrum

Infrared spectrum from autocorrelation function of total dipole moment in the harmonic approximation:

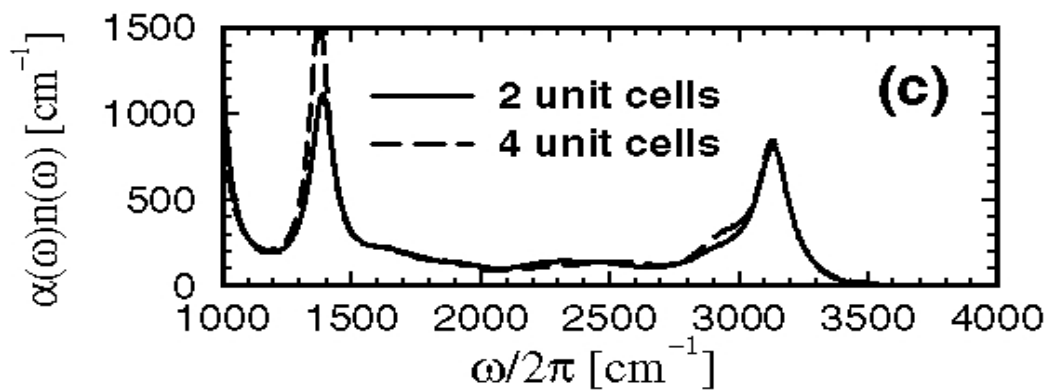
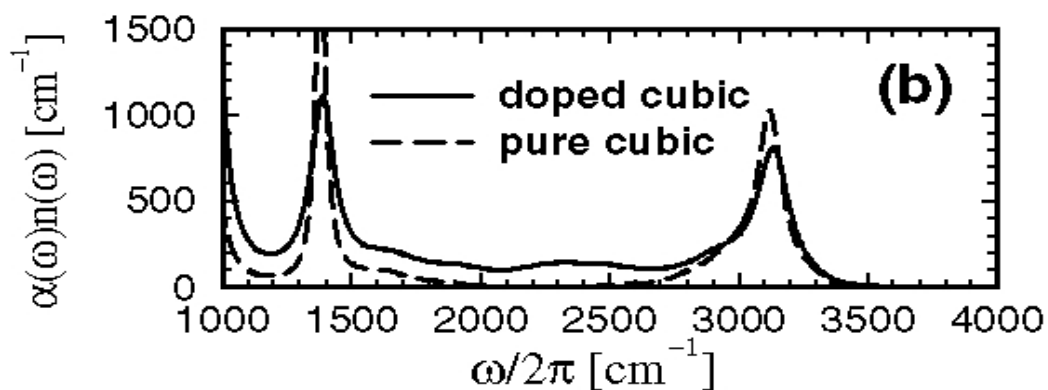
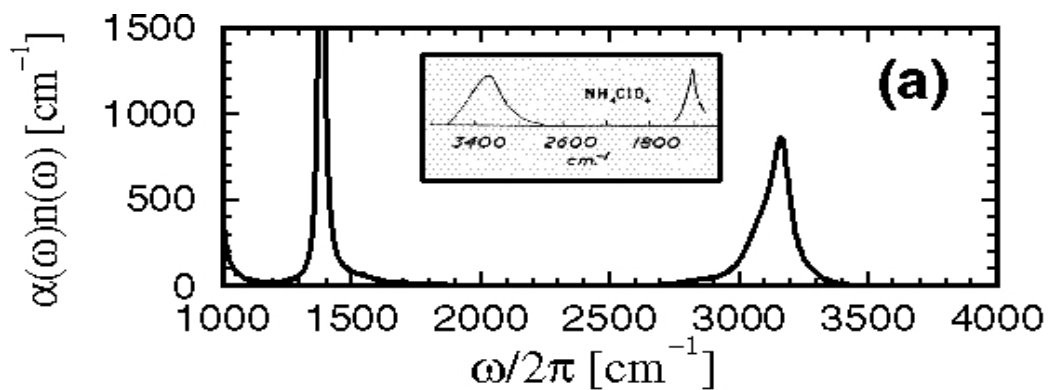
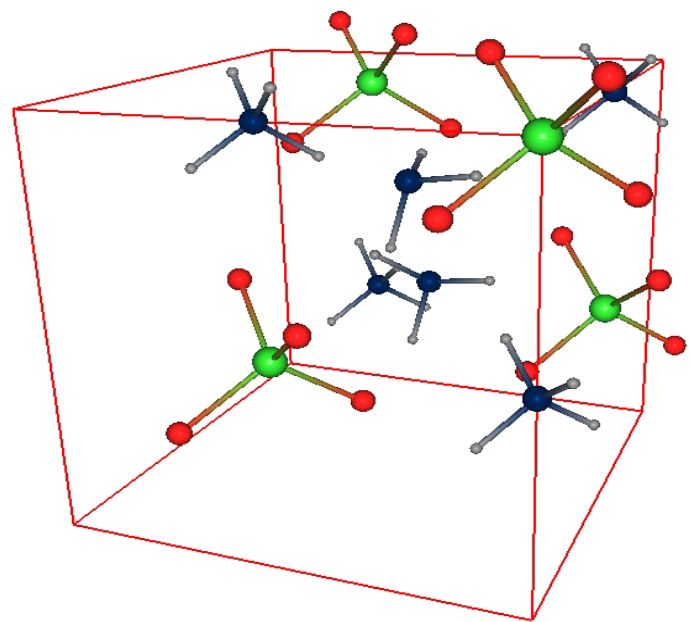
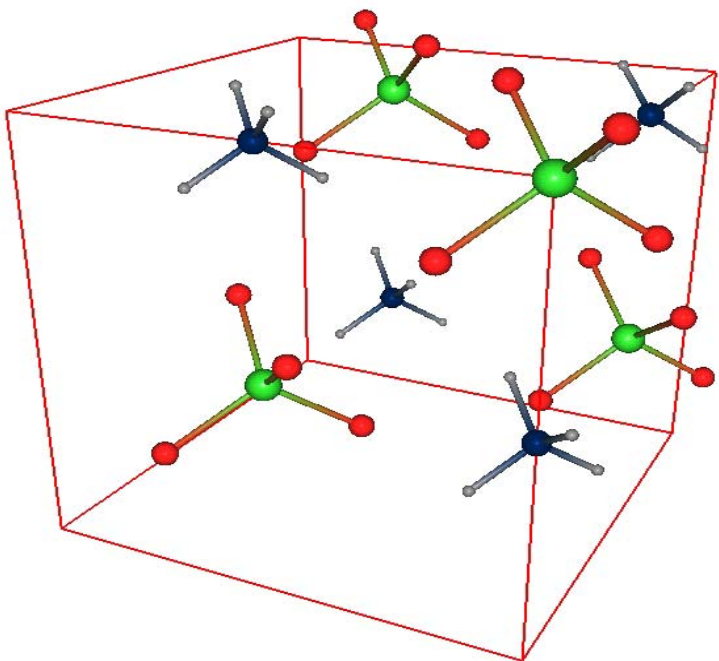
$$\begin{aligned}\alpha(\omega) &= \frac{4\pi\beta\omega^2}{3\hbar n(\omega)cV\epsilon_0} \int d\omega e^{-i\omega t} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle_{cl} \\ &= \frac{4\pi\beta}{3\hbar n(\omega)cV\epsilon_0} \int d\omega e^{-i\omega t} \langle \dot{\mathbf{M}}(0) \cdot \dot{\mathbf{M}}(t) \rangle_{cl}\end{aligned}$$

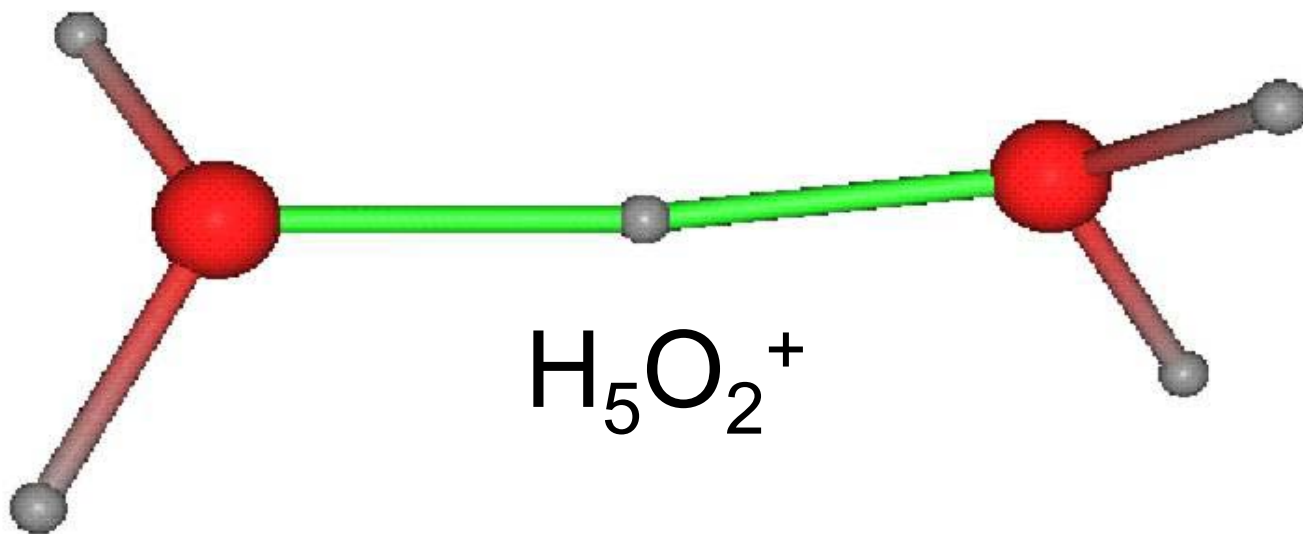
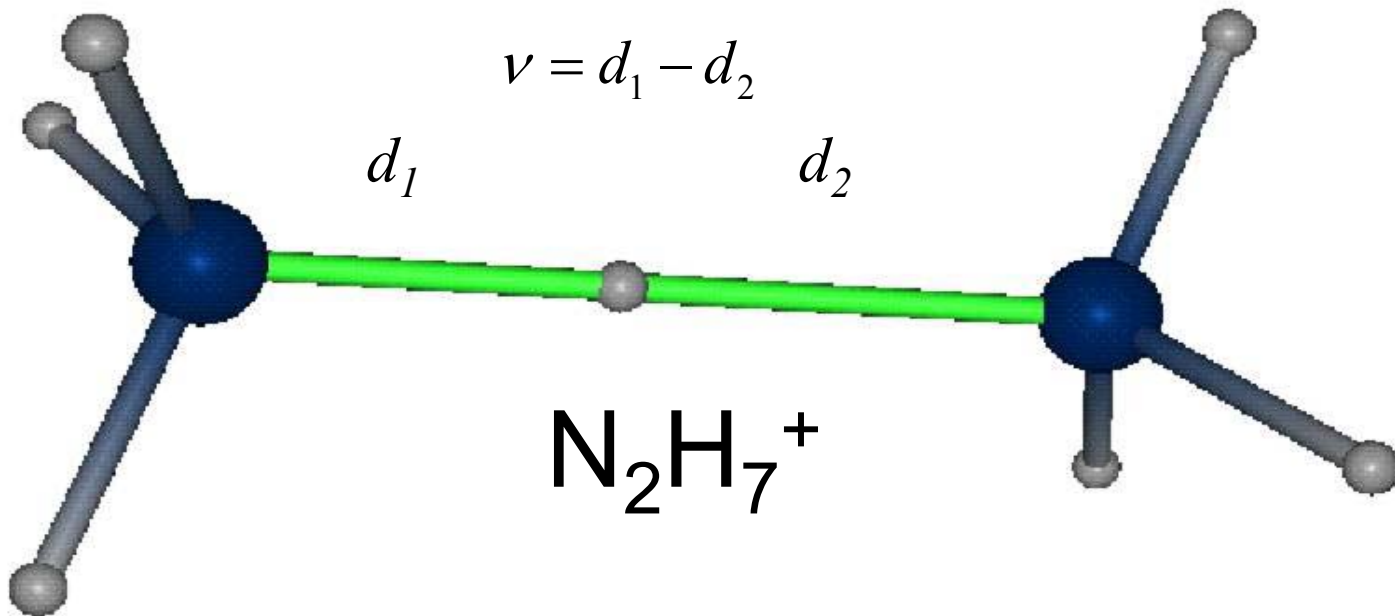
Total electronic position operator: $\mathbf{r} = \sum_i \mathbf{r}_i$

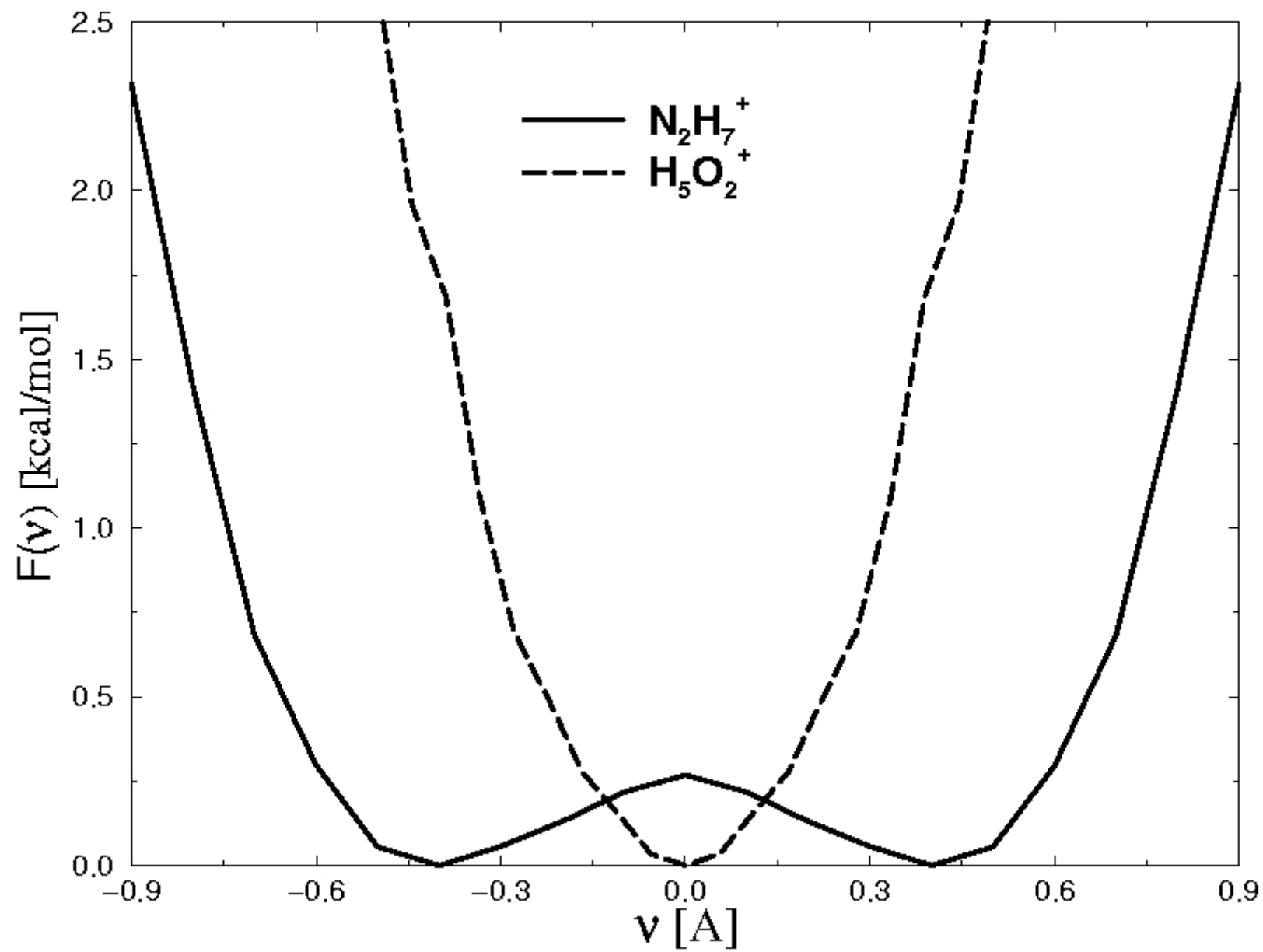
Electronic contribution: [R. Resta, *Phys. Rev. Lett.* **80**, 1800 (1998)]

$$M_{\alpha}^{(\text{elec})} = \frac{eL}{2\pi} \text{Im} \ln \det R_{\alpha} e^{-2\pi i r_{\alpha} / L} \Psi_0(\tau)$$

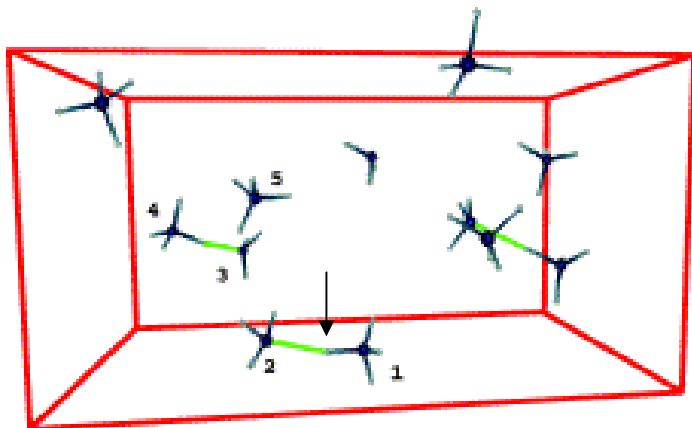
$$R_{\alpha,ij} = \langle \psi_i | e^{-2\pi i r_{\alpha} / L} | \psi_j \rangle$$



