Understanding Hydration, One Water Molecule at the Time

Francesco Paesani
Department of Chemistry and Biochemistry
University of California, San Diego

Temple University, November 4, 2016

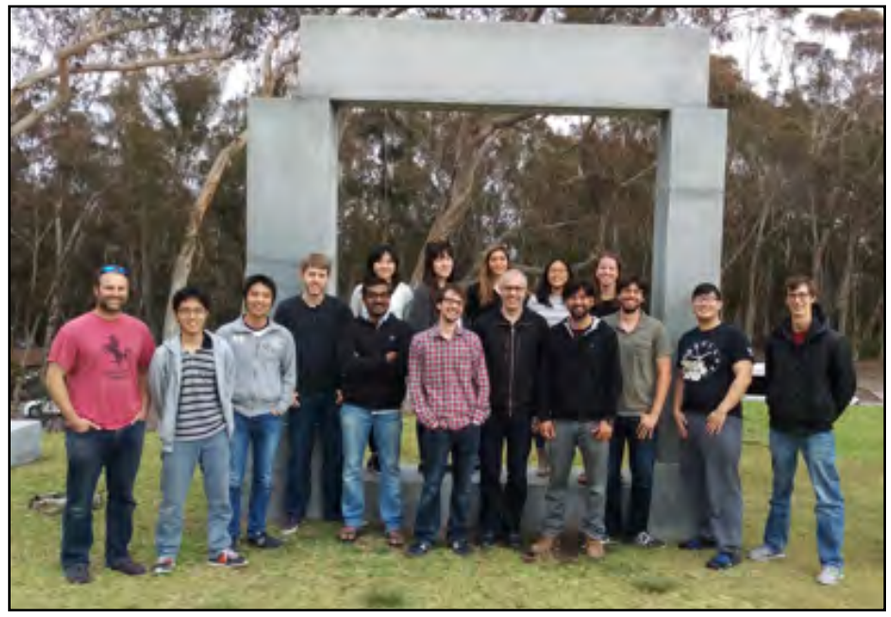
Acknowledgments

Current Members

Pushp Bajaj
Shelby Straight
Sandeep Reddy
Huy Pham
Santosh Kumar
Karl Chen
Renee Luo
Marc Riera
Colin Egan
Daniel Moberg
Gianmarc Grazioli
Sandra Brown
Debbie Zhuang
Minyue Fan

Collaborators

Vladimir Mandelshtam (UCI)
Andy Götz (SDSC)
Andrea Zonca (SDSC)
Miguel Morales (LLNL)
Anh Pham (LLNL)
Chris Knight (ANL)



Current Members

Greg Medders (Penn)
Volodymyr Babin (Schrödinger)

UC San Diego

CCI: Center for Aerosol Impacts on Climate and the Environment

CHE
DMR

DOE

AFOSR

ARO

Hellman Fellows

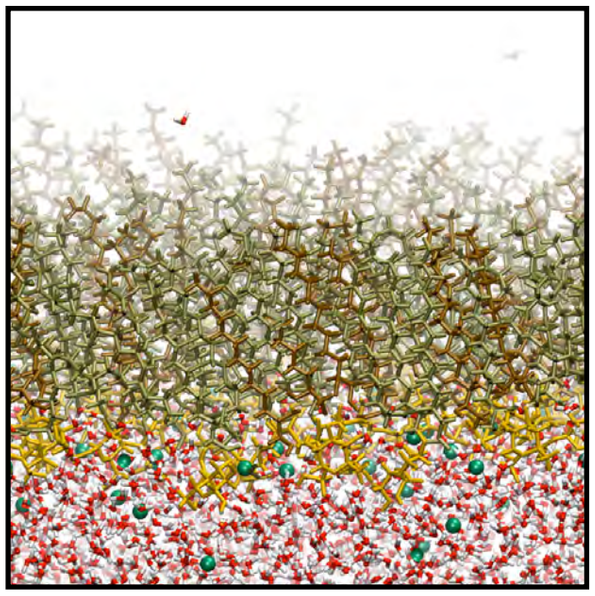
NERSC

XSEDE
Extreme Science and Engineering Discovery Environment

NVIDIA

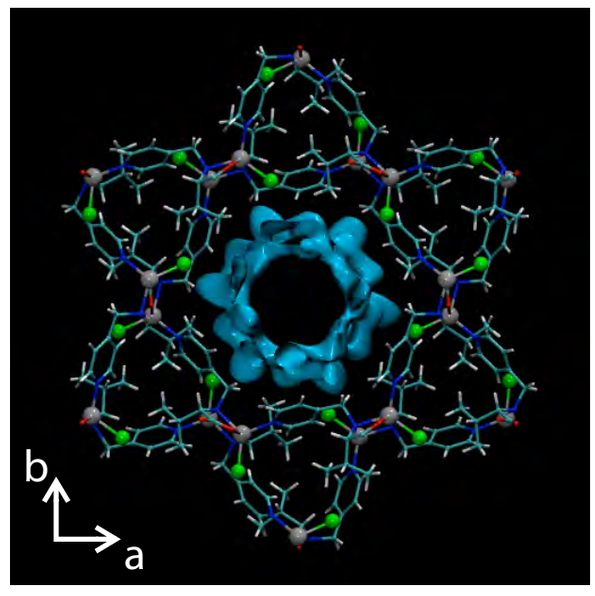
Triton Resource

Molecular Dynamics in Complex Systems



chemistry in aqueous environments

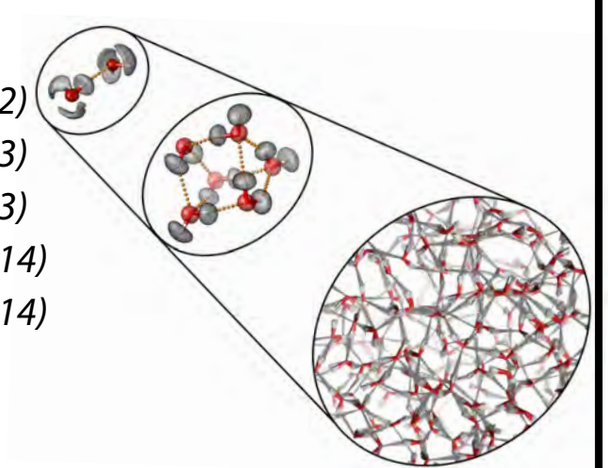
multifunctional porous materials



Chemistry in Aqueous Environments

many-body effects from the gas to the condensed phase

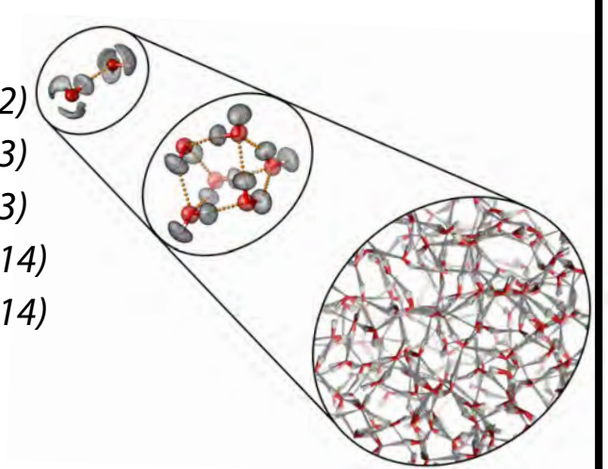
J. Phys. Chem. Lett. 3, 3765 (2012)
J. Chem. Theory Comput. 9, 1103 (2012)
J. Chem. Theory Comput. 9, 4844 (2013)
J. Chem. Theory Comput. 9, 5395 (2013)
J. Chem. Theory Comput. 10, 1599 (2014)
J. Chem. Theory Comput. 10, 2906 (2014)
J. Chem. Phys. 143, 104102 (2015)
Chem. Rev. 116, 7501 (2016)
Acc. Chem. Res. 48, 1844 (2016)



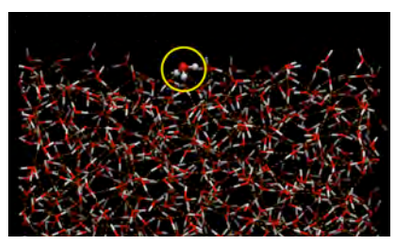
Chemistry in Aqueous Environments

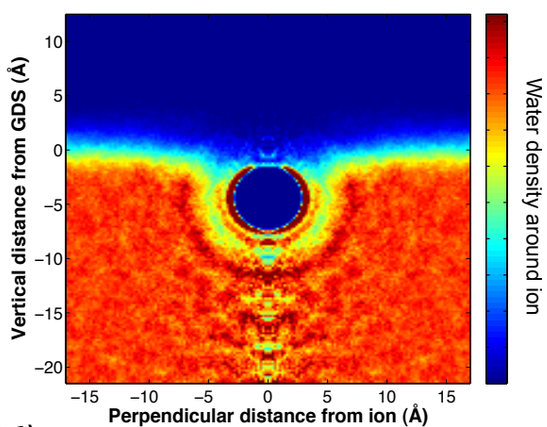
many-body effects from the gas to the condensed phase

J. Phys. Chem. Lett. 3, 3765 (2012)
J. Chem. Theory Comput. 9, 1103 (2012)
J. Chem. Theory Comput. 9, 4844 (2013)
J. Chem. Theory Comput. 9, 5395 (2013)
J. Chem. Theory Comput. 10, 1599 (2014)
J. Chem. Theory Comput. 10, 2906 (2014)
J. Chem. Phys. 143, 104102 (2015)
Chem. Rev. 116, 7501 (2016)
Acc. Chem. Res. 48, 1844 (2016)



ion hydration: clusters vs. bulk vs. interfaces



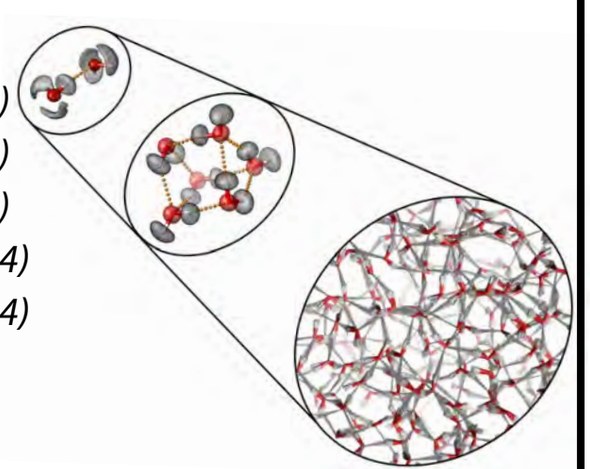


J. Phys. Chem. Lett. 4, 779 (2013)
J. Phys. Chem. A 119, 1859 (2015)
J. Phys. Chem. B 120, 1822 (2016)
J. Chem. Theory Comput. 12, 2698 (2016)
Phys. Chem. Chem. Phys., in press, DOI: 10.1039/C6CP02553F

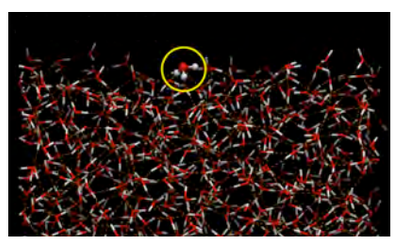
Chemistry in Aqueous Environments

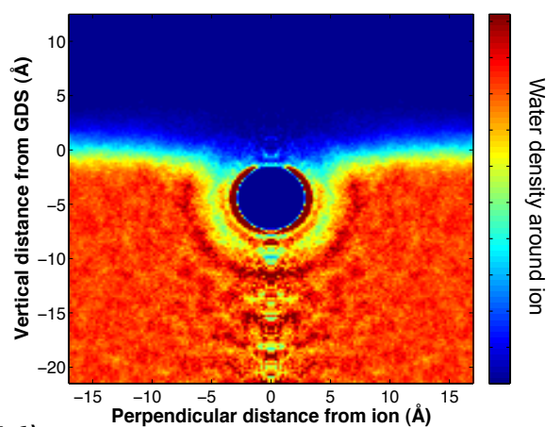
many-body effects from the gas to the condensed phase

J. Phys. Chem. Lett. 3, 3765 (2012)
J. Chem. Theory Comput. 9, 1103 (2012)
J. Chem. Theory Comput. 9, 4844 (2013)
J. Chem. Theory Comput. 9, 5395 (2013)
J. Chem. Theory Comput. 10, 1599 (2014)
J. Chem. Theory Comput. 10, 2906 (2014)
J. Chem. Phys. 143, 104102 (2015)
Chem. Rev. 116, 7501 (2016)
Acc. Chem. Res. 48, 1844 (2016)



ion hydration: clusters vs. bulk vs. interfaces

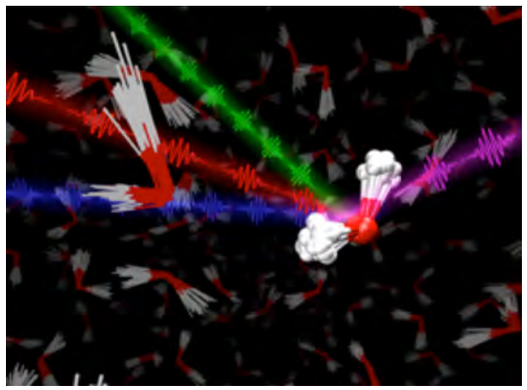




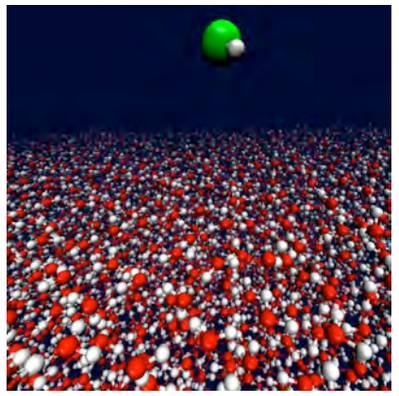
J. Phys. Chem. Lett. 4, 779 (2013)
J. Phys. Chem. A 119, 1859 (2015)
J. Phys. Chem. B 120, 1822 (2016)
J. Chem. Theory Comput. 12, 2698 (2016)
Phys. Chem. Chem. Phys., in press, DOI: 10.1039/C6CP02553F

nonlinear multidimensional vibrational spectroscopy

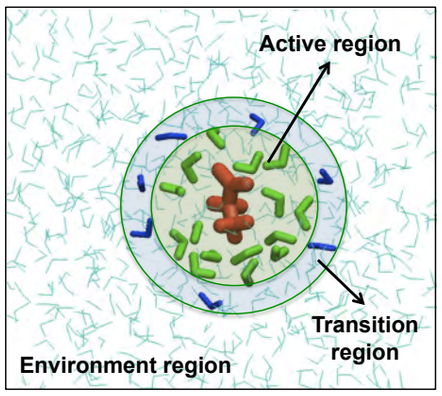
J. Phys. Chem. A 115, 6861 (2011)
Phys. Chem. Chem. Phys. 13, 19865 (2011)
J. Phys. Chem. B 116, 13774 (2012)
J. Chem. Theory Comput. 11, 1145 (2015)
J. Chem. Phys. 142, 212411 (2015)
J. Am. Chem. Soc. 138, 3912 (2016)
J. Phys. Chem. B 120, 8539 (2016)



chemical reactions: clusters vs. bulk vs. interfaces



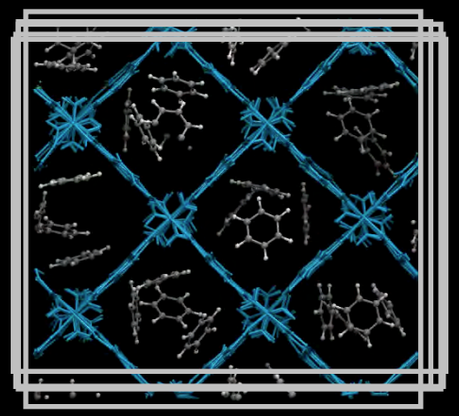
J. Chem. Theory Comput. 8, 2868 (2012)
J. Phys. Chem. B 118, 8081 (2014)



J. Phys. Chem. A 119, 4450 (2015)

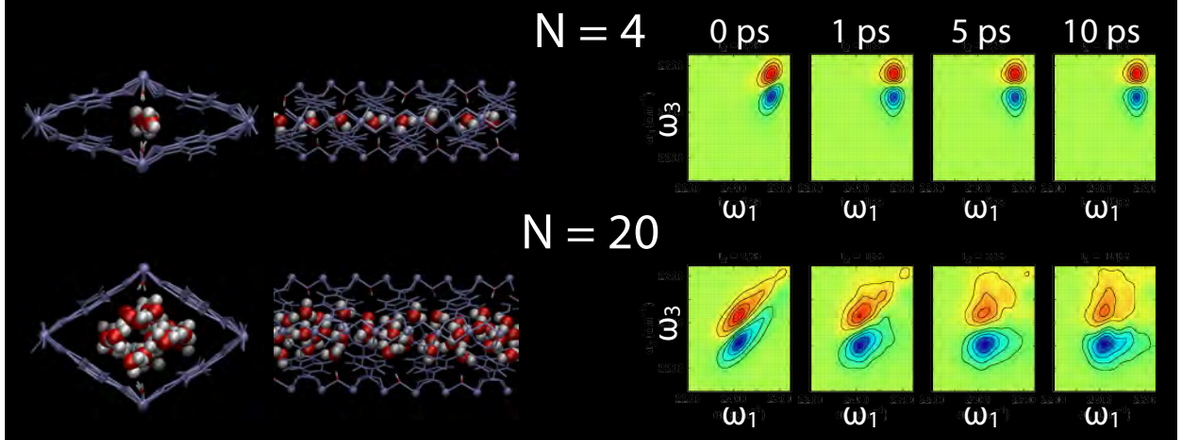
Multifunctional Porous Materials

Breathing effect & cross linking



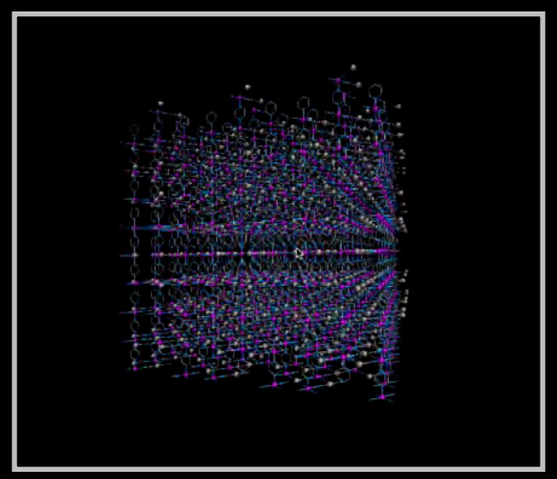
J. Am. Chem. Soc. 134, 4207 (2012)
Chem. Comm. 49, 3200 (2013)
Phys. Chem. Chem. Phys. 18, 8196 (2016)

Guest structure and dynamics



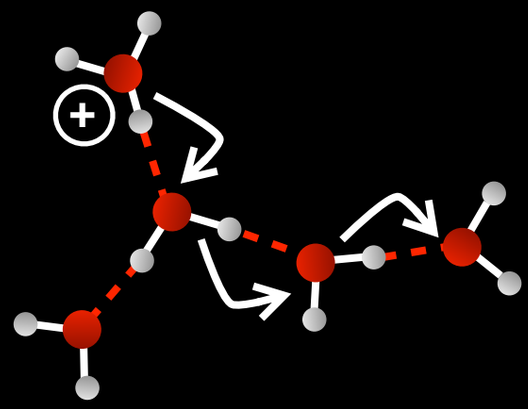
Mol. Simul. 38, 631 (2012)
J. Chem. Phys. 137, 054704 (2012)
J. Phys. Chem. Lett. 5, 2897 (2014)
J. Phys. Chem. C 119, 18239 (2015)

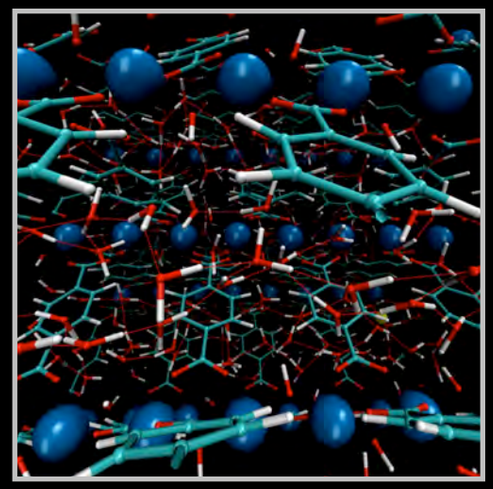
Spin crossover



Inorg. Chem. 53, 11020 (2014)
J. Am. Chem. Soc. 138, 6123 (2016)
J. Phys. Chem. Lett. 7, 4022 (2016)

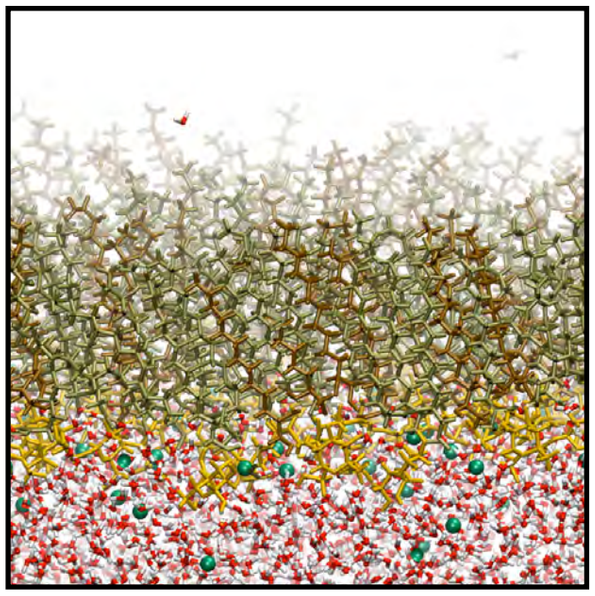
Proton conduction





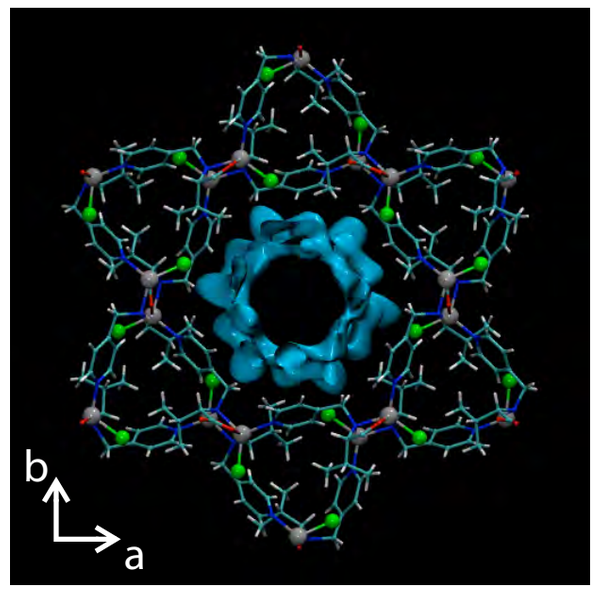
J. Phys. Chem. C 117, 19508 (2013)
Angew. Chem. Int. Ed. 55, 3319 (2016)
Chem. Mater., under review

How Realistic Are the Simulations?

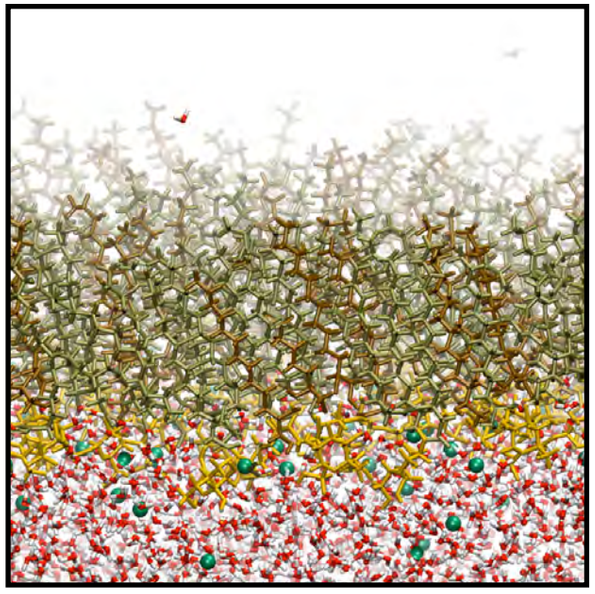


chemistry in aqueous environments

multifunctional porous materials

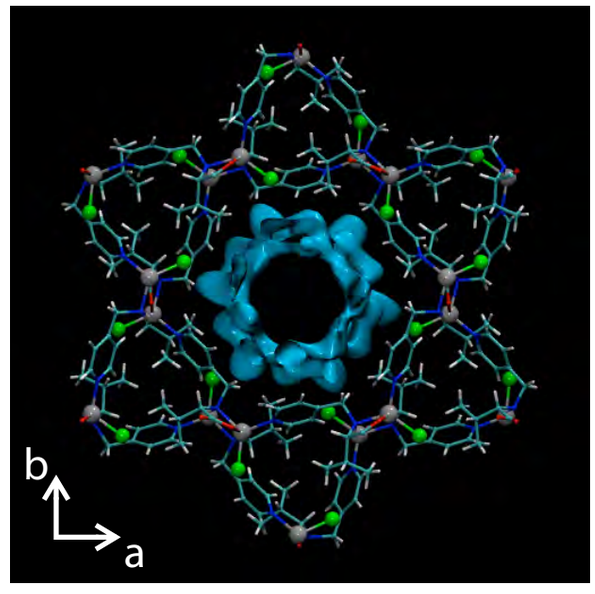


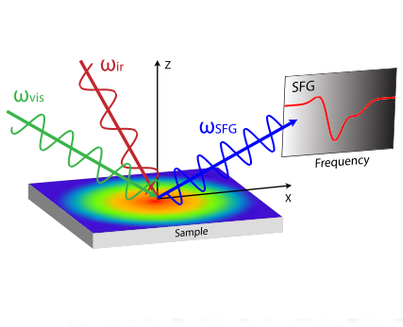
Vibrational Spectroscopy for Reality Check

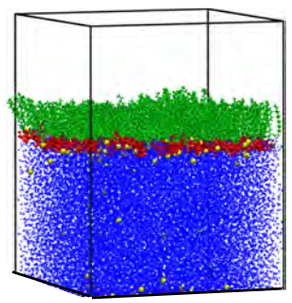


chemistry in aqueous environments

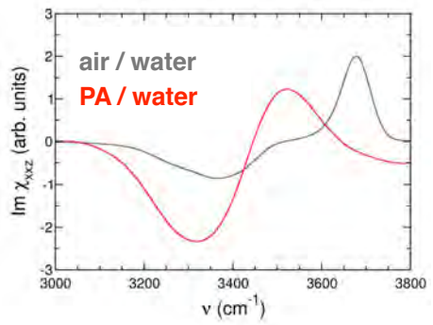
multifunctional porous materials





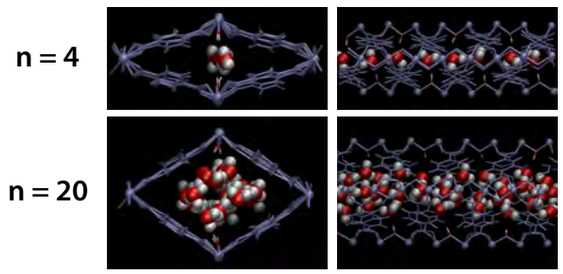


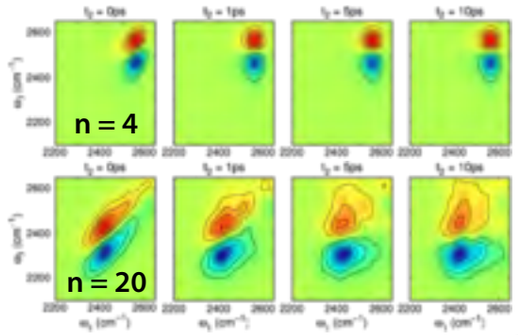
interface & SFG spectra



J. Chem. Theory Comput. 8, 2868 (2012)
J. Phys. Chem. Lett. 4, 779 (2013)
J. Phys. Chem. B 118, 8081 (2014)
Langmuir 31, 2147 (2015)
J. Am. Chem. Soc. 138, 3912 (2016)

adsorption & 2D-IR spectra





J. Am. Chem. Soc. 134, 4207 (2012)
J. Phys. Chem. C 117, 19508 (2013)
J. Phys. Chem. Lett. 5, 2897 (2014)
J. Phys. Chem. C 119 ,18239 (2015)
J. Am. Chem. Soc. 138, 6123 (2016)

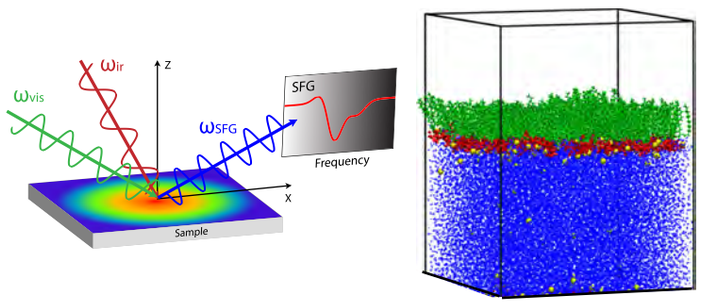
Molecular Simulations & Vibrational Spectroscopy

Infrared: $I_{IR} \propto \int e^{-i\omega t} \langle \mu(t)\mu(0) \rangle dt$

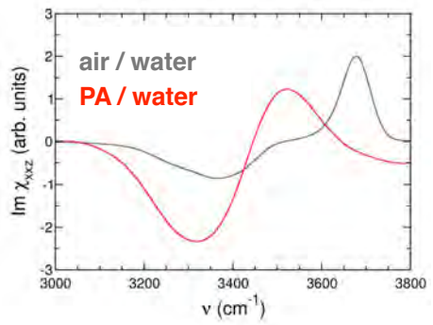
Raman: $I_{Raman} \propto \int e^{-i\omega t} \langle \alpha(t)\alpha(0) \rangle dt$

Sum-frequency generation: $I_{SFG} \propto \int e^{-i\omega t} \langle \alpha(t)\mu(0) \rangle dt$

…and nonlinear multidimensional analogs

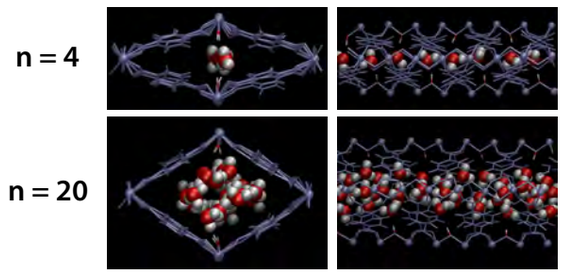


interface & SFG spectra

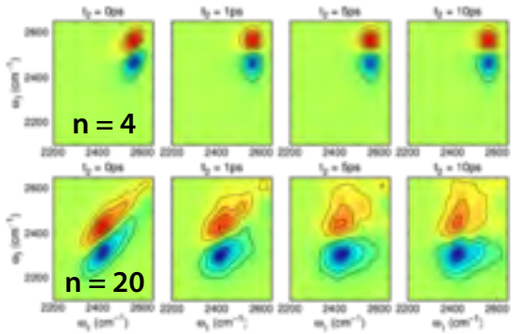


J. Chem. Theory Comput. 8, 2868 (2012)
J. Phys. Chem. Lett. 4, 779 (2013)
J. Phys. Chem. B 118, 8081 (2014)
Langmuir 31, 2147 (2015)
J. Am. Chem. Soc. 138, 3912 (2016)

adsorption & 2D-IR spectra



J. Am. Chem. Soc. 134, 4207 (2012)
J. Phys. Chem. C 117, 19508 (2013)
J. Phys. Chem. Lett. 5, 2897 (2014)
J. Phys. Chem. C 119 ,18239 (2015)
J. Am. Chem. Soc. 138, 6123 (2016)