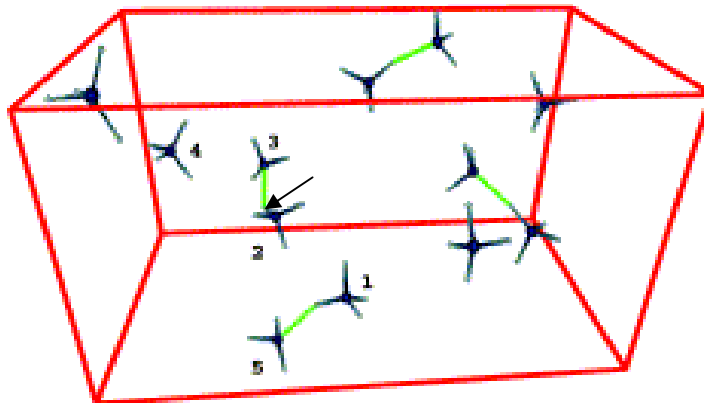




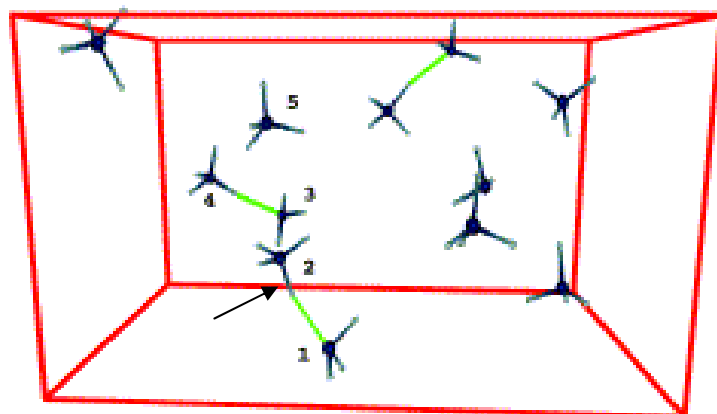
(a)



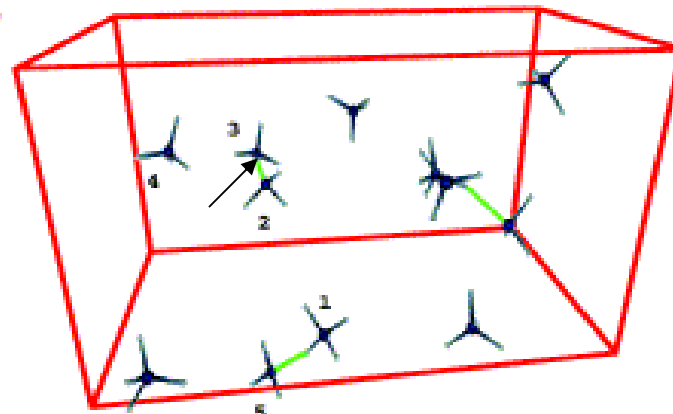
(d)



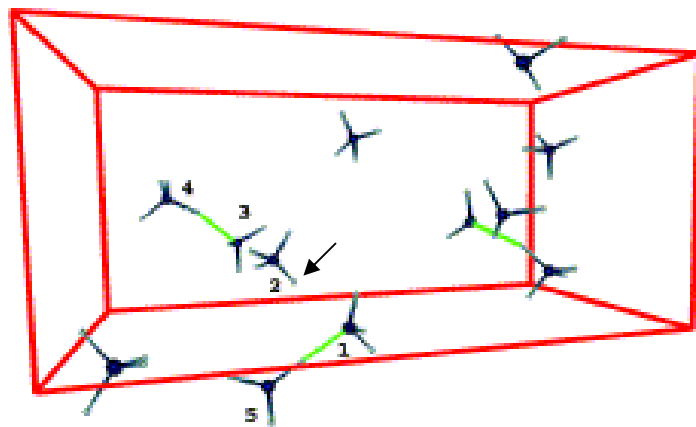
(b)



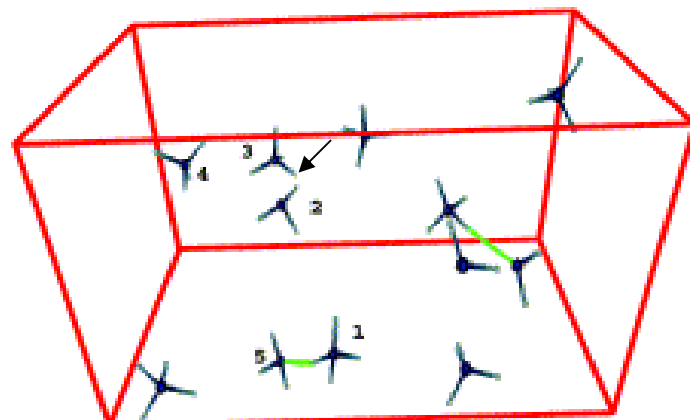
(e)

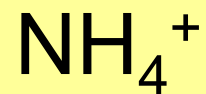
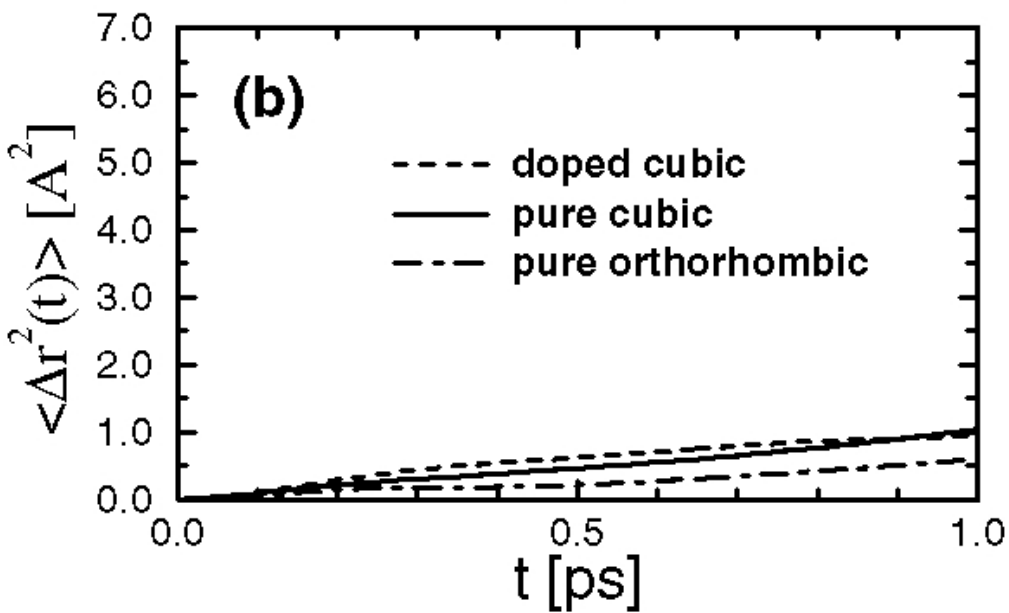
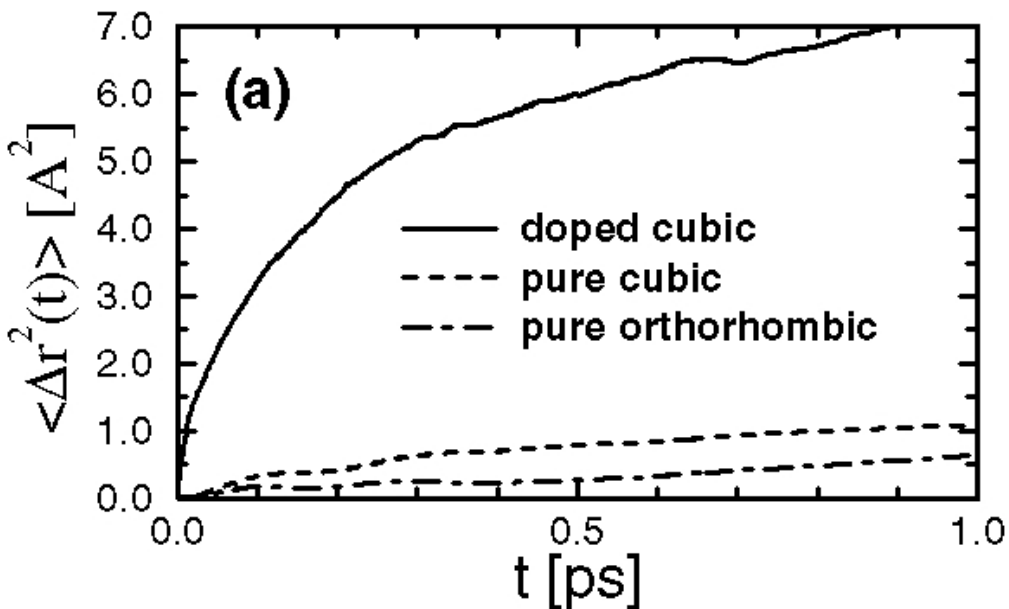


(c)



(f)





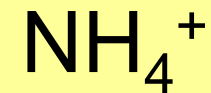
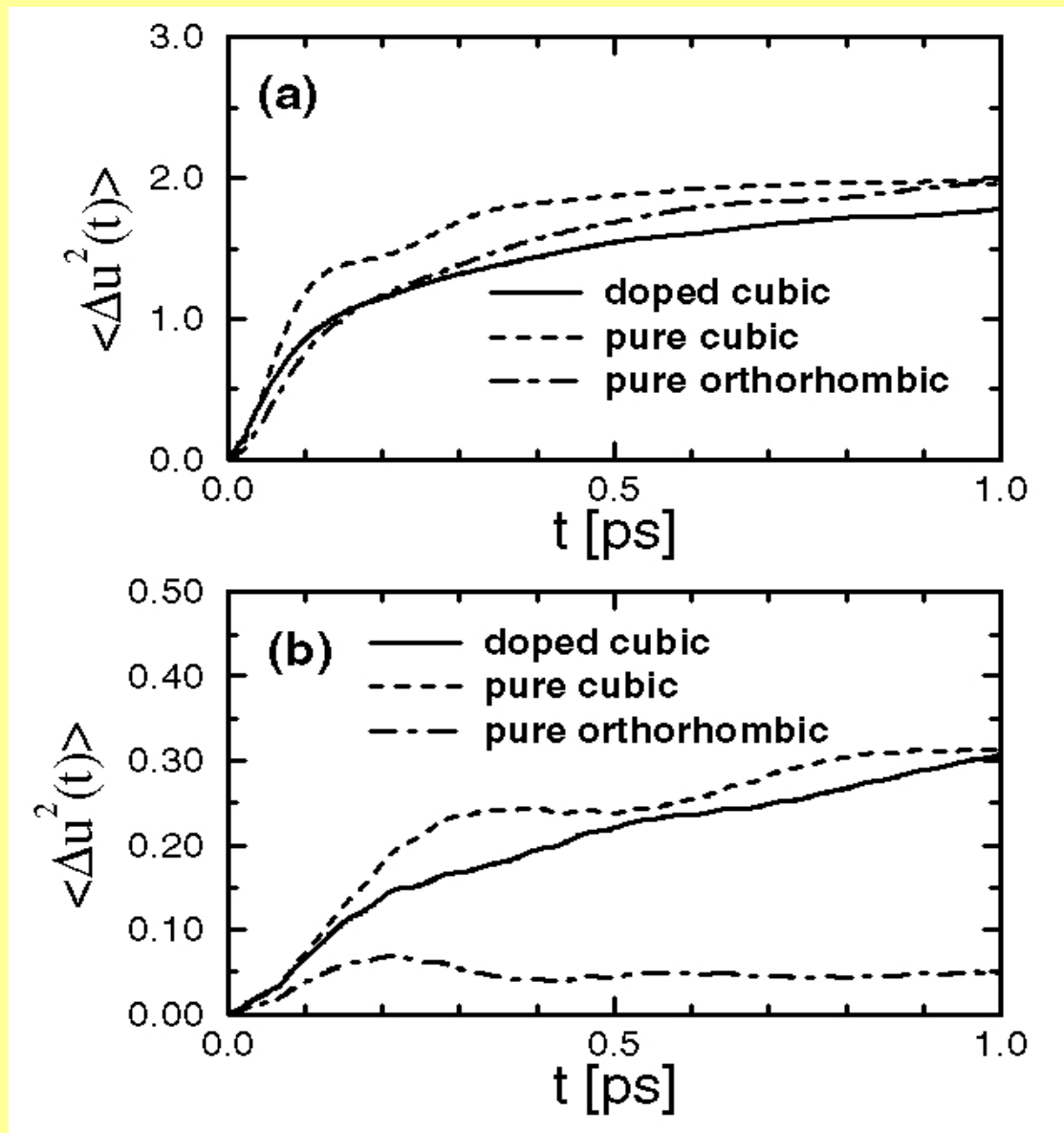
$$D(\text{doped})/D(\text{pure})=4.9$$

$$\sigma(\text{doped})/\sigma(\text{pure})=4.5$$

H. Wise, JPC 71, 2843 (1967)

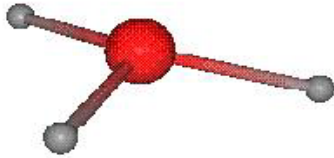


Rotational mean-square displacements

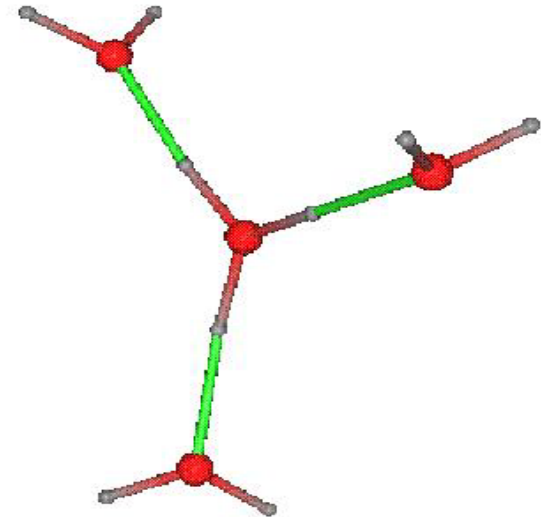


Structures of the excess proton in water

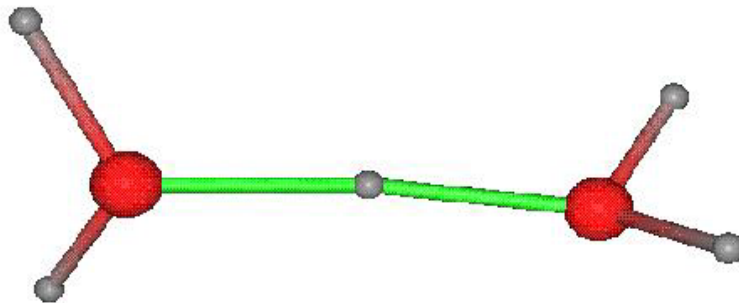
Hydronium ion:



Eigen cation:



Zundel cation:



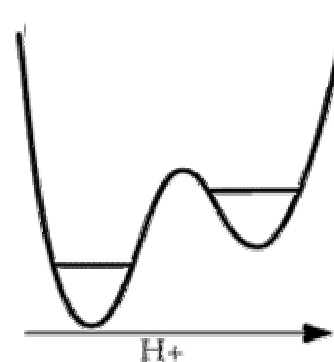
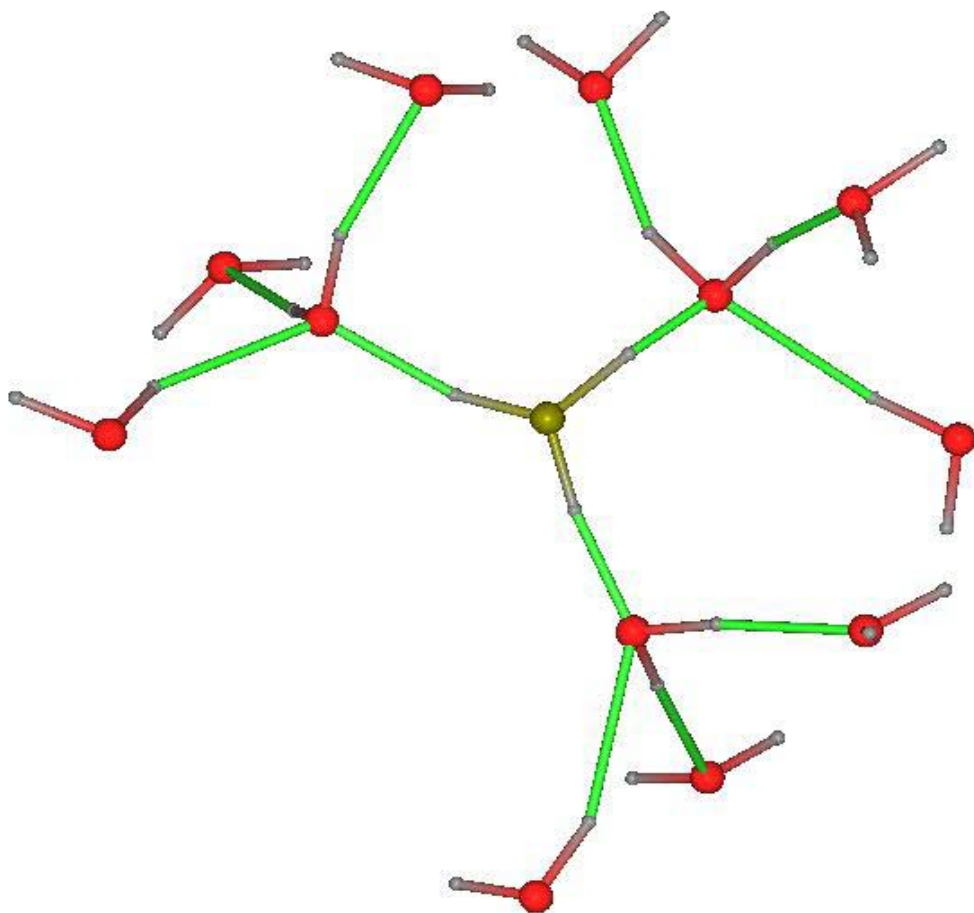
The Grotthuss mechanism in water

MET, *et al.*, JPC, **99**, 5749 (1995); JCP **103**, 150 (1995)