Molecular Simulations & Vibrational Spectroscopy

Infrared: $I_{IR} \propto \int e^{-i\omega t} \langle \mu(t)\mu(0) \rangle dt$

Raman: $I_{Raman} \propto \int e^{-i\omega t} \langle \alpha(t)\alpha(0) \rangle dt$

Sum-frequency generation: $I_{SFG} \propto \int e^{-i\omega t} \langle \alpha(t)\mu(0) \rangle dt$

…and nonlinear multidimensional analogs

What goes into these expressions:

Molecular configurations, dipoles, polarizabilities

Correlation functions

Energy Landscape

Molecular mechanics = Force fields

$$V(\vec{R}^N) = \sum_{bonds} \frac{k_b}{2}(r_b - r_{b,o})^2 + \sum_{angles} \frac{k_a}{2}(\theta_a - \theta_{a,o})^2 + \sum_{torsion} \left[\sum_n \frac{V_n}{2}(1 + \cos(n\omega - \gamma)) \right]$$

$$+ \sum_{i<j} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}} \right\}$$

Hill, J. Chem. Phys. 14, 465 (1946) / Westheimer & Mayer, J. Chem. Phys. 14, 733 (1946)

Lifson & Warshel, J. Chem. Phys. 49, 5116 (1968)

Energy Landscape

Molecular mechanics = Force fields

$$V(\vec{R}^N) = \sum_{bonds} \frac{k_b}{2}(r_b - r_{b,o})^2 + \sum_{angles} \frac{k_a}{2}(\theta_a - \theta_{a,o})^2 + \sum_{torsion} \left[\sum_n \frac{V_n}{2}(1 + \cos(n\omega - \gamma)) \right]$$

$$+ \sum_{i<j} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}} \right\}$$

Hill, J. Chem. Phys. 14, 465 (1946) / Westheimer & Mayer, J. Chem. Phys. 14, 733 (1946)

Lifson & Warshel, J. Chem. Phys. 49, 5116 (1968)

Quantum mechanics = Ab initio

$$\hat{H}\Psi = E\Psi$$

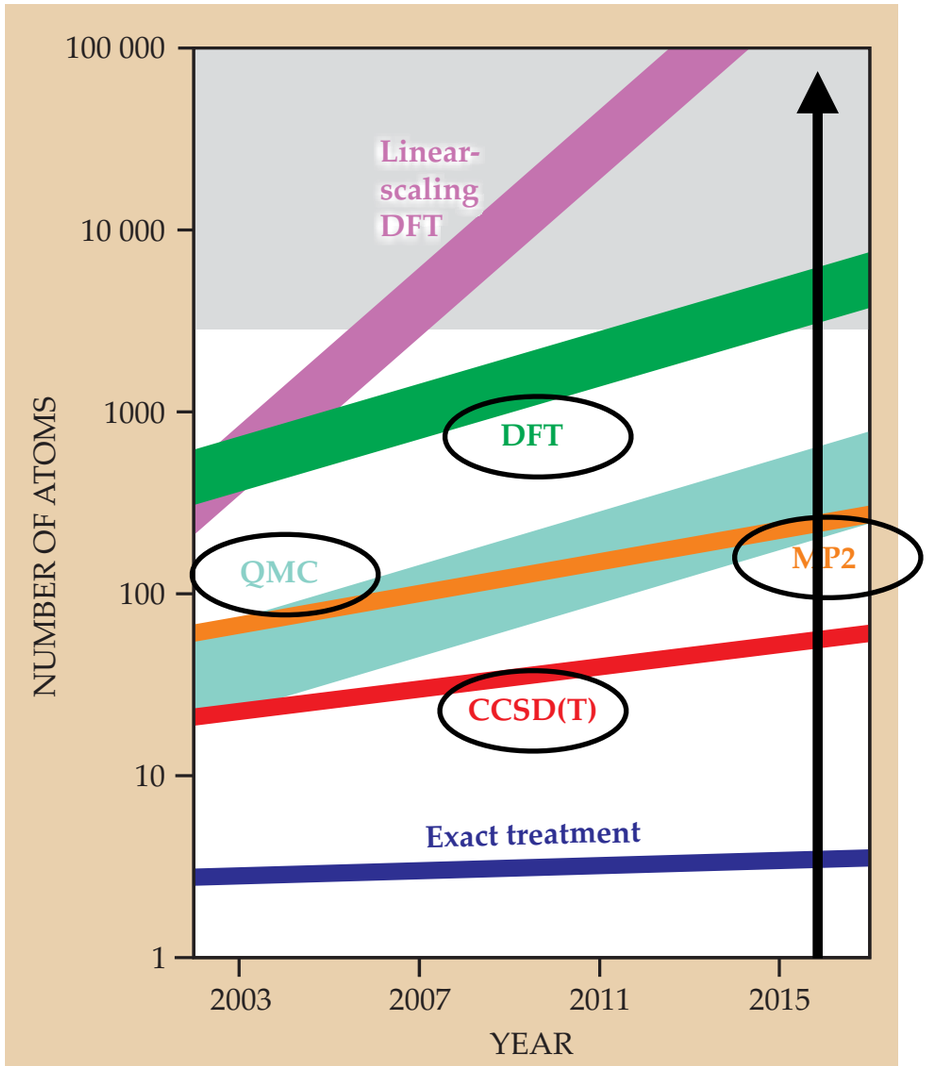
$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{xc}[\rho]$$

1930: Hartree-Fock equations

1951: Hartree-Fock-Roothan equations

1965: Kohn & Sham equations

1966: Coupled-Cluster equations



Head-Gordon & Artacho, Phys. Today 61, 58 (2008)

Molecular Simulations & Vibrational Spectroscopy

Infrared: $I_{IR} \propto \int e^{-i\omega t} \langle \mu(t)\mu(0) \rangle dt$

Raman: $I_{Raman} \propto \int e^{-i\omega t} \langle \alpha(t)\alpha(0) \rangle dt$

Sum-frequency generation: $I_{SFG} \propto \int e^{-i\omega t} \langle \alpha(t)\mu(0) \rangle dt$

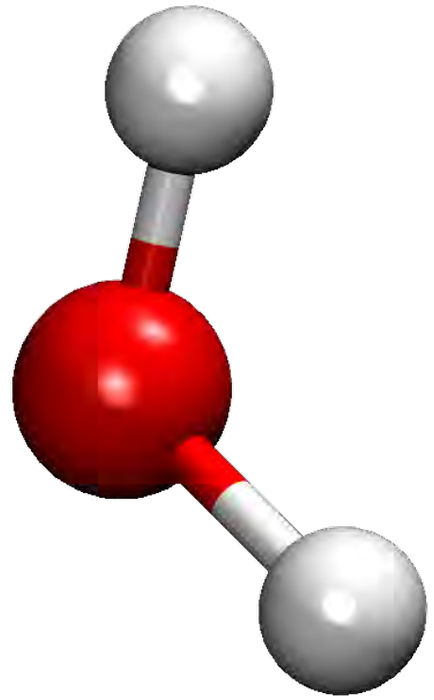
…and nonlinear multidimensional analogs

What goes into these expressions:

Molecular configurations, dipoles, polarizabilities

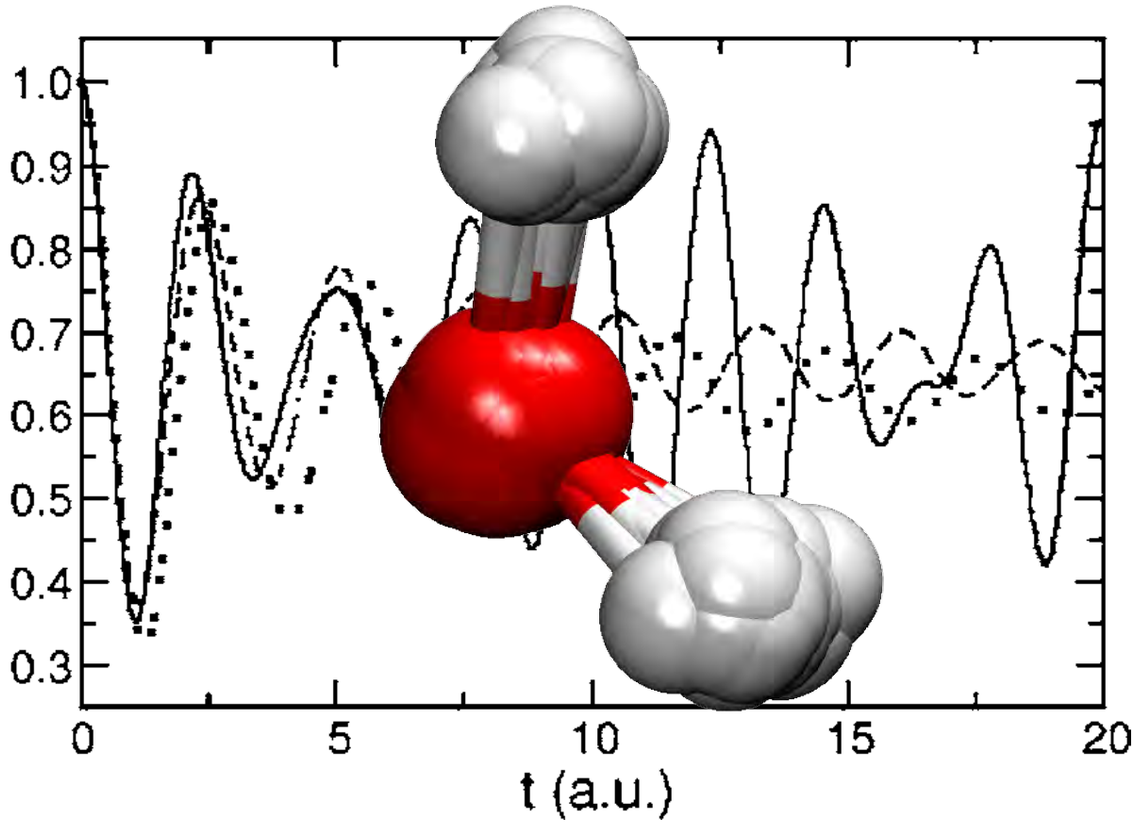
Correlation functions

Molecular Dynamics



classical

Newton equation



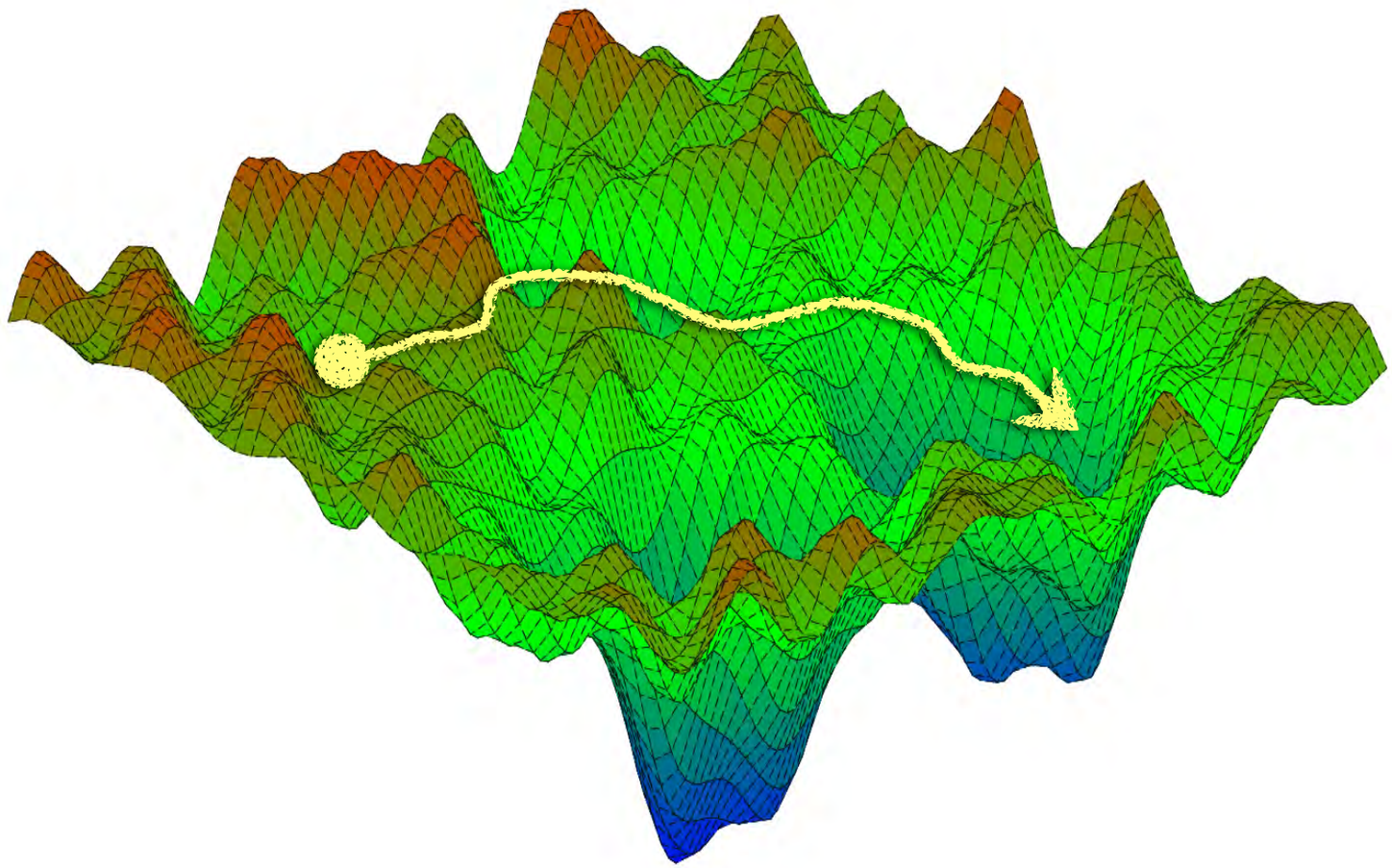
quantum

TD Schrödinger equation

Defining Chemical and Spectroscopic Accuracy

Energy landscape

force fields or ***CCSD(T)***



Molecular dynamics

Newton eq. or ***TD Schrödinger eq.***

How Can We Do It?

Quantum Chemist:
"It is all about
chemical accuracy"
(what about sampling?)

Statistical Mechanician:
"It is all about
averages and fluctuations"
(what about E_i in $Z = \sum_i e^{-\beta E_i}$?)

Computer Scientist:
"I don't know
what you are talking about
but I know
how to win at Go"

CCSD(T) only for 10-20 atoms!!!

quantum dynamics is a hard problem!!!

Where We Started: Many-Body Representations

$$E_N = \sum_i^N V^{1B}(i) \qquad \text{1-body}$$

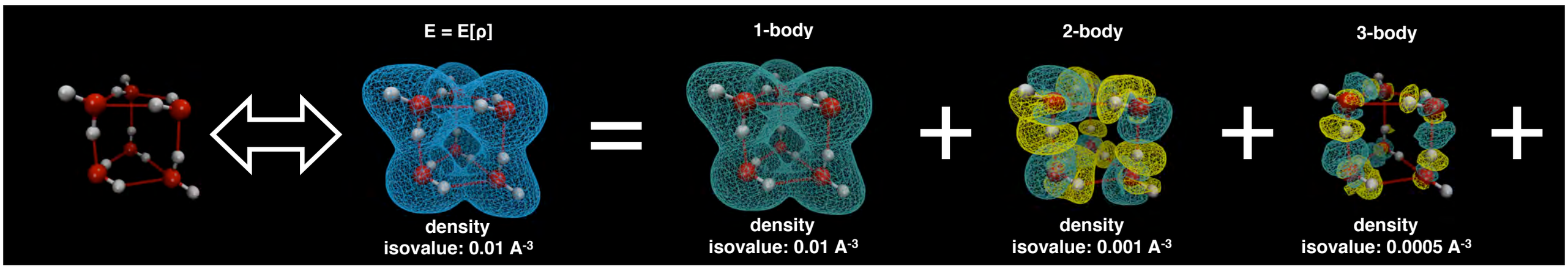
$$+ \sum_{i<j}^N V^{2B}(i,j) \qquad \text{2-body}$$

$$+ \sum_{i<j<k}^N V^{3B}(i,j,k) \qquad \text{3-body}$$

$$+ \ldots$$

$$+ V^{NB}(1,\ldots,N) \qquad \text{N-body}$$

Hankins, Moskowitz & Stillinger, J. Chem. Phys. 53, 4544 (1970)
Popkie, Kistenmacher & Clementi, J. Chem. Phys. 59, 1325 (1973)



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Where We Started: Many-Body Representations

$$E_N = \sum_i^N V^{1B}(i)$$ 1-body *~100 kcal mol^{-1}*

$$+ \sum_{i<j}^N V^{2B}(i,j)$$ 2-body *~10 kcal mol^{-1}*

$$+ \sum_{i<j<k}^N V^{3B}(i,j,k)$$ 3-body *~1 kcal mol^{-1}*

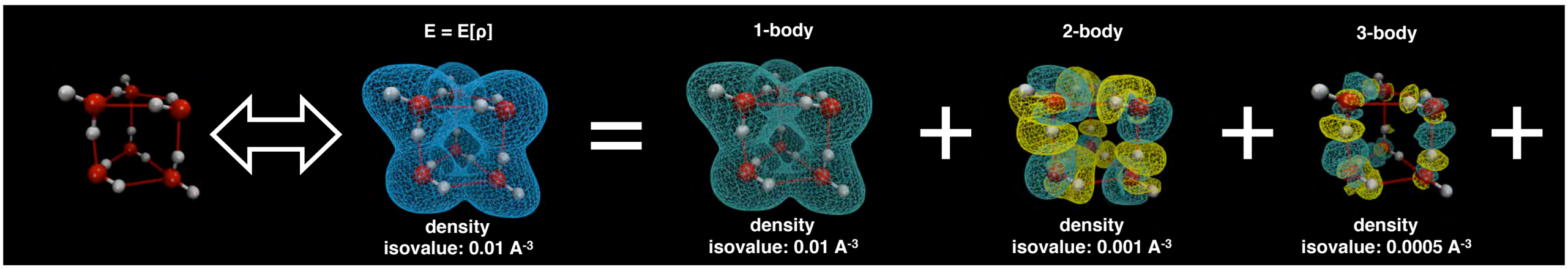
$$+ \ldots$$ 4-body *~0.1 kcal mol^{-1}*

$$+ V^{NB}(1,\ldots,N)$$ N-body

MB expansion for insulators (like water) converges quickly

see: Clementi, Stillinger, Xantheas, Jordan, Szalewicz, Bowman, ...

Hankins, Moskowitz & Stillinger, J. Chem. Phys. 53, 4544 (1970)
Popkie, Kistenmacher & Clementi, J. Chem. Phys. 59, 1325 (1973)



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Neither the First Nor the Only Ones

1973 - Clementi: 2B from HF data (rigid)

1976 - Clementi: 2B + (3B + 4B) polarization (rigid)

1989 - Clementi: 2B + 3B from MP4 and HF data (rigid)

1992 - Stone: ASP potential from intermolecular perturbation theory (rigid)

2000 - Szalewicz & van der Avoird: SAPT potentials (rigid)

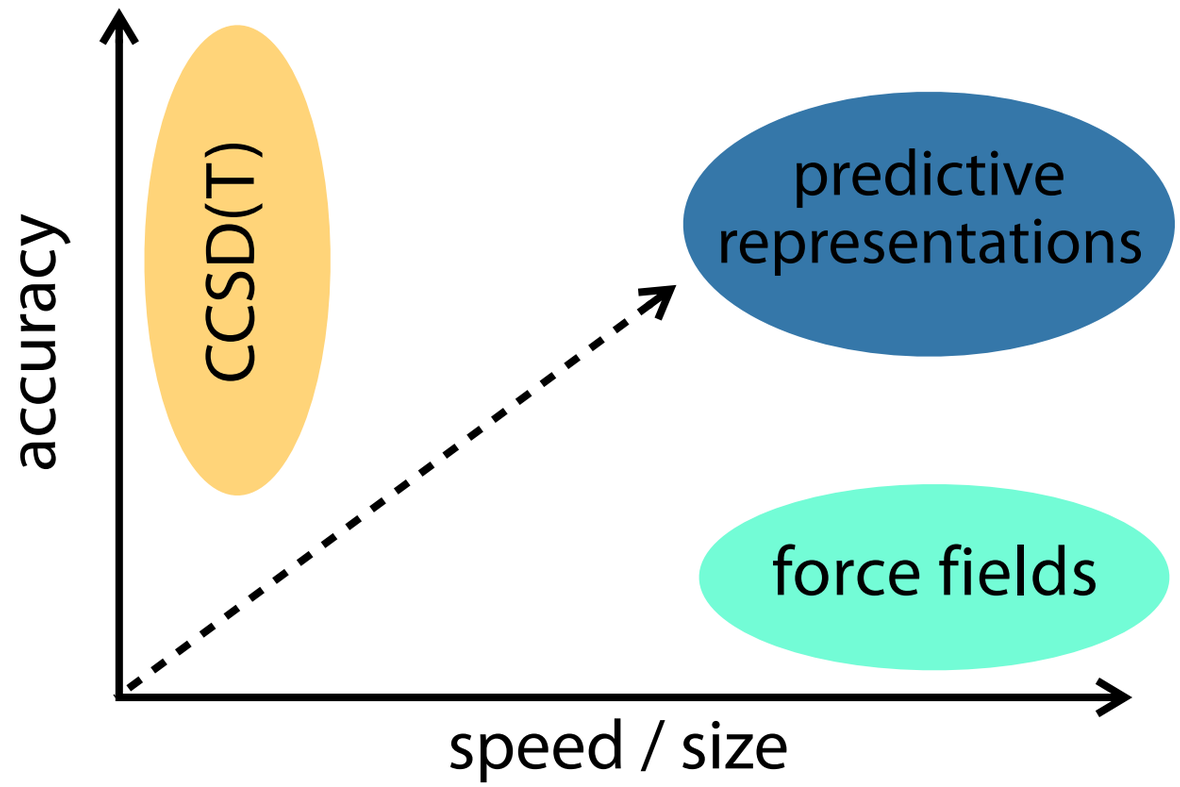
2007 - Szalewicz & van der Avoird: CC-pol (1B + 2B + 3B + NB) from MP2/CCSD(T) and SAPT (rigid)

2008 - Xantheas / Burnham: TTM3-F / TTM4-F (1B + NB) from MP2 data (flexible)

2011 - Bowman: WHBB (1B + 2B + 3B) from CCSD(T) and MP2 data (flexible)

2012/2014 - Our group: HBB2-pol & MB-pol

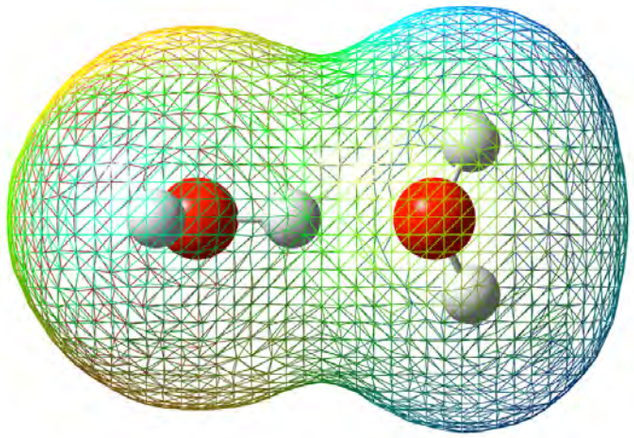
20XX - …



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Molecular Interactions & Electronic Structure

Interactions depend
on the density overlap

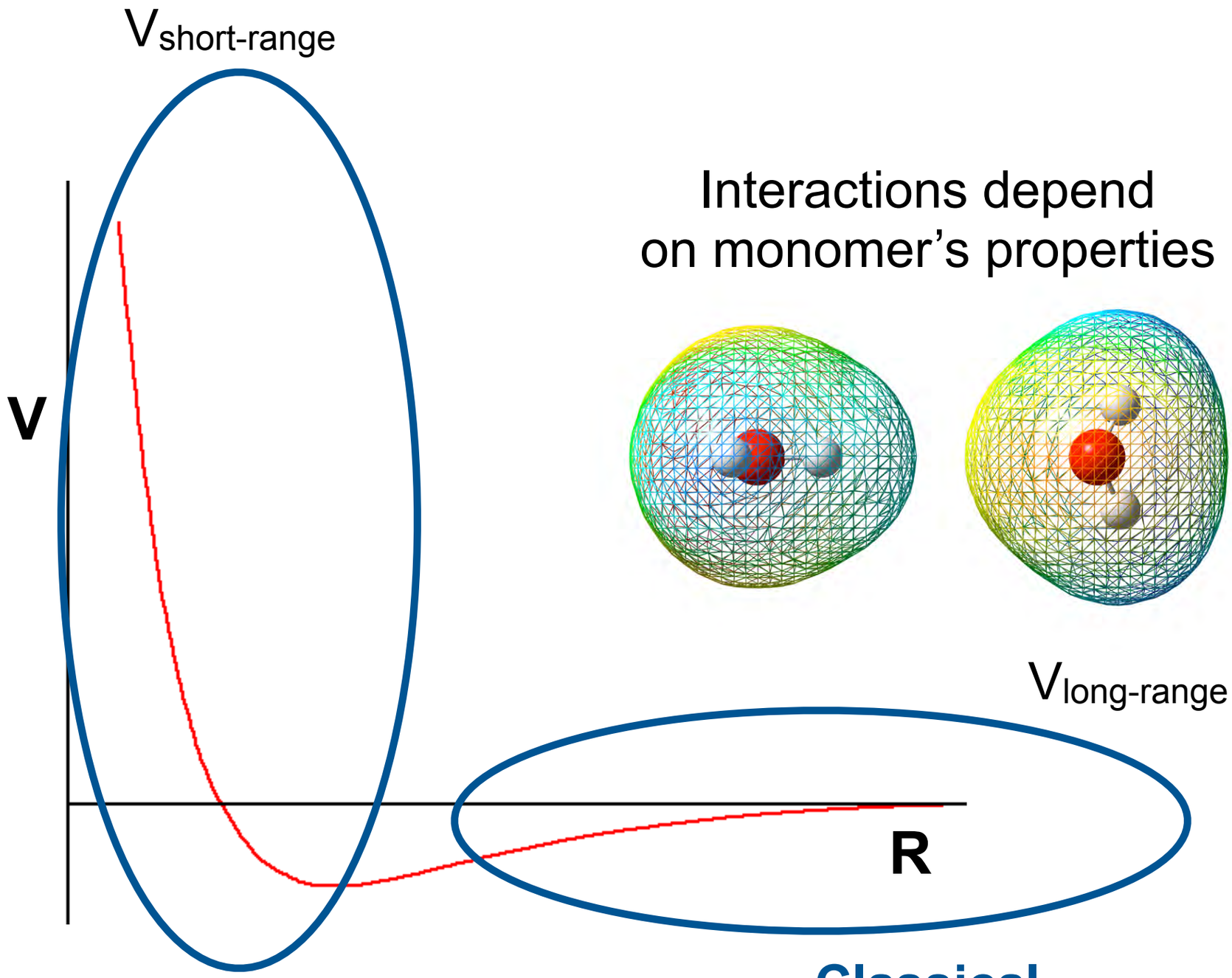


Multidimensional fits to highly-correlated ab initio data

Suhm
Chem. Phys. Lett. 223, 474 (1994)

Marquardt & Quack
J. Chem. Phys. 109, 10628 (1998)

Braams & Bowman,
Int. Rev. Phys. Chem. 28, 577 (2009)

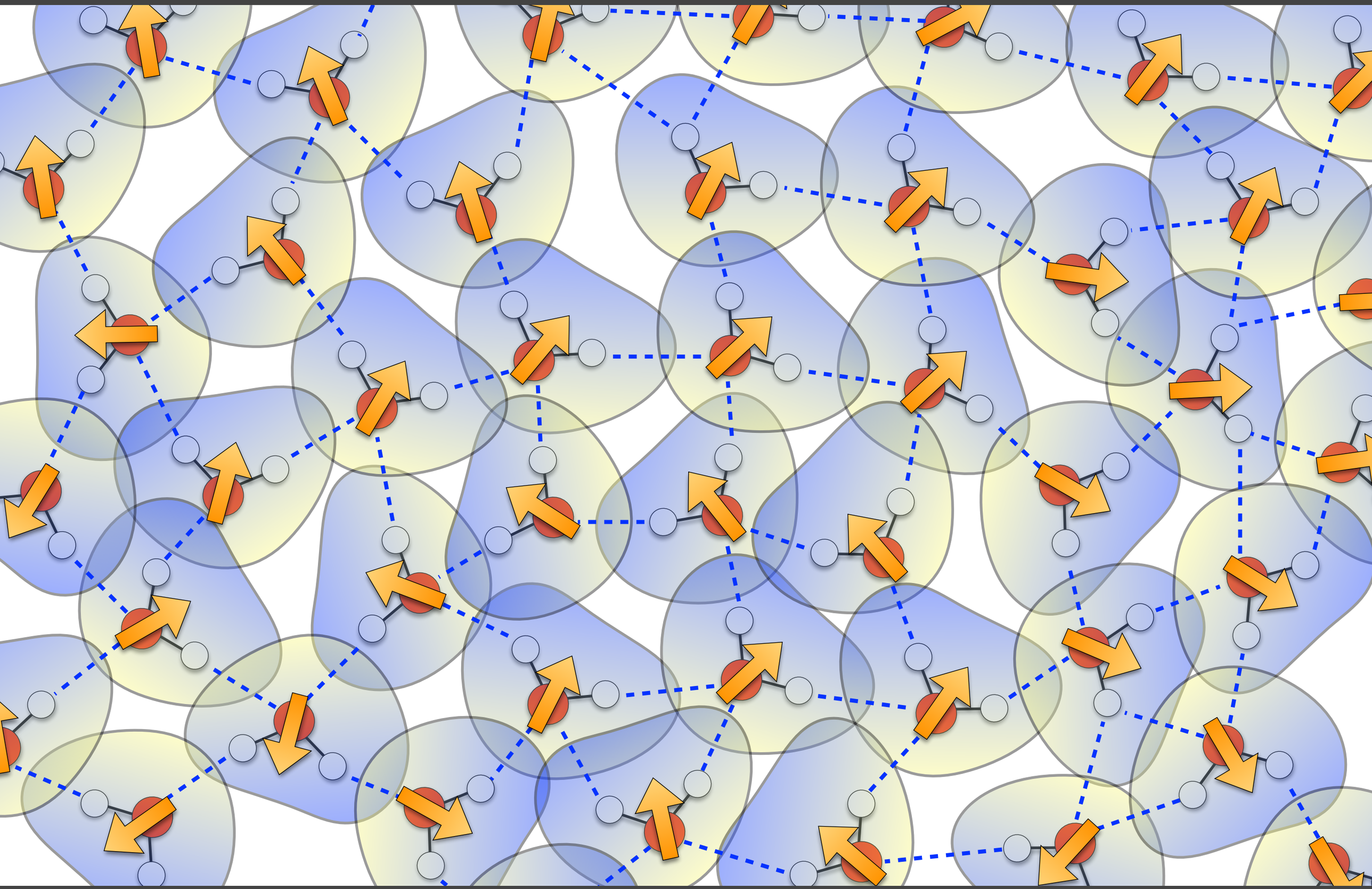


Interactions depend
on monomer's properties

Classical electrostatics

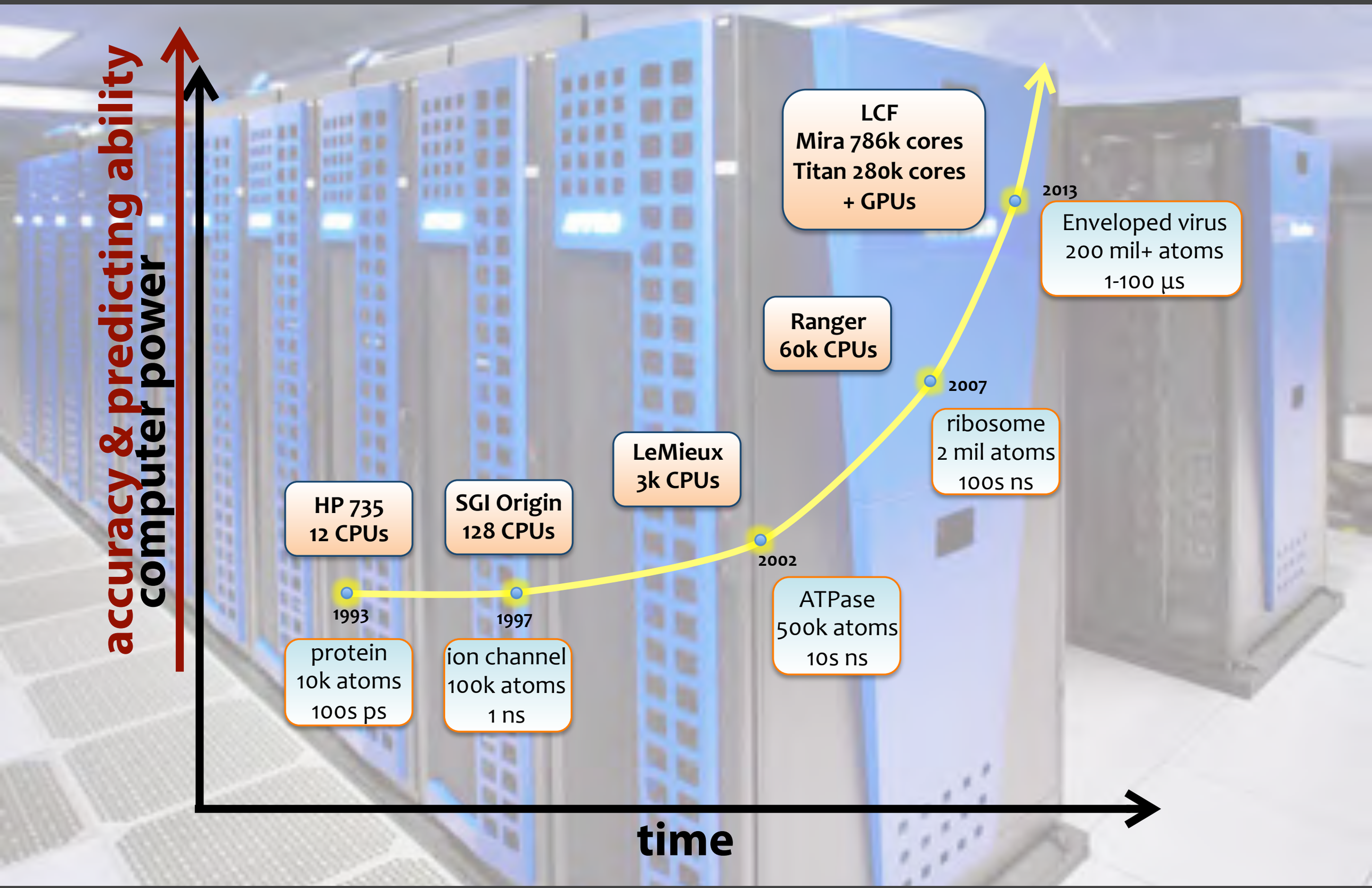
Stone, "Intermolecular Interactions"

Molecular Interactions & Electronic Structure



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

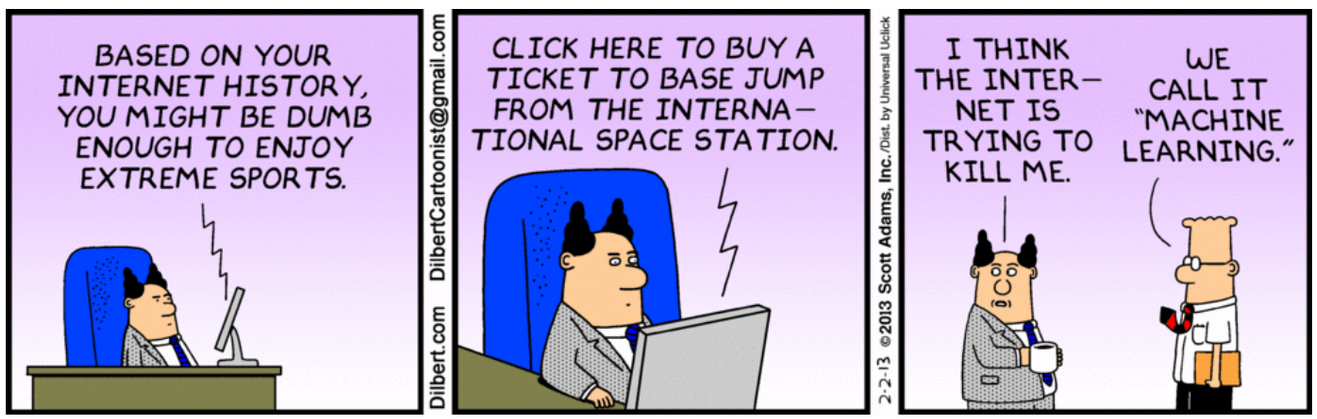
Molecular Interactions & Scientific Computing



Courtesy of Rommie Amaro (UCSD/SanDiego)

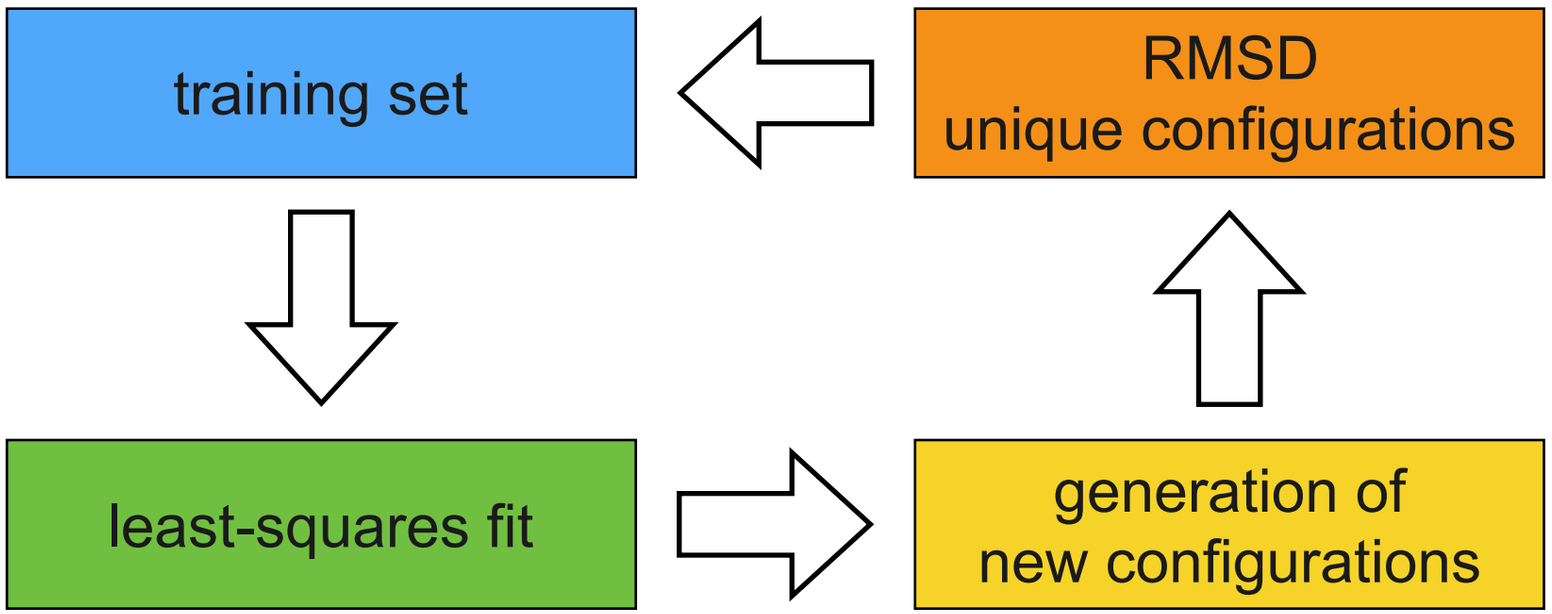
Molecular Interactions & Big Data

Machine learning

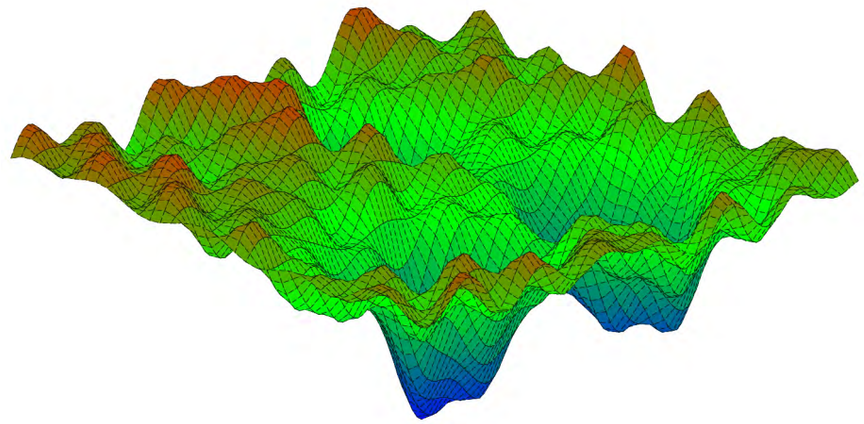


- Google
- Amazon
- Facebook
- LinkedIn

Supervised learning



optimization of
multidimensional functions



Abu-Mostafa & Magdon-Ismail, "Learning from data"

MB-pol: A "CCSD(T)" Many-Body Water Potential

$$E_N = \sum_i^N V^{1B}(i) \qquad \text{1-body}$$

$$+ \sum_{i<j}^N V^{2B}(i,j) \qquad \text{2-body}$$

$$+ \sum_{i<j<k}^N V^{3B}(i,j,k) \qquad \text{3-body}$$

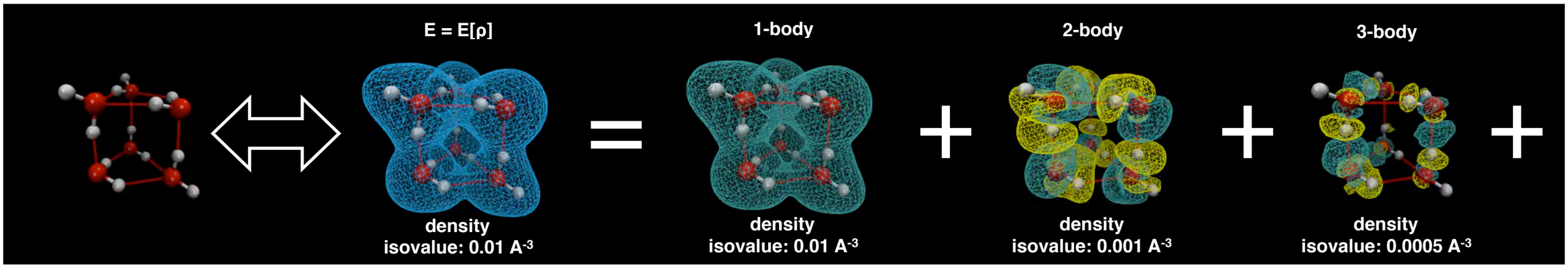
$$+ \ldots$$

$$+ V^{NB}(1,\ldots,N) \qquad \text{N-body}$$

Hankins, Moskowitz & Stillinger, J. Chem. Phys. 53, 4544 (1970)
Popkie, Kistenmacher & Clementi, J. Chem. Phys. 59, 1325 (1973)

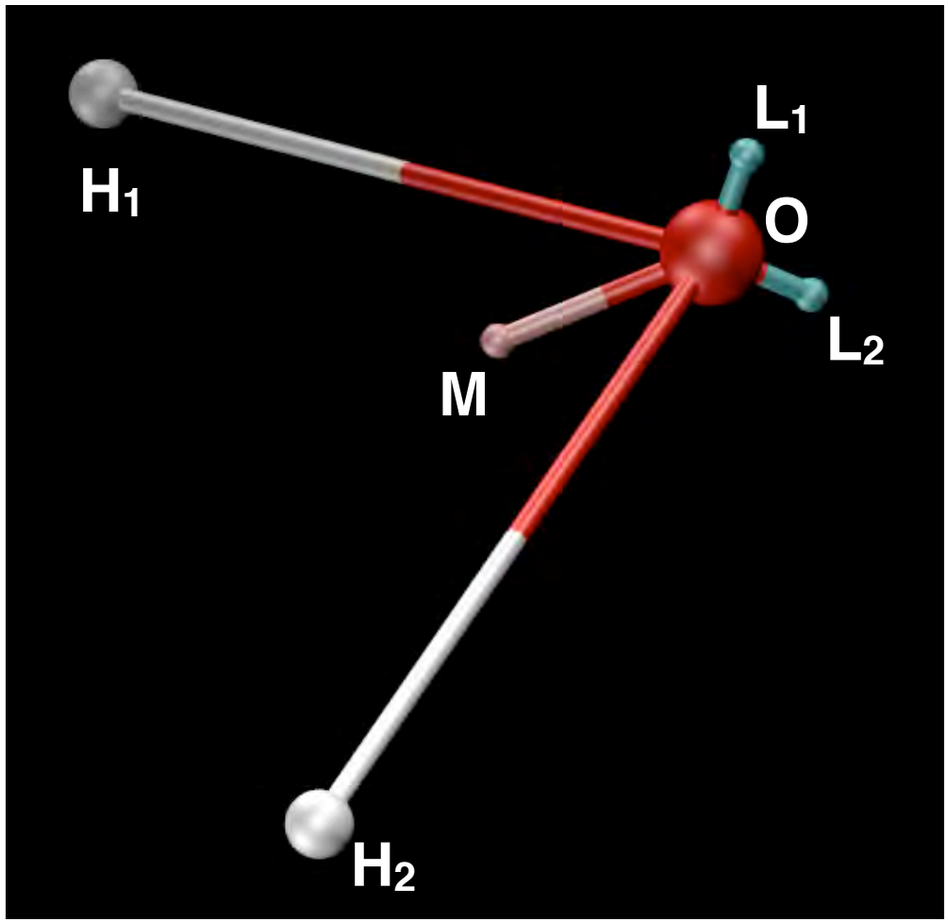
explicit 1B term
+
N-body polarization
+
explicit 2B and 3B terms from CCSD(T)/CBS

- *J. Phys. Chem. Lett. 3, 3765 (2012)*
- *J. Chem. Theory Comput. 9, 1103 (2013)*
- *J. Chem. Theory Comput. 9, 4844 (2013)*
- *J. Chem. Theory Comput. 9, 5395 (2013)*
- *J. Chem. Theory Comput. 10, 1599 (2014)*
- *J. Chem. Theory Comput. 10, 2906 (2014)*
- *J. Chem. Theory Comput. 11, 1145 (2015)*



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

MB-pol: A "CCSD(T)" Many-Body Water Potential



$$V^{1B} = V^{1B}_{PS}$$ *Partridge & Schwenke, J. Chem. Phys. 106, 4618 (1997)*

permanent electrostatics

$$V^{2B} = s_2 V^{2B}_{poly} + V^{2B}_{elect} + V^{2B}_{ind} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R^6_{ij}}$$

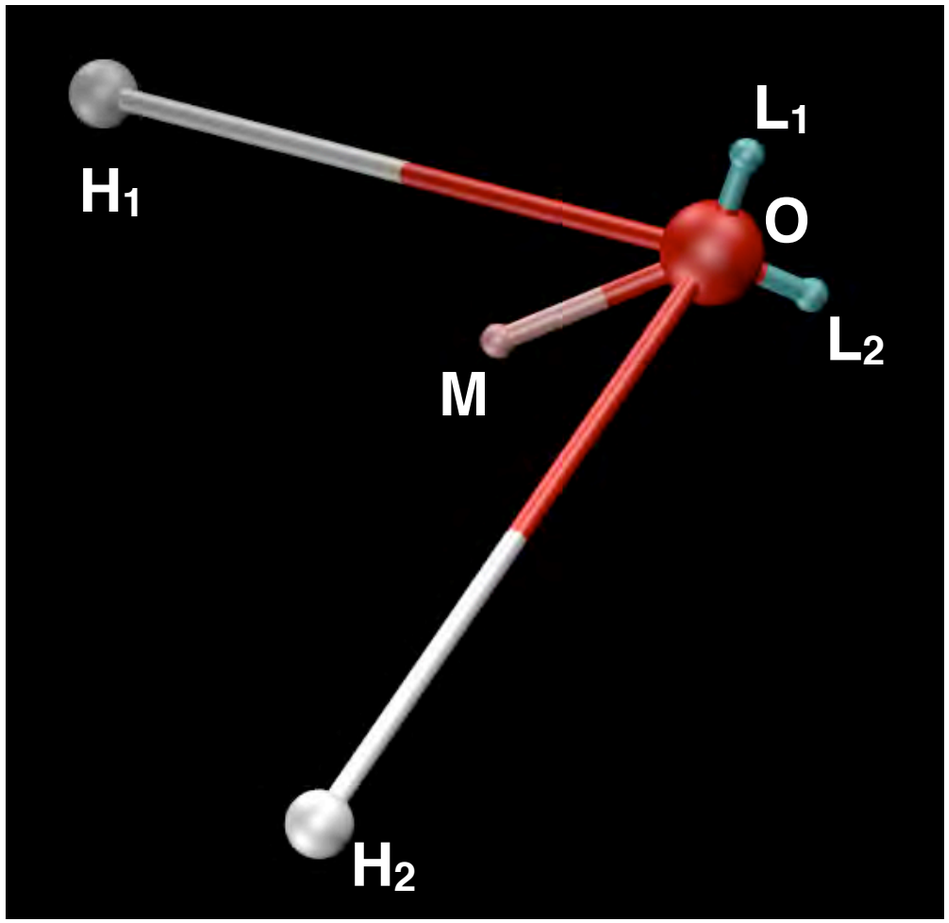
2B dispersion

$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

$$V^{>3B} = V^{>3B}_{ind}(1, \ldots, N)$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A "CCSD(T)" Many-Body Water Potential



$$V^{1B} = V^{1B}_{PS}$$

Partridge & Schwenke, J. Chem. Phys. 106, 4618 (1997)

permanent electrostatics

$$V^{2B} = s_2 V^{2B}_{poly} + V^{2B}_{elect} + V^{2B}_{ind} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R^6_{ij}}$$

2B dispersion

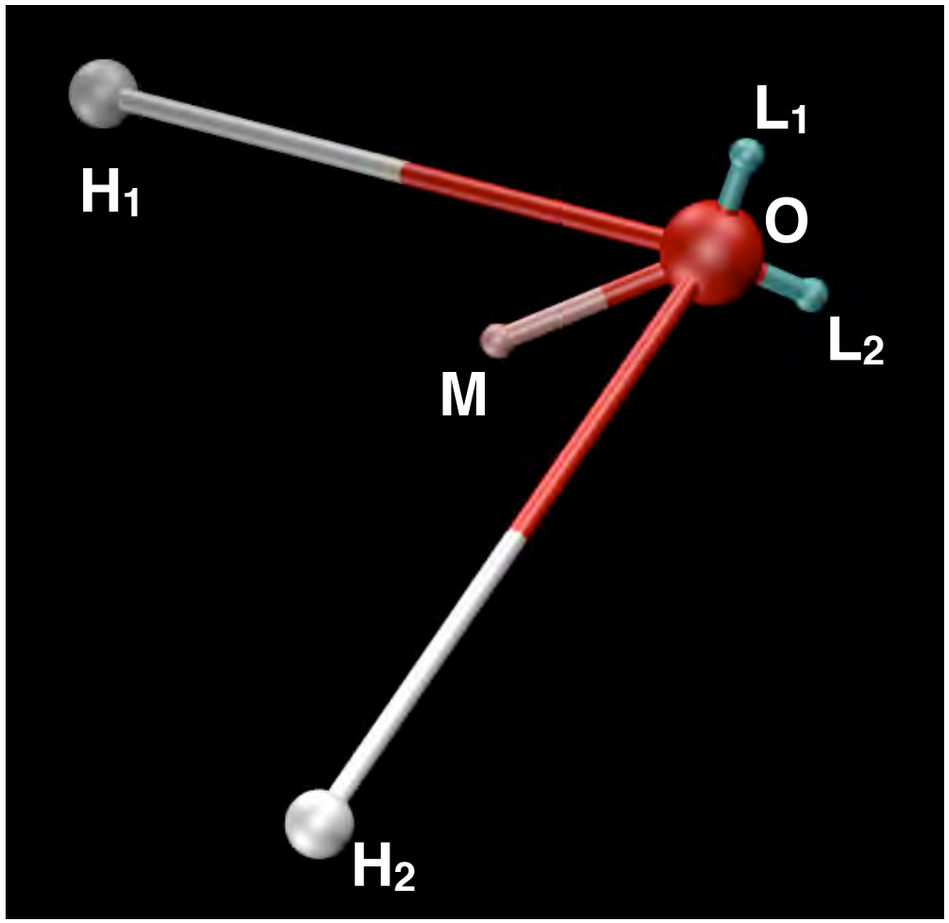
$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

NB induction

$$V^{>3B} = V^{>3B}_{ind}(1, \ldots, N)$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A "CCSD(T)" Many-Body Water Potential



$$V^{1B} = V^{1B}_{PS}$$

Partridge & Schwenke, J. Chem. Phys. 106, 4618 (1997)

permanent electrostatics

$$V^{2B} = s_2 V^{2B}_{poly} + V^{2B}_{elect} + V^{2B}_{ind} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R^6_{ij}}$$

short-range interactions

2B dispersion

$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

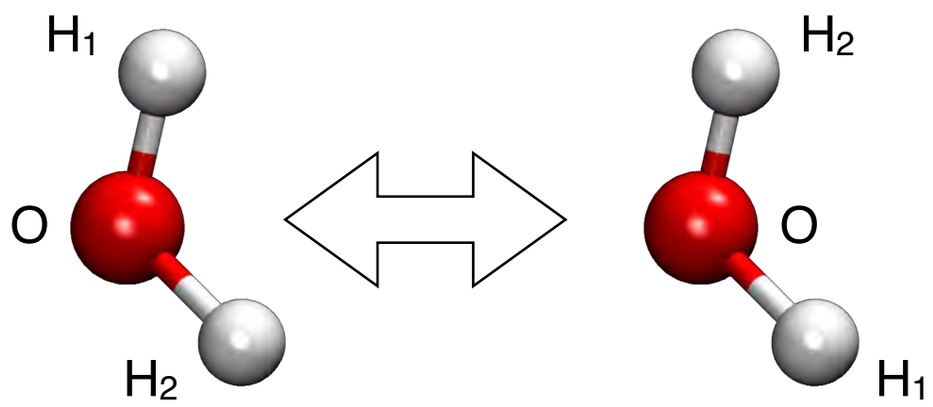
NB induction

$$V^{>3B} = V^{>3B}_{ind}(1, \ldots, N)$$

Permutationally invariant polynomials

Marquardt & Quack, J. Chem. Phys. 109, 10628 (1998)

Braams & Bowman, Int. Rev. Phys. Chem. 28, 577 (2009)



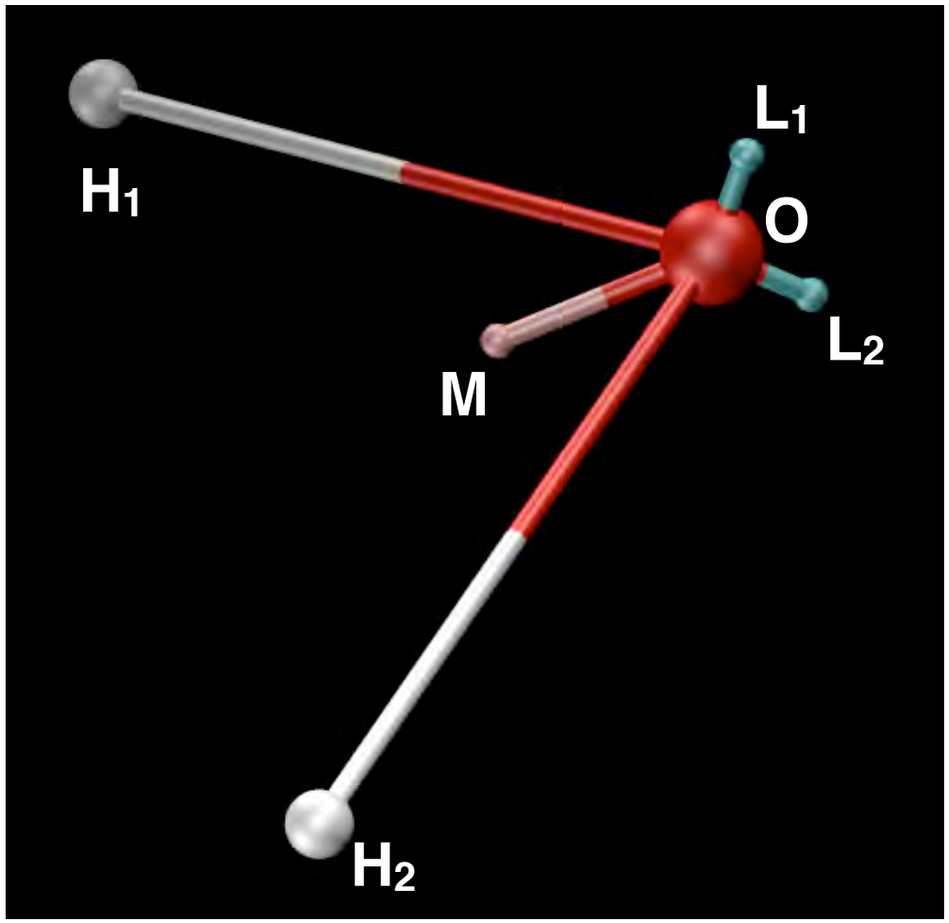
$$V = \sum_{m=a+b+c=0}^{M} D_{abc} \left\{ y_{12}^a \left[y_{13}^b y_{23}^c + y_{13}^c y_{23}^b \right] \right\}$$

Morse variables

$$y_{ij} = e^{-k r_{ij}} \qquad y_{ij} = \frac{e^{-k r_{ij}}}{r_{ij}}$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A "CCSD(T)" Many-Body Water Potential



$$V^{1B} = V^{1B}_{PS}$$

Partridge & Schwenke, J. Chem. Phys. 106, 4618 (1997)

permanent electrostatics

$$V^{2B} = s_2 V^{2B}_{poly} + V^{2B}_{elect} + V^{2B}_{ind} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R^6_{ij}}$$

short-range interactions

2B dispersion

$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

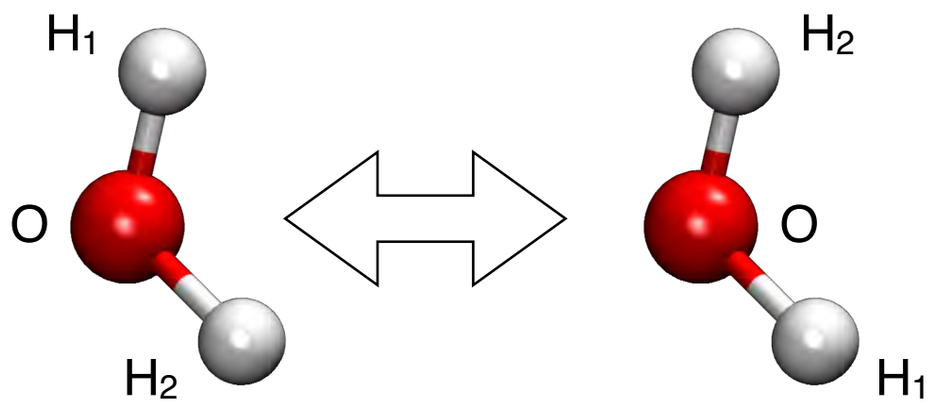
NB induction

$$V^{>3B} = V^{>3B}_{ind}(1, \ldots, N)$$

Permutationally invariant polynomials

Marquardt & Quack, J. Chem. Phys. 109, 10628 (1998)

Braams & Bowman, Int. Rev. Phys. Chem. 28, 577 (2009)



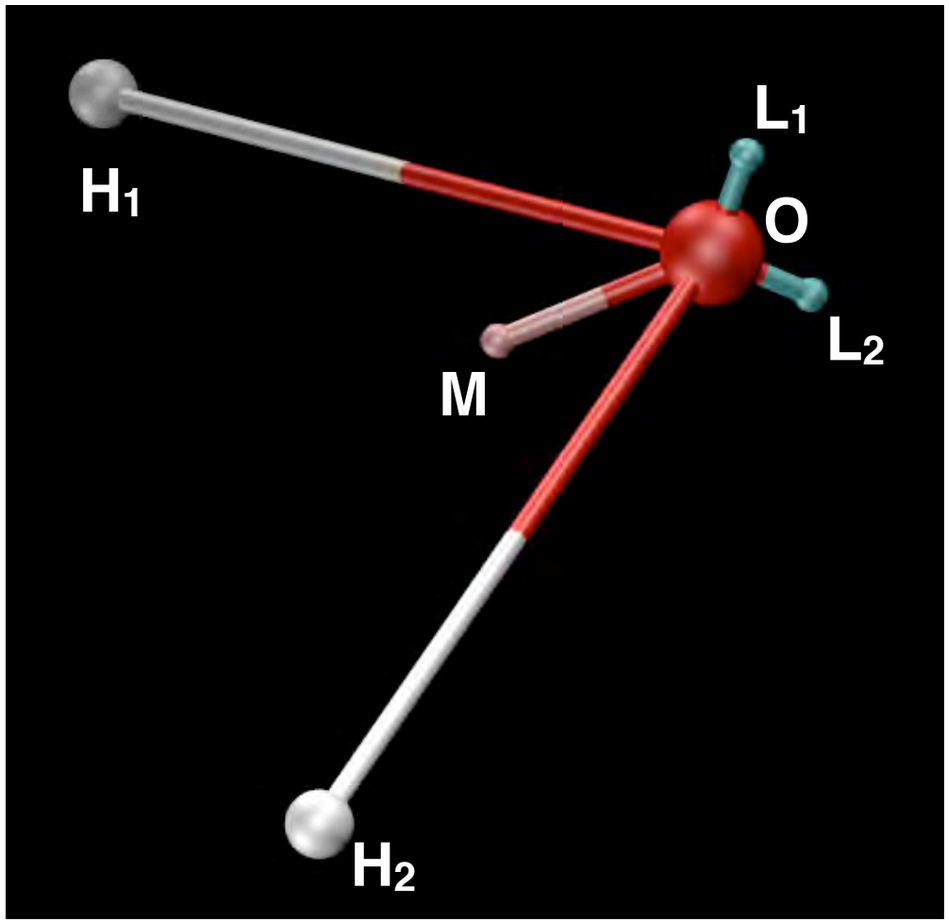
Alternative basis functions

Gaussian approximation potentials

Bartok, Payne, Kondor & Csanyi, Phys. Rev. Lett. 104, 136403 (2010)

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A "CCSD(T)" Many-Body Water Potential



$$V^{1B} = V^{1B}_{PS}$$ *Partridge & Schwenke, J. Chem. Phys. 106, 4618 (1997)*

permanent electrostatics

$$V^{2B} = s_2 V^{2B}_{poly} + V^{2B}_{elect} + V^{2B}_{ind} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R^6_{ij}}$$

short-range interactions

2B dispersion

$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

NB induction

$$V^{>3B} = V^{>3B}_{ind}(1, \ldots, N)$$

V2B and V3B from CCSD(T)/CBS data

supervised learning & Tikhonov regression

$$\chi^2 = \sum_{n \in \mathcal{S}} w_n [V_2^{\text{model}}(n) - V_2^{\text{ref}}(n)]^2 + \Gamma^2 \sum_{l=1}^{1153} c_l^2$$