D. Marx, MET, M. Parrinello, *Nature* **397**, 601 (1999).

N. Agmon, *Chem. Phys. Lett.* **244**, 456 (1995)

T. J. F. Day, *et al.* *J. Am. Chem. Soc.* **122**, 12027 (2000)



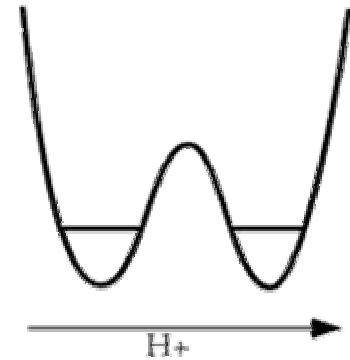
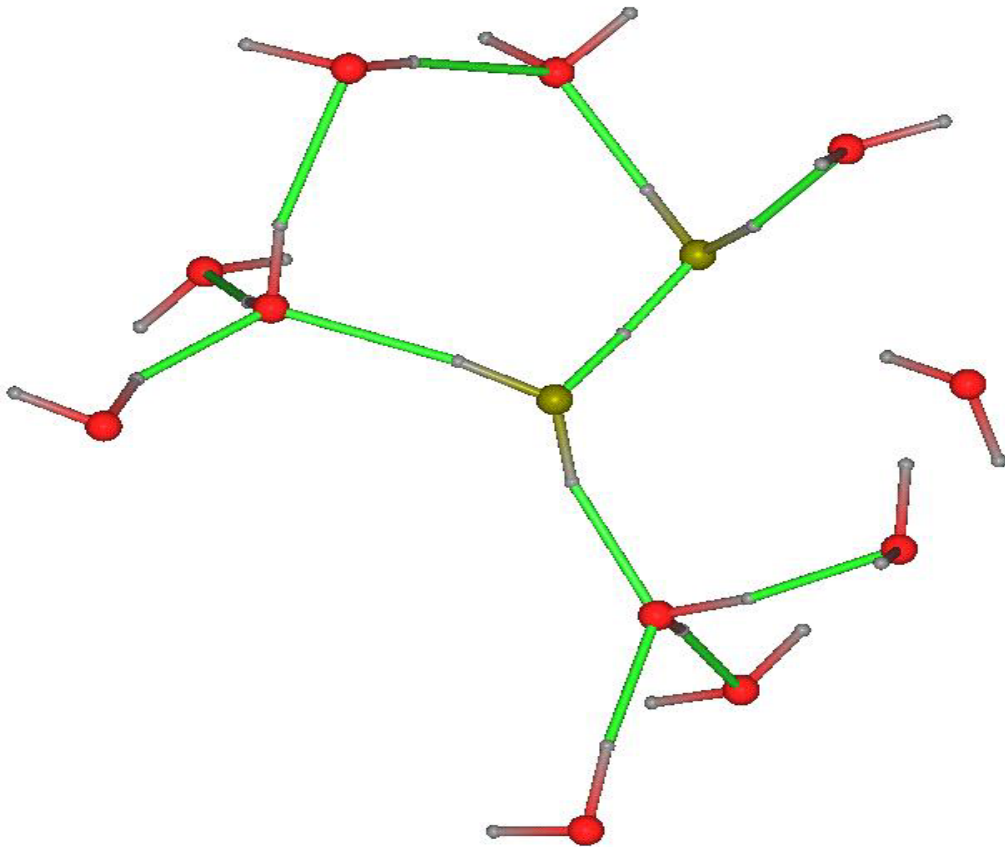
Solvent coordinate view:

P. M. Kiefer, J. T. Hynes

J. Phys. Chem. A **108**, 11793 (2004)

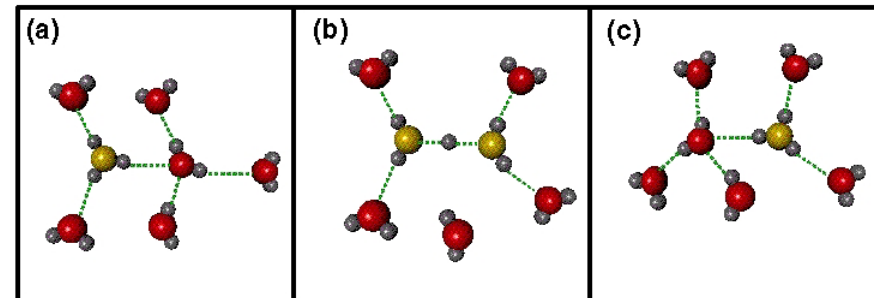
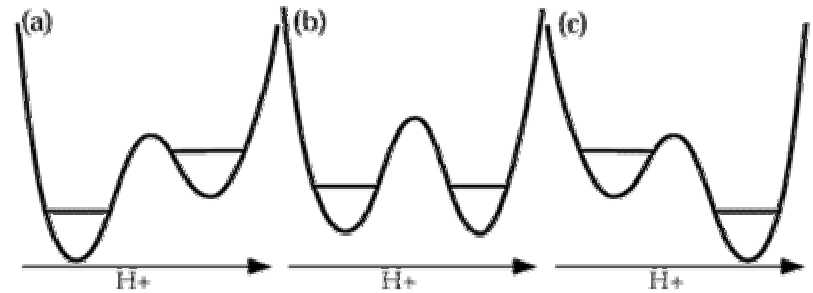
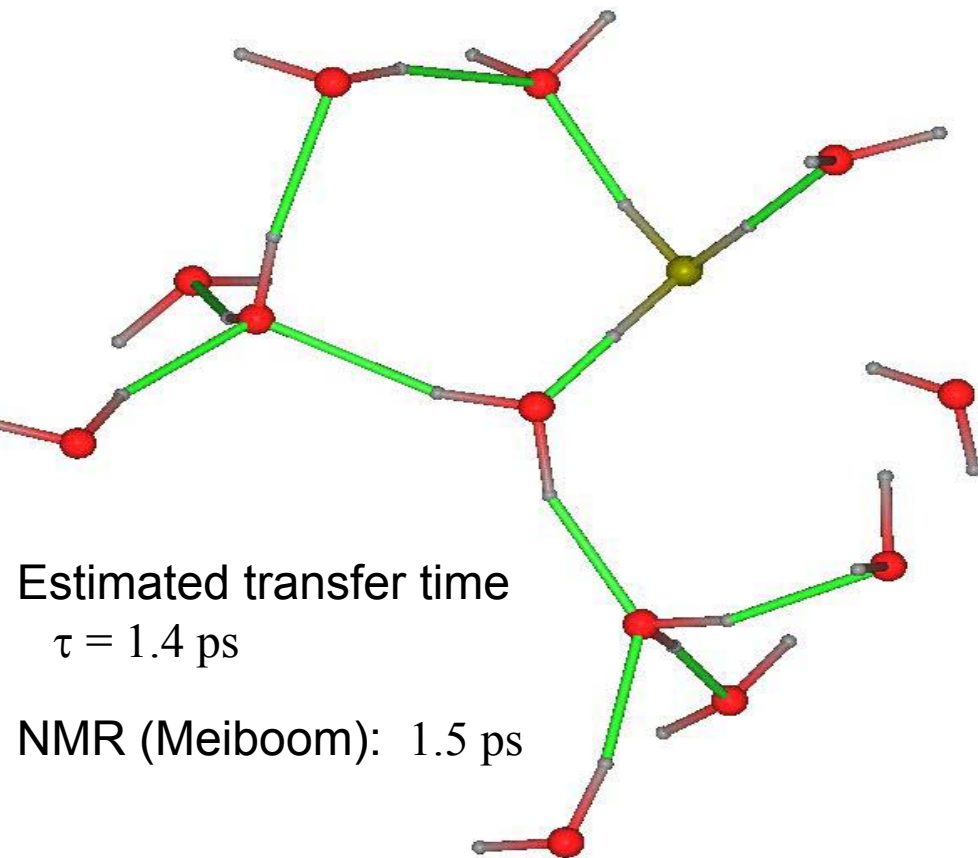
The Grotthuss mechanism in water

Second solvation shell H-bond breaking followed by formation of intermediate Zundel complex:



The Grotthuss mechanism in water

Transfer of proton resulting in ``diffusion'' of solvation structure:



Decomposition of the dipole moment

R. Iftimie and MET, *J. Chem. Phys.* (in press)

Dipole moment:

$$M_{\alpha}^{(\text{elec})} = \frac{eL}{2\pi} \text{Im} \ln \det \mathbf{R}_{\alpha}$$

If \mathbf{R} is diagonal with eigenvalues \mathbf{r} :

$$\mathbf{M} = \sum_i \boldsymbol{\mu}_i = \sum_m \boldsymbol{\mu}_m$$

where

$$\boldsymbol{\mu}_m = \sum_{j \in m} \left[Z_j \mathbf{R}_j - \sum_{k \in j} \mathbf{r}_k \right]$$

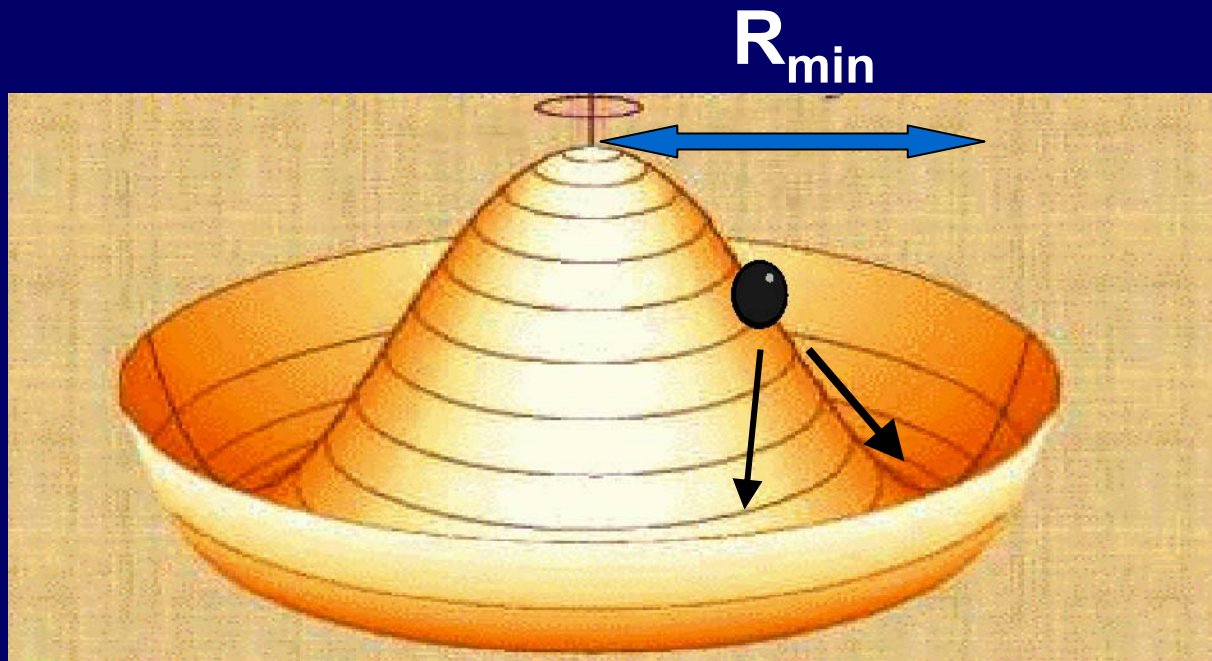
Correlation function:

$$C(t) = \left\langle \dot{\mathbf{M}}(0) \cdot \dot{\mathbf{M}}(t) \right\rangle_{cl} = \sum_m \left\langle \dot{\boldsymbol{\mu}}_m(0) \cdot \dot{\mathbf{M}}(t) \right\rangle_{cl}$$

Unitary (Gauge) Invariance and localized orbitals

Total energy invariant under static unitary transformations:

$$\tilde{\psi}_i(\mathbf{r}, t) = \sum_j U_{ij} \psi_j(\mathbf{r}, t) = \sum_j (e^{iB})_{ij} \psi_j(\mathbf{r}, t)$$



If we only care about distance from center at the potential minimum, then a point $Z = R_{min} e^{i\theta}$ is acceptable for any choice of θ

Decomposition of the dipole moment

Dipole moment determined by the matrix

$$R_{\alpha,ij} = \langle \psi_i | e^{2\pi i r_\alpha / L} | \psi_j \rangle$$

Different components do not commute with each other

$$[R_\alpha, R_\beta] \neq 0 \quad \text{if } \alpha \neq \beta$$

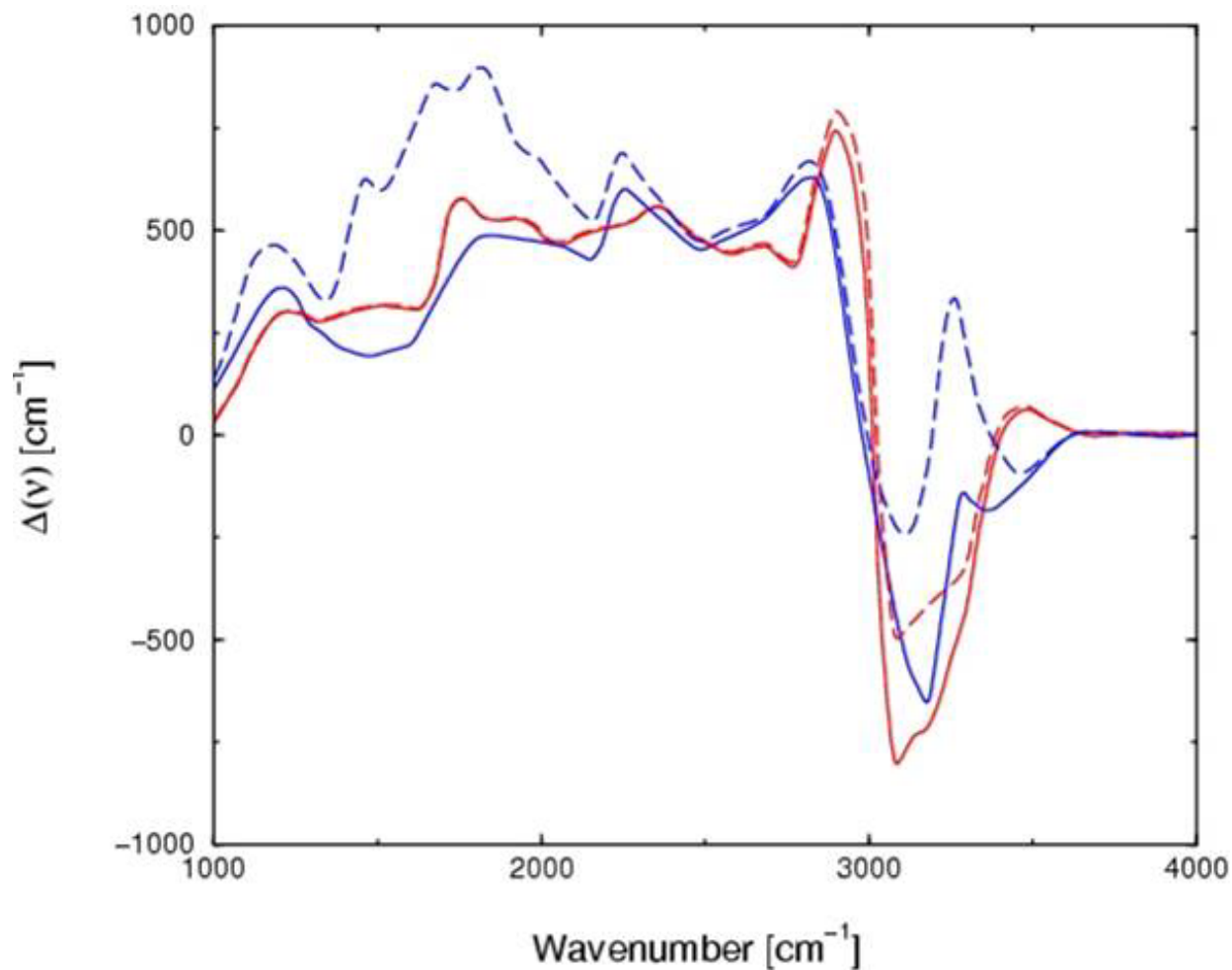
Cannot simultaneously diagonalize all three components. Define

$$\Omega[\psi] = \sum_i \left[|R_{x,ii}|^2 + |R_{y,ii}|^2 + |R_{z,ii}|^2 \right]$$

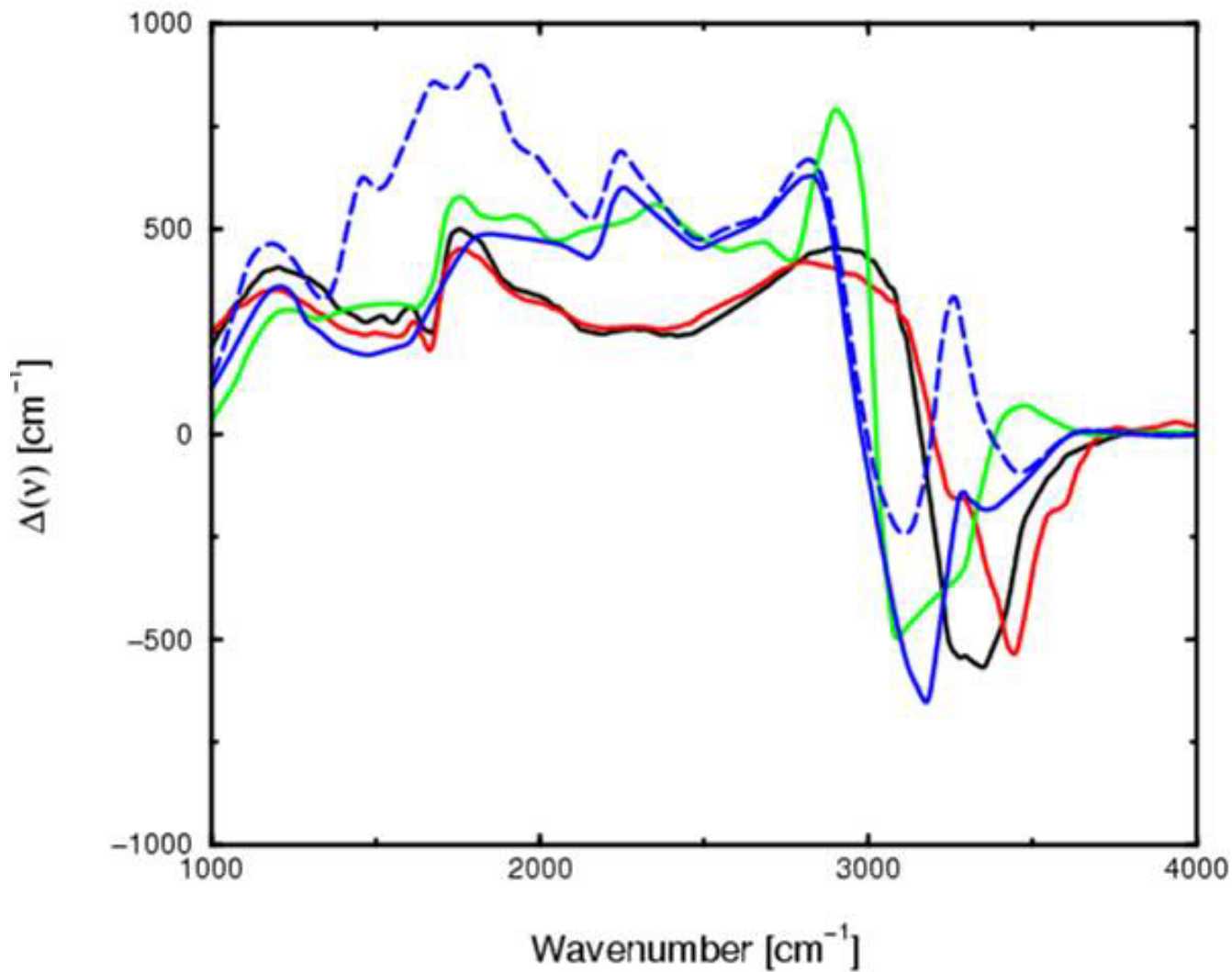
Choose U such that $\Omega[\tilde{\psi}]$ is maximal. The orbitals that result are known as Wannier functions. Because they maximize the diagonal elements of the translationally invariant position operator, their spatial spread is minimal.

DFT = BLYP, Cutoff = 80 Ry, System = 64 molecules + 1 HCl or 1 H₂F₂ time = 20 ps

— 0.9 M HCl – water – Cl- — 0.9 M H₂F₂ – water – FHF-
- - - 0.9 M HCl - water - - - 0.9 M H₂F₂ – water



- Expt. (3.6 M HBr)
- Expt. (8.8 M HBr)
- Theor. (0.9 M HCl)
- - - Theor. (0.9 M H₂F₂)
- Theor. (0.9 M H₂F₂) – FHF⁻ spectrum



Ab Initio Path Integrals

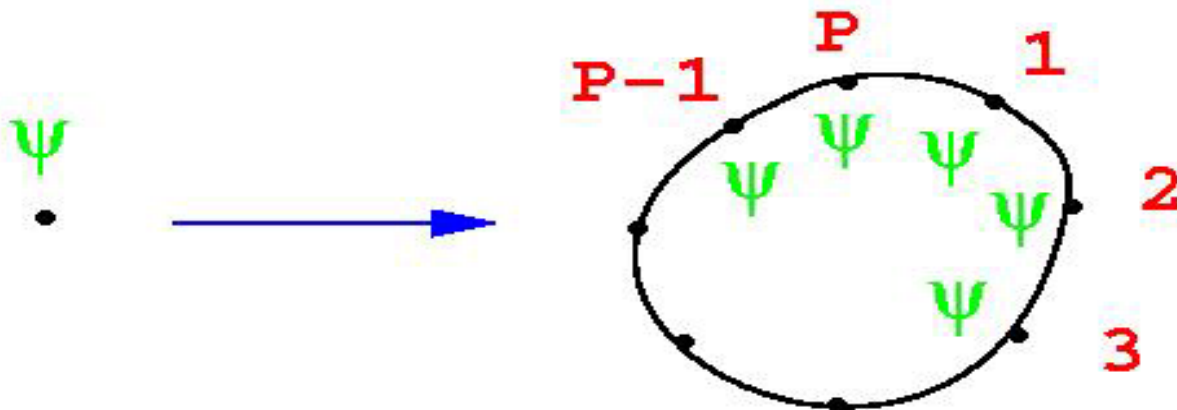
M. E. Tuckerman, *et al*, JCP **104**, 5579 (1996).

Quantum canonical partition function

$$Q = \text{Tr}(e^{-\beta H})$$
$$= \oint \mathcal{D}\mathbf{R}_1 \cdots \mathcal{D}\mathbf{R}_N \exp \left\{ - \int_0^\beta d\tau \left[\sum_{I=1}^N \frac{1}{2} M_I \dot{\mathbf{R}}_I^2(\tau) + E_0(\{\mathbf{R}_I(\tau)\}) \right] \right\}$$

Limit of discretized integral

$$Q = \lim_{P \rightarrow \infty} \left[\prod_{I=1}^N \mathcal{N} \int d\mathbf{R}_I^{(1)} \cdots d\mathbf{R}_I^{(P)} \int d\mathbf{P}_I^{(1)} \cdots d\mathbf{P}_I^{(P)} \right]$$
$$\times \exp \left\{ -\beta \sum_{s=1}^P \left[\sum_{I=1}^N \left(\frac{(\mathbf{P}_I^{(s)})^2}{2M_I'} + \frac{1}{2\beta^2} M_I P (\mathbf{R}_I^{(s)} - \mathbf{R}_I^{(s+1)})^2 \right) + \frac{1}{P} E_0(\{\mathbf{R}_I\}^{(s)}) \right] \right\}$$



Exact when:

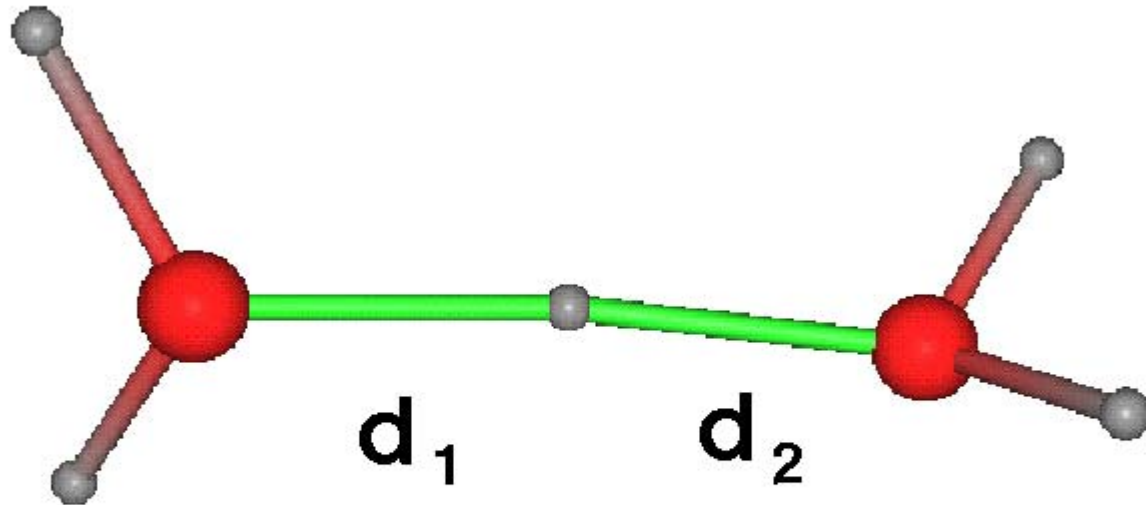
$$P \rightarrow \infty$$

Simulation specifics

Marx, MET, Hutter, Parrinello, *Nature* 397, 601 (1999).

- **Temperature:** $T = 300 \text{ K}$
- **Box:** $L = 9.87 \text{ \AA}$
- **System:** $31 \text{ H}_2\text{O} + 1 \text{ H}_3\text{O}^+$
- **Path integral discretization:** $P = 8$,
Classical: $P=1$
- **Simulation Lengths:**
 - Quantum:** 322,000 configurations (40 ps)
 - Classical (P=1):** 345,000 configurations (60 ps)

Coordinates that follow the proton

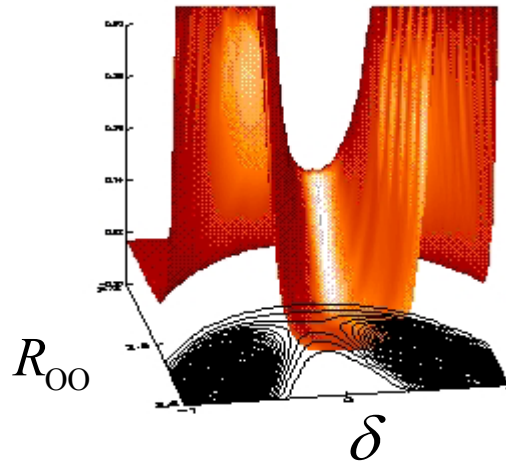


$$\delta = d_1 - d_2$$

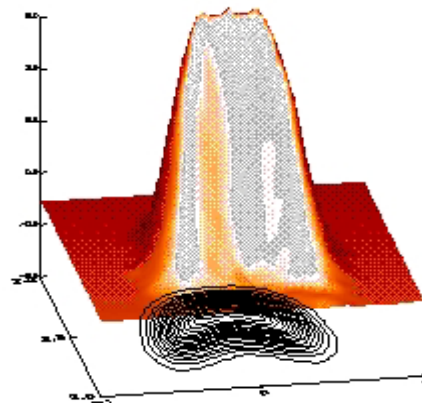
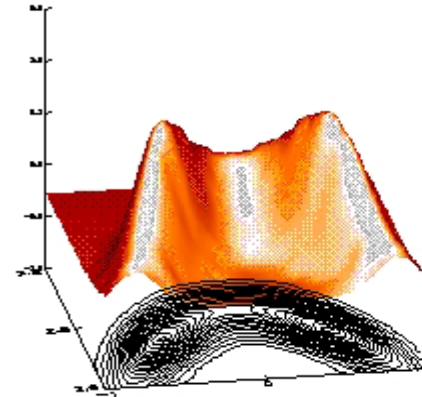
$$R_{OO} = \left| \mathbf{R}_{O_1} - \mathbf{R}_{O_2} \right|$$

Project out the Defect Site

All hydrogen bonds:

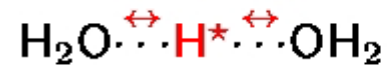


H_3O^+ hydrogen bonds:

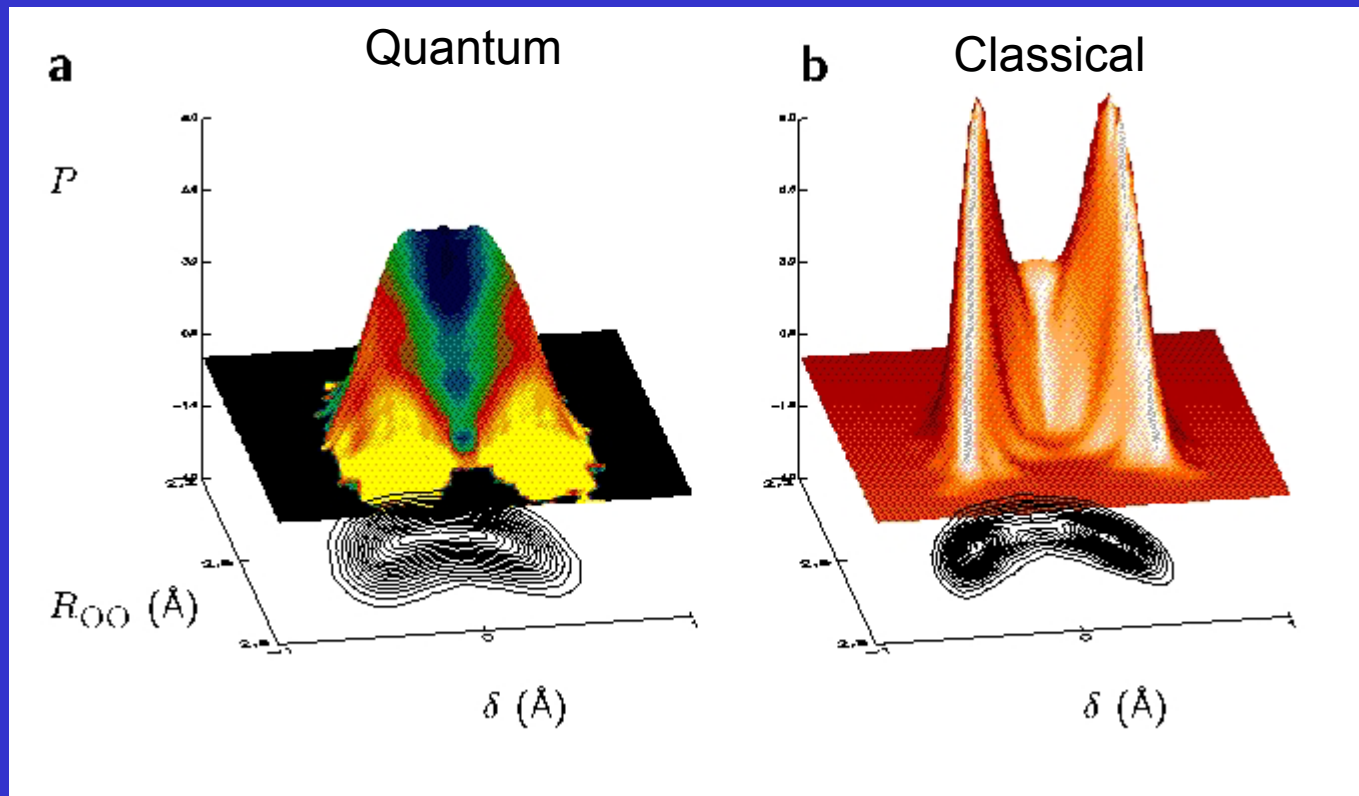


$\Leftarrow \min[\delta]$ criterion

Most active hydrogen bond:

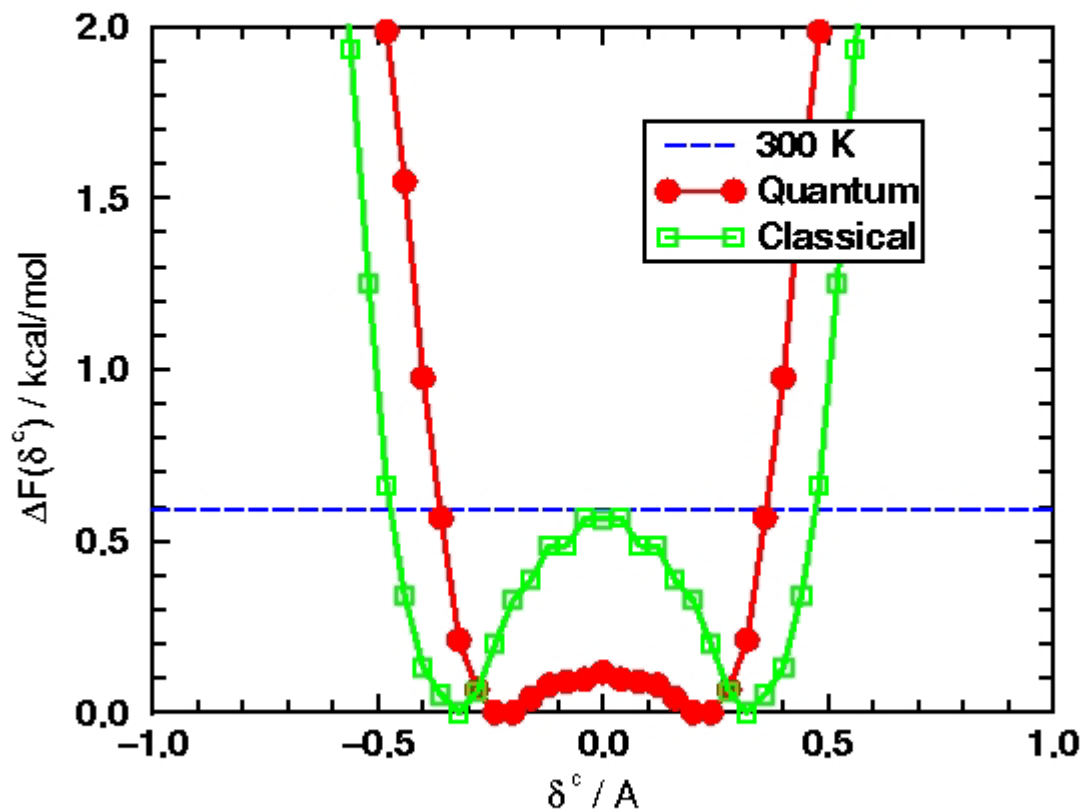


Probability distribution functions



Proton Rattling: Free Energy Profile

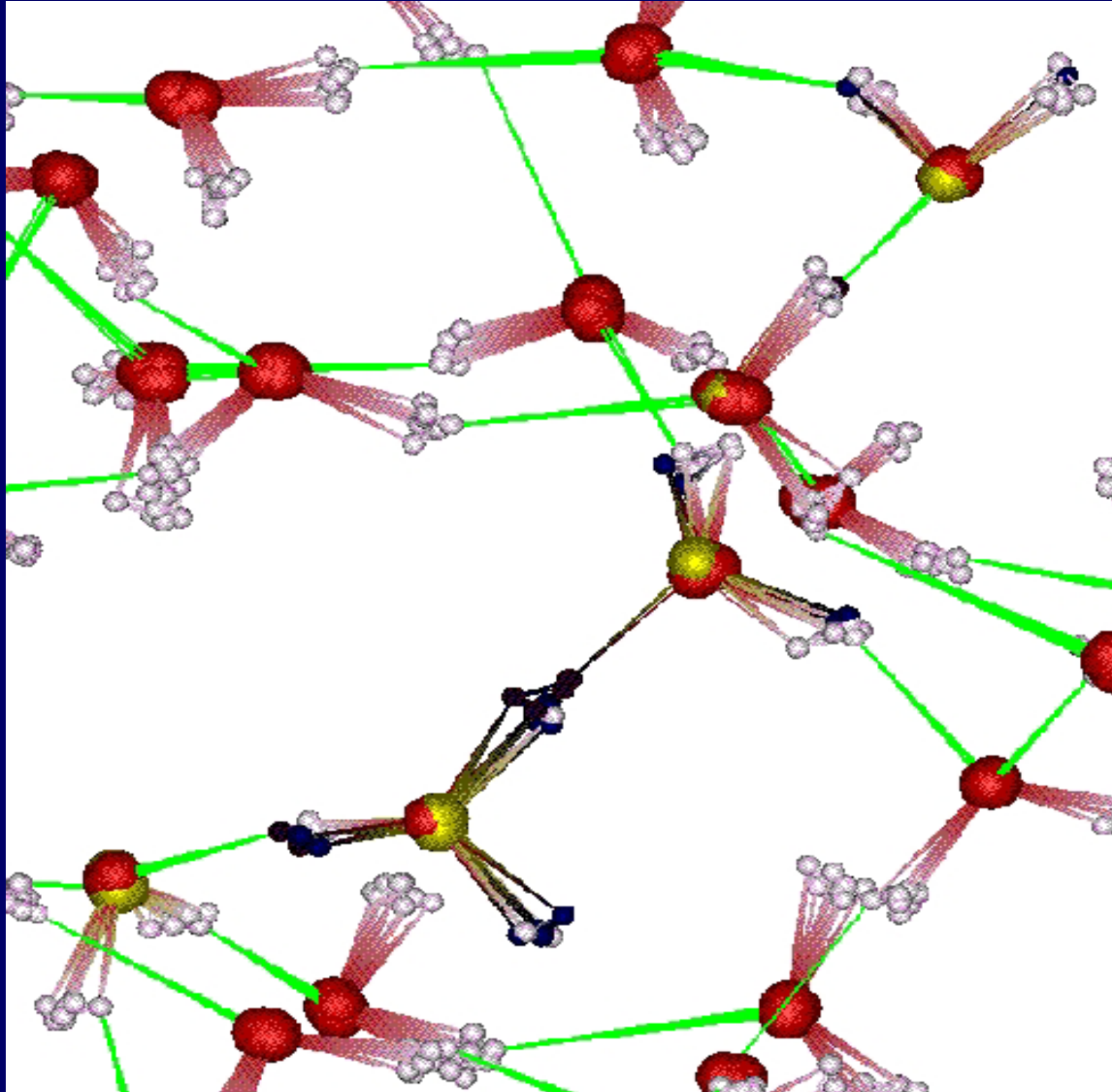
For analysis: 1D proton transfer coordinate ¹