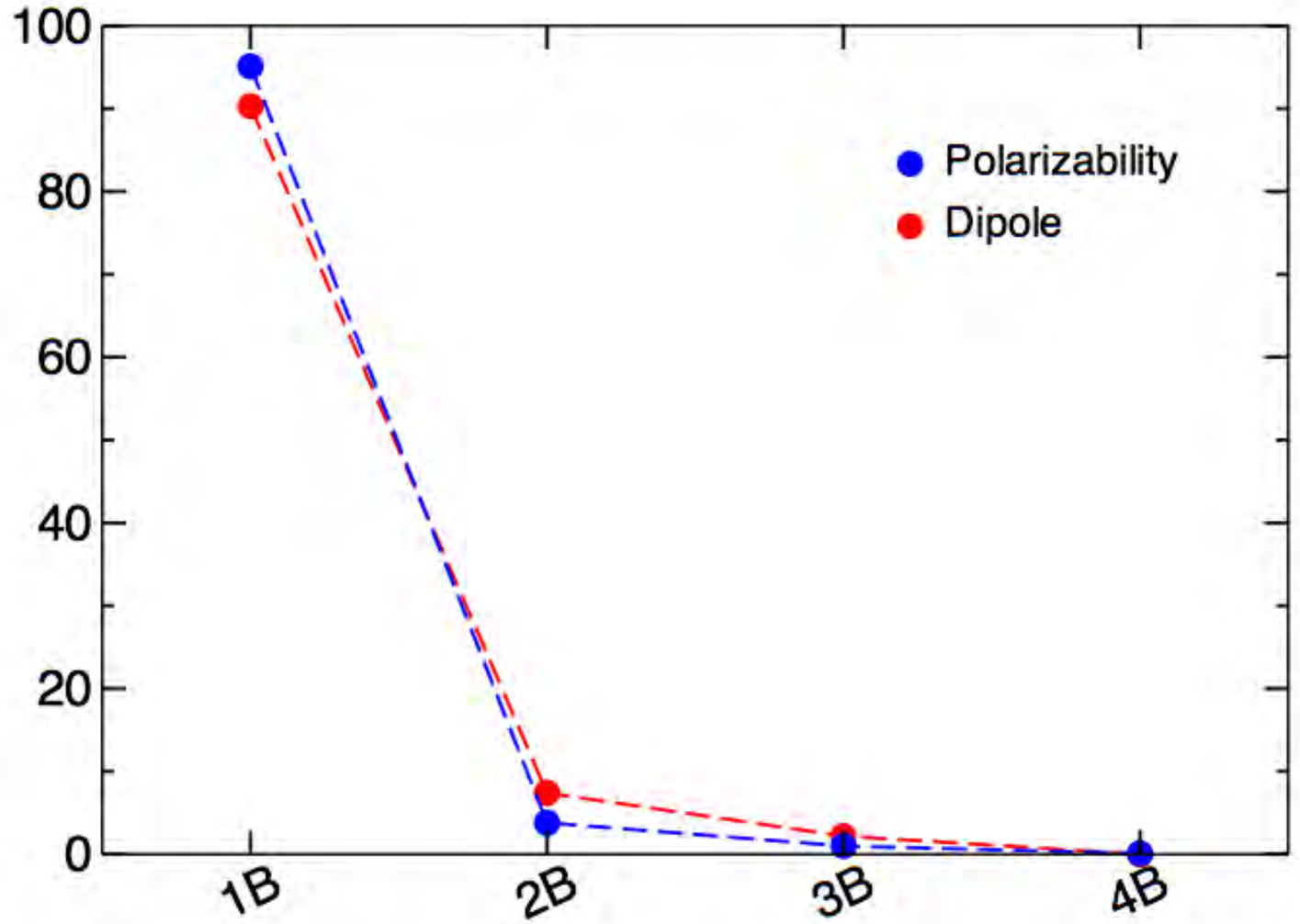
$$w(E) = \left(\frac{\Delta E}{E - E_{\text{min}} + \Delta E} \right)^2$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

Electrostatic Properties from Many-Body Expansions

Energy of a molecular system in an external field

$$E = E_0 - \mu_\alpha F_\alpha - \frac{1}{2} F_\alpha \alpha_{\alpha\beta} F_\beta$$



More than 95% of both dipole moment and polarizability are recovered at the two-body level

Medders & FP, J. Chem. Theory Comput. 9, 4844 (2013); Medders & FP, J. Chem. Theory Comput. 11, 1145 (2015)

Molecular Simulations & Vibrational Spectroscopy

Infrared: $I_{IR} \propto \int e^{-i\omega t} \langle \mu(t)\mu(0) \rangle dt$

Raman: $I_{Raman} \propto \int e^{-i\omega t} \langle \alpha(t)\alpha(0) \rangle dt$

Sum-frequency generation: $I_{SFG} \propto \int e^{-i\omega t} \langle \alpha(t)\mu(0) \rangle dt$

…and nonlinear multidimensional analogs

What goes into these expressions:

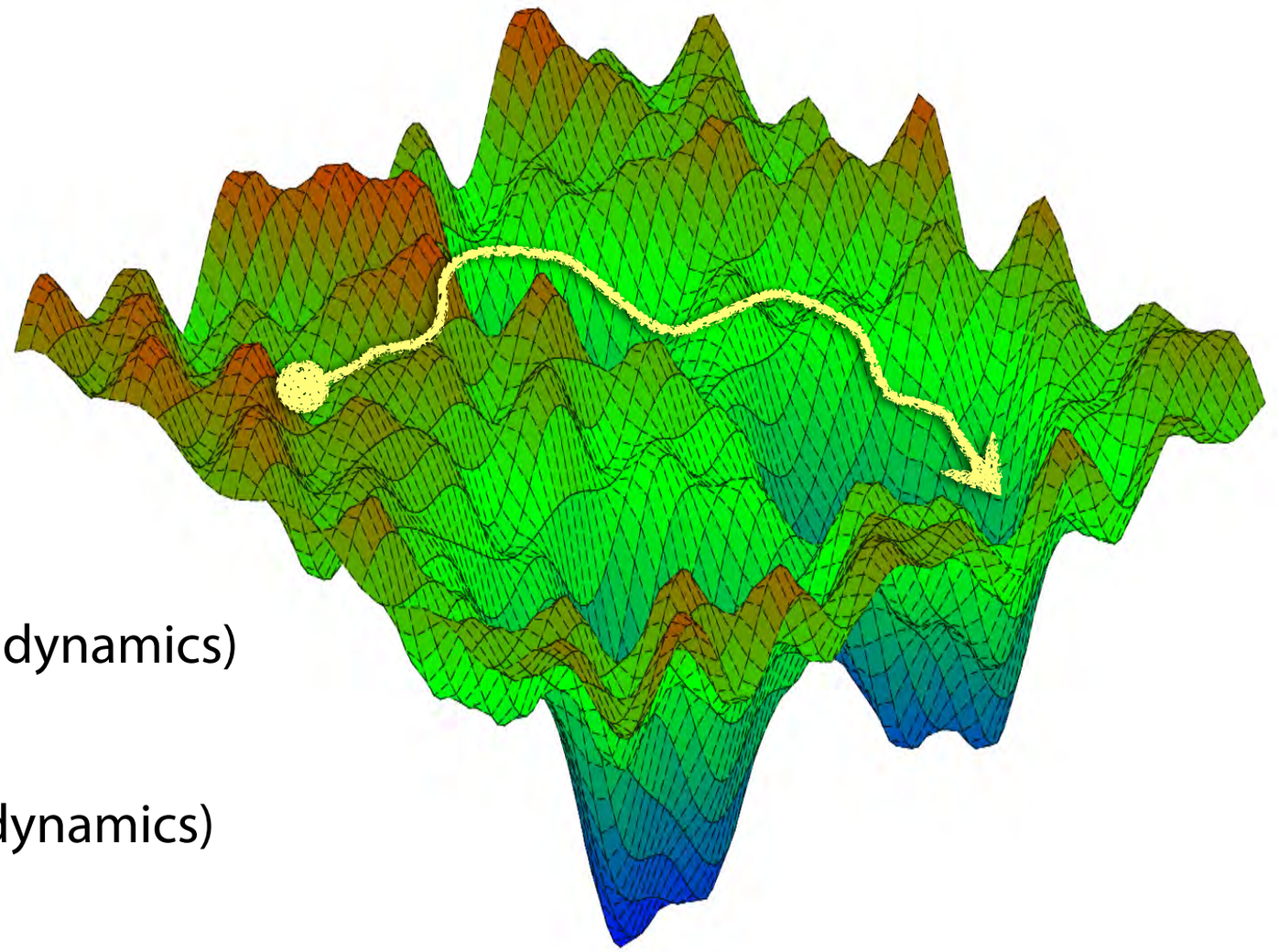
Configurations, dipoles, polarizabilities ⟶ many-body representations

Correlation functions

Quantum Dynamics: It's a Hard Problem!

MB-pol ⟺ Born-Oppenheimer potential energy surface

Nuclear quantum effects must be included
explicitly in molecular simulations



Methods based on:

- **Basis set expansions**
  with Leforestier, Wang & Carrington, Steele
  (clusters: vibrational spectra)
- **Self-Consistent Phonons**
  with Brown & Mandelshtam
  (clusters: structure, thermodynamics, and dynamics)
- **Path-integral molecular dynamics**
  (condensed phase: structure and thermodynamics)
- **Centroid molecular dynamics**
  (condensed phase: dynamics)

Molecular Simulations & Vibrational Spectroscopy

Infrared: $I_{IR} \propto \int e^{-i\omega t} \langle \mu(t)\mu(0) \rangle dt$

Raman: $I_{Raman} \propto \int e^{-i\omega t} \langle \alpha(t)\alpha(0) \rangle dt$

Sum-frequency generation: $I_{SFG} \propto \int e^{-i\omega t} \langle \alpha(t)\mu(0) \rangle dt$

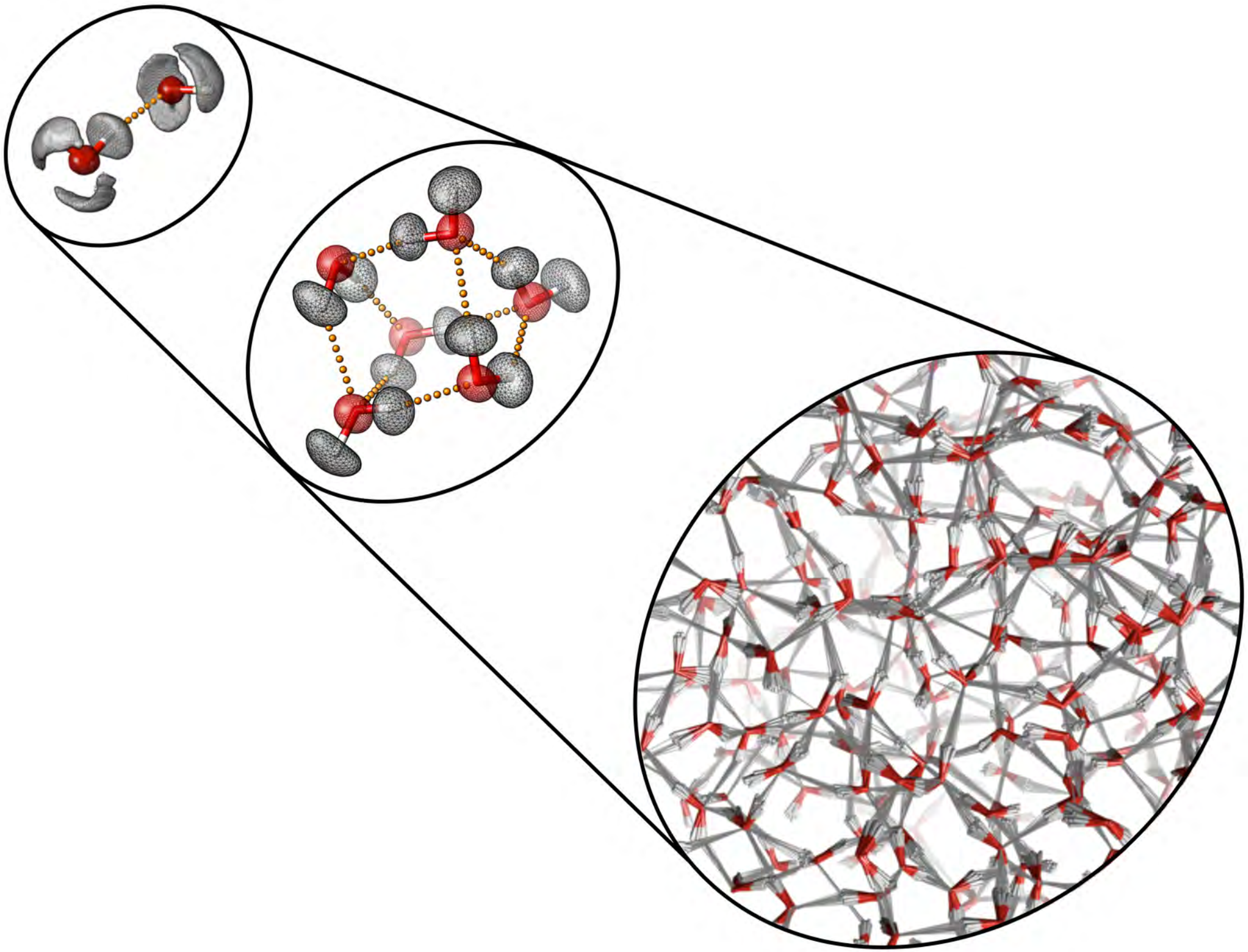
…and nonlinear multidimensional analogs

Many-Body Molecular Dynamics (MB-MD)

Configurations, dipoles, polarizabilities ⟶ many-body representations

Correlation functions ⟶ path-integral methods

Chemical Accuracy Across Phases



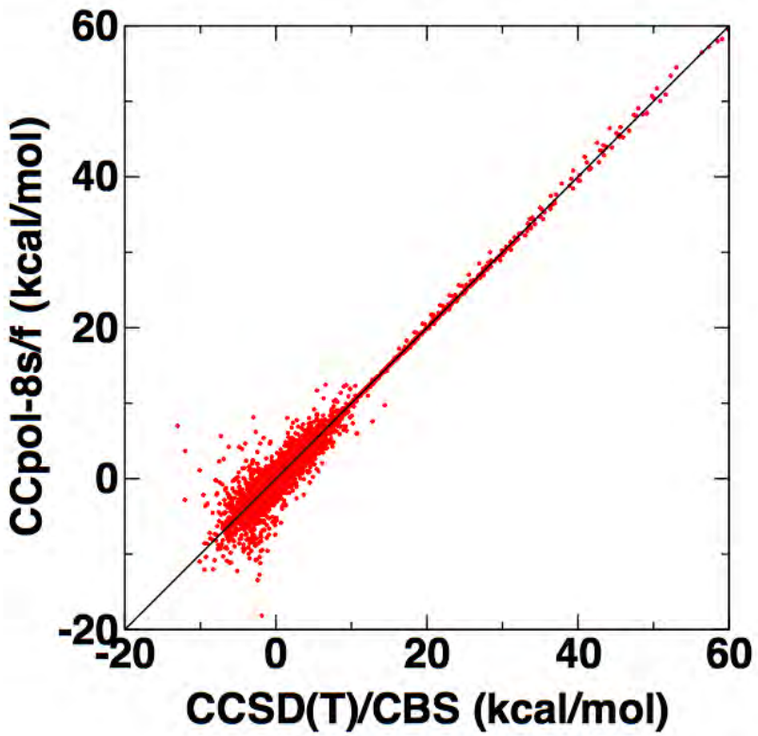
FP, Acc. Chem. Res. 49, 1844 (2016)

Water Dimer: Energies

Many-body potentials

CCpol-8s/f

Leforestier, Szalewicz & van der Avoird, J. Chem. Phys. 137, 014305 (2012)

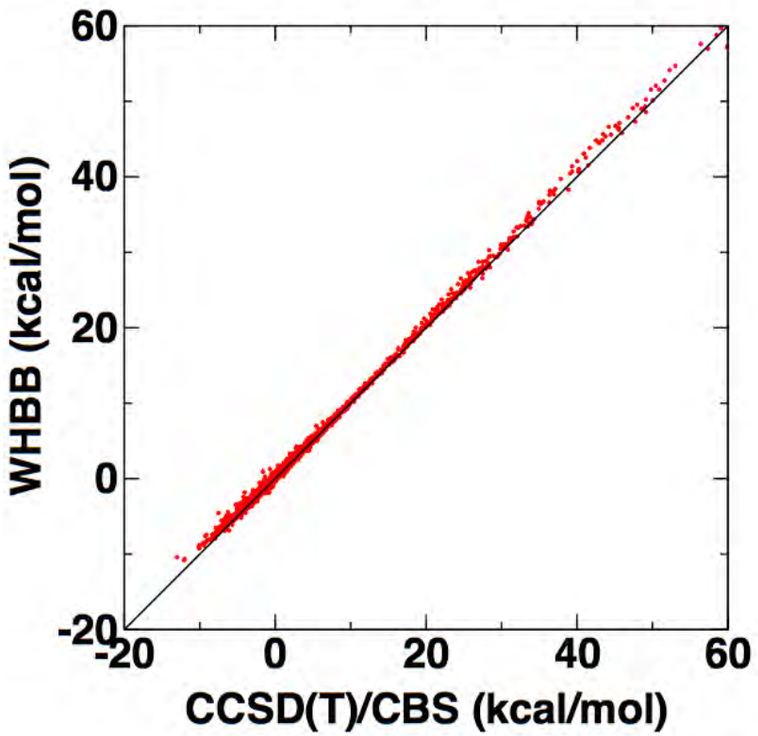


RMSD = 0.42 kcal/mol

for E_{tot} < 25 kcal/mol
RMSD = 0.18 kcal/mol

WHBB

Wang, Shepler, Braams & Bowman, J. Chem. Phys. 131, 054511 (2009)

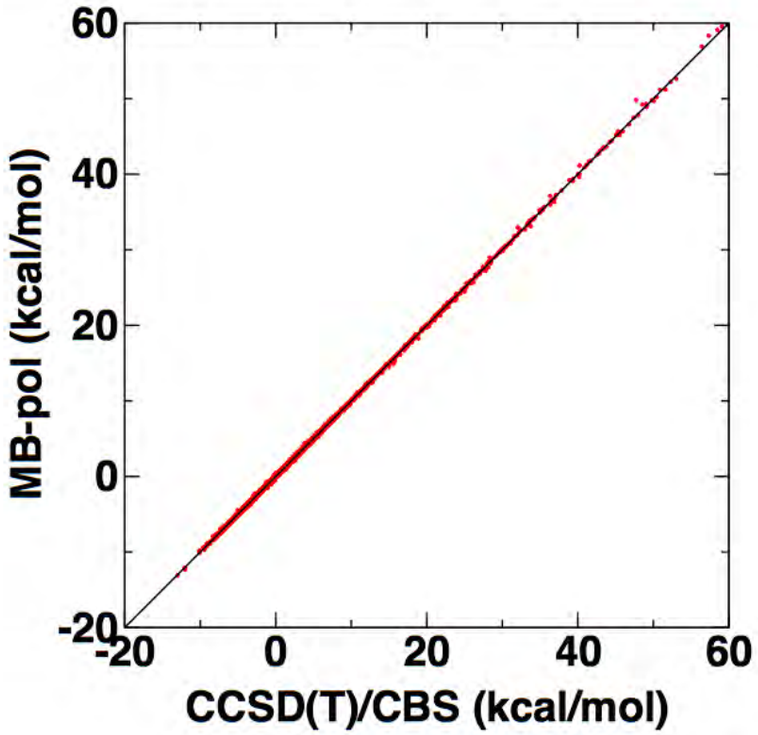


RMSD = 0.15 kcal/mol

for E_{tot} < 25 kcal/mol
RMSD = 0.07 kcal/mol

MB-pol

Babin, Leforestier & FP J. Chem. Theory Comput. 9, 5395 (2013)



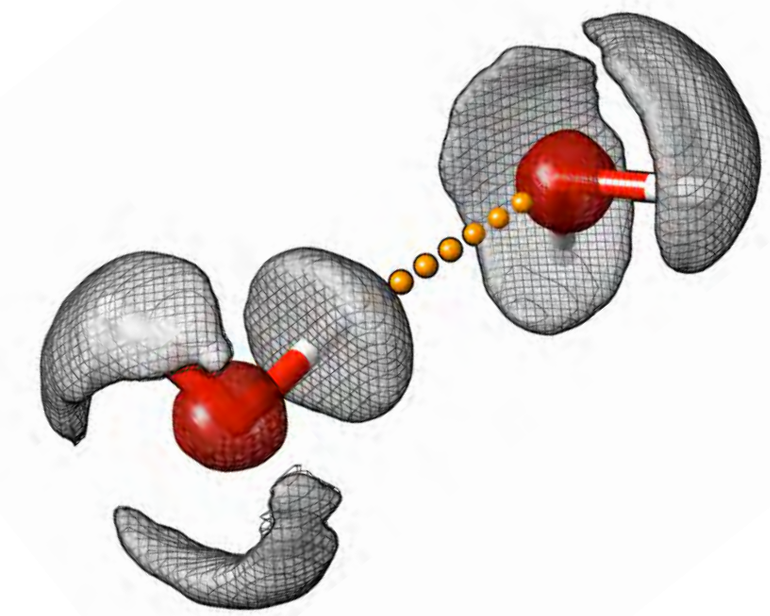
RMSD = 0.05 kcal/mol

for E_{tot} < 25 kcal/mol
RMSD = 0.03 kcal/mol

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

Water Dimer: Vibration-Rotation Tunneling Spectrum

Collaboration with Leforestier, Wang & Carrington

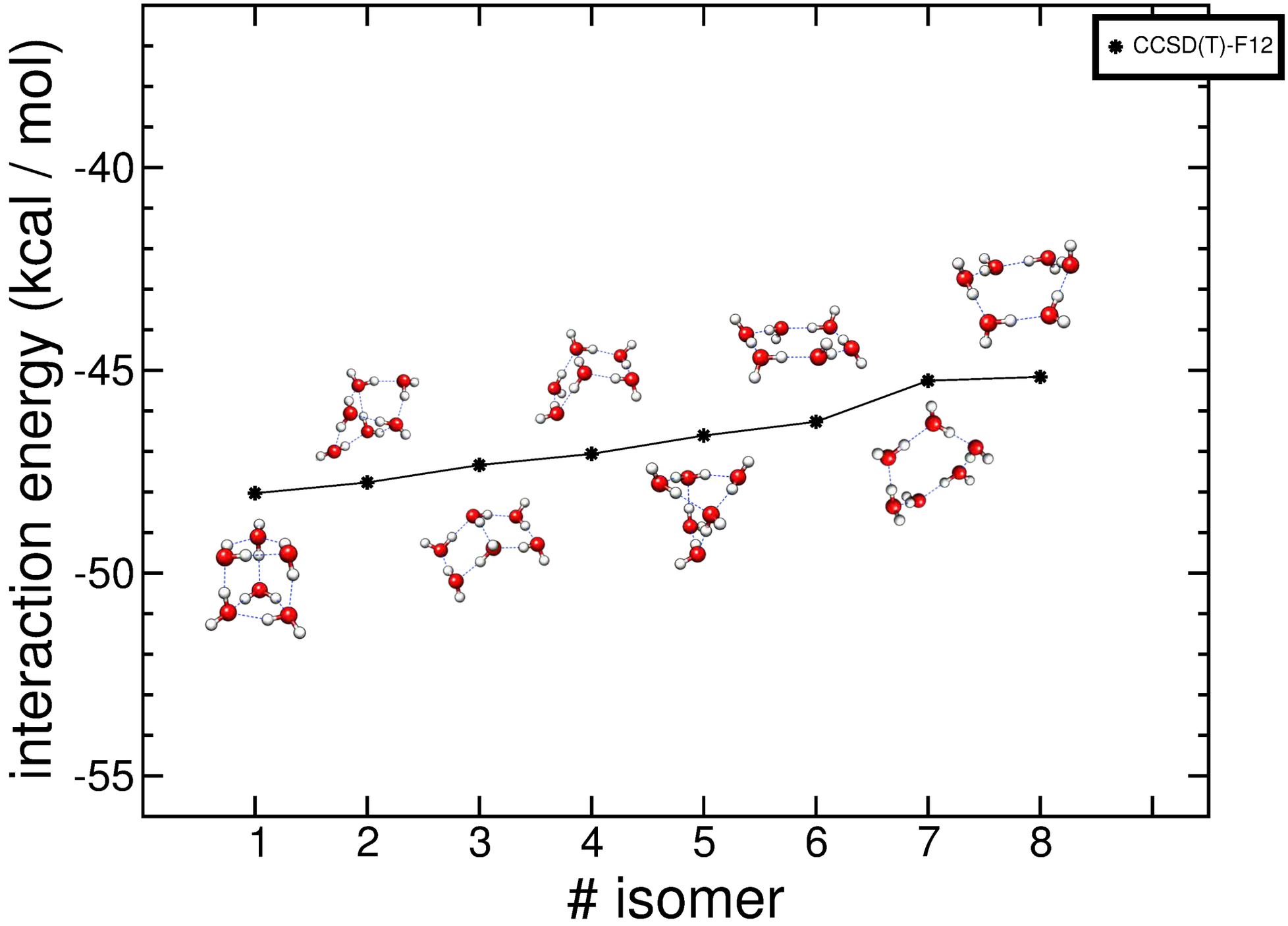


- **hydrogen tunneling**
- **energy level splitting**

Mode		Experiment (cm^{-1})	MB-pol (cm^{-1})
intermolecular stretch	2	153.62	154.77
	1		149.05
acceptor twist	1		129.49
	2	120.19	119.23
acceptor wag	2	108.89	109.14
	1	107.93	108.76
donor torsion	1		113.18
	2	64.52	61.24
ground state	2	11.18	11.88
	1	0	0

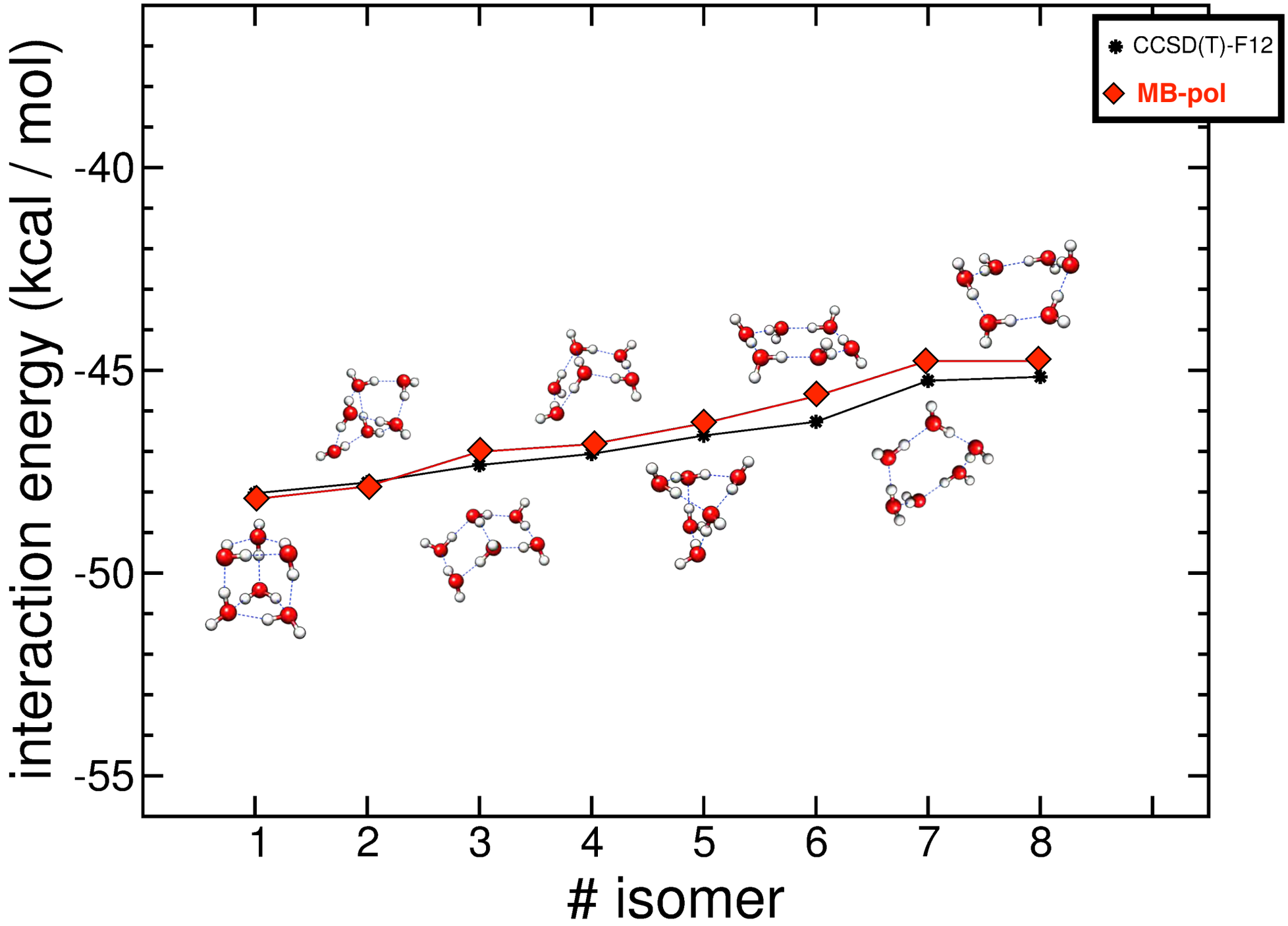
Water Hexamer: Energies

Interaction energies: MB-pol vs. CCSD(T)-F12/VTZ-F12



Water Hexamer: Energies

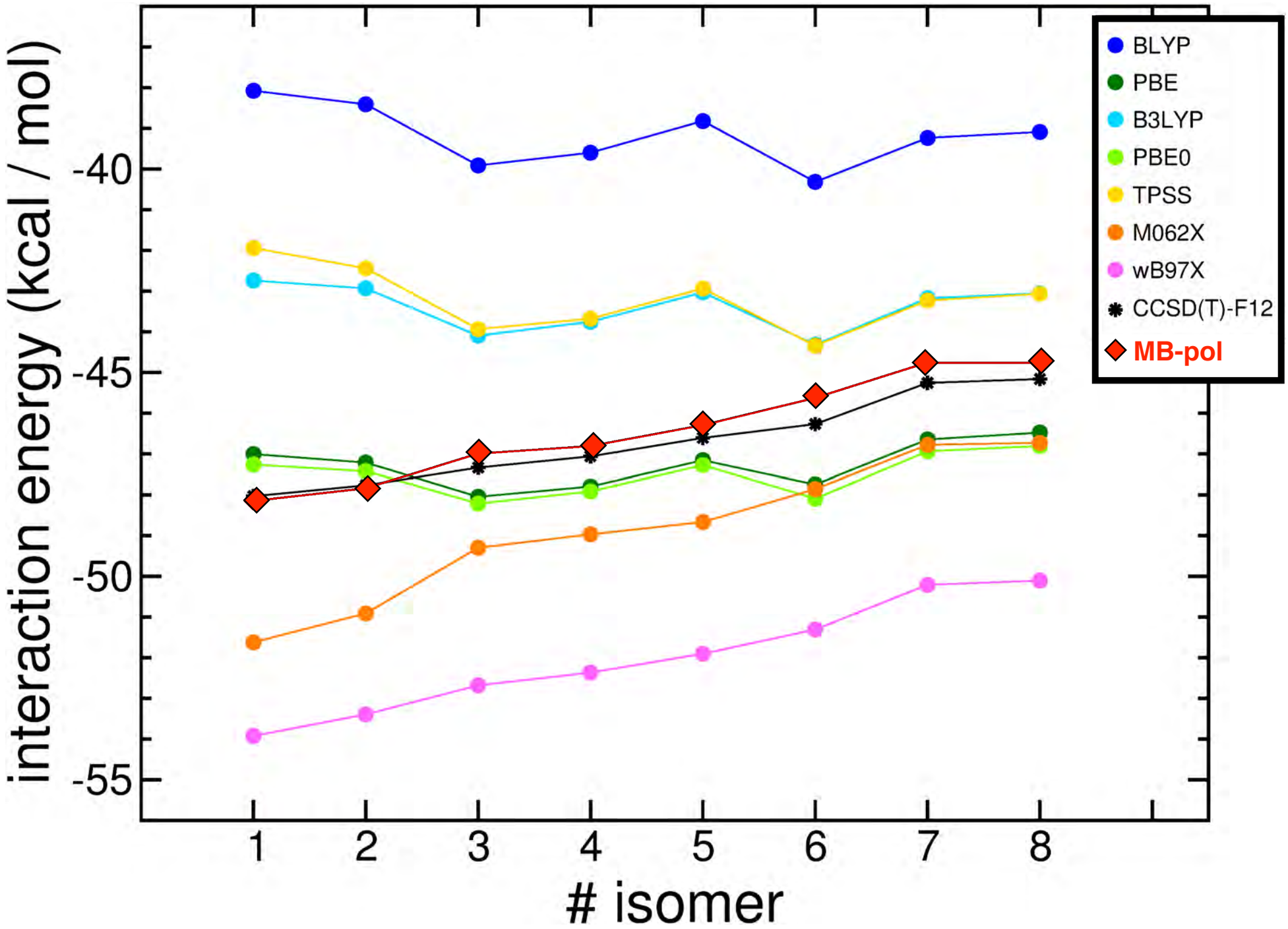
Interaction energies: MB-pol vs. CCSD(T)-F12/VTZ-F12