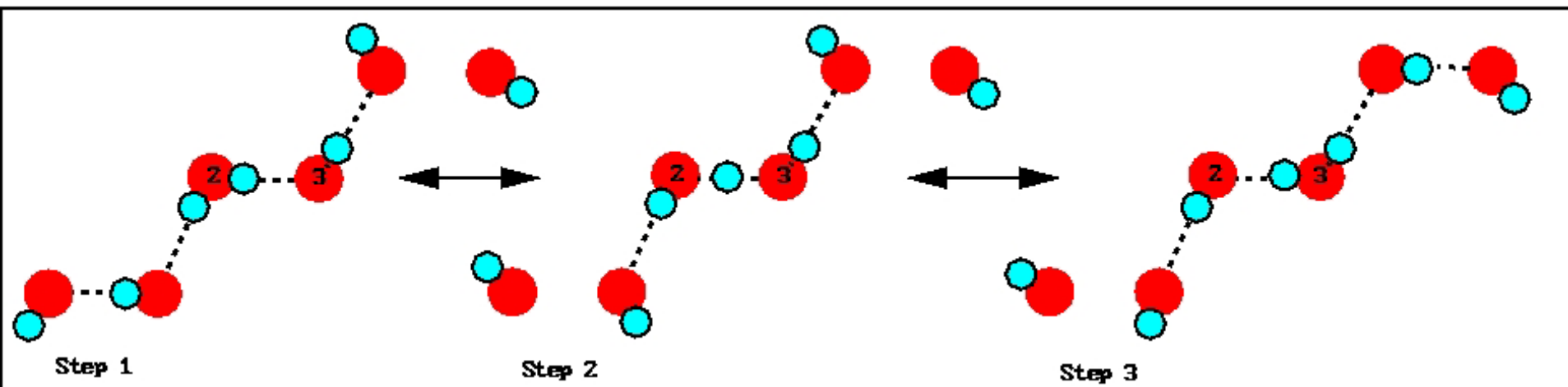
Proton rattling in H_5O_2^+ complex: $\text{H}_2\text{O} \cdots \text{H}^* \cdots \text{OH}_2$

Quantum delocalization of structural defect

D. Marx, MET, J. Hutter and M. Parrinello *Nature* 397, 601 (1999)



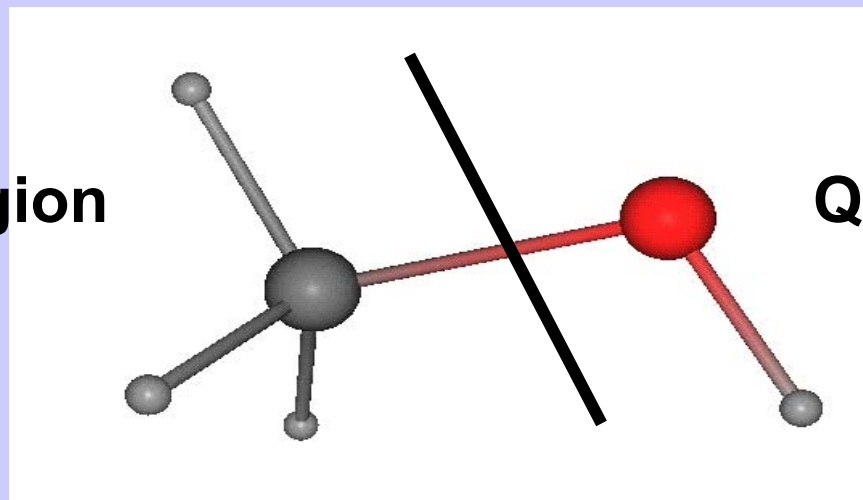
Proposed Structural Diffusion Mechanism in MeOH



H. -C. Chang, *et al*, *J. Phys. Chem. A* **103**, 2941 (1999).

Bond Cutting

MM region

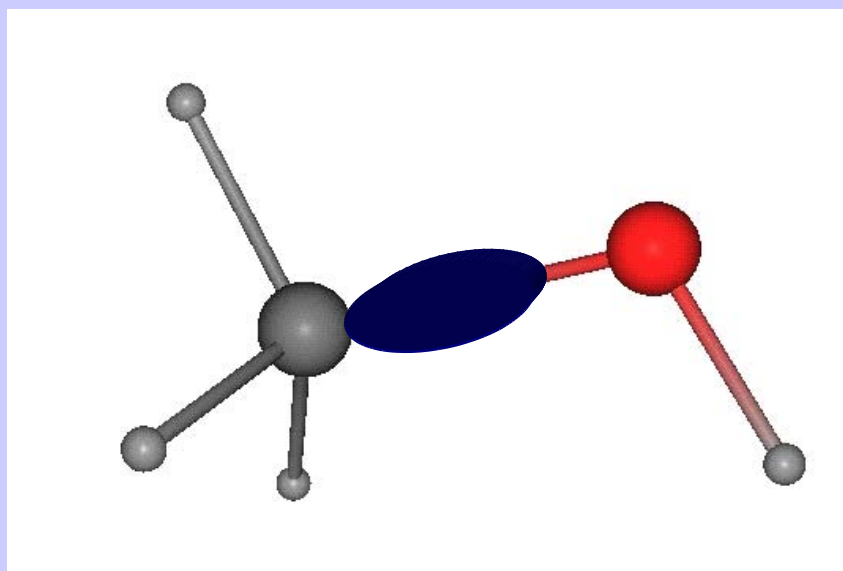


QM region

Use of monovalent
Carbon pseudopotential

U. Röthlisberger, private comm.

Y. Zhang, T. Lee, W. Yang
JCP 110, 46 (1999).



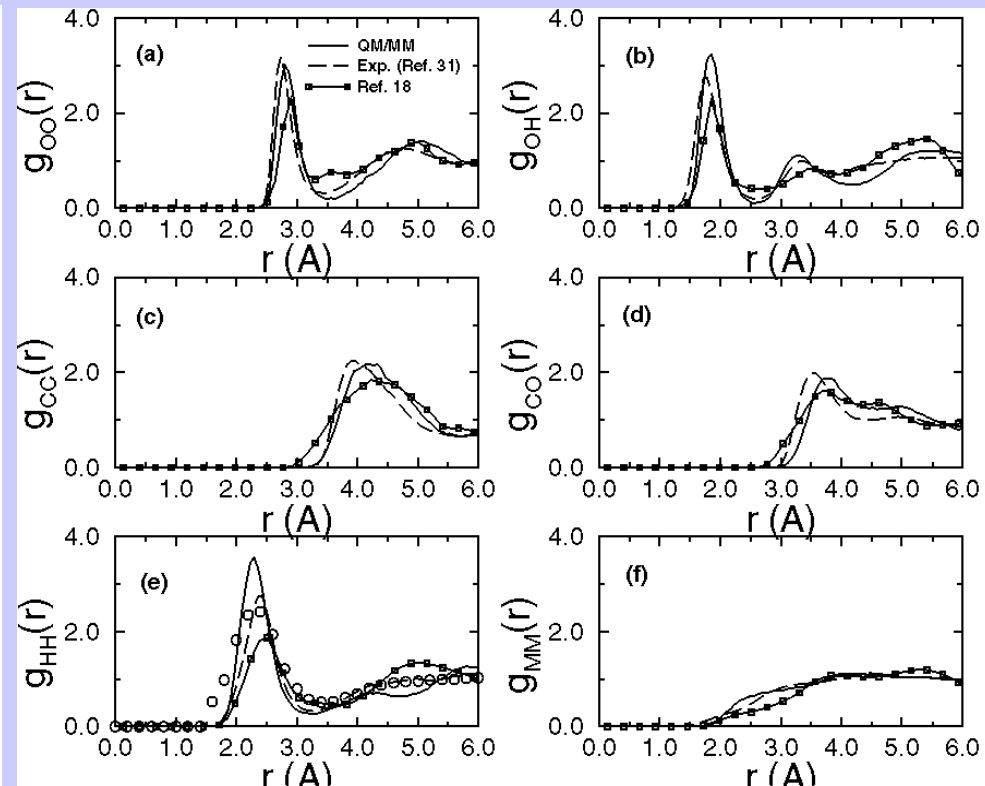
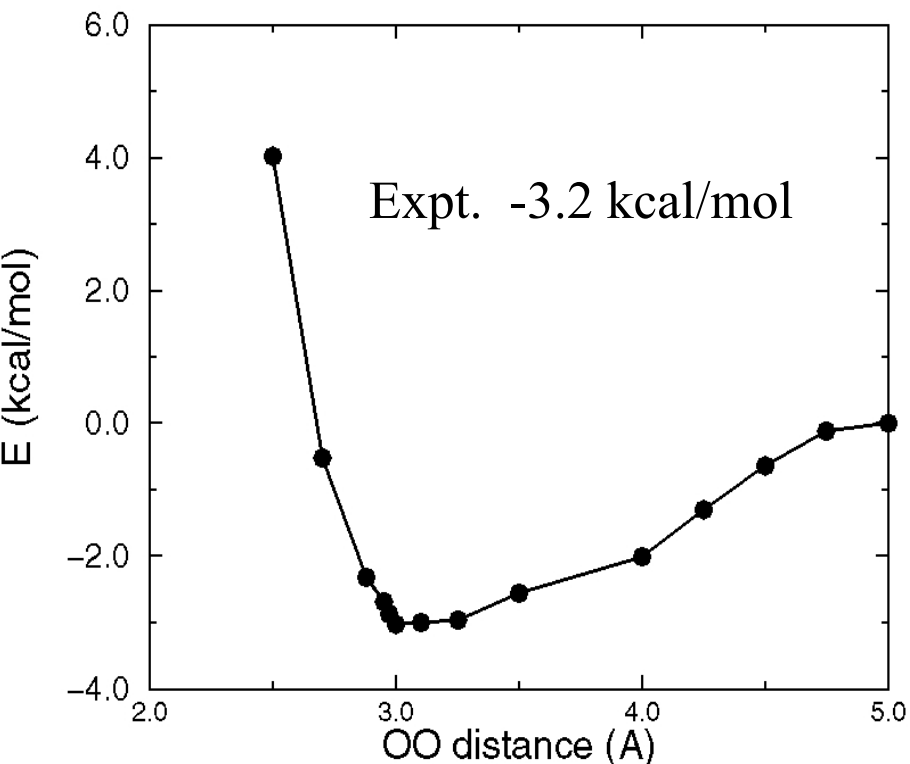
Results on structure of liquid methanol

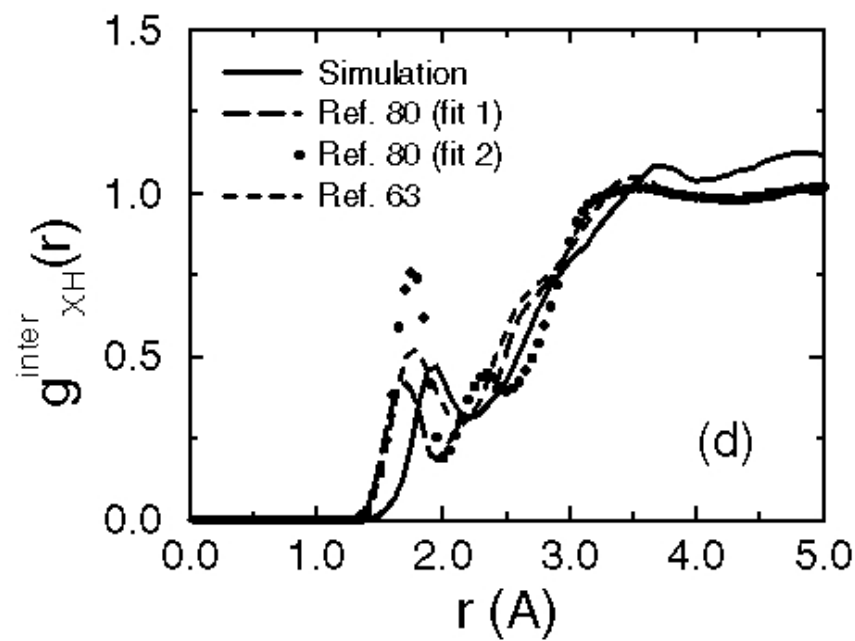
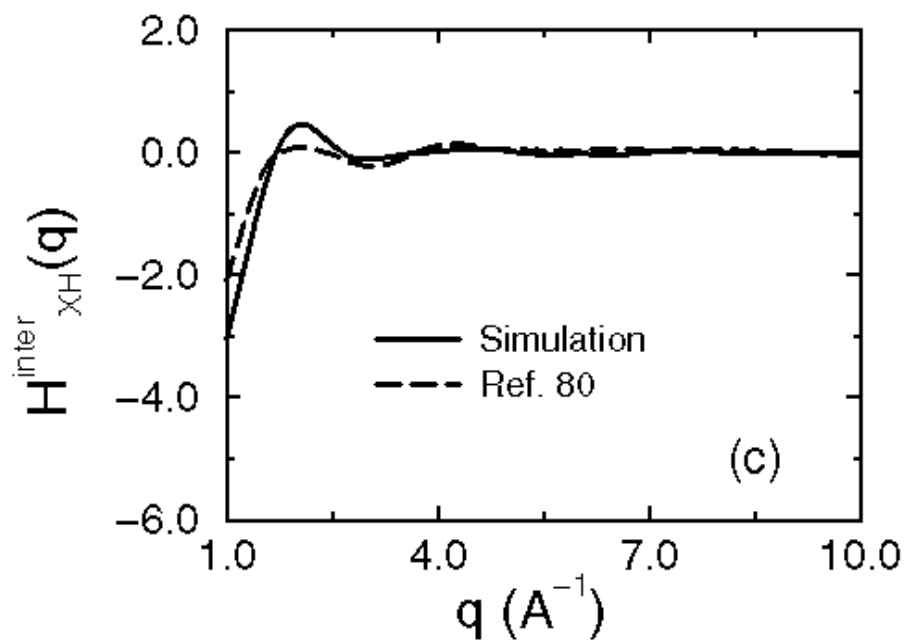
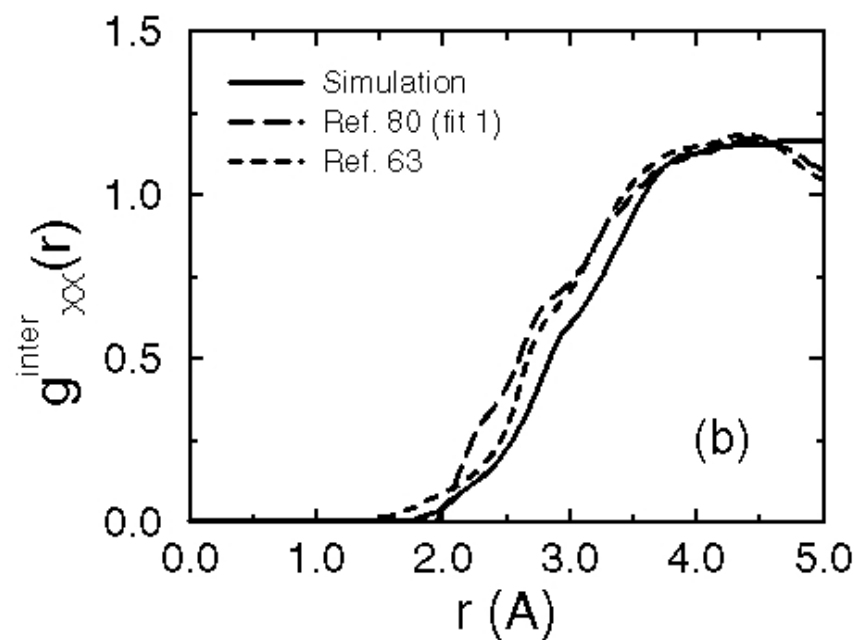
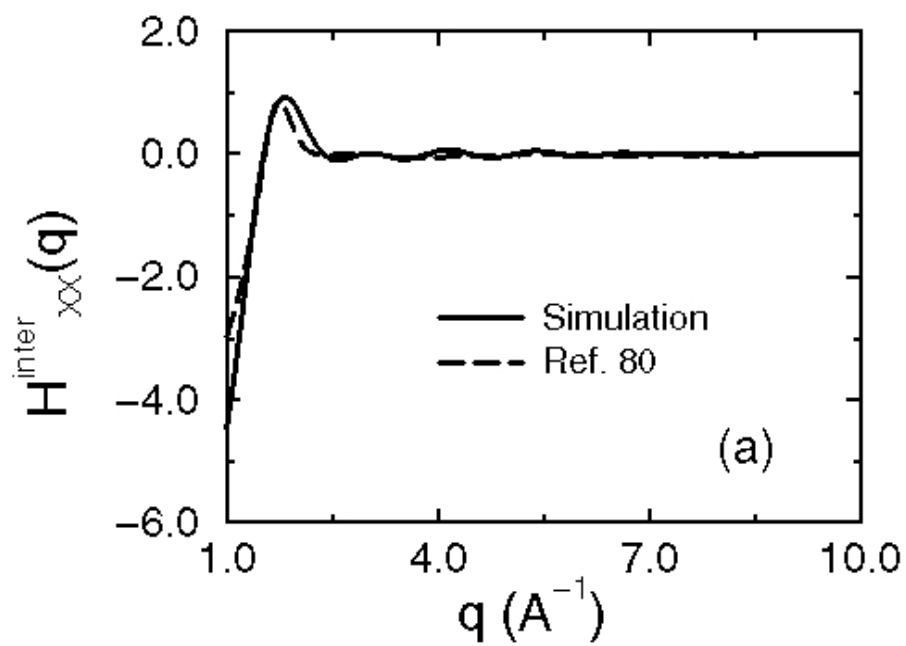
DFT Level: **BLYP** Force Field: **AMBER95** CO bond cutting: **Pseudobond**
System size: **32 molecules** Sim. Length: **10 ps**

Electron-methyl H pseudopotential: $V_{e-M}(r) = Ae^{-\gamma r}$

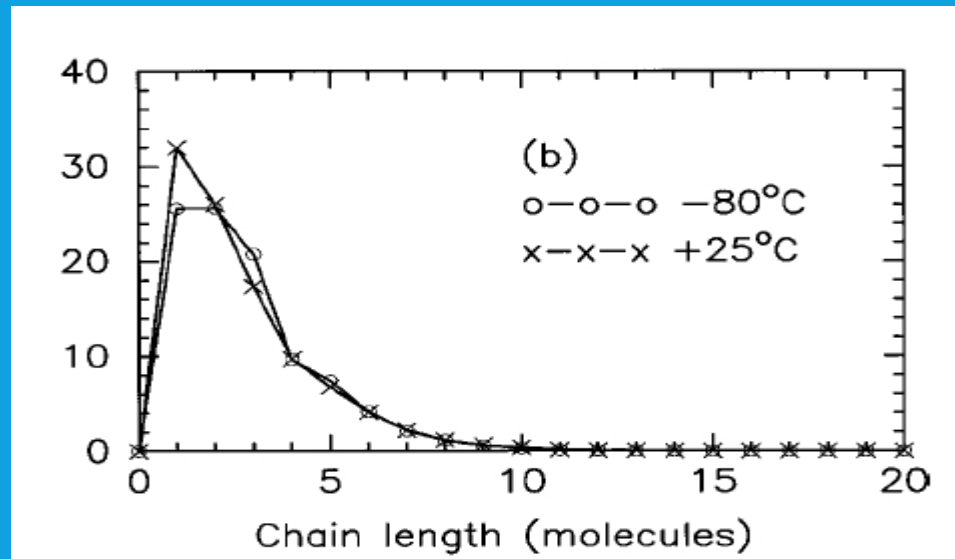
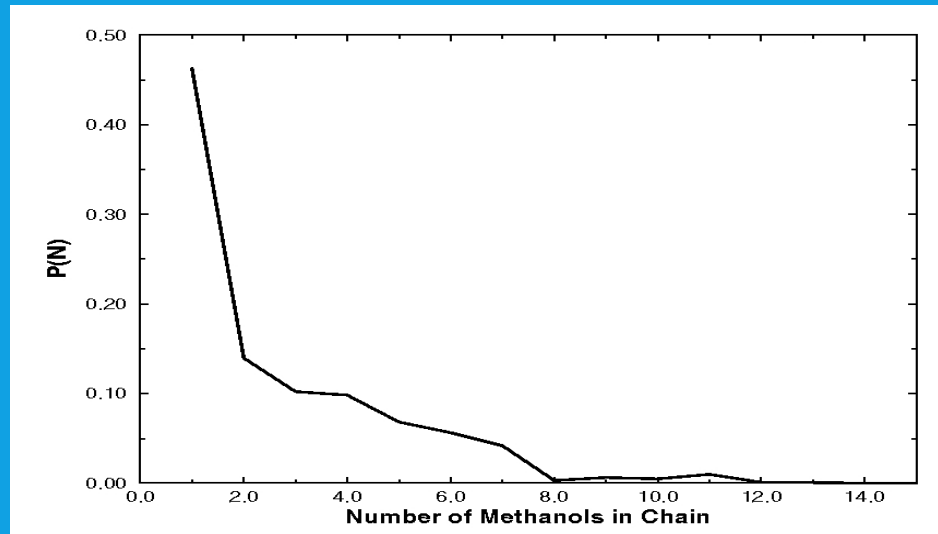
$A=18.5763$ kcal/mol

$\gamma = 0.5292$ Å





H-bond chain length statistics



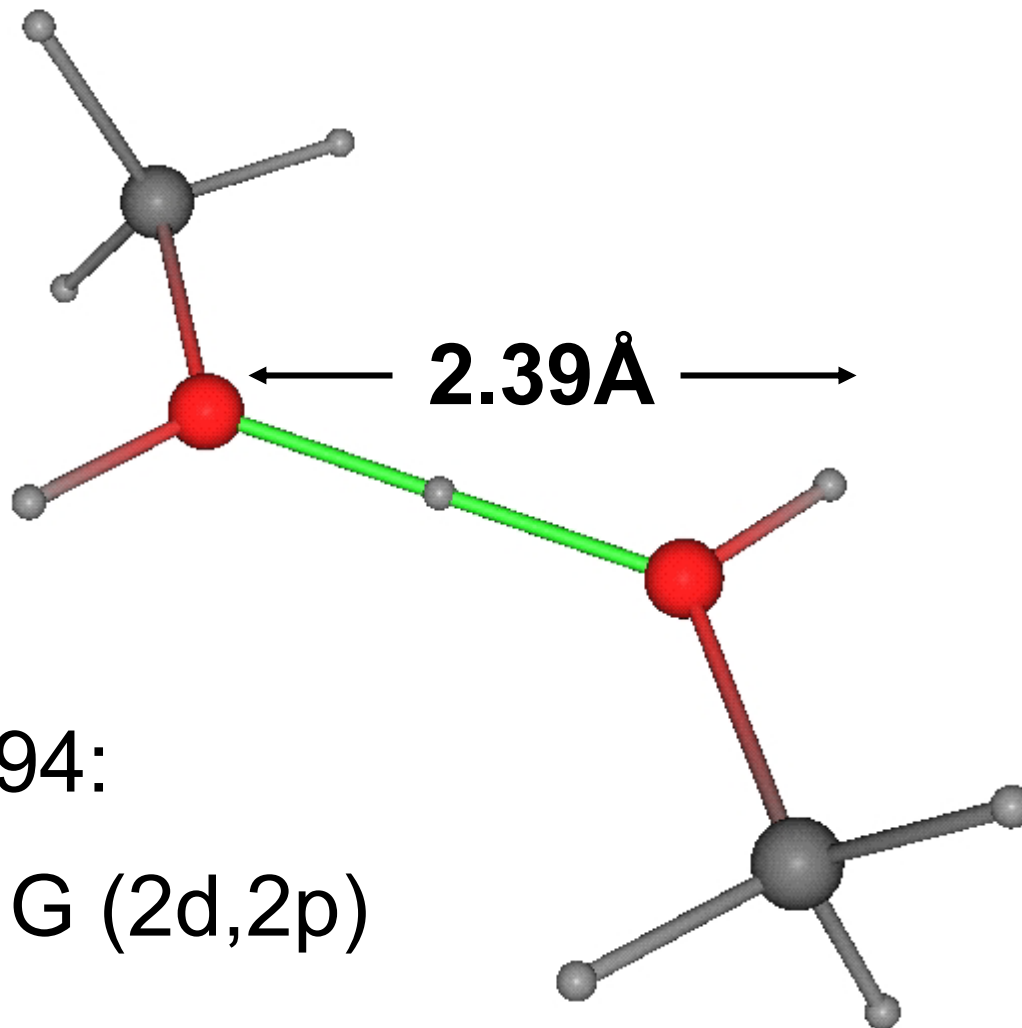
Simulation specifics

J. A. Morrone and MET, *J. Chem. Phys.* **117**, 4403 (2002).

J. A. Morrone and MET, *Chem. Phys. Lett.* **370**, 406 (2003).

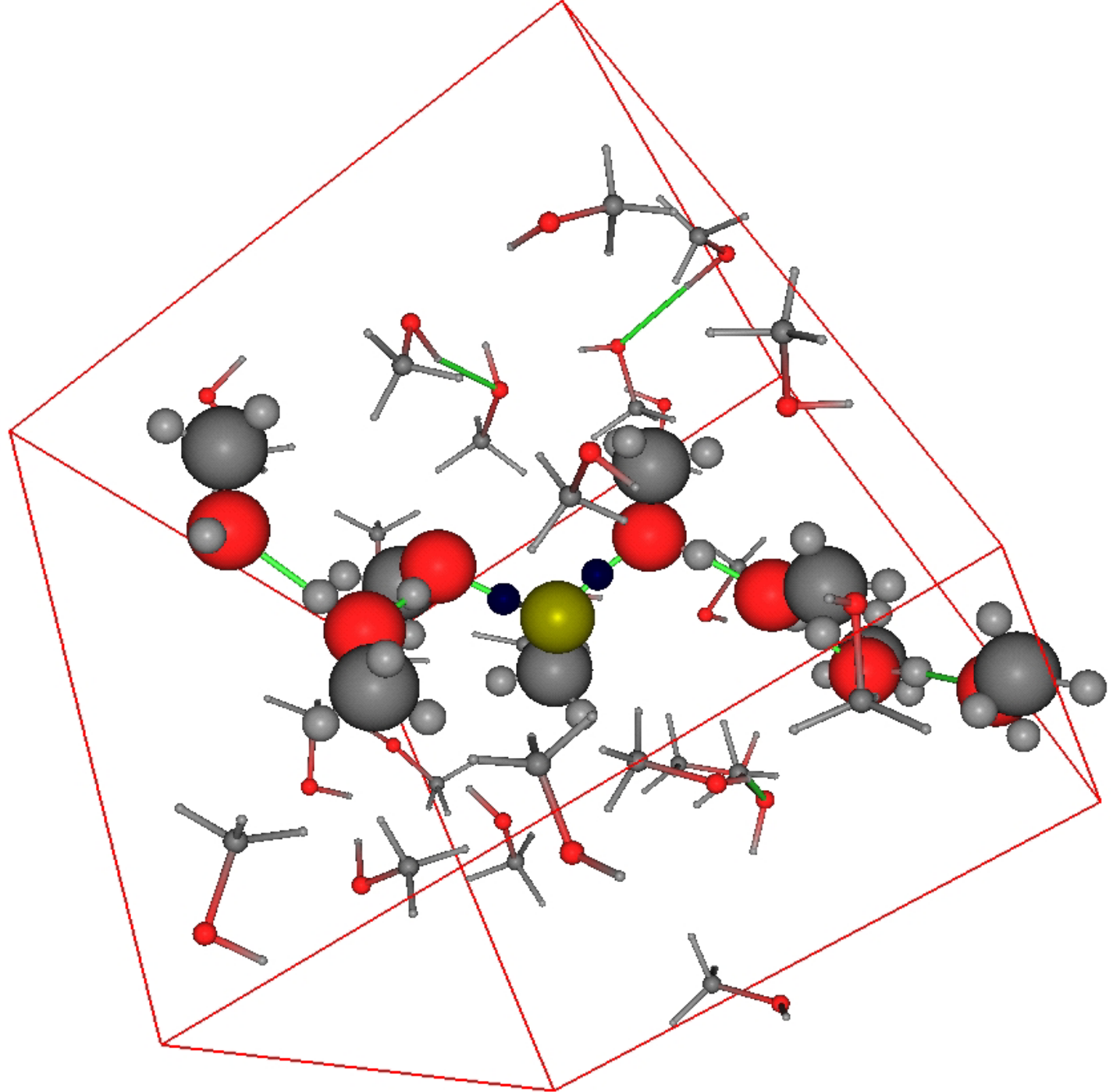
- **Temperature:** $T = 300$ K
- **Box:** $L = 12.93$ Å
- **System:** 32 MeOH and 32 MeOH + 1 H⁺
- **All H are D**
- **Simulation Lengths:** 60 ps
- **BLYP** treatment of OH group
- **AMBER** treatment of Me
- **Monovalent pseudopotential** in “cut” bond
- **e-M pseudopotential** $V(r) = Ae^{-\gamma r}$

Geometry of the protonated methanol dimer



Gaussian 94:

MP2 6-311G (2d,2p)



The Hazard Plot

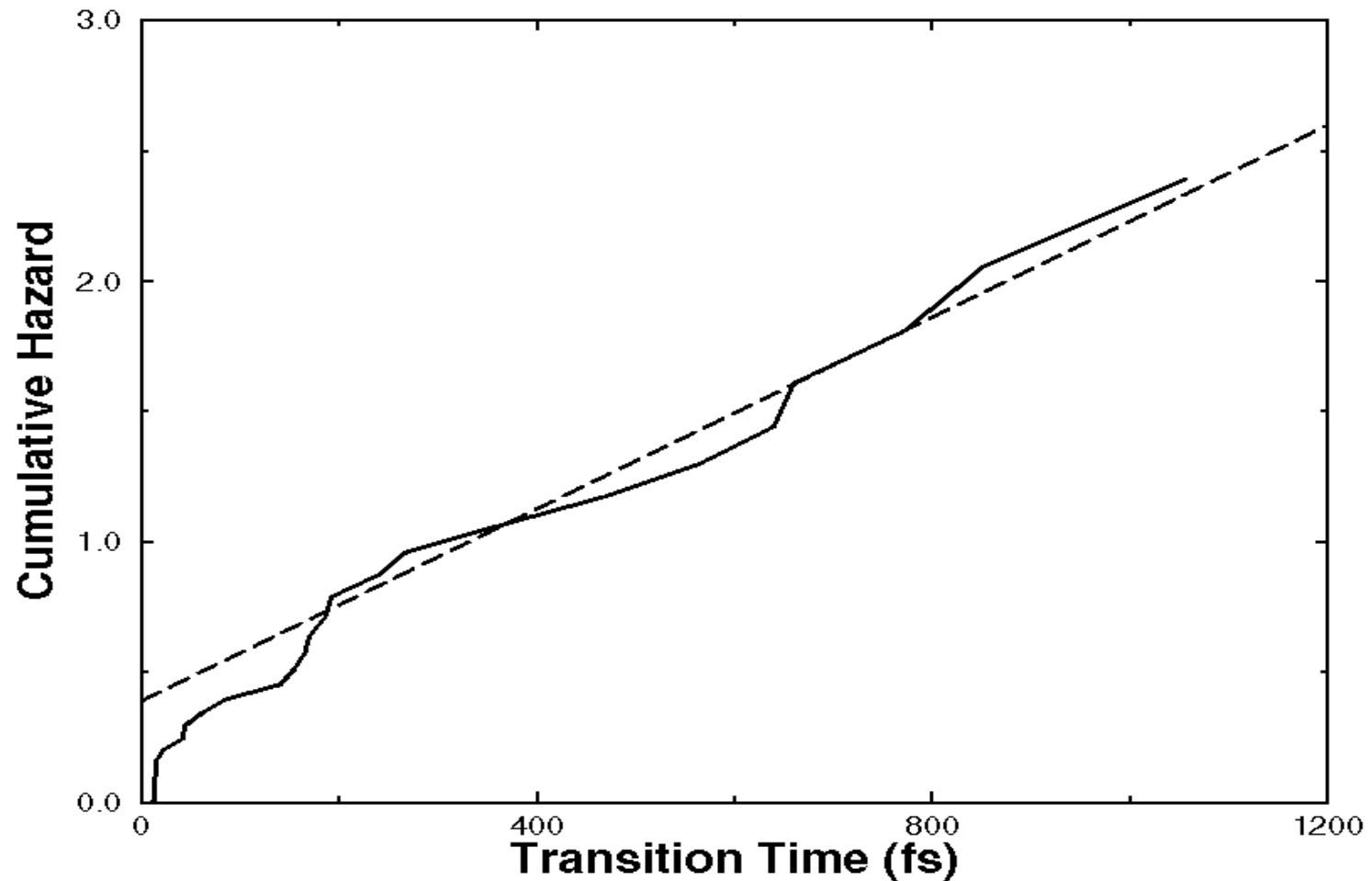
Suppose a system which can undergo a particular process has survived up to time t without undergoing the process. Let $h(t)dt$ be the probability that the process will occur between t and $t + dt$ (called the hazard). Define the cumulative hazard:

$$H(t) = \int_0^t dt' h(t')$$

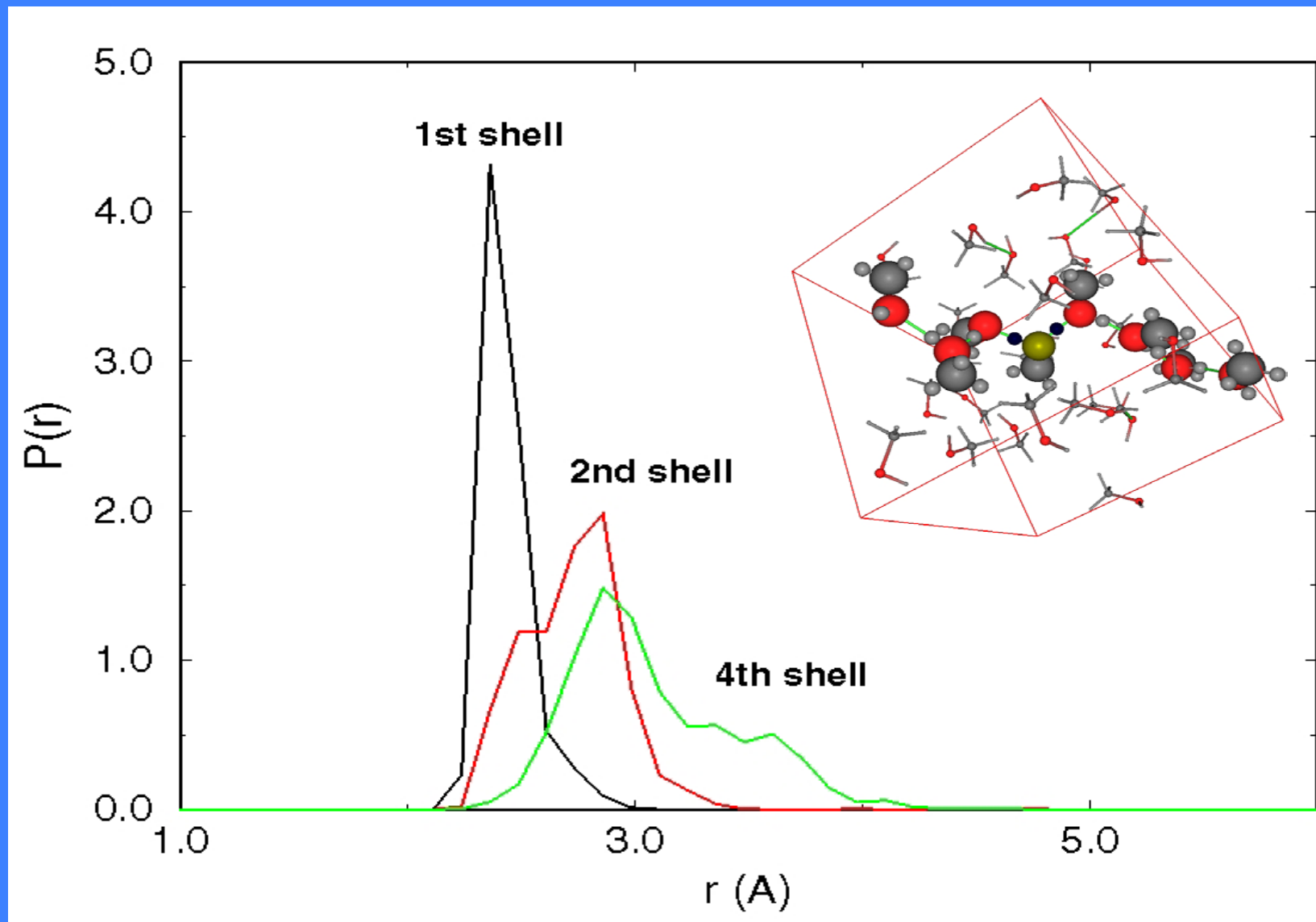
Plot $H(t)$ vs. transition time.