Medders, Götz, Morales, Bajaj & FP, J. Chem. Phys. 143, 104102 (2015)

Water Hexamer: Energies

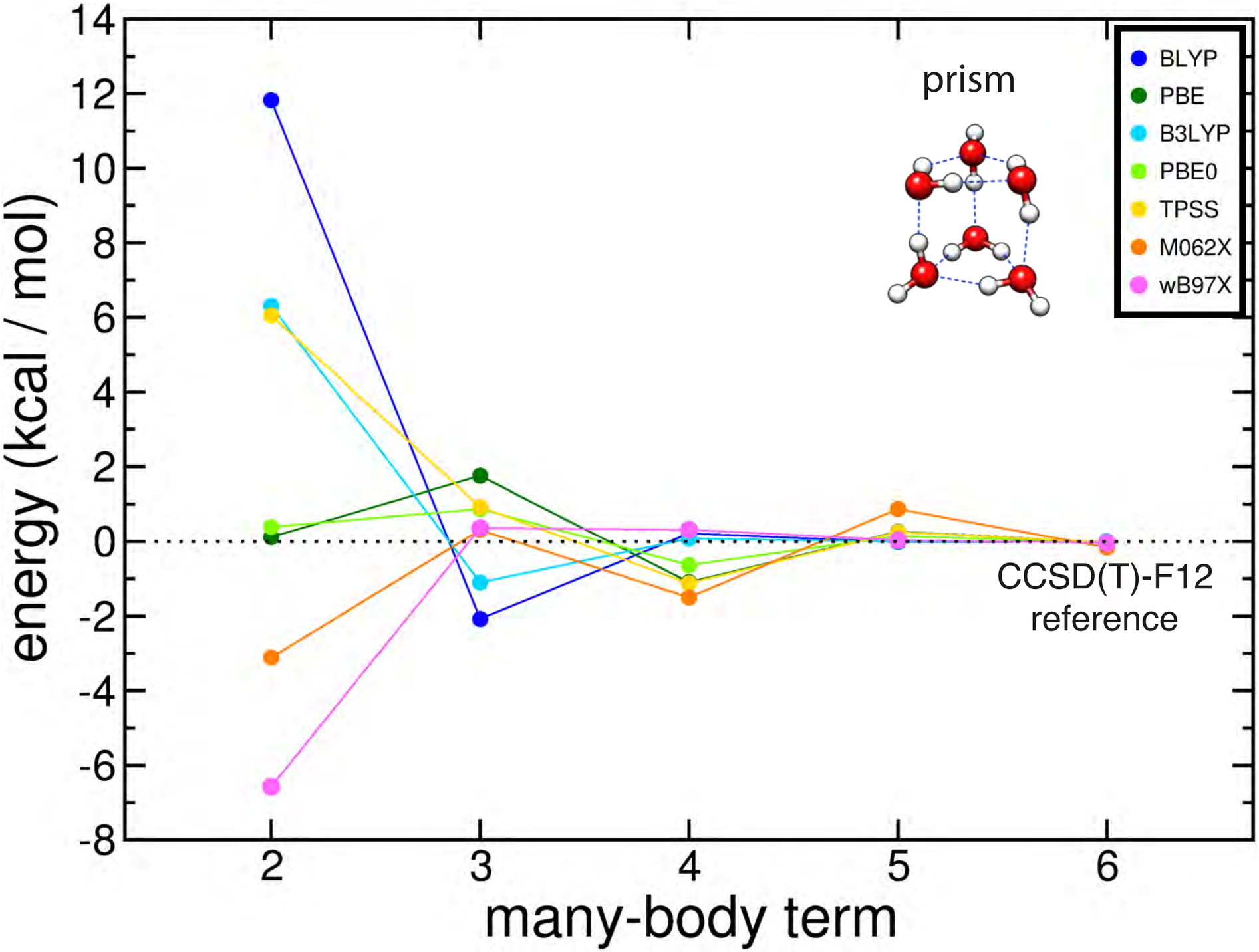
Interaction energies: DFT vs. MB-pol



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Water Hexamer: Energies

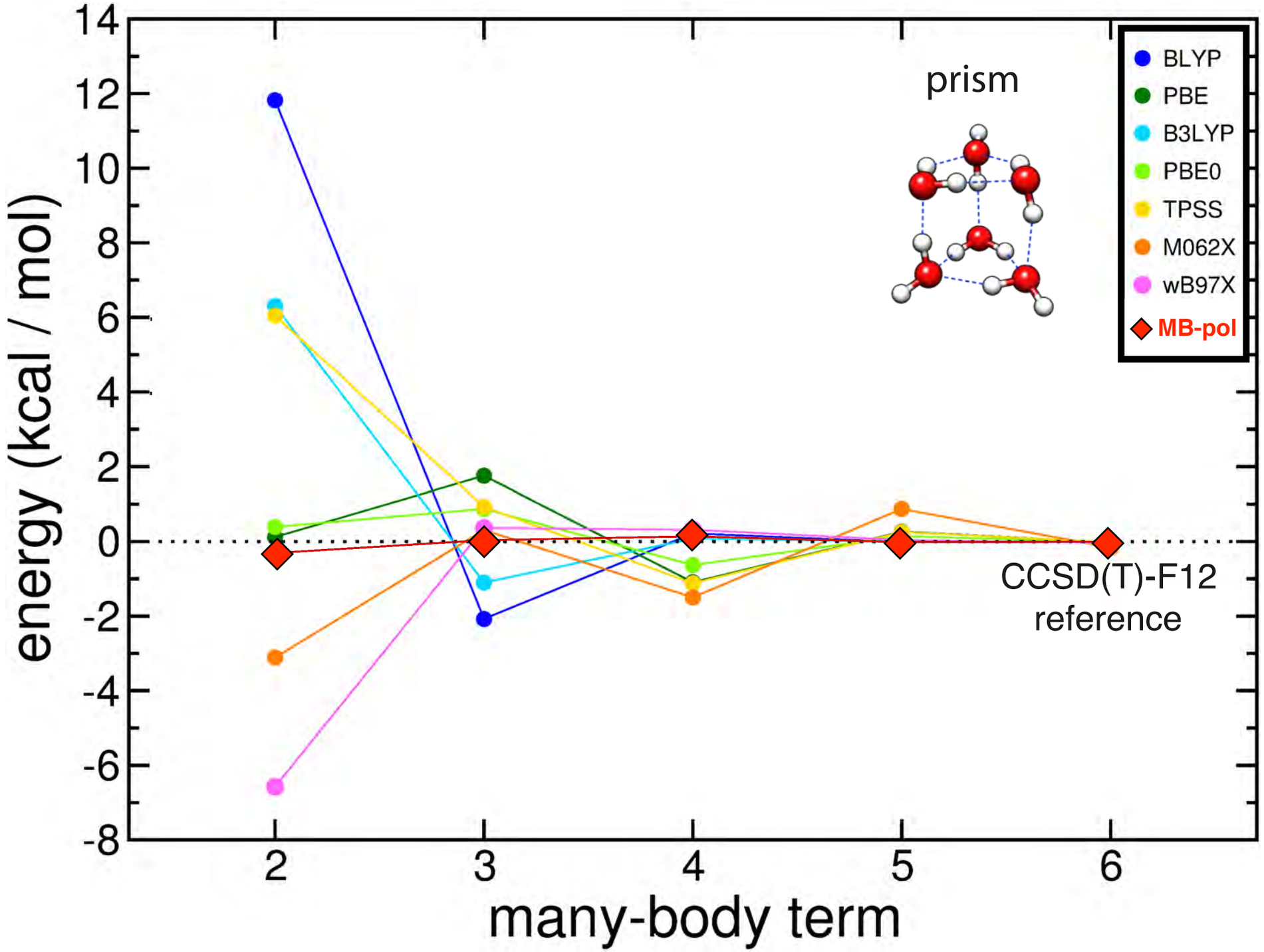
Many-body decomposition: DFT vs. MB-pol



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Water Hexamer: Energies

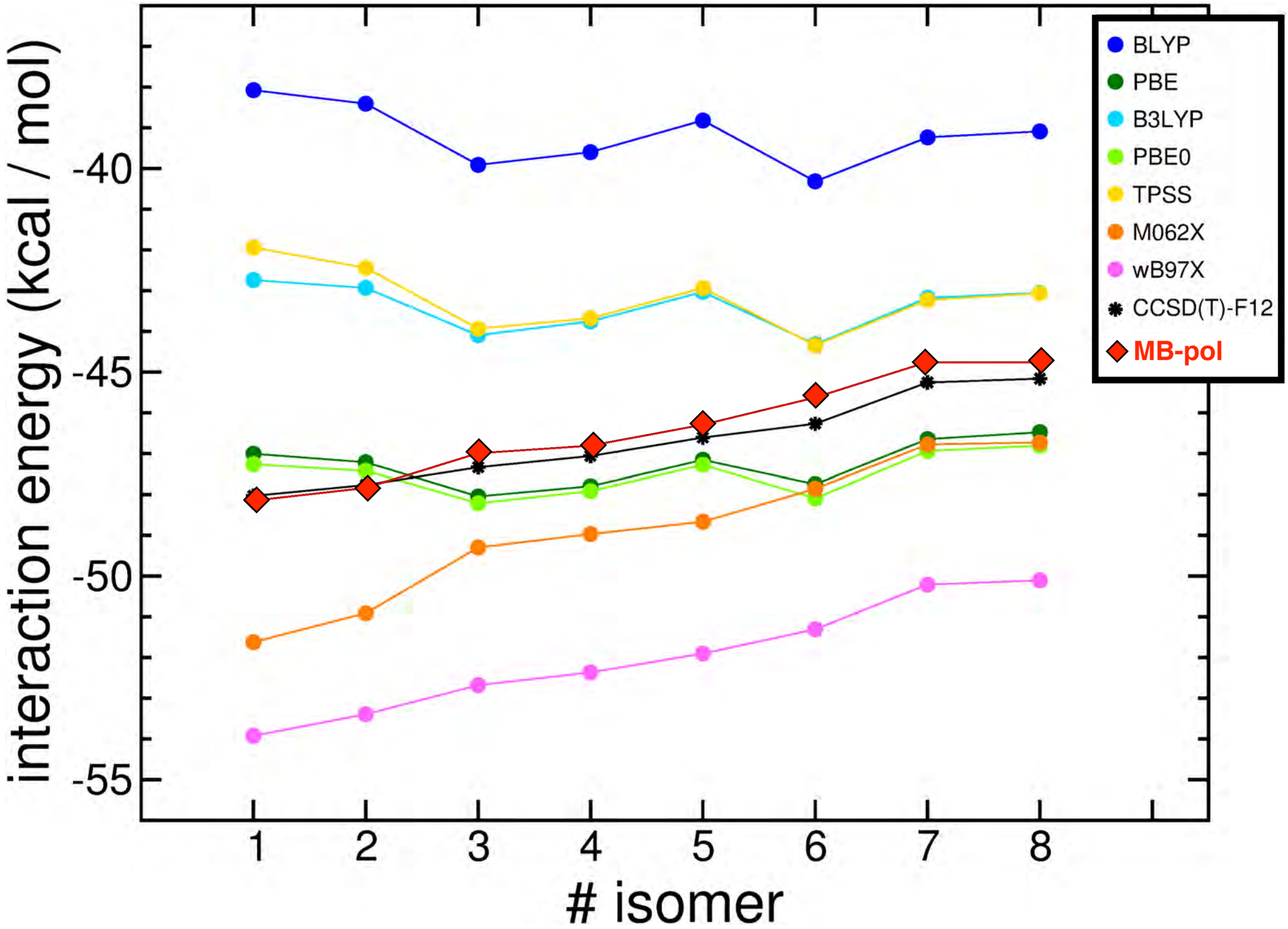
Many-body decomposition: DFT vs. MB-pol



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Water Hexamer: Energies

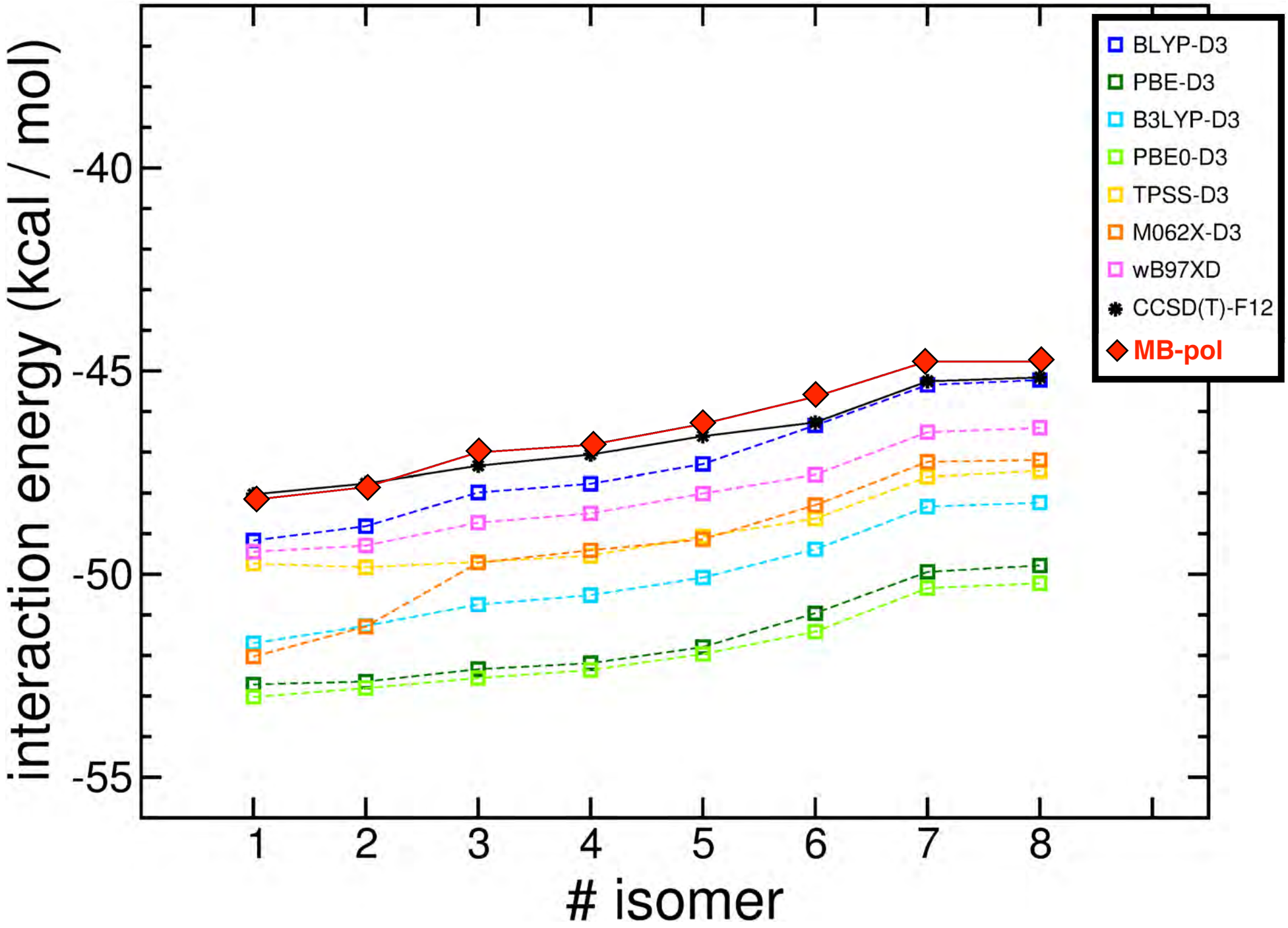
Interaction energies: DFT vs. MB-pol



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Water Hexamer: Energies

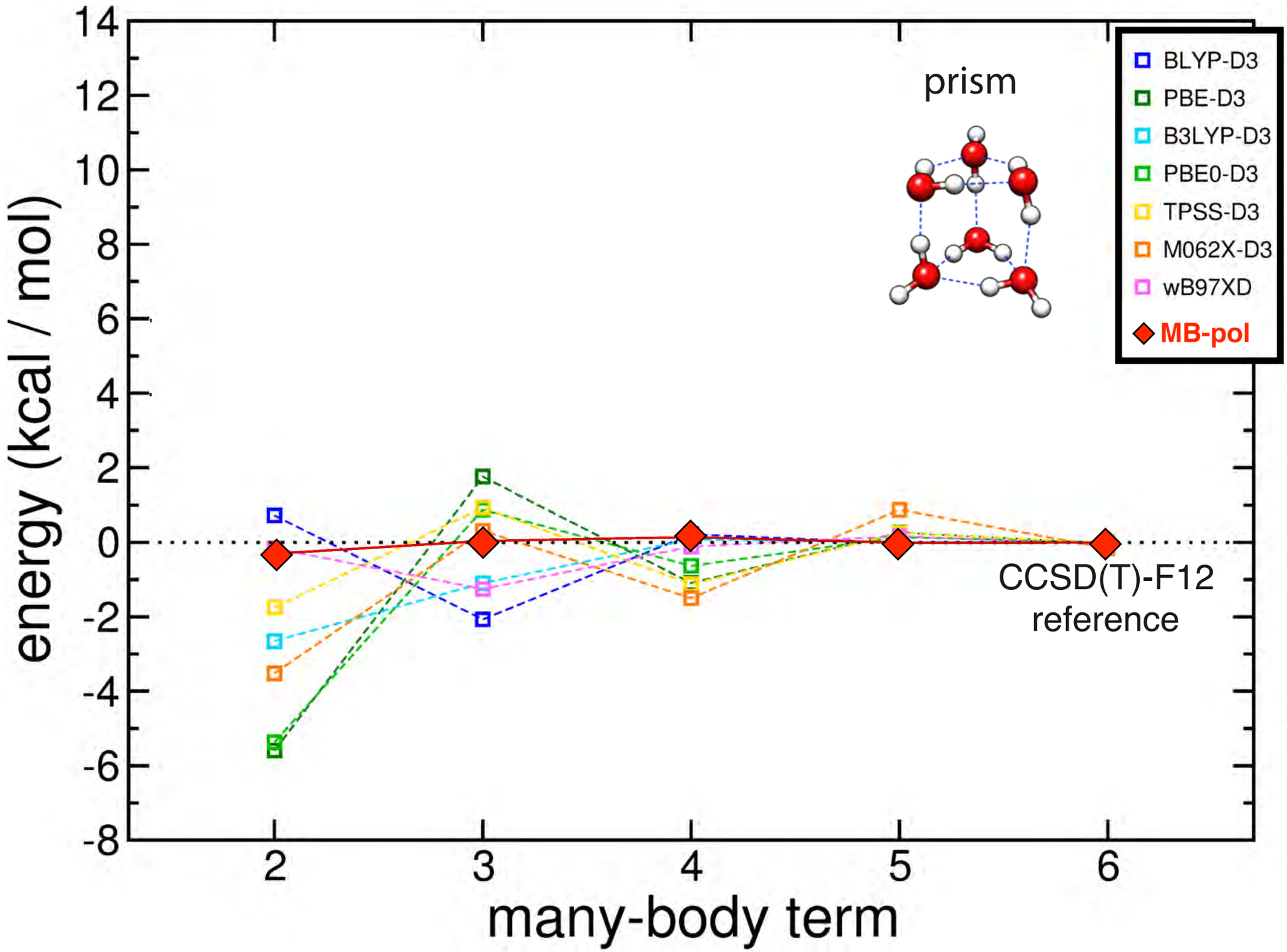
Interaction energies: DFT-D3 vs. MB-pol



Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Water Hexamer: Energies

Interaction energies: DFT-D3 vs. MB-pol

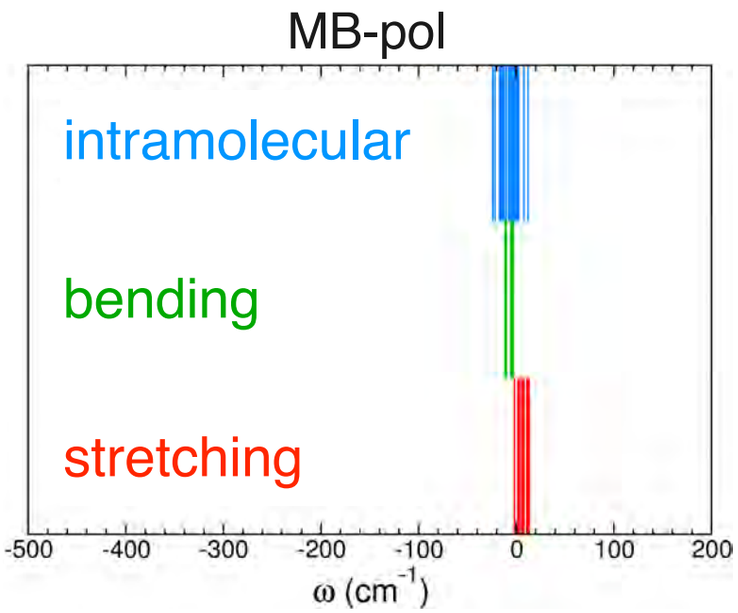


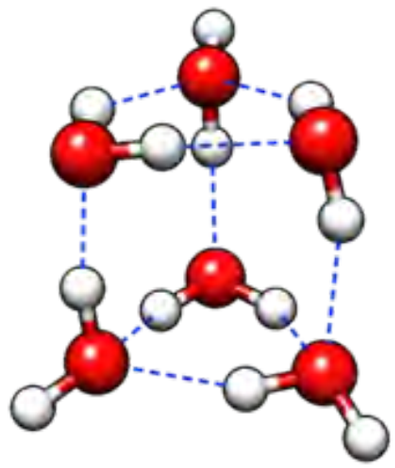
Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Hexamer: Infrared Spectra

Harmonic frequencies relative to CCSD(T):MP2
prism isomer

Howard & Tschumper, J. Chem. Theory Comput. 11, 2126 (2015)



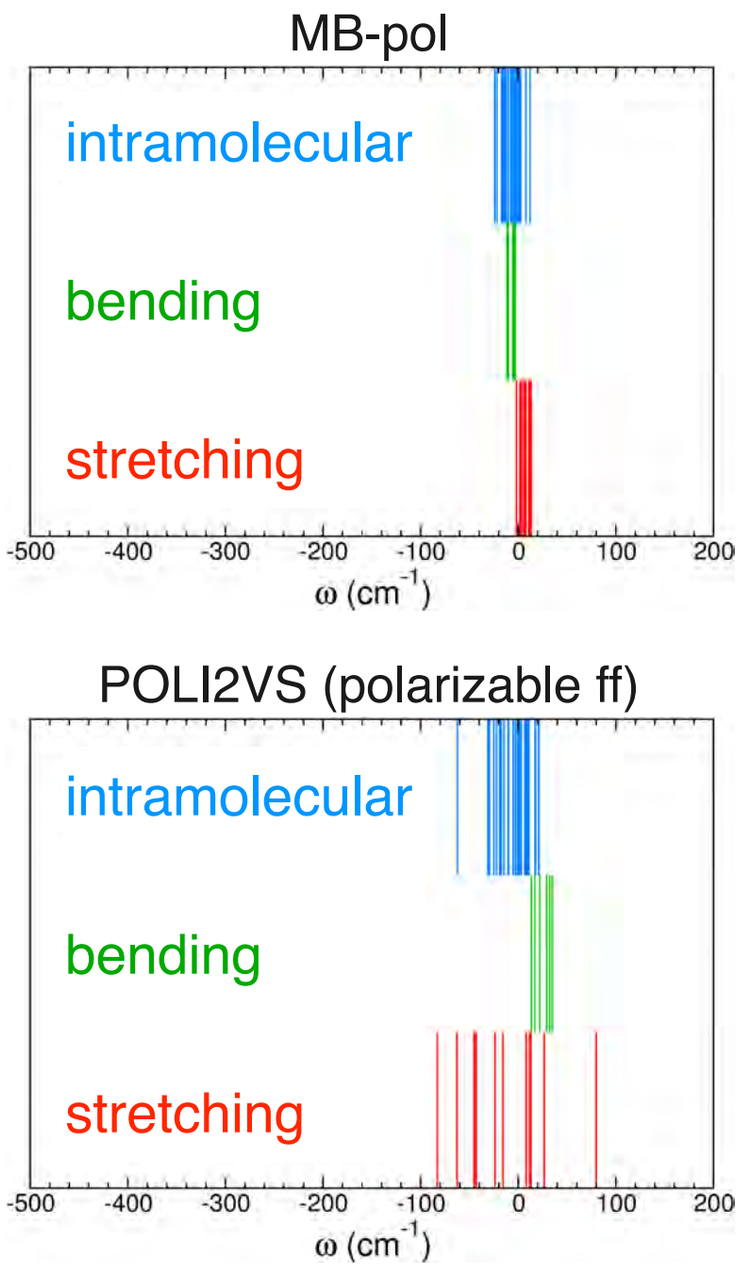


Medders, Götz, Morales, Bajaj & FP, J. Chem. Phys. 143, 104102 (2015)

Hexamer: Infrared Spectra

Harmonic frequencies relative to CCSD(T):MP2 prism isomer

Howard & Tschumper, J. Chem. Theory Comput. 11, 2126 (2015)

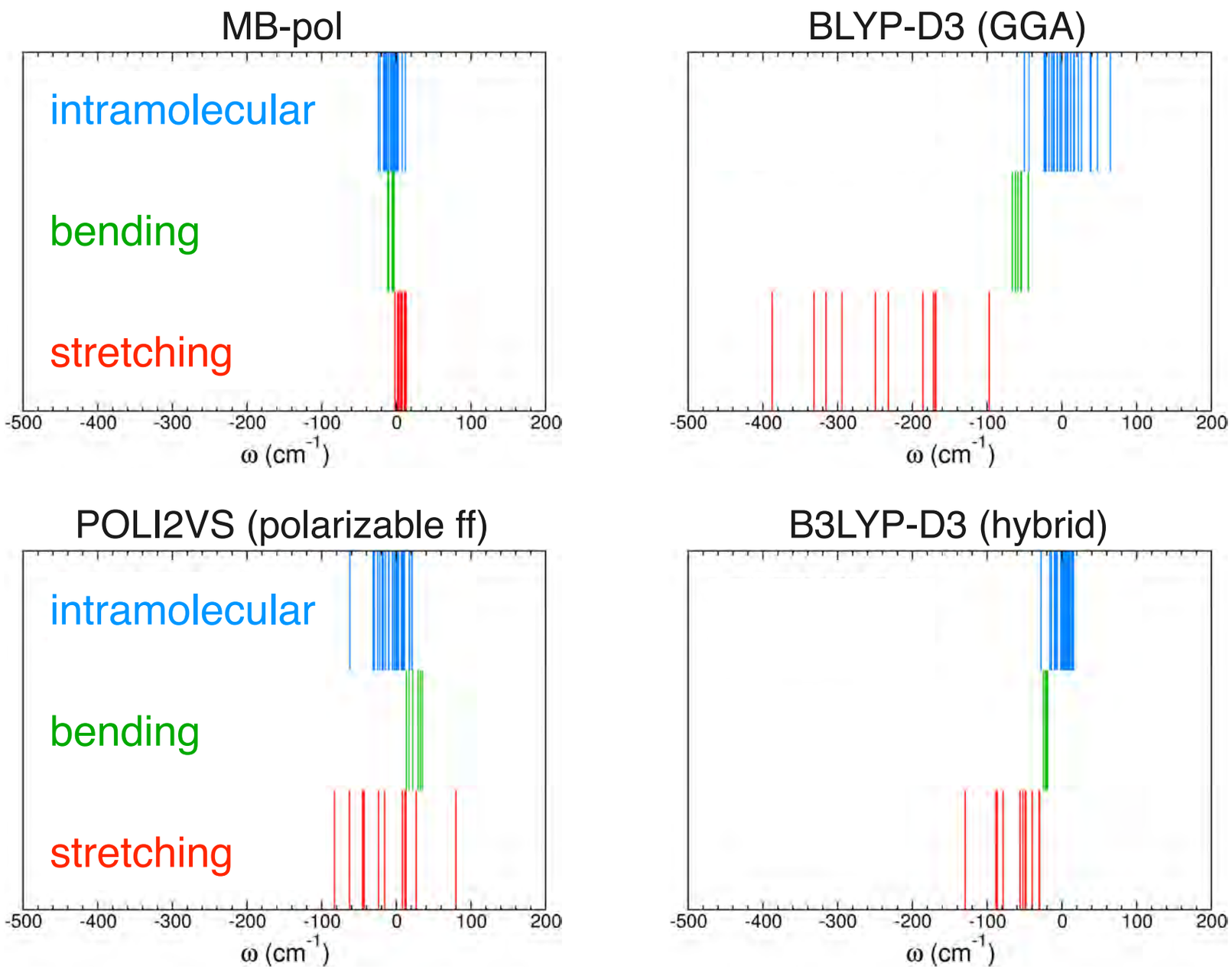


Medders, Götz, Morales, Bajaj & FP, J. Chem. Phys. 143, 104102 (2015)

Hexamer: Infrared Spectra

Harmonic frequencies relative to CCSD(T):MP2 prism isomer

Howard & Tschumper, J. Chem. Theory Comput. 11, 2126 (2015)



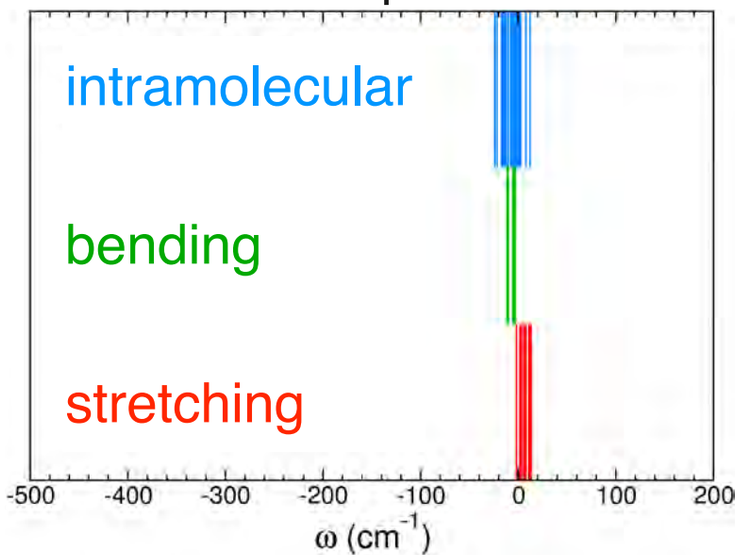
Medders, Götz, Morales, Bajaj & FP, J. Chem. Phys. 143, 104102 (2015)