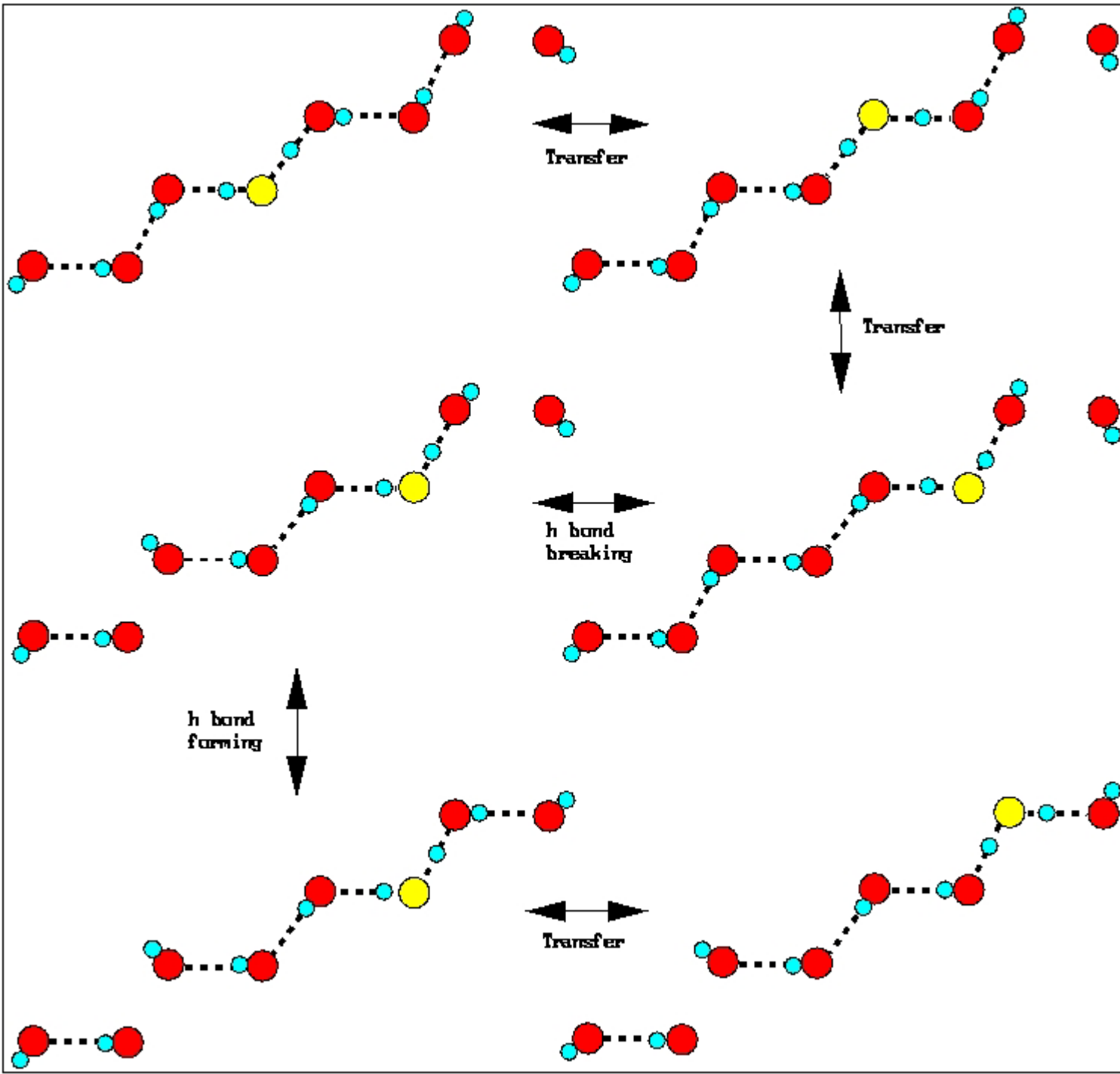
If process is random, then at long time, $h(t) = \lambda$,
 $H(t) = \lambda t$.

Proton transfer event statistics



Defect H-bond length distributions





Activation
Enthalpy:
2 kcal/mol
(NMR)

Methanol-
Methanol
H-bond strength:
3.2 kcal/mol
(spectroscopy)

Methanol-water mixtures

Competition between chain formation of methanol and tetrahedral network of water

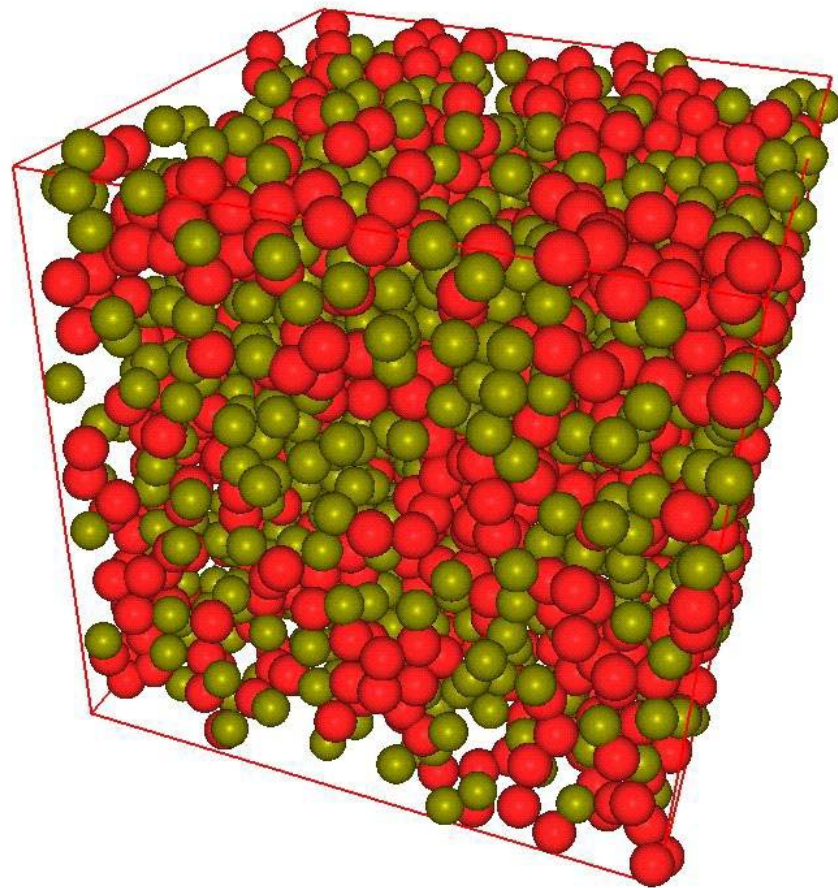
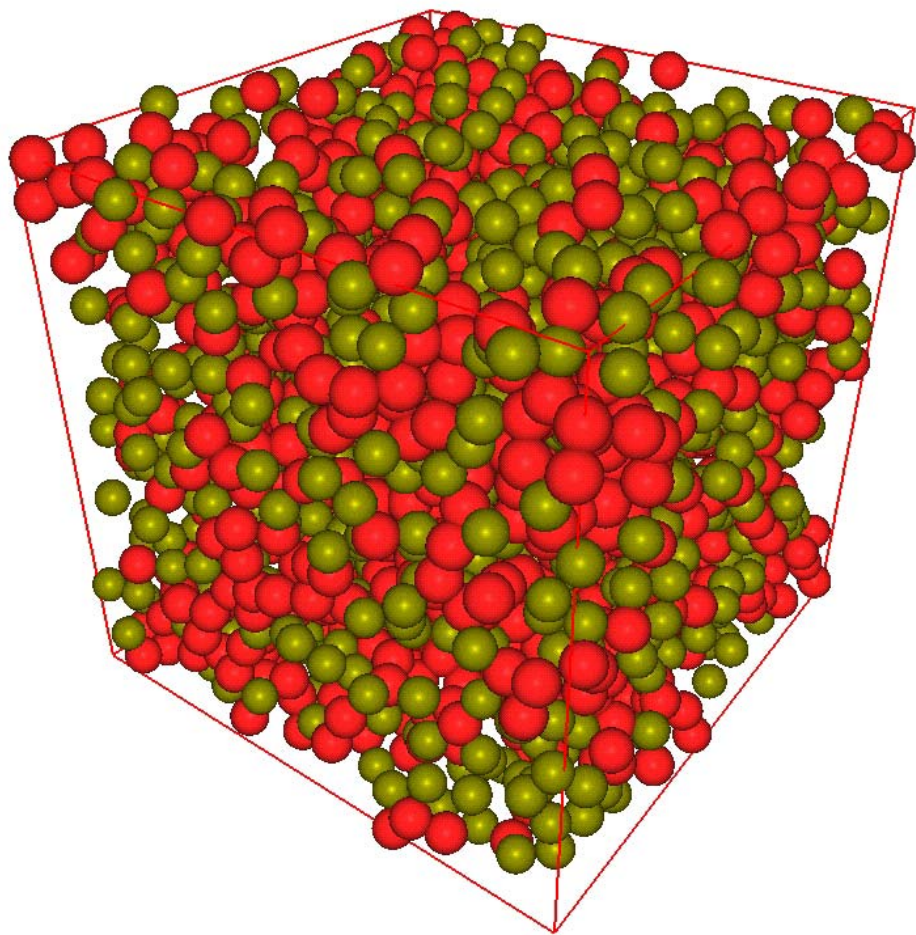
Recent neutron diffraction experiments suggest that between $X=0.27$ and $x=0.54$, molecular segregation occurs, leading to separate “percolating networks”.

S. Dixit, et al. *Nature* **416**, 829 (2002); L. Dougan, et al. *J. Chem. Phys.* **121**, 6456 (2004)

Water cluster sizes mostly less than 10 at $x=0.27$ and less than 20 for $x=0.54$.

Suppression of methanol tendency to form hydrogen-bonded chains as x increases.

From a classical MD run using 1024 MeOH + 1024 H₂O (x=0.5)



Simulation specifics

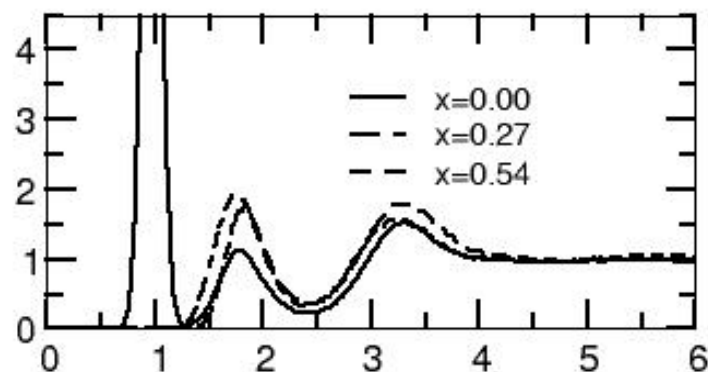
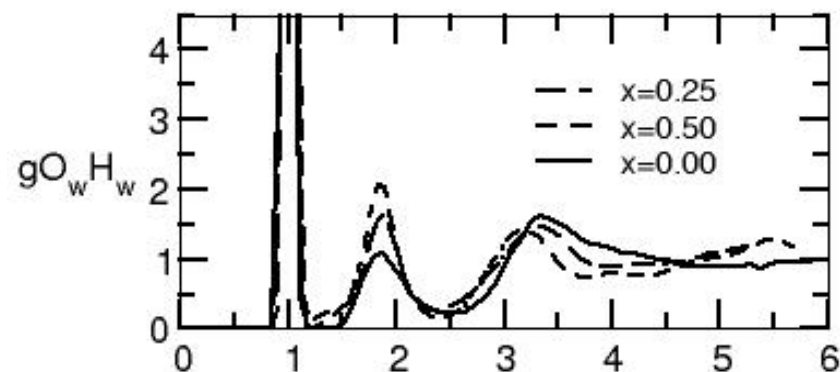
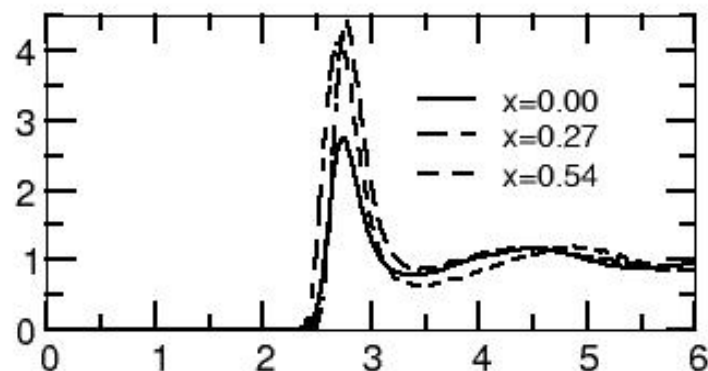
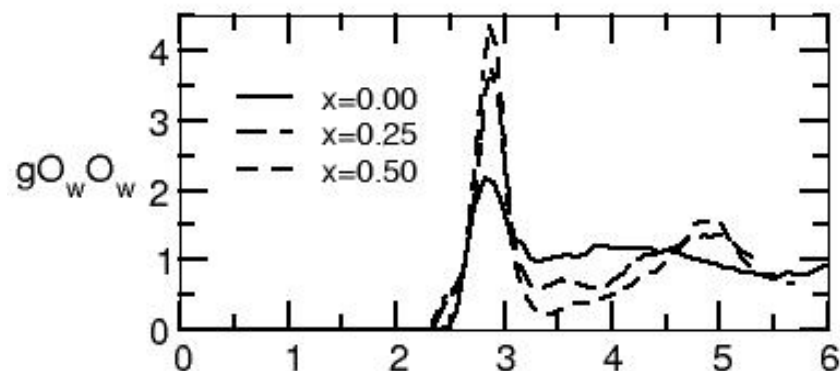
K. E. Haslinger, J. A. Morrone and MET (in preparation)

- **Temperature:** $T = 300 \text{ K}$
- **Box:** $L = 11.46 \text{ \AA}$ ($x=0.5$), 10.69 \AA ($x=0.25$)
- **System:** 16 MeOH and 16 H₂O (+ 1 H⁺): $x=0.5$
- **System:** 8 MeOH and 24 H₂O: $x=0.25$
- **All H are D**
- **Simulation Lengths:** 100 ps
- **Vanderbilt Ultrasoft Pseudopotentials**

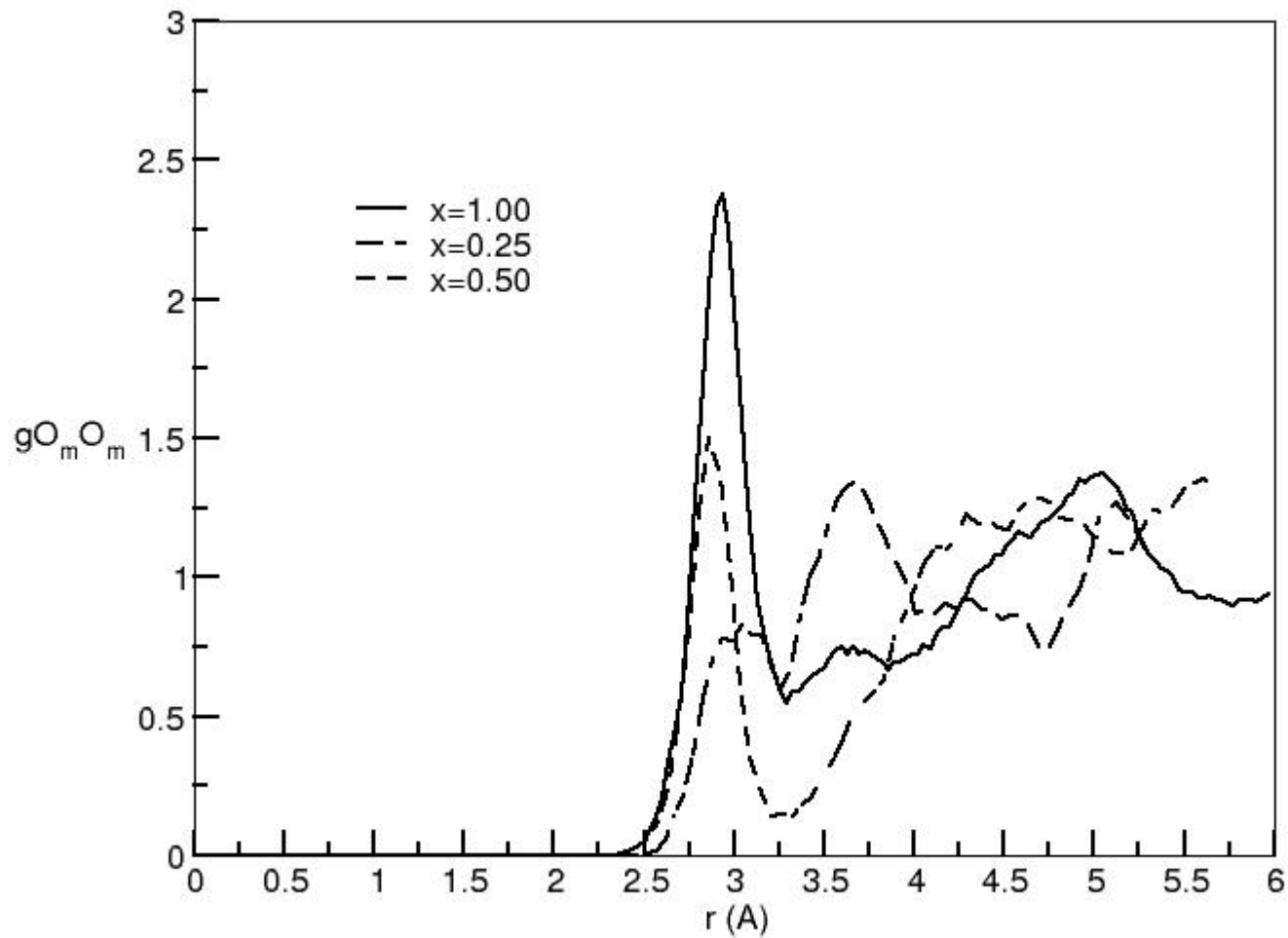
Water-water radial distribution functions