Hexamer: Infrared Spectra

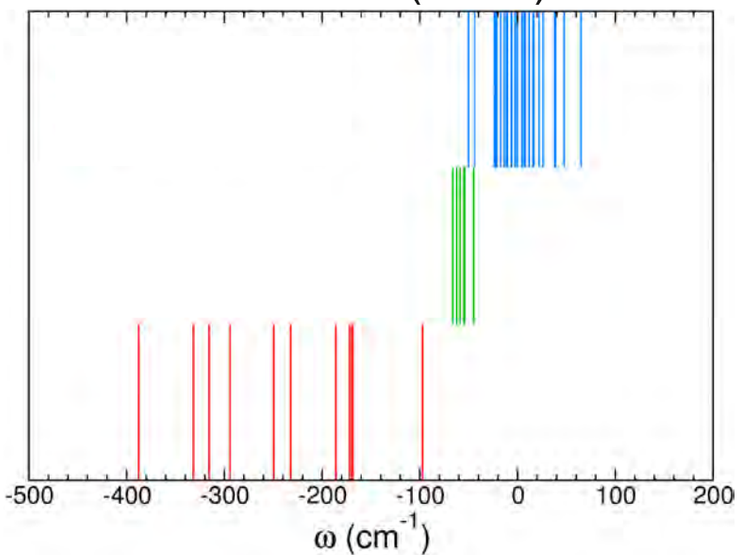
Harmonic frequencies relative to CCSD(T):MP2 prism isomer

Howard & Tschumper, J. Chem. Theory Comput. 11, 2126 (2015)

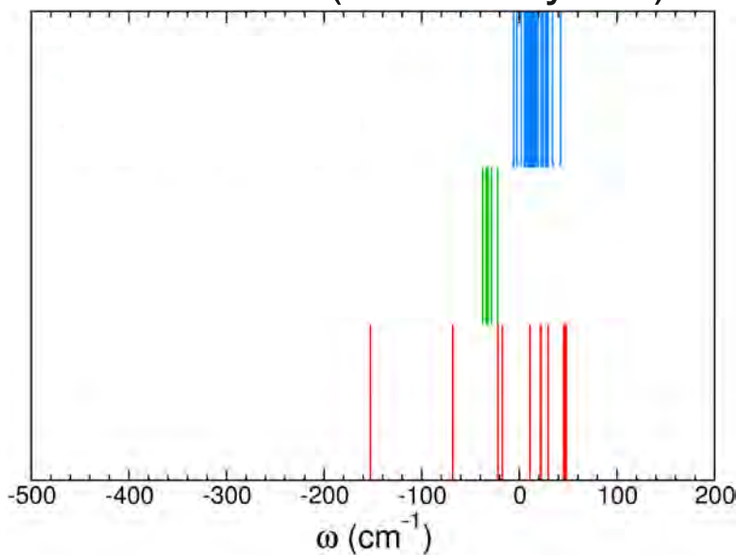
MB-pol



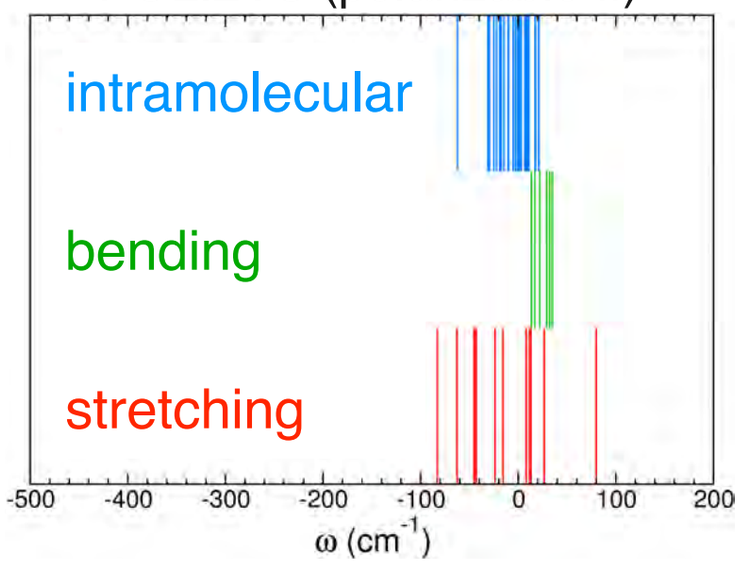
BLYP-D3 (GGA)



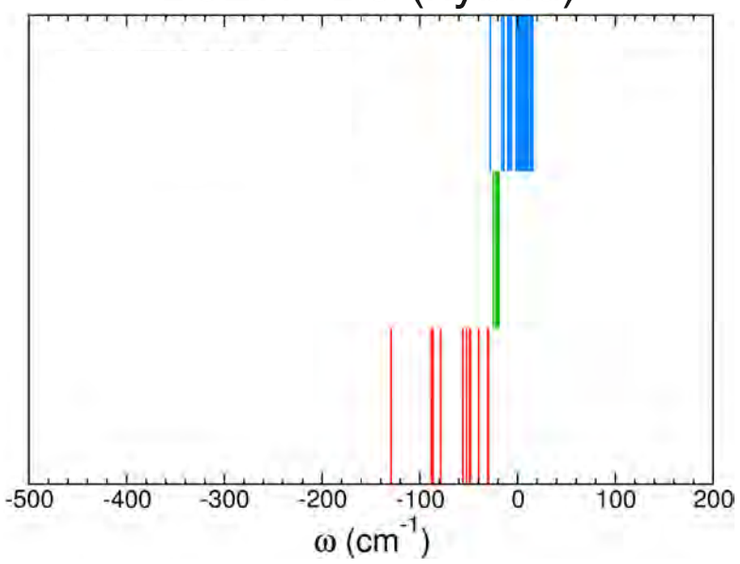
M062X-D3 (meta & hybrid)



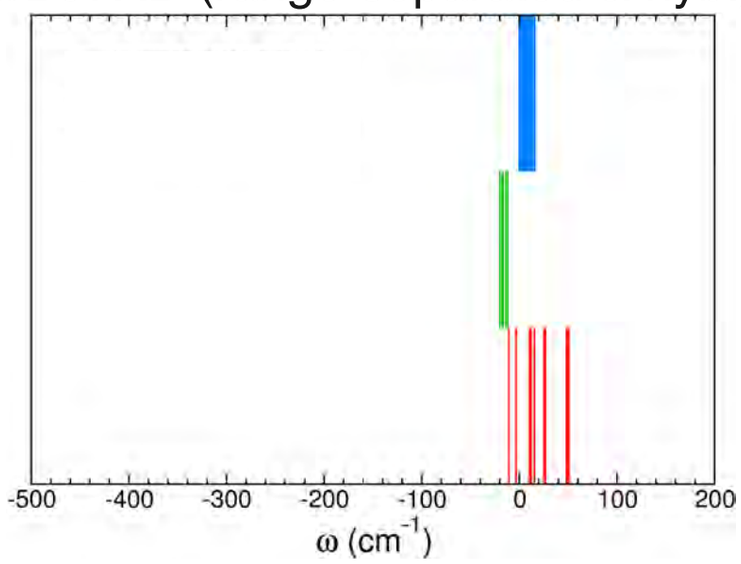
POLI2VS (polarizable ff)



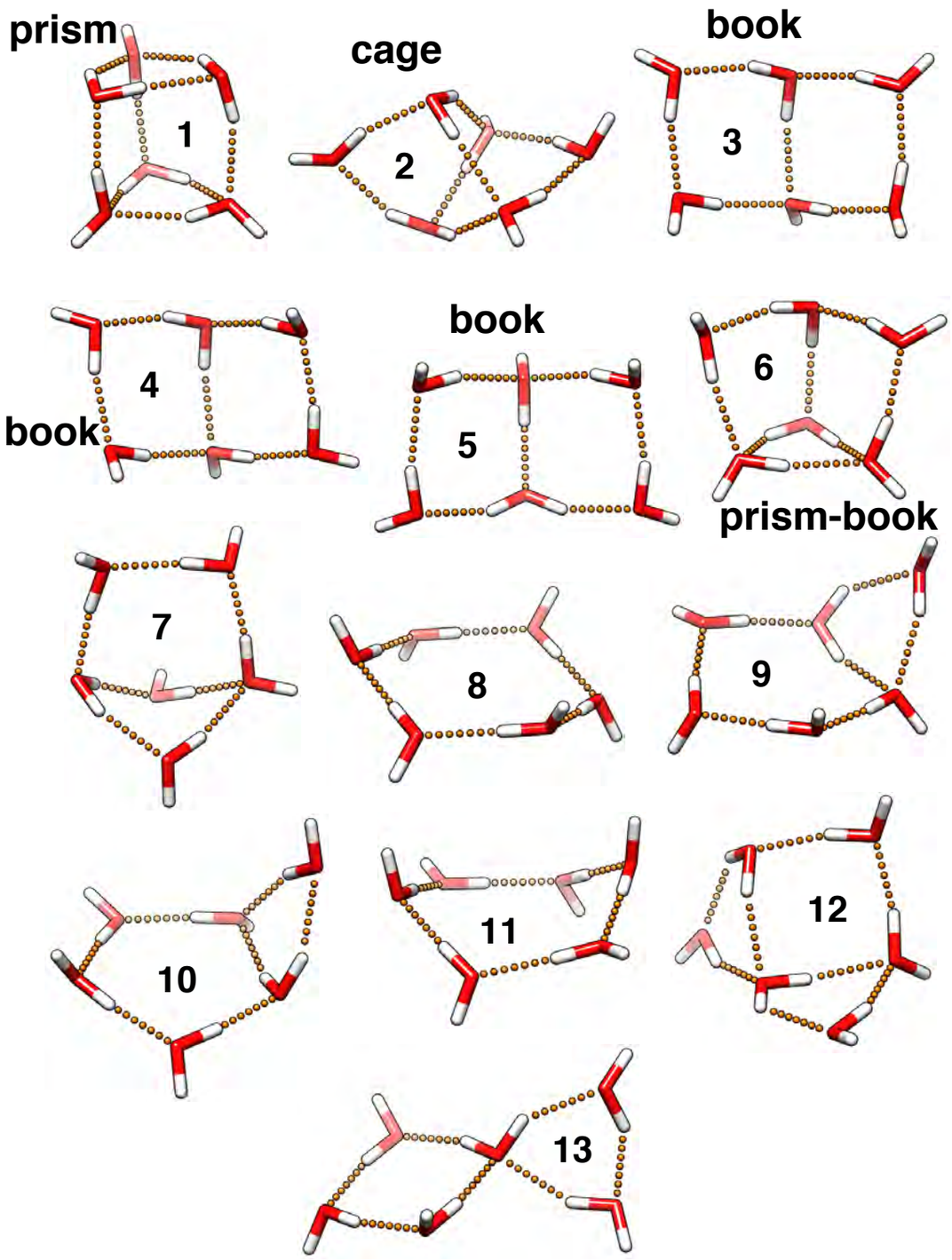
B3LYP-D3 (hybrid)



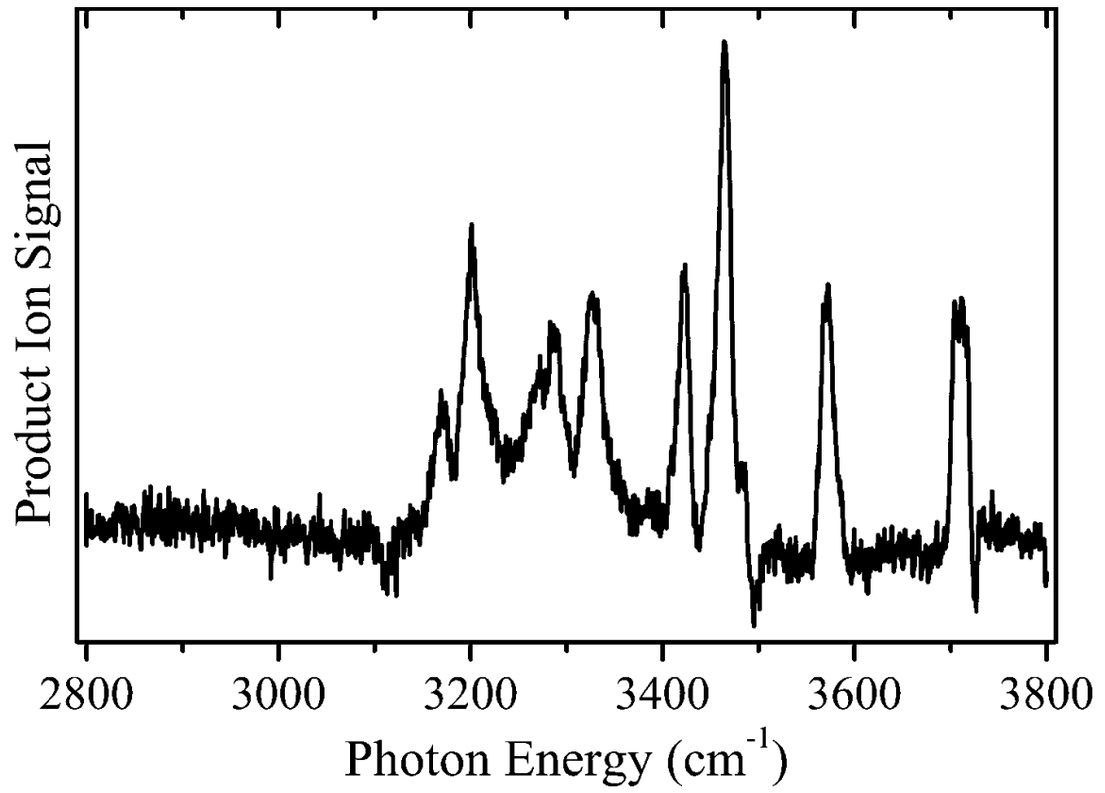
ωB97XD (range-separated & hyb.)



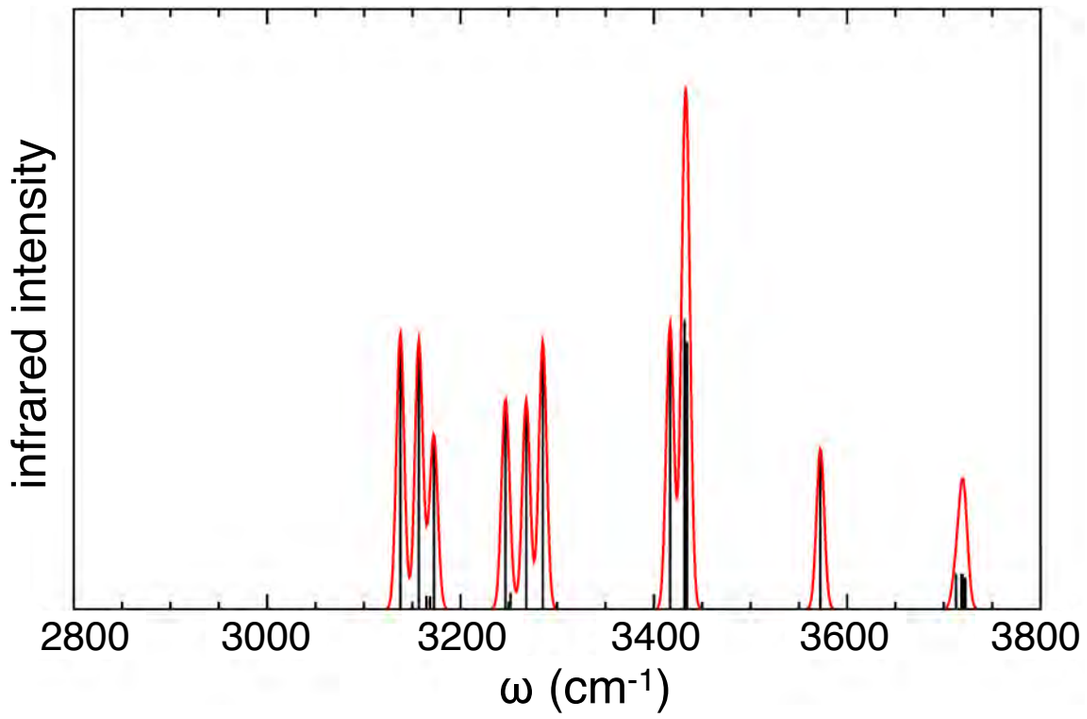
Hexamer: Infrared Spectra



13 isomers within 4 kcal/mol

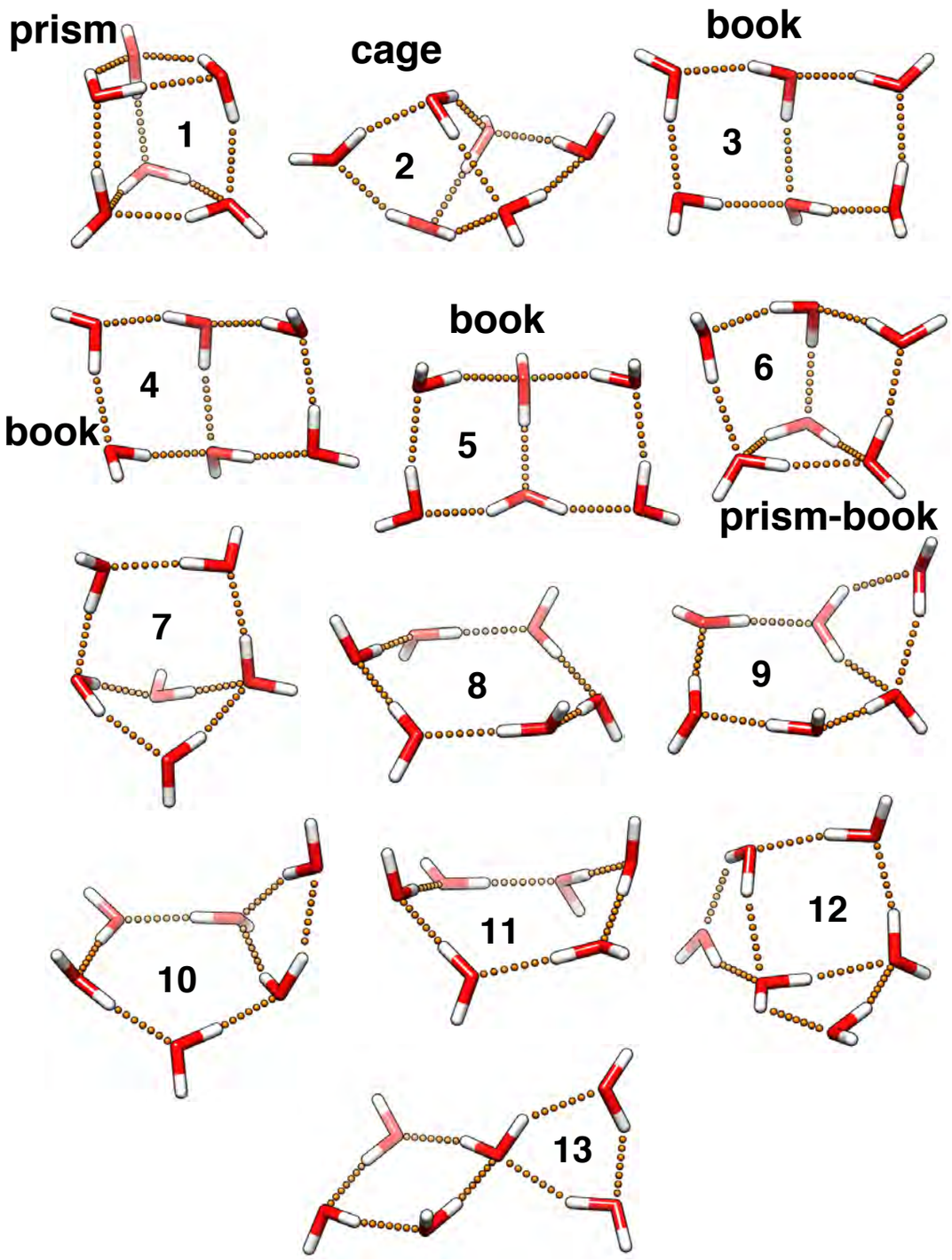


Diken, Robertson & Johnson, J. Phys. Chem. A 108, 64 (2005)

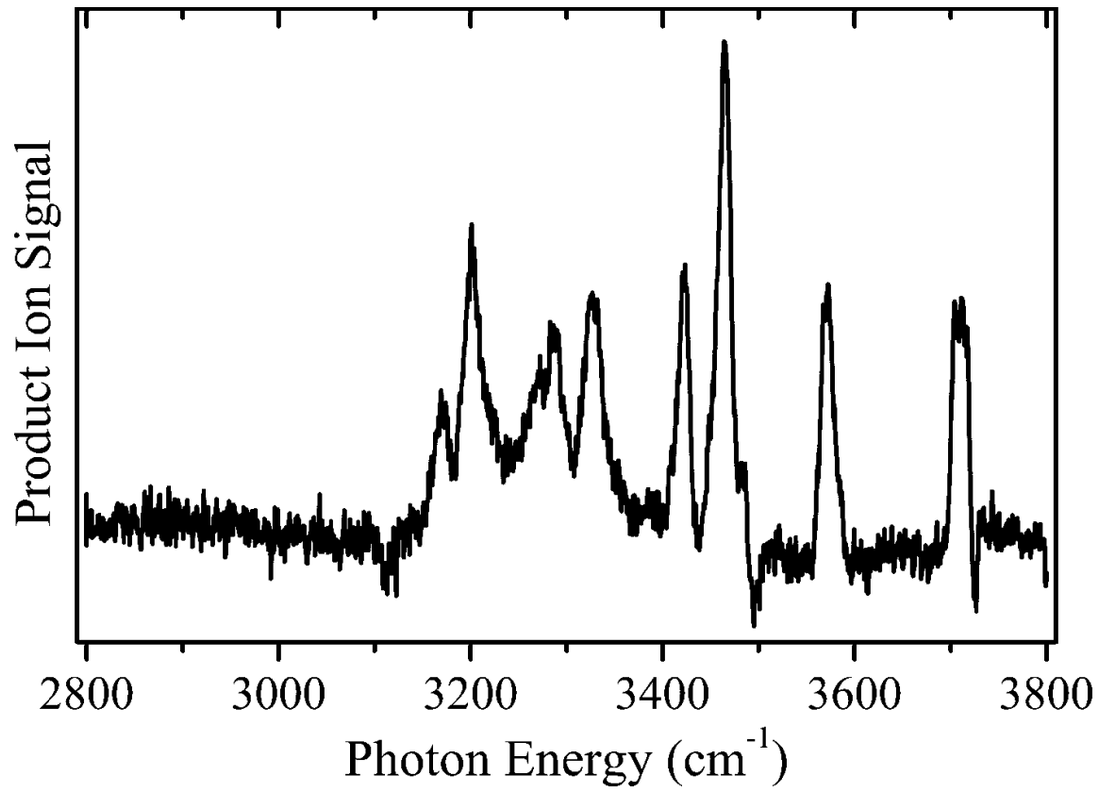


Götz, Brown, Steele, Mandelshtam, FP, to be submitted

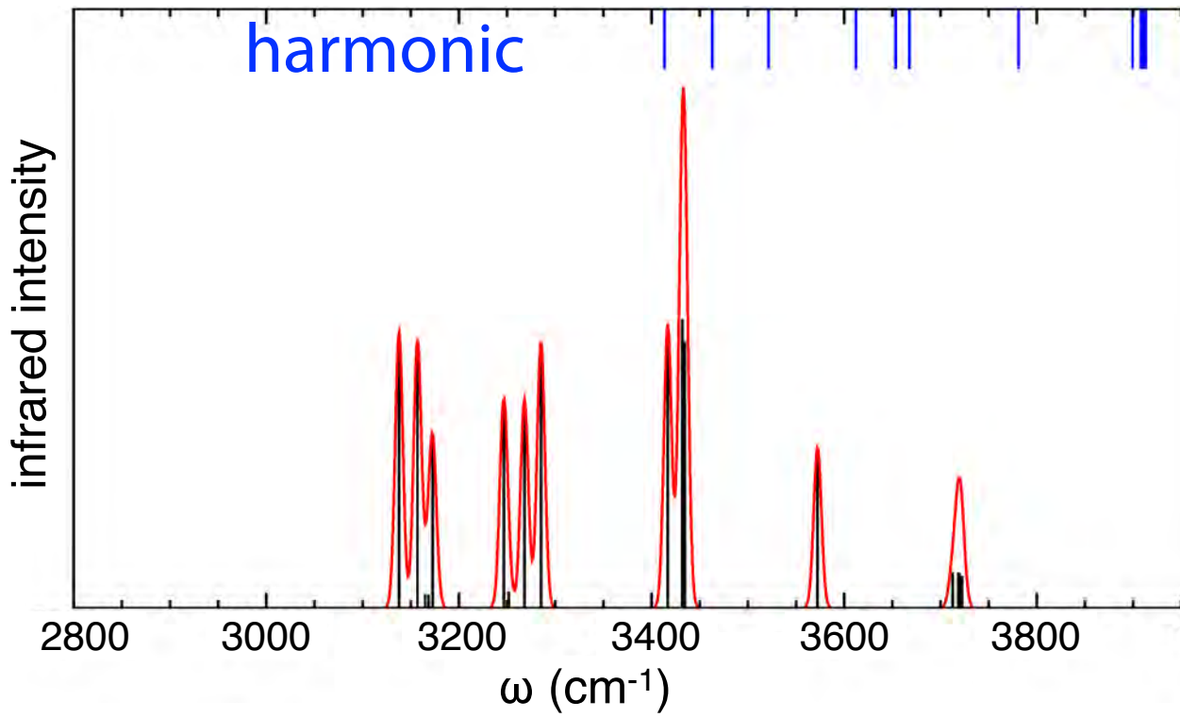
Hexamer: Infrared Spectra



13 isomers within 4 kcal/mol



Diken, Robertson & Johnson, J. Phys. Chem. A 108, 64 (2005)



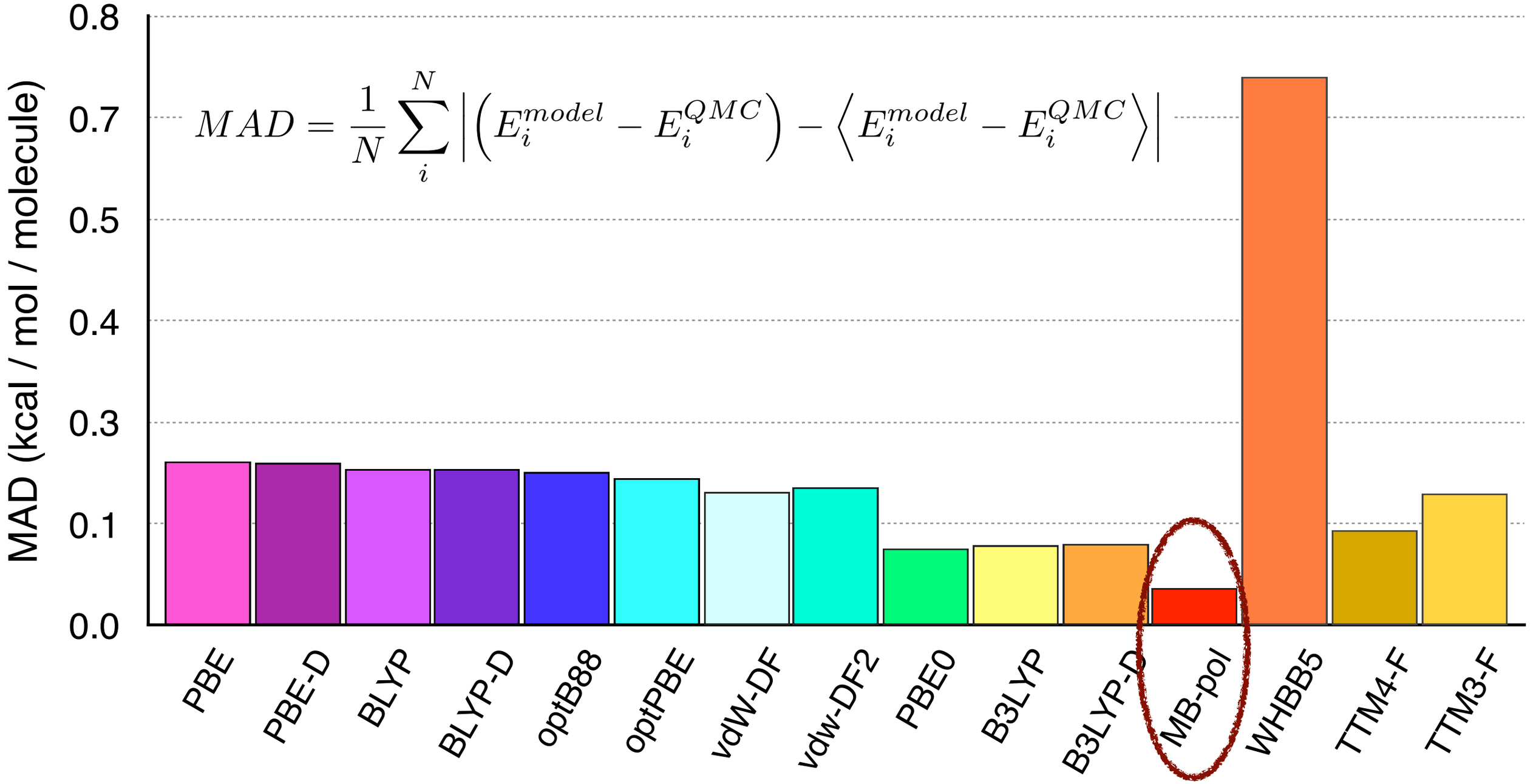
Götz, Brown, Steele, Mandelshtam, FP, to be submitted

Liquid Water: Energies

Mean absolute deviations relative to Quantum Monte Carlo

Molecular configurations from MD simulations with vdW-DF and vdW-DF2

$$MAD = \frac{1}{N}\sum_{i}^{N}\left|\left(E_i^{model} - E_i^{QMC}\right) - \left\langle E_i^{model} - E_i^{QMC}\right\rangle\right|$$

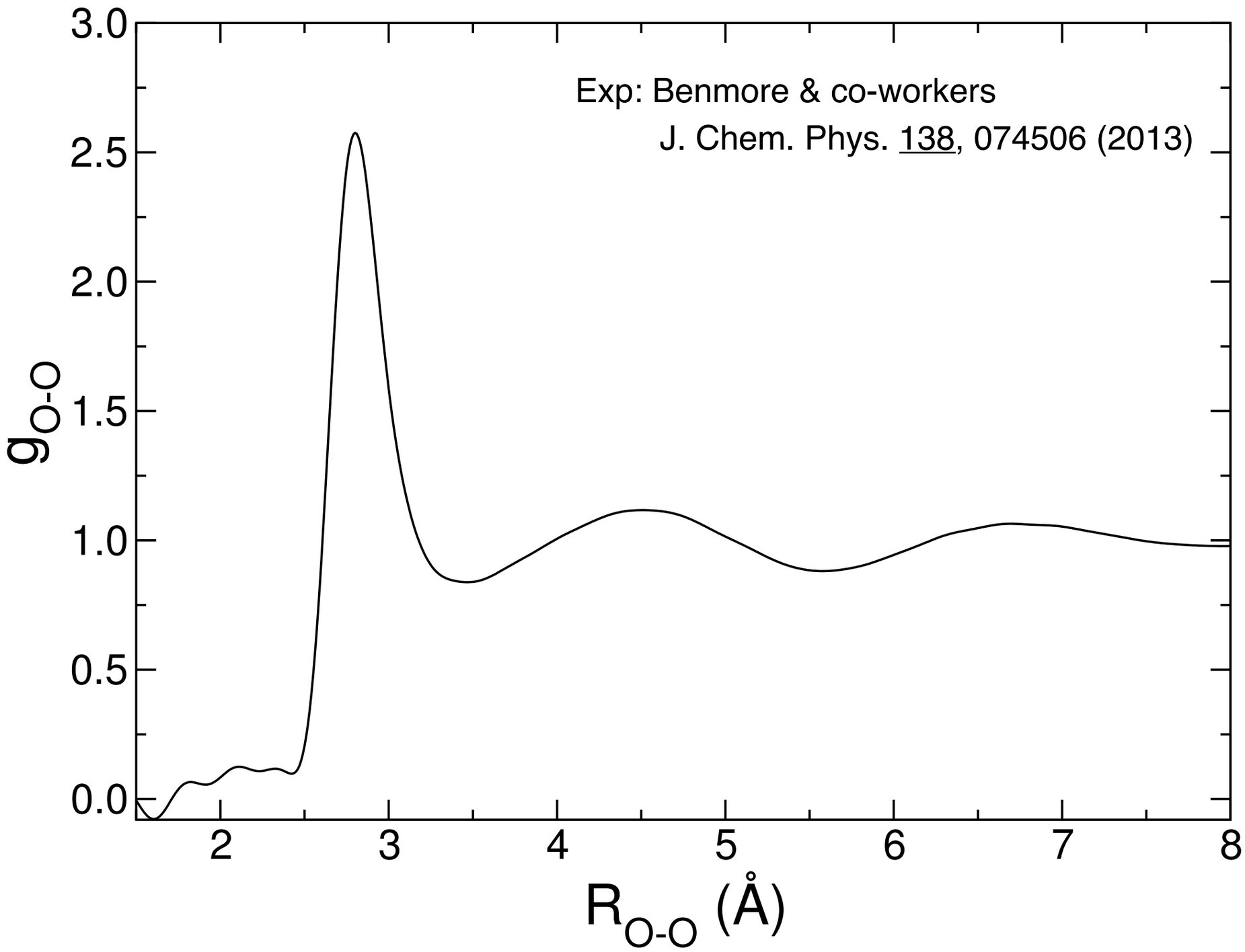


QMC: *Morales, Gergely, McMinis, McMahon, Kim & Ceperley, J. Chem. Theory Comput. 10, 2355 (2014)*

Medders, Götz, Morales, Bajaj & FP, J. Chem. Phys. 143, 104102 (2015)

Liquid Water: Structure

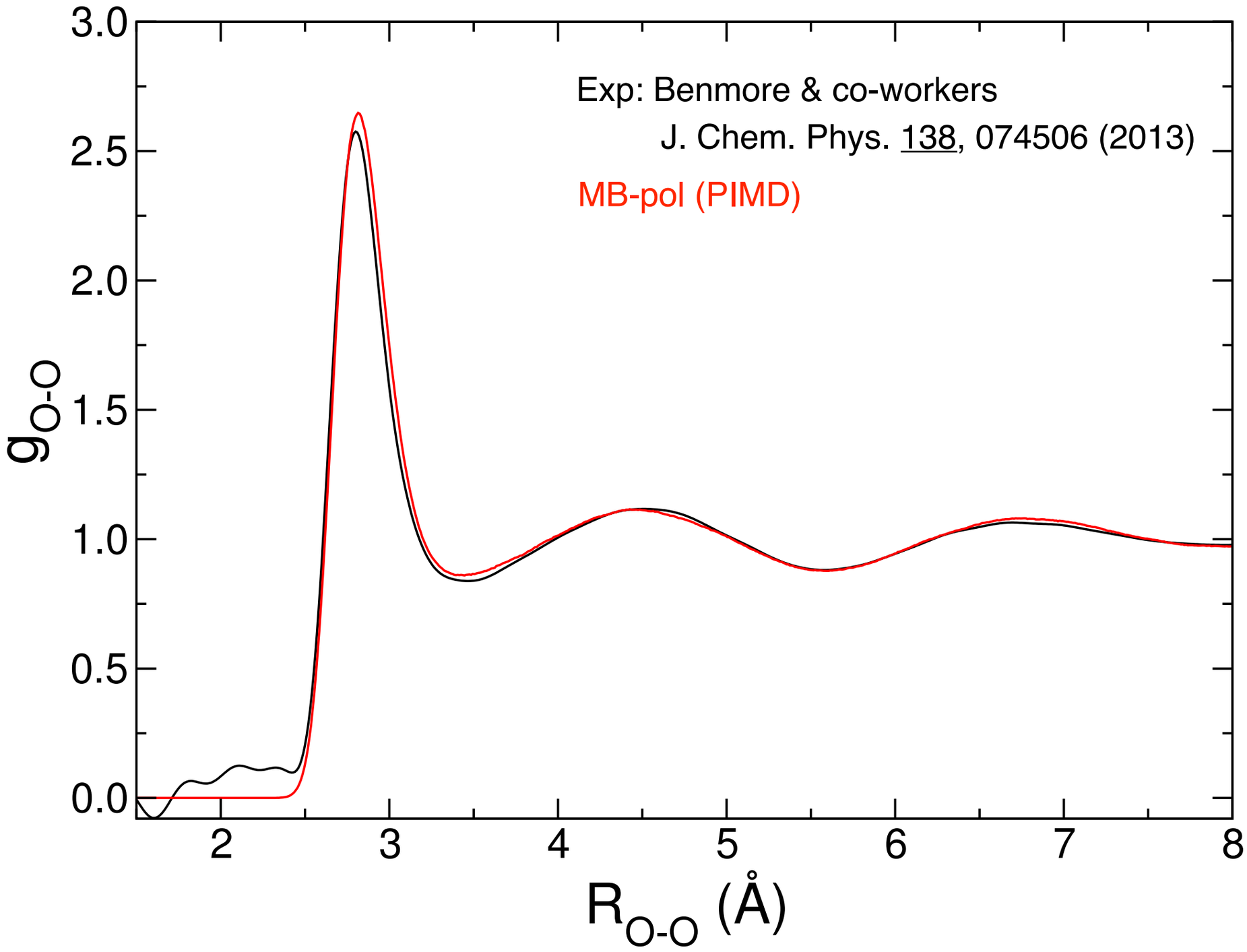
Oxygen-oxygen radial distribution function



Medders, Babin & FP, J. Chem. Theory Comput. 10, 2906 (2014)

Liquid Water: Structure

Oxygen-oxygen radial distribution function

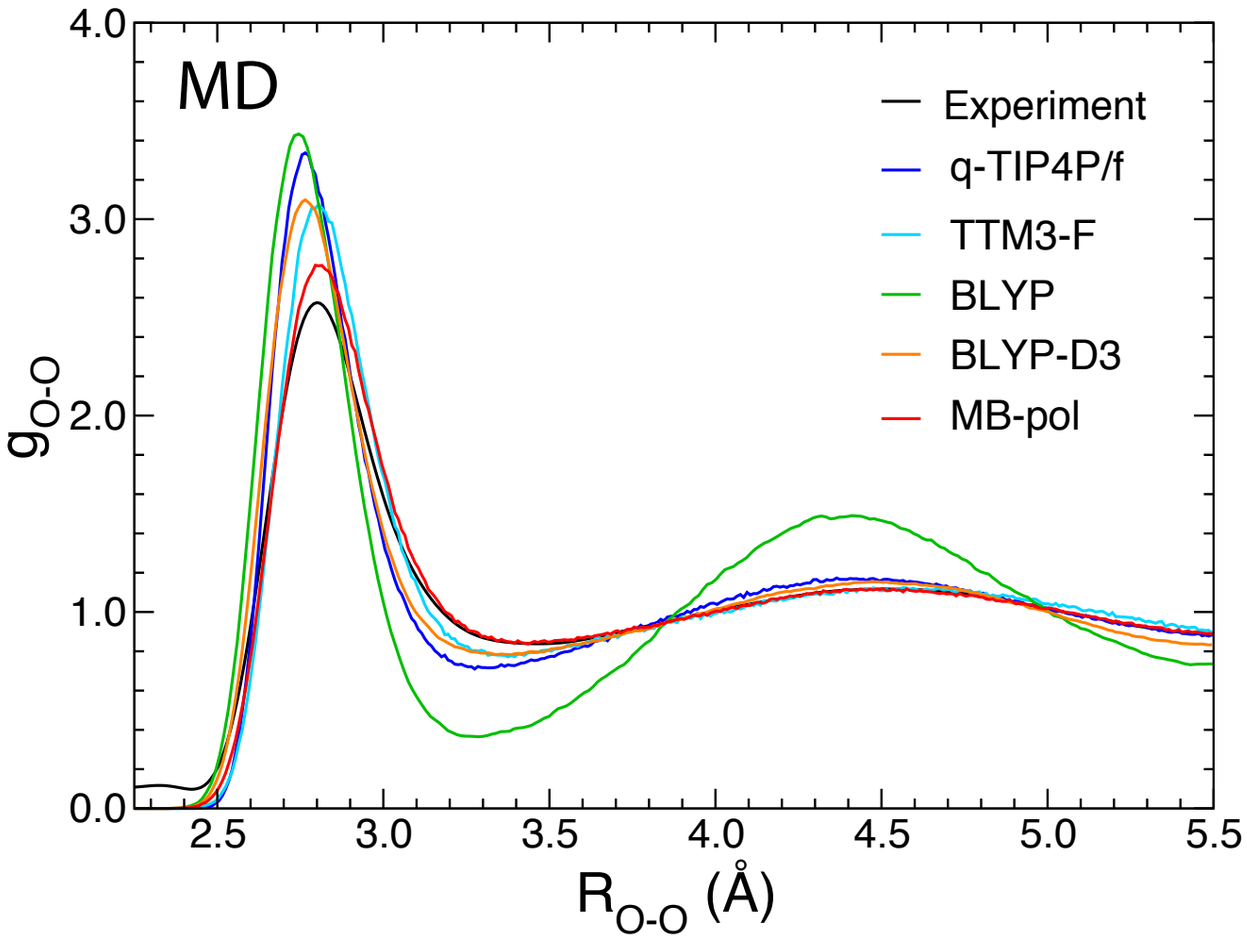


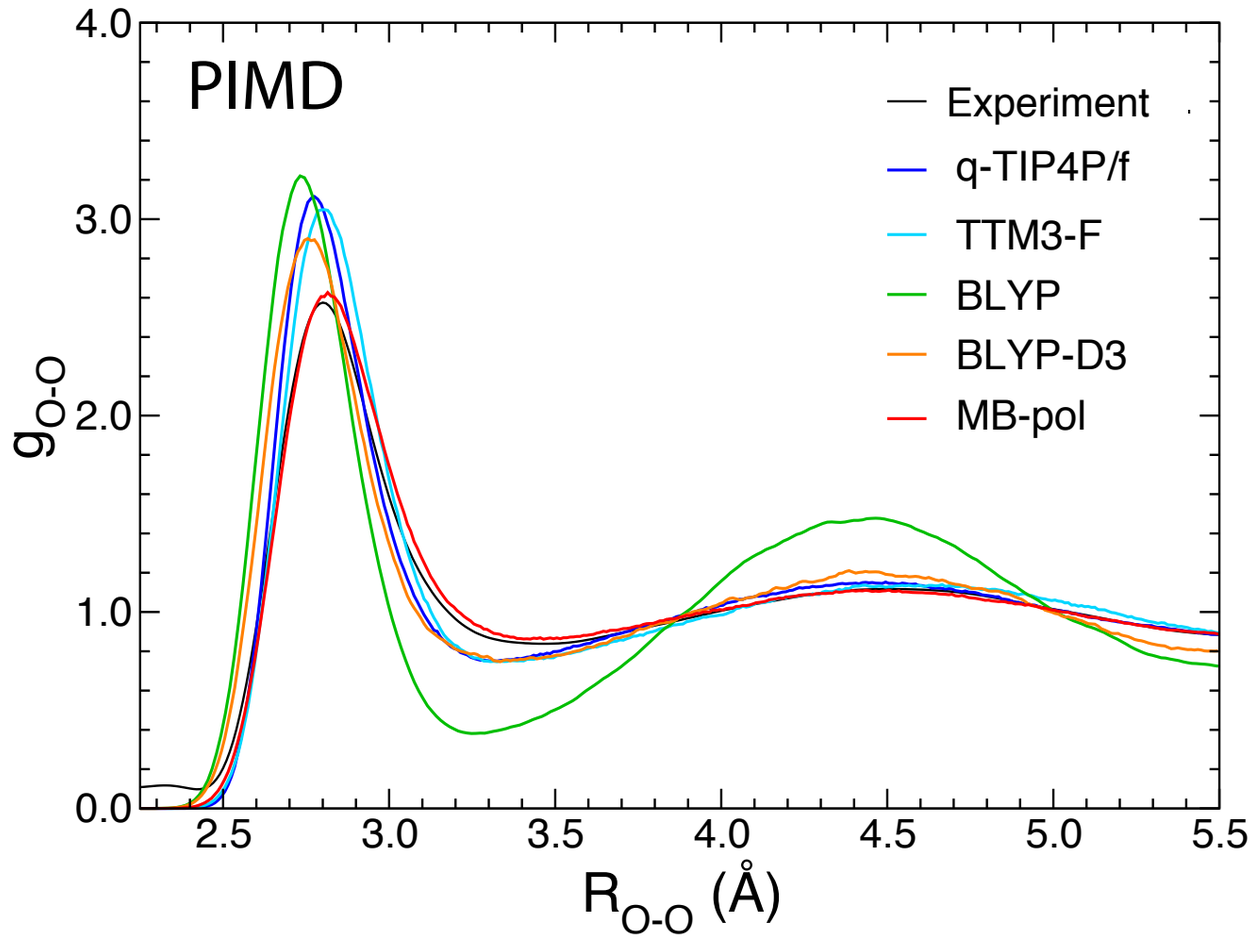
Medders, Babin & FP, J. Chem. Theory Comput. 10, 2906 (2014)

Liquid Water: Some Insights

Oxygen-oxygen radial distribution function

Nuclear quantum effects and model dependence



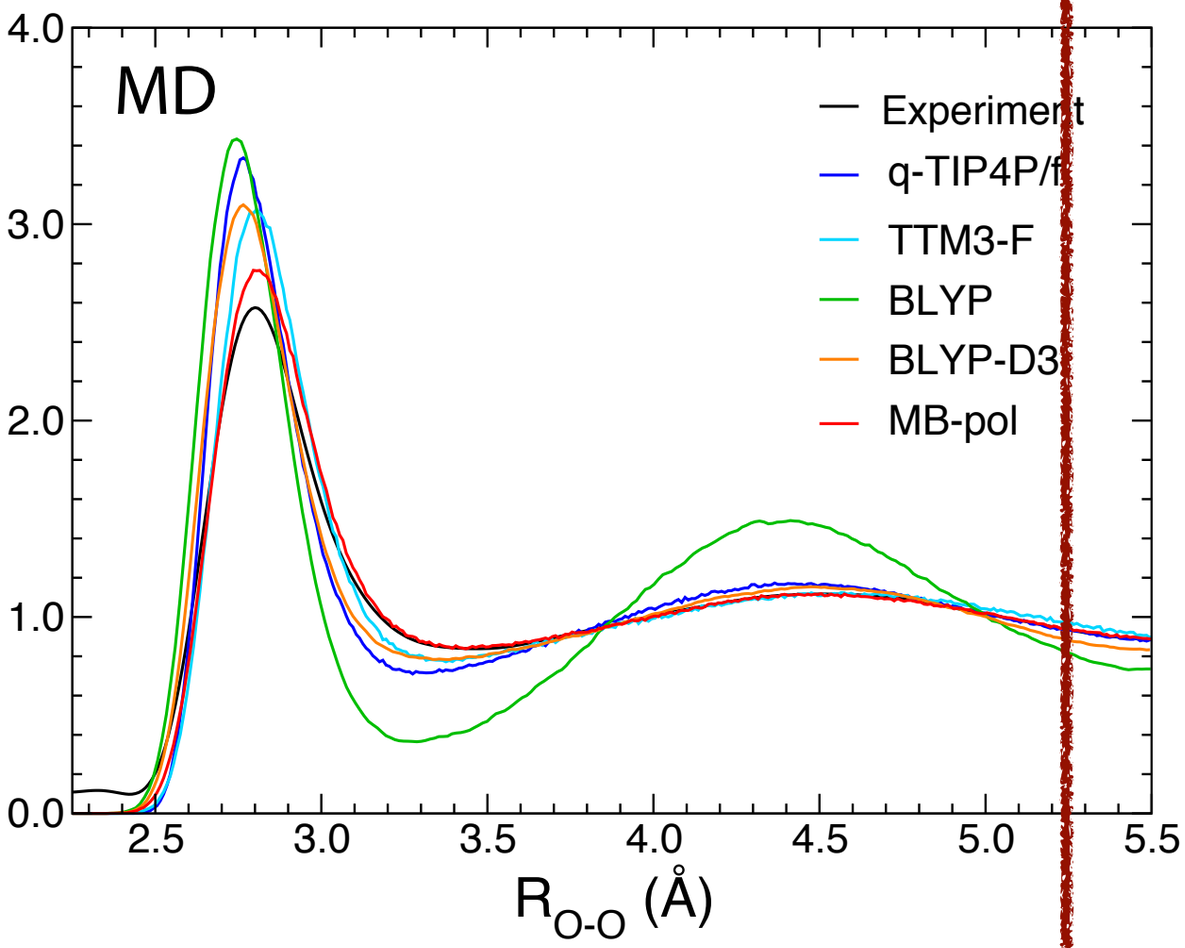


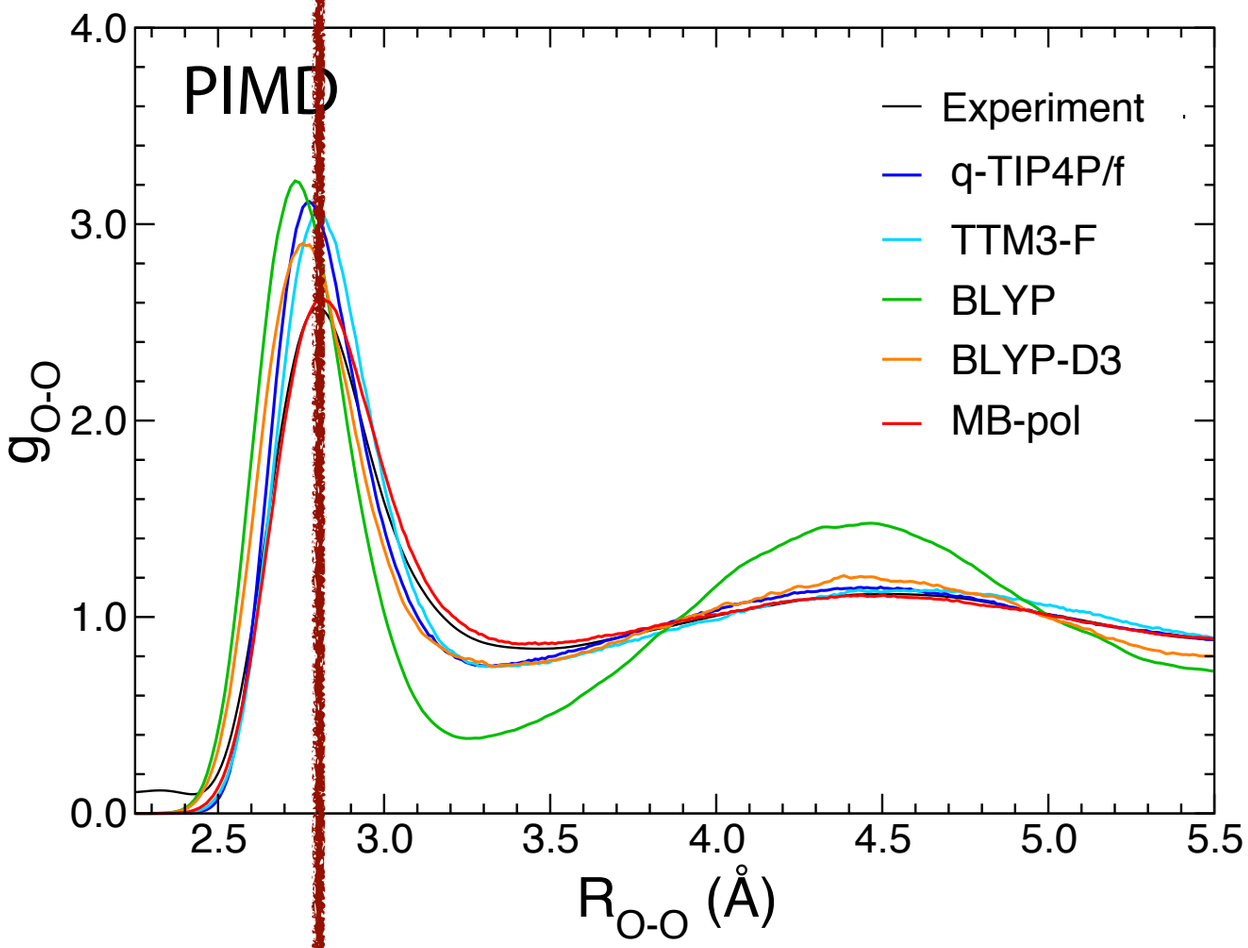
BLYP & BLYP-D3: *Wang, Ceriotti & Markland, J. Chem. Phys. 141, 104502 (2014)*

Liquid Water: Some Insights

Oxygen-oxygen radial distribution function

Nuclear quantum effects and model dependence





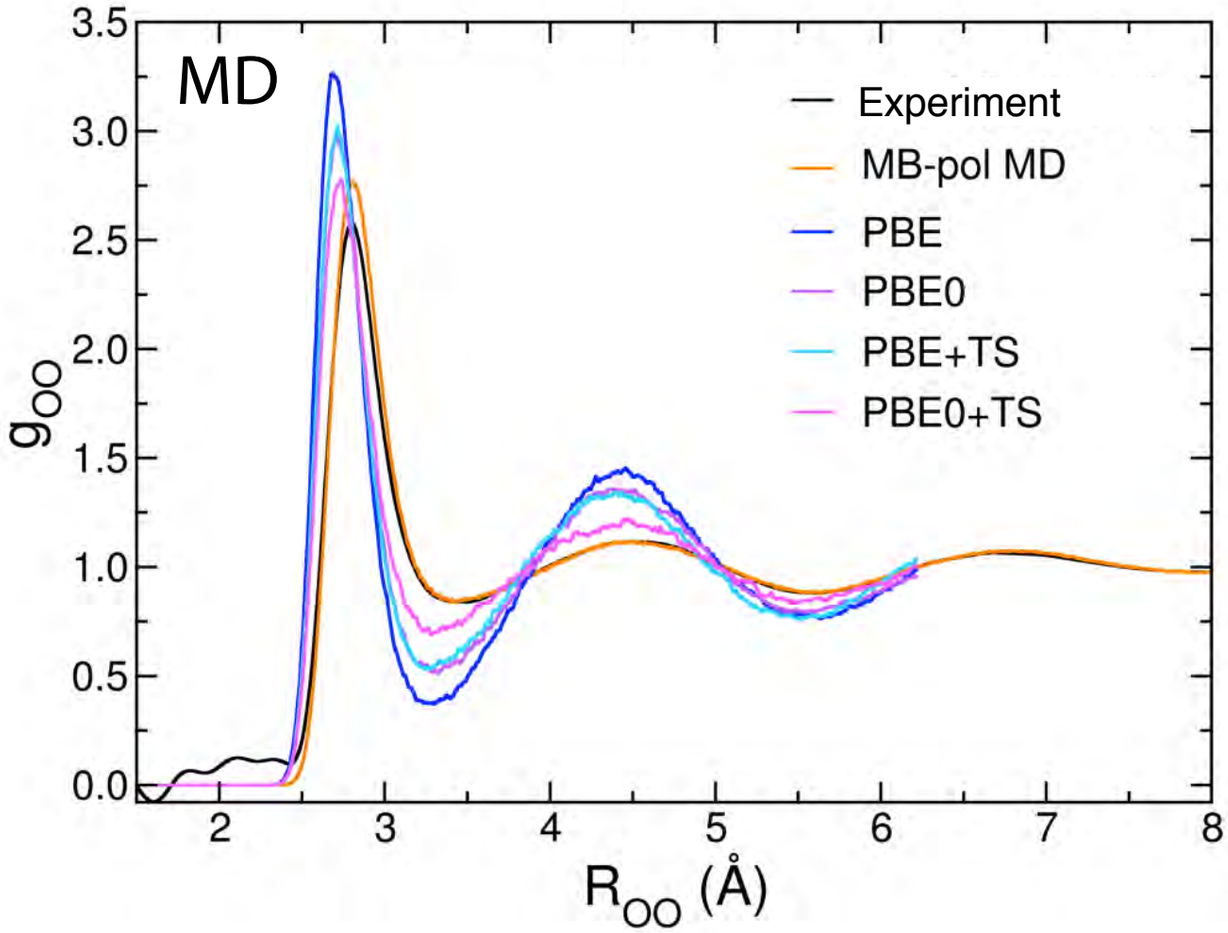
BLYP & BLYP-D3: *Wang, Ceriotti & Markland, J. Chem. Phys. 141, 104502 (2014)*

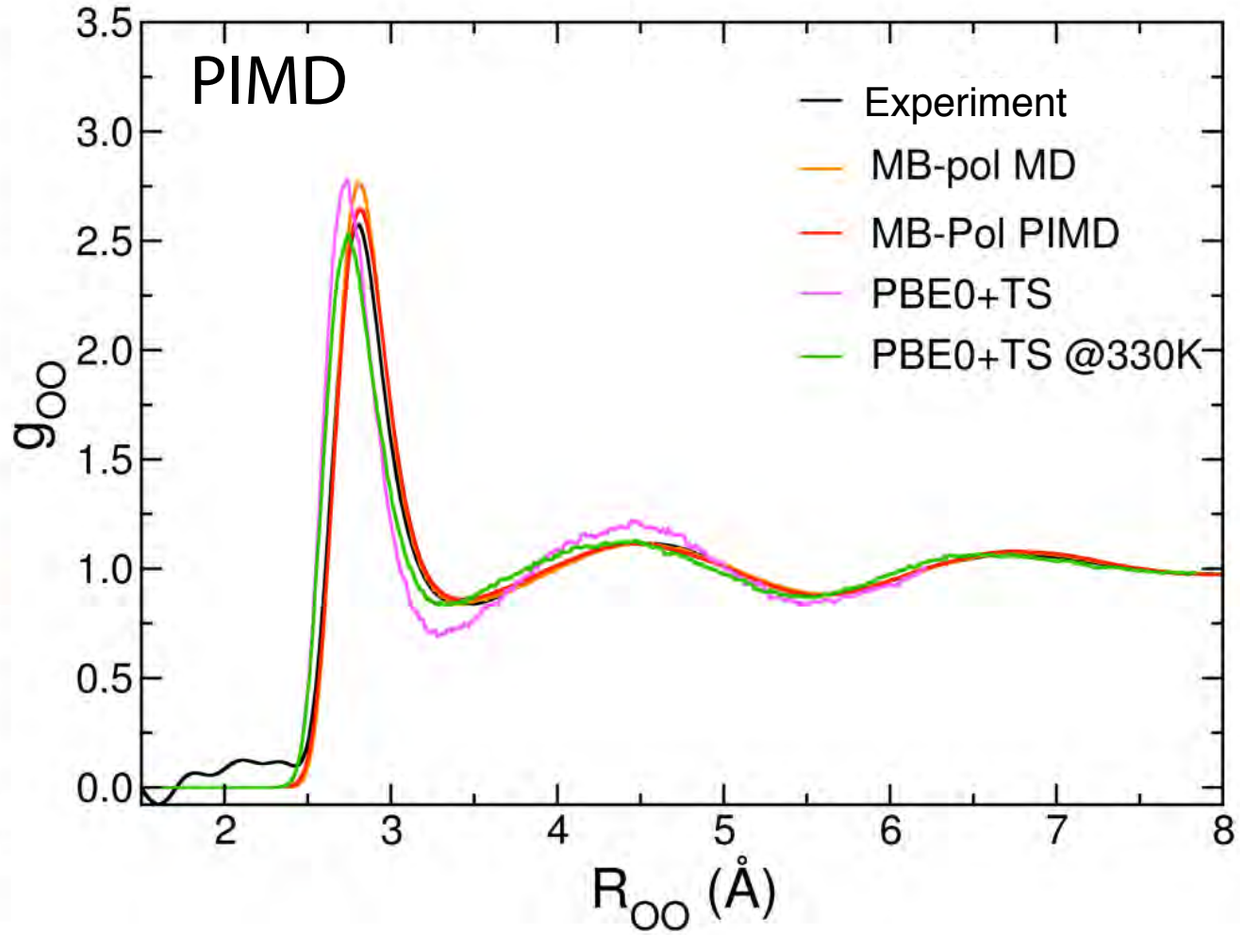
Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Liquid Water: Some Insights

Oxygen-oxygen radial distribution function

Nuclear quantum effects and model dependence





PBE & PBE0: *DiStasio, Santra, Li, Wu & Car, J. Chem. Phys. 141, 084502 (2014)*

Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Liquid Water: Thermodynamics & Dynamics