Theory

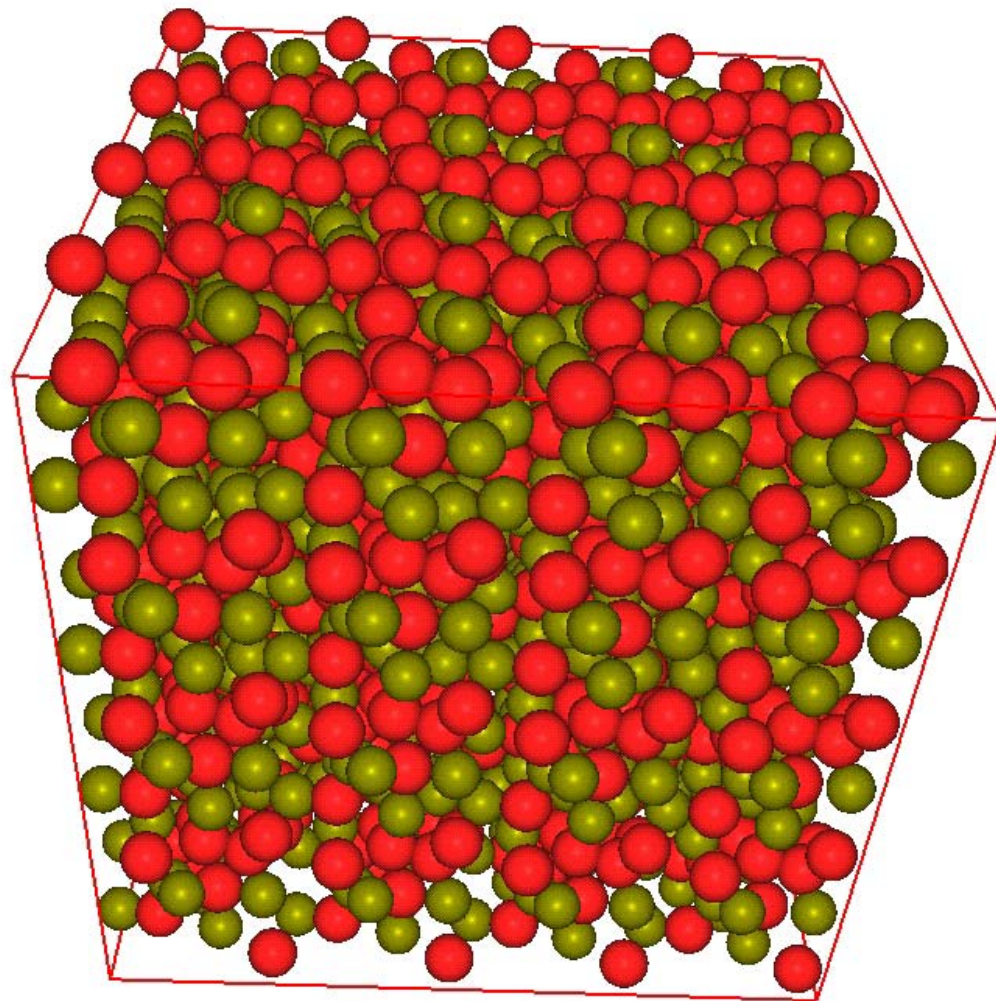
Experiment



Methanol-methanol radial distribution function



From ab initio MD run ($x=0.5$)

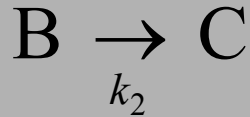
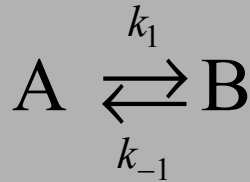


A simple kinetic model

Let A be the most active hydrogen bond.

Let B be an adjacent hydrogen bond.

Let C be a more “distant” situation.



$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = -(k_2 + k_{-1})[B] + k_1[A]$$

Solution of the kinetic model

$$[A](t) = \frac{1}{2\lambda} \left[(\lambda - k_1 + K) e^{-(k_1 + K - \lambda)t/2} + (\lambda + k_1 - K) e^{-(k_1 + K + \lambda)t/2} \right]$$

$$= [A]_{\text{slow}}(t) + [A]_{\text{fast}}(t)$$

$$[B](t) = \frac{k_1}{\lambda} \left[e^{-(k_1 + K - \lambda)t/2} - e^{-(k_1 + K + \lambda)t/2} \right]$$

$$= [B]_{\text{slow}}(t) + [B]_{\text{fast}}(t)$$

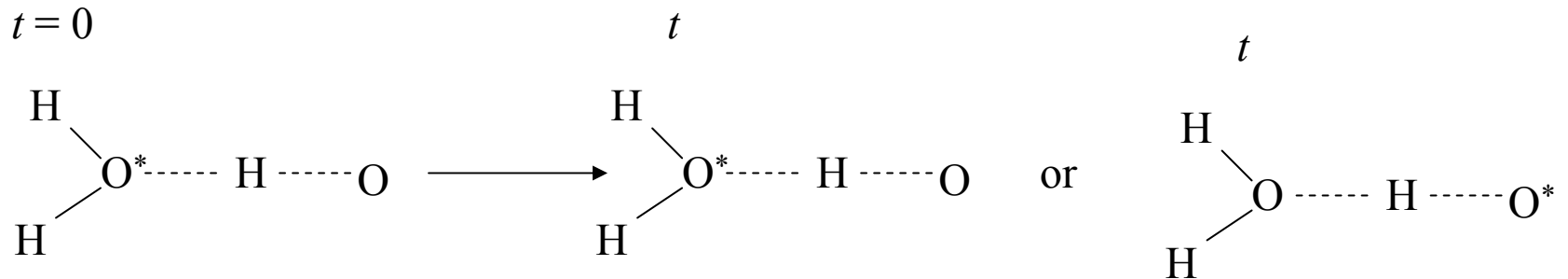
$$\lambda = \sqrt{(k_1 - K)^2 + 4k_1k_{-1}}$$

$$K = k_2 + k_{-1}$$

Using the model with the MD data

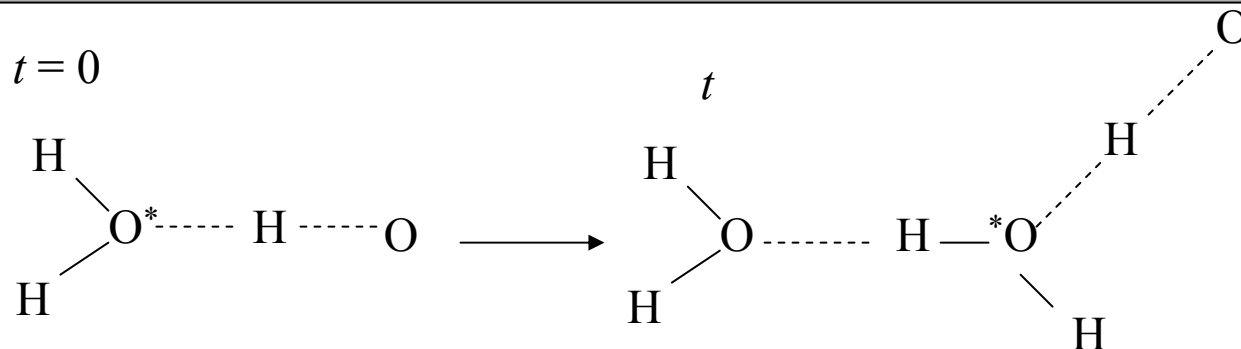
$$[A](t) \rightarrow \langle f(0)f(t) \rangle$$

$$f(t) = \begin{cases} 1 & \text{if most active H-bond has same identity at } t \text{ as at } t=0 \\ 0 & \text{otherwise} \end{cases}$$

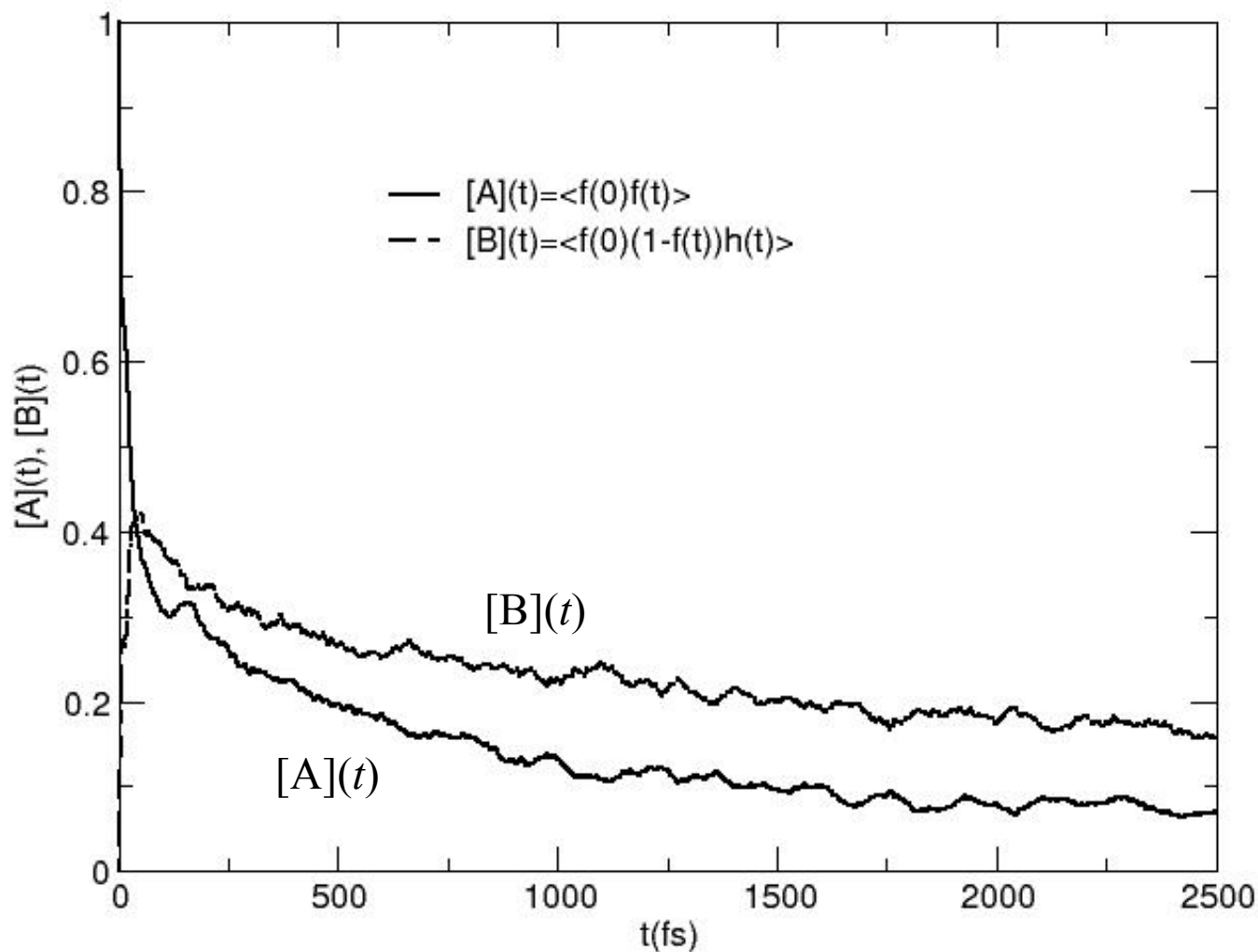


$$[B](t) \rightarrow \langle f(0)(1-f(t))h(t) \rangle$$

$$h(t) = \begin{cases} 1 & \text{if most active H-bond moves to an adjacent location at } t, \\ & \text{but original O* remains undercoordinated} \\ 0 & \text{otherwise} \end{cases}$$



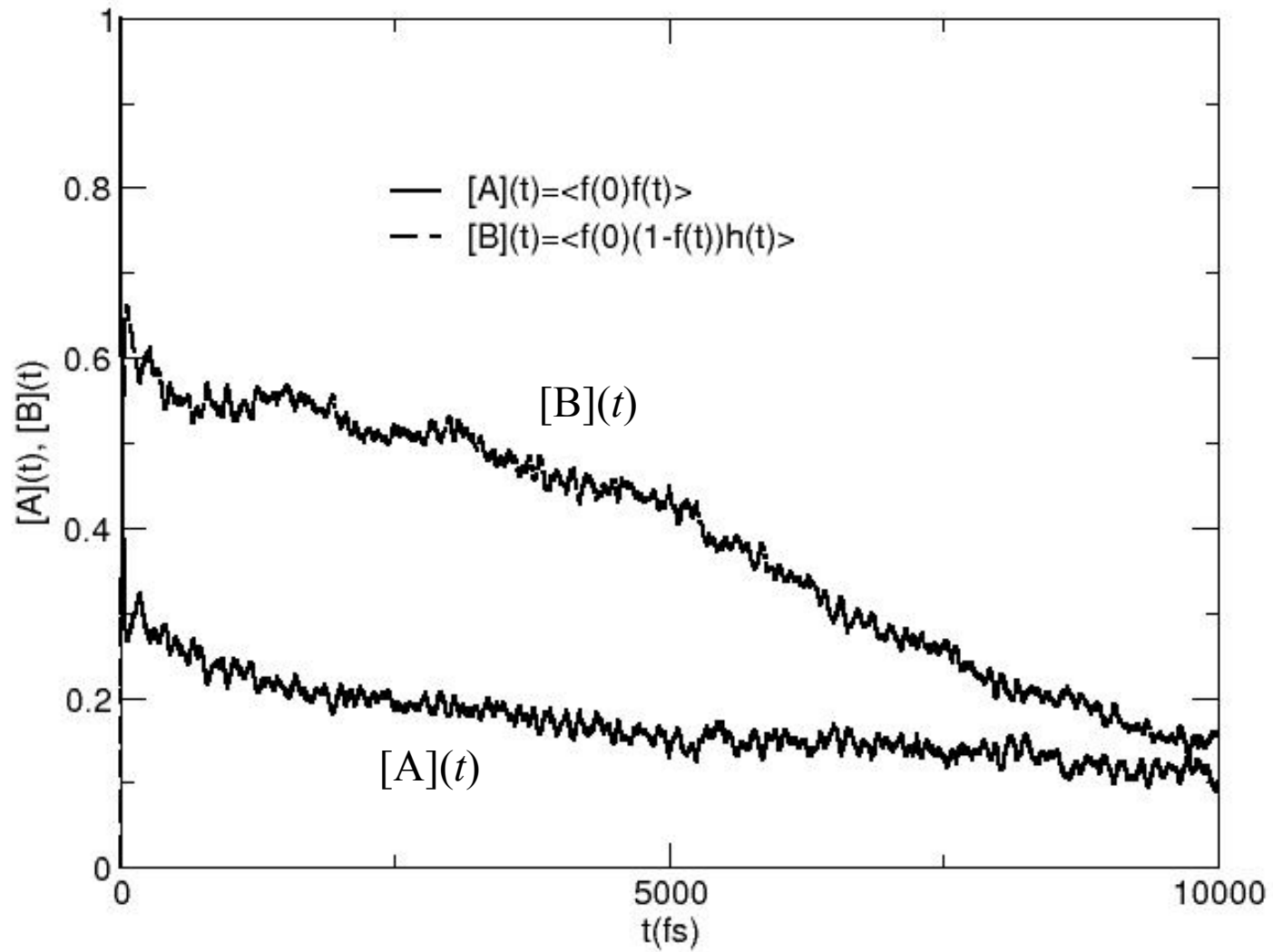
Correlation functions for a proton in a 50:50 methanol/water mixture



From a LLSQ fit:

$$k_1 = 20.9 \text{ ps}^{-1} \quad k_{-1} = 22.6 \text{ ps}^{-1} \quad k_2 = 0.8 \text{ ps}^{-1}$$

Correlation functions for hydroxide mobility in water



Calculated approximate branching ratios

<u>Reaction</u>	<u>Fraction</u>
$\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_3\text{O}^+$	47.0%
$\text{H}_3\text{O}^+ + \text{MeOH} \rightarrow \text{H}_2\text{O} + \text{MeOH}_2^+$	25.0%
$\text{MeOH}_2^+ + \text{H}_2\text{O} \rightarrow \text{MeOH} + \text{H}_3\text{O}^+$	25.0%
$\text{MeOH}_2^+ + \text{MeOH} \rightarrow \text{MeOH} + \text{MeOH}_2^+$	3.0%

Acknowledgments

Students past and present

- Zhongwei Zhu
- Yi Liu
- Joseph A. Morrone
- Kiryn E. Haslinger
- Lula Rosso

Postdocs

- Giuseppe Brancato
- Radu Iftimie
- Hee-Seung Lee
- Dawn A. Yarne

Collaborators

- Glenn Martyna
- Dominik Marx
- Michele Parrinello

Funding

- NSF - CAREER
- NYU Whitehead Award
- NSF – Chemistry, ITR
- Camille and Henry Dreyfus Foundation