T = 298.15 K and P = 1 atm

Density

Experiment: 0.997 g cm^{-3}

MD: 1.004 ± 0.001 g cm^{-3}

PIMD: 0.999 ± 0.002 g cm^{-3}

Diffusion

Experiment: 0.23 $Å^2$ ps^{-1}

MD: 0.23 ± 0.01 $Å^2$ ps^{-1}

CMD: 0.22 ± 0.02 $Å^2$ ps^{-1}

Enthalpy of vaporization

Experiment: 10.52 kcal / mol^{-1}

MD: 10.9 ± 0.1 kcal / mol^{-1}

PIMD: 10.1 ± 0.4 kcal / mol^{-1}

Orientational relaxation

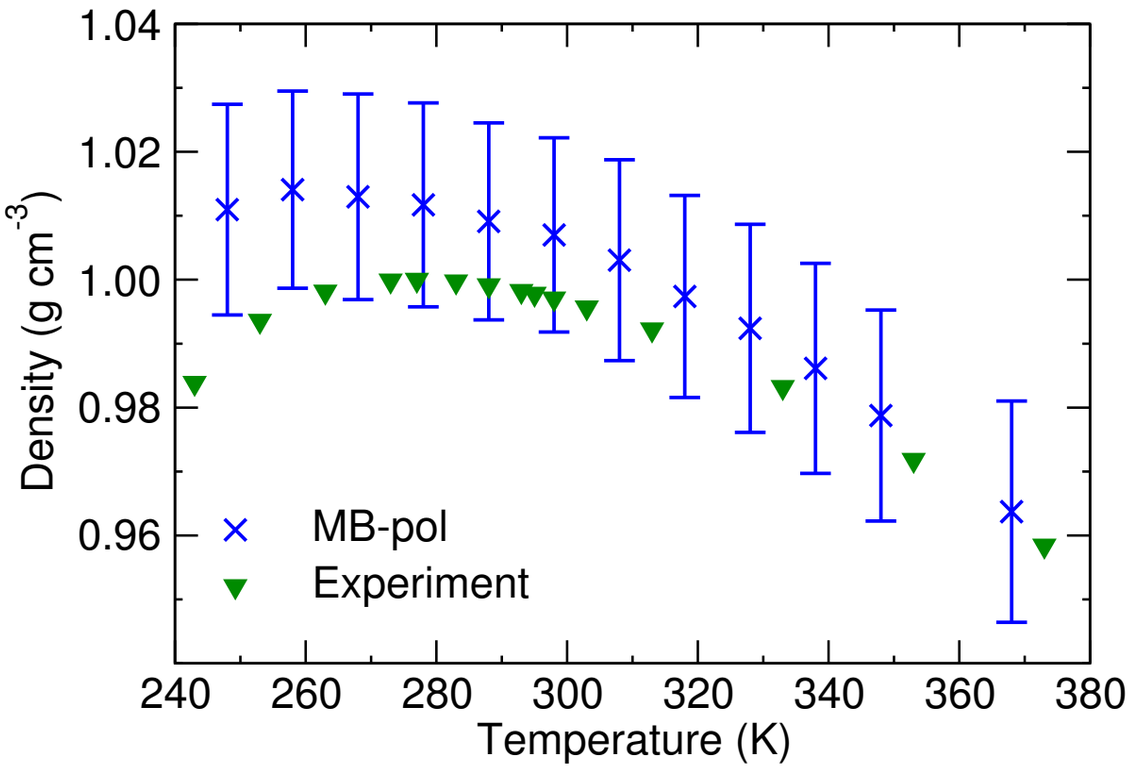
Experiment: 2.5 ps

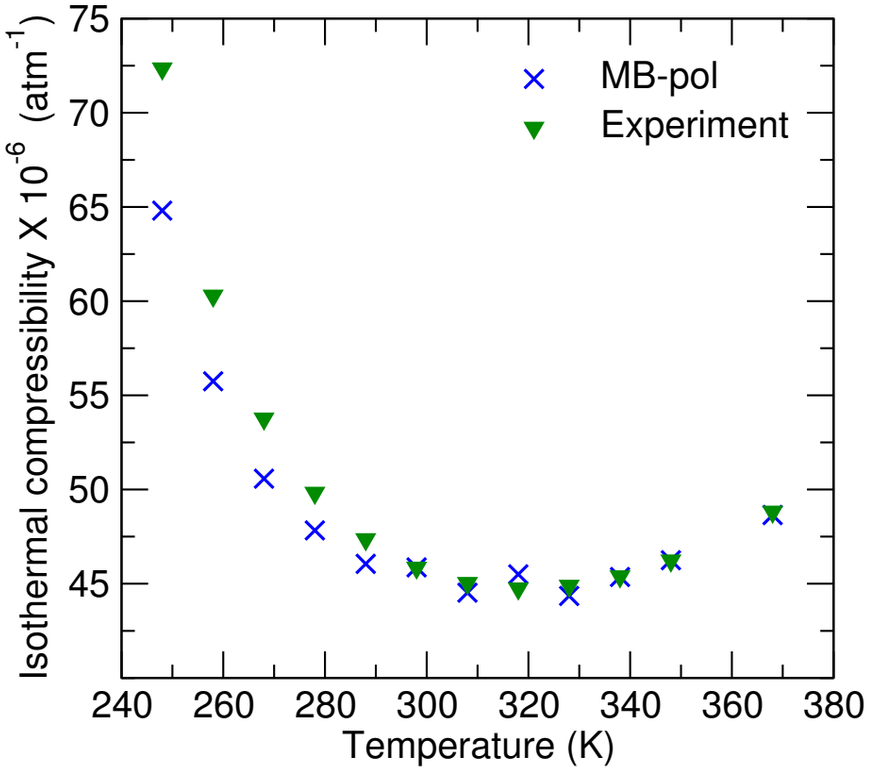
MD: 5.3 ± 0.1 ps

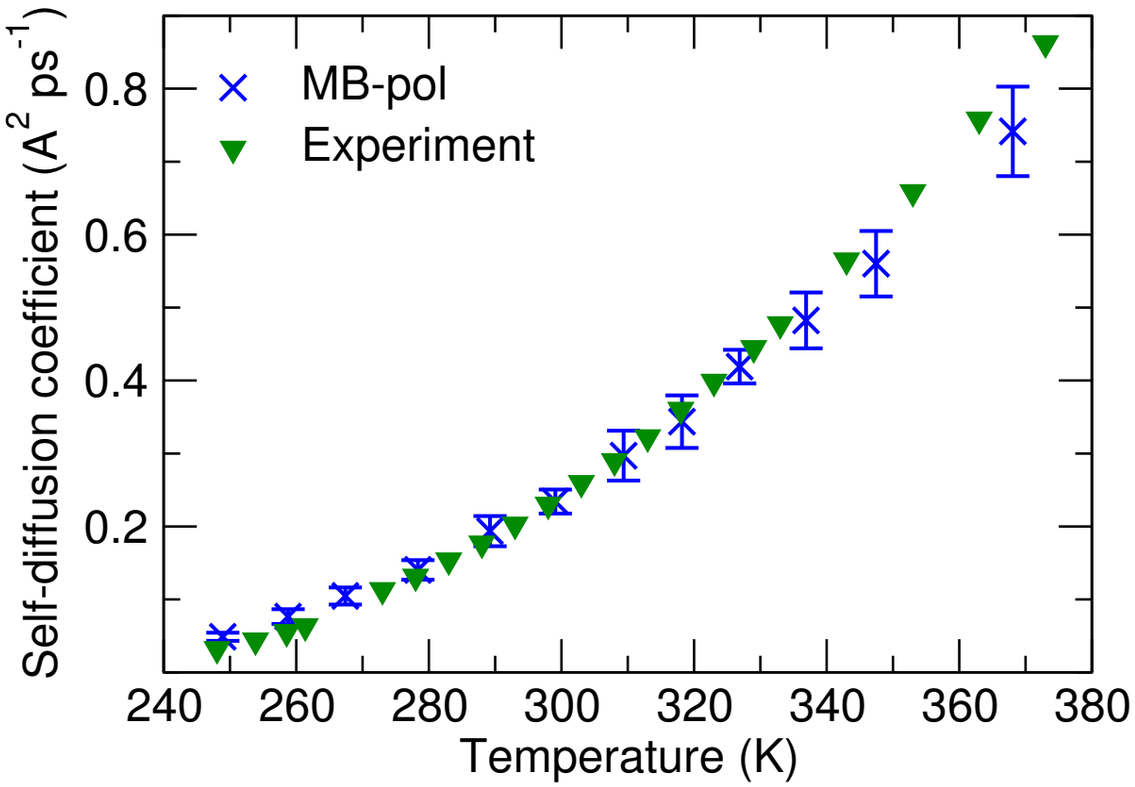
CMD: 2.6 ± 0.2 ps

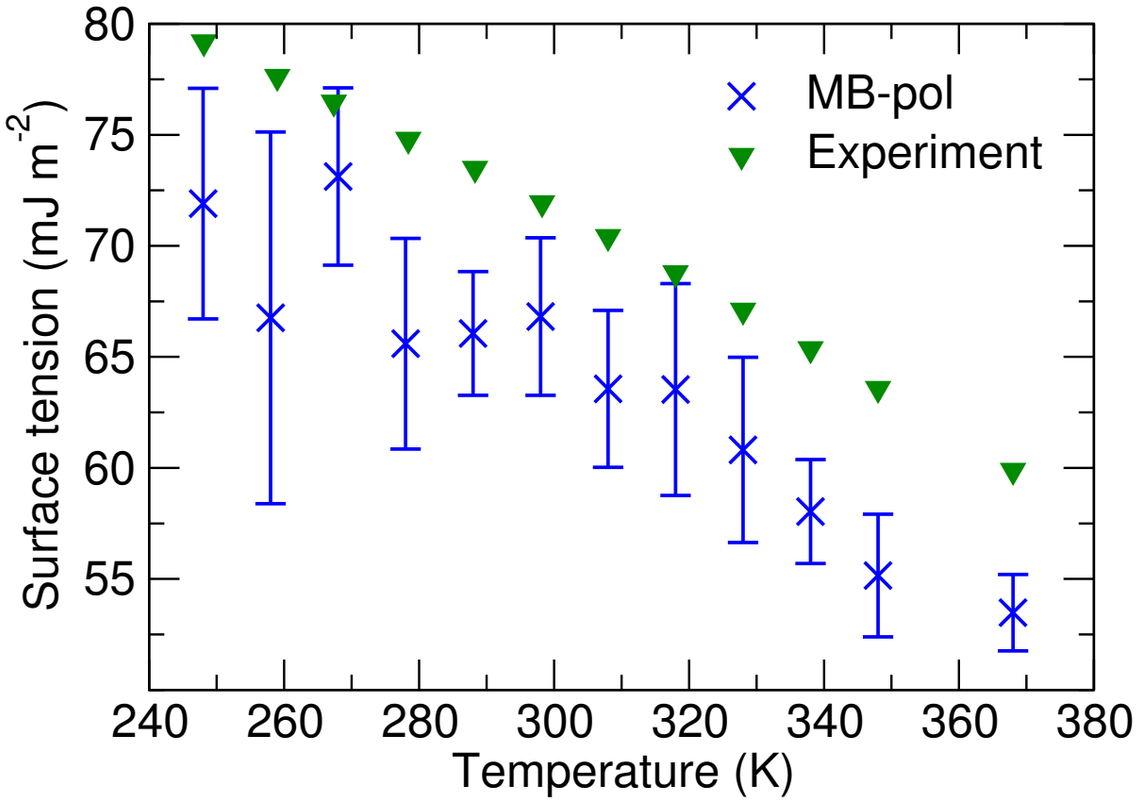
Babin, Medders & FP, J. Phys. Chem. Lett. 3, 3765 (2012); Medders, Babin & FP, J. Chem. Theory Comput. 10, 2906 (2014)

Liquid Water: Thermodynamics & Dynamics







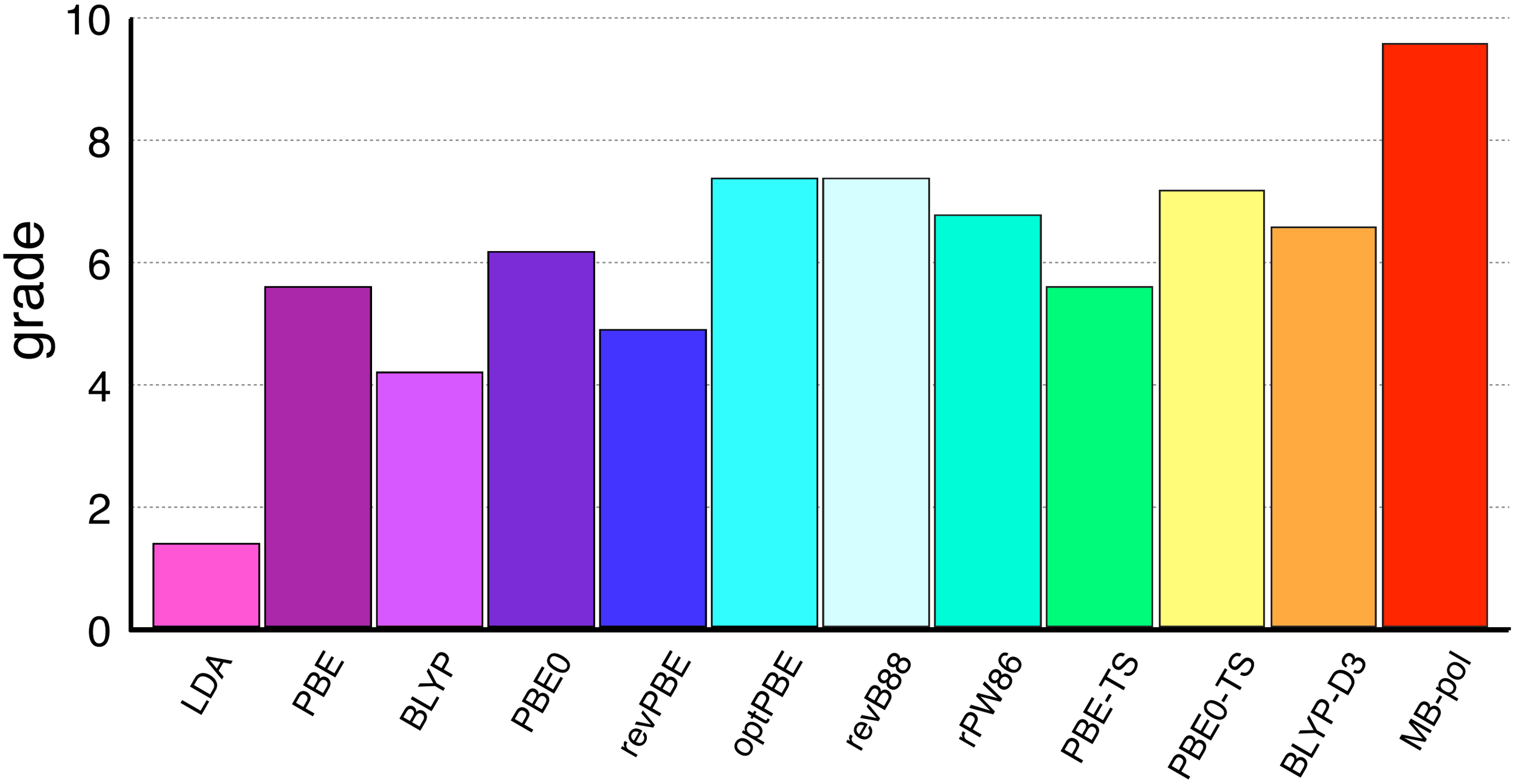


Reddy, Straight, Bajaj, Pham, Riera, Moberg, Morales, Knight, Götz, FP, J. Chem. Phys., in press, arxiv.org/abs/1609.02884

MB-pol: "CCSD(T) Accuracy" Across Phases

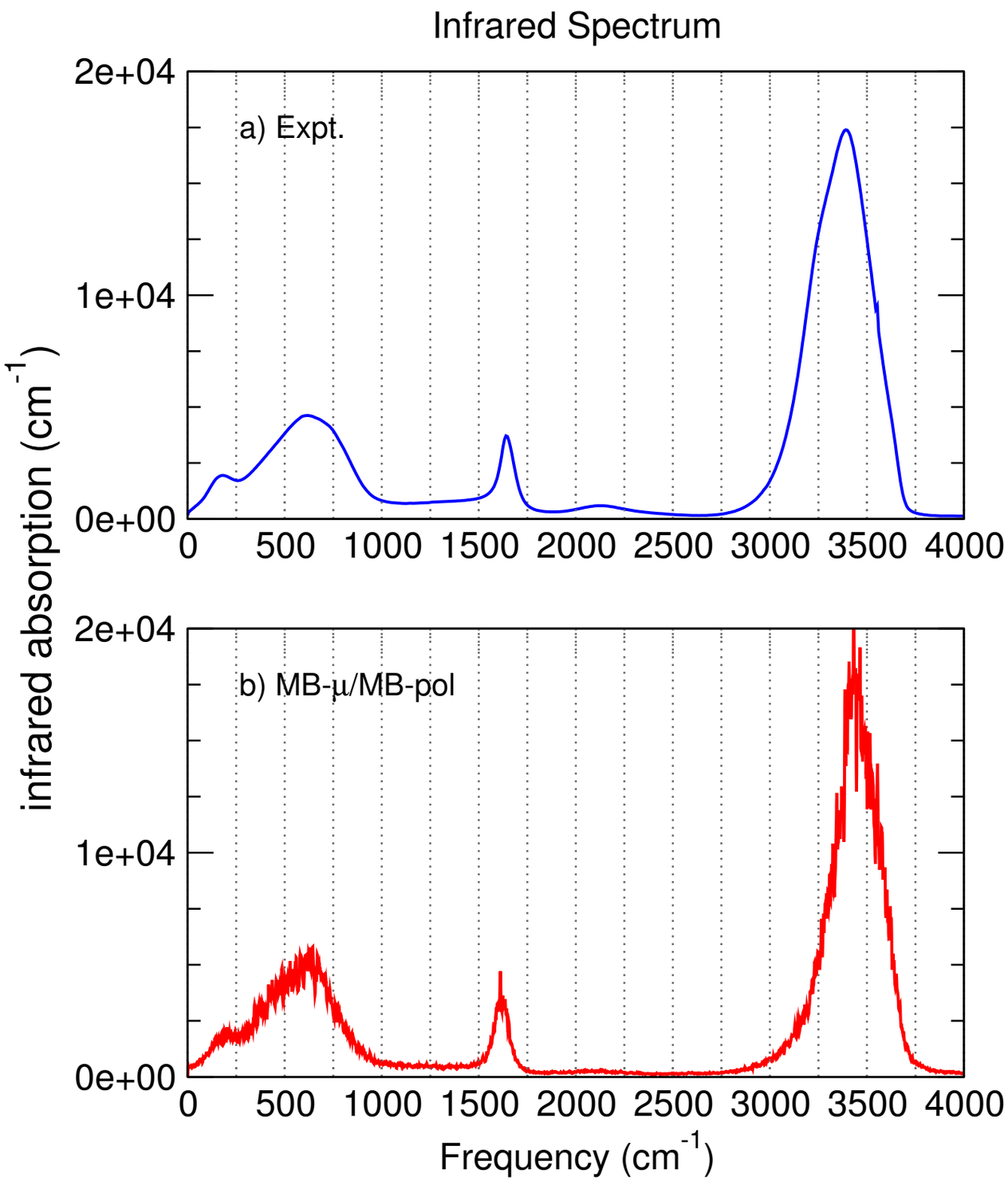
Reference data from monomer, dimer, hexamer, and ice

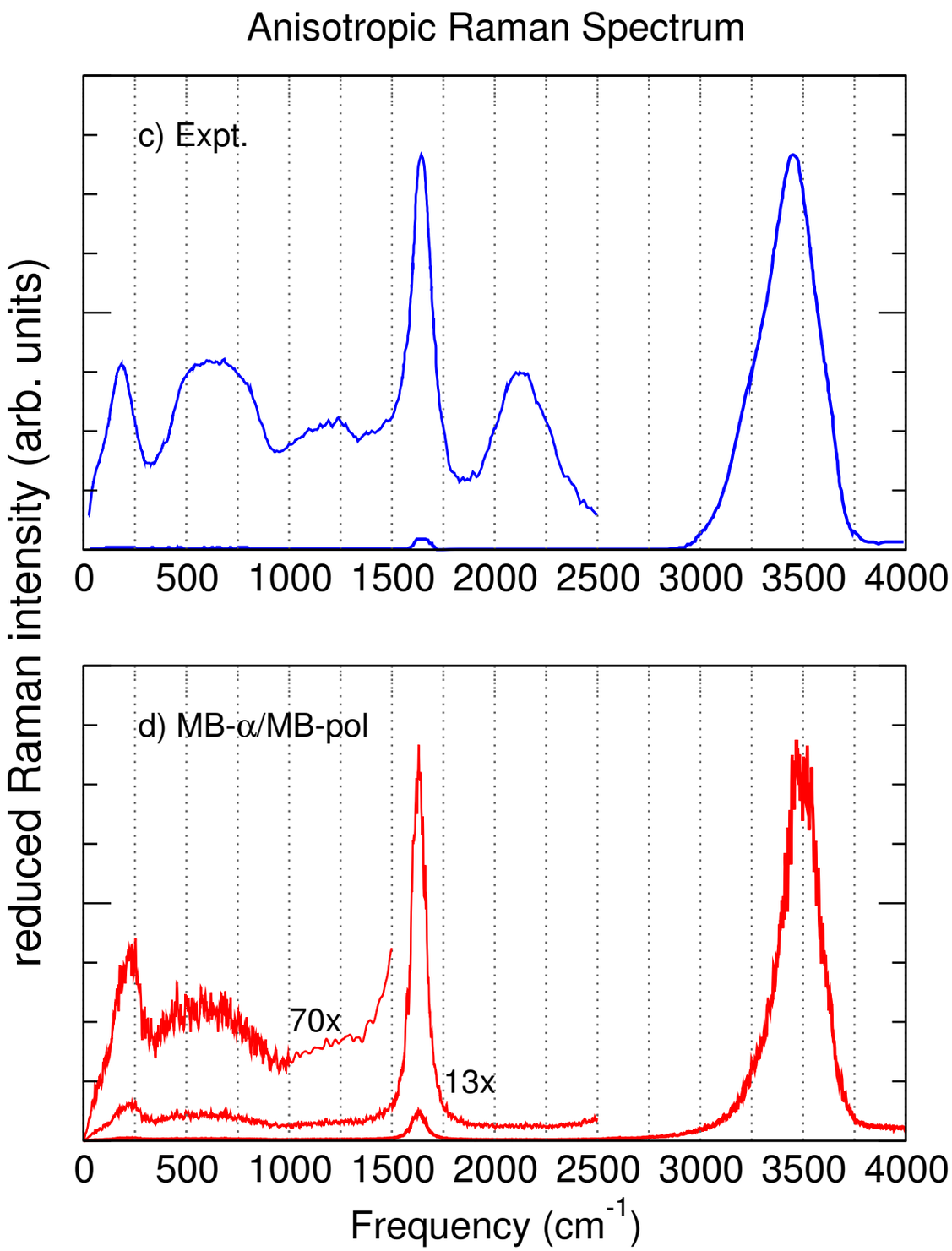
Gillan, Alfé, Michaelides, "Perspective: How Good Is DFT for Water?", J. Chem. Phys. 144, 130901 (2016)



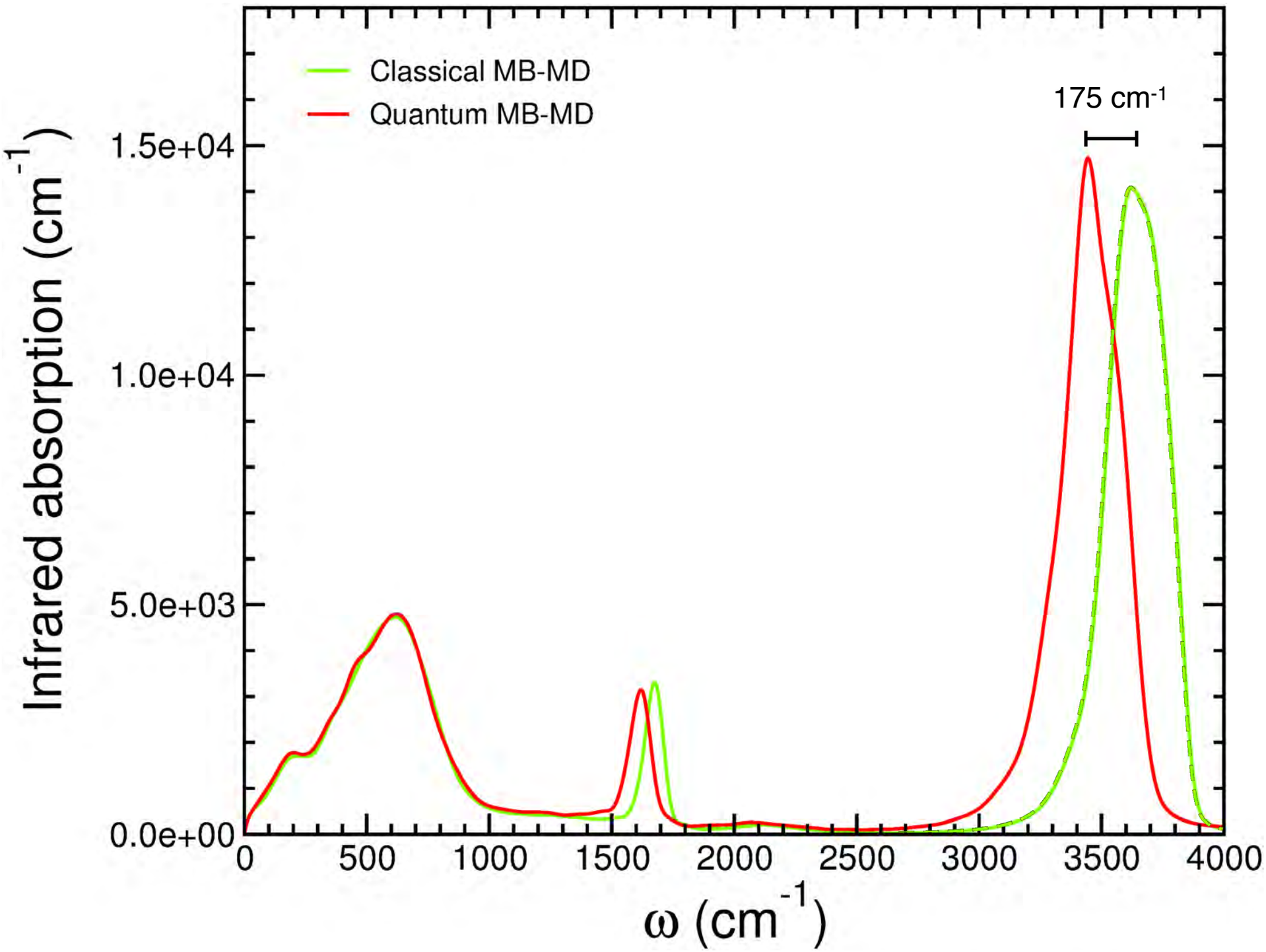
Cisneros, Wikfeldt, Ojamäe, Lu, Xu, Torabifard, Bartók-Pártay, Csányi, Molinero & FP, Chem. Rev. 116, 7501 (2016)

Liquid Water: Infrared & Raman Spectra





Liquid Water: Classical vs. Quantum IR Spectrum



Medders & FP, J. Chem. Theory Comput. 11, 1145 (2015)

A New Look at the Air/Water Interface

Vibrational sum-frequency generation spectrum

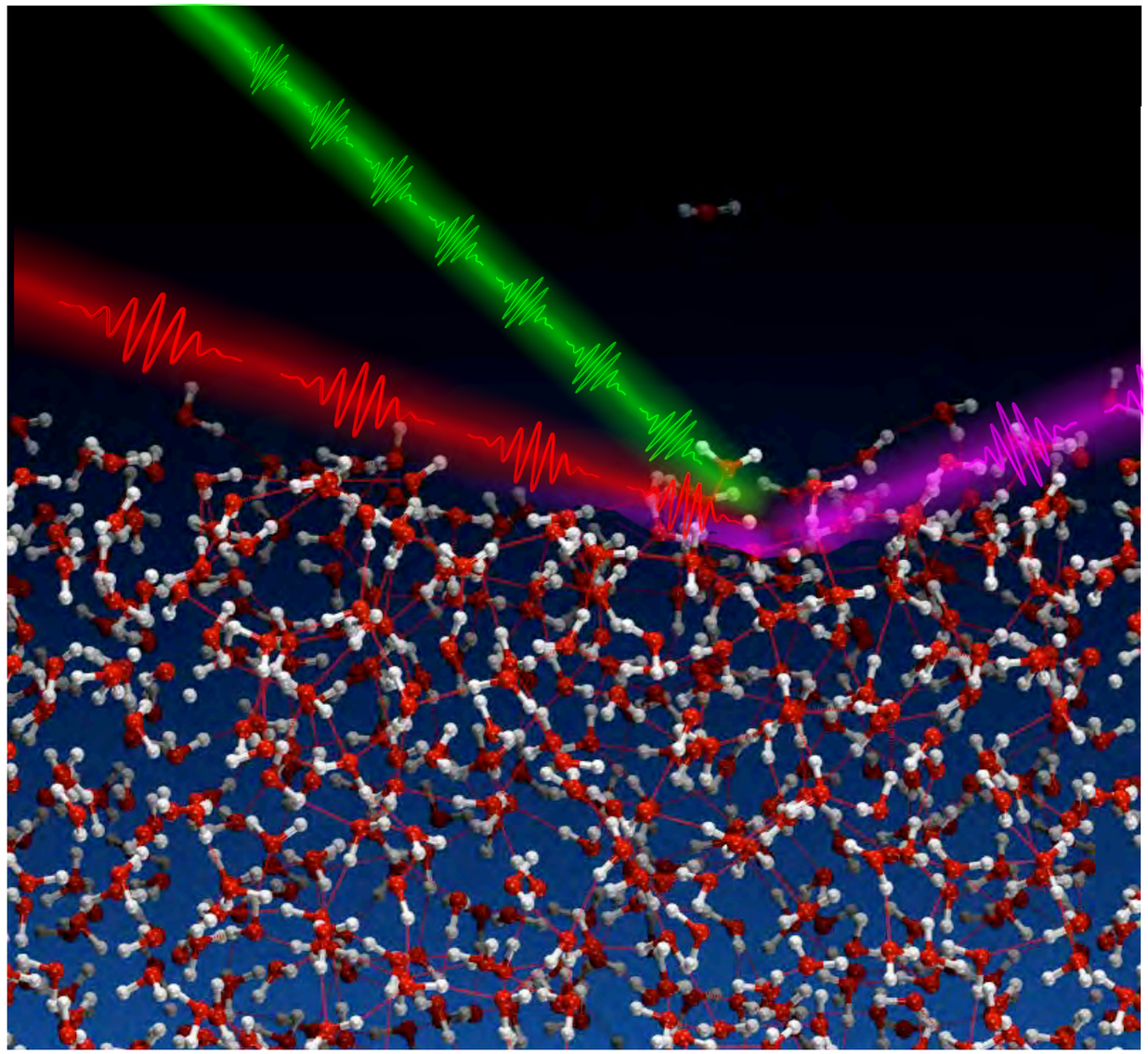
$$Im[\chi^{\mathrm{R},(2)}_{ijk}(\omega)] = Im\left[\frac{i\omega}{k_B T}\int_0^\infty dt e^{-i\omega t}\langle\alpha_{ij}(t)\mu_k(0)\rangle\right]$$

i = polarization of sum-frequency beam

j = polarization of visible beam

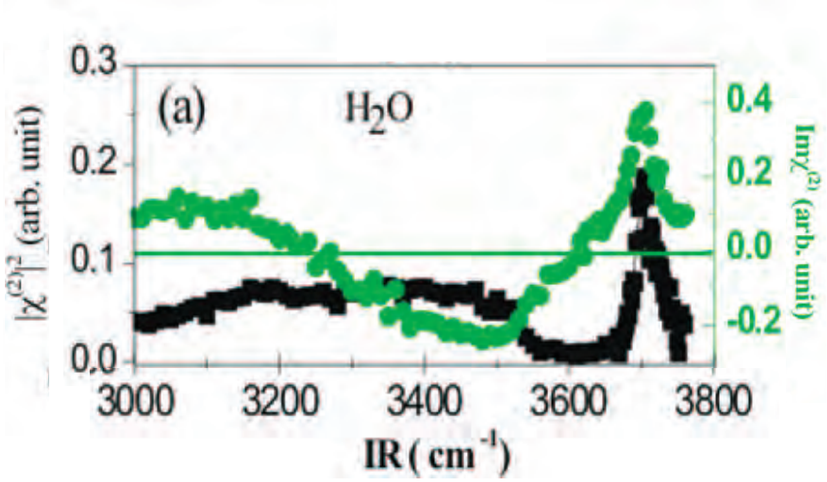
k = polarization of infrared beam

SSP combination: i = x; j = x; k = z

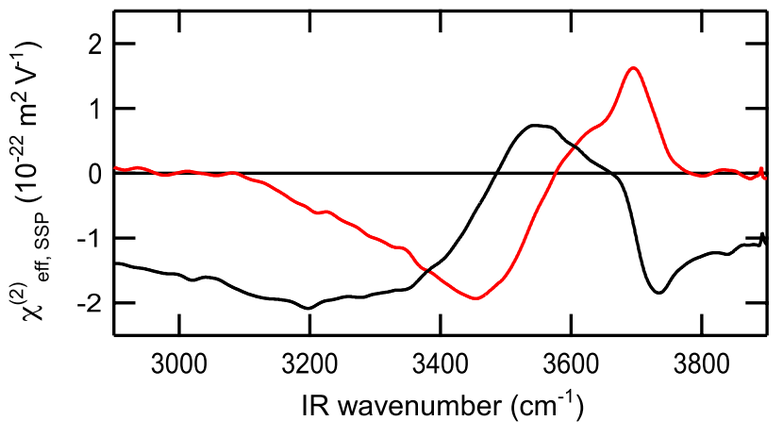


A New Look at the Air/Water Interface

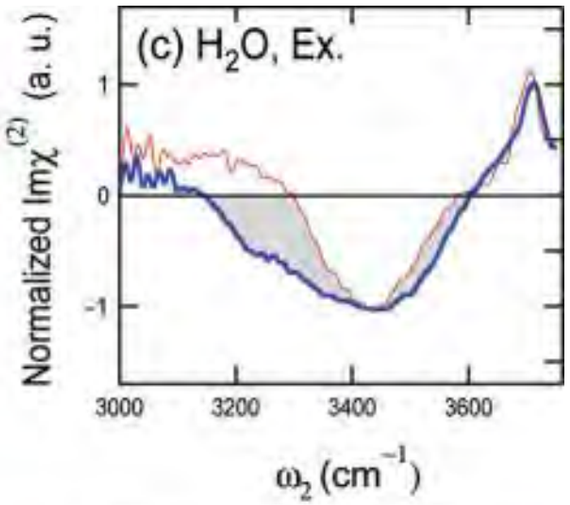
Experiment



Tian & Shen
J. Am. Chem. Soc. 31, 2790 (2009)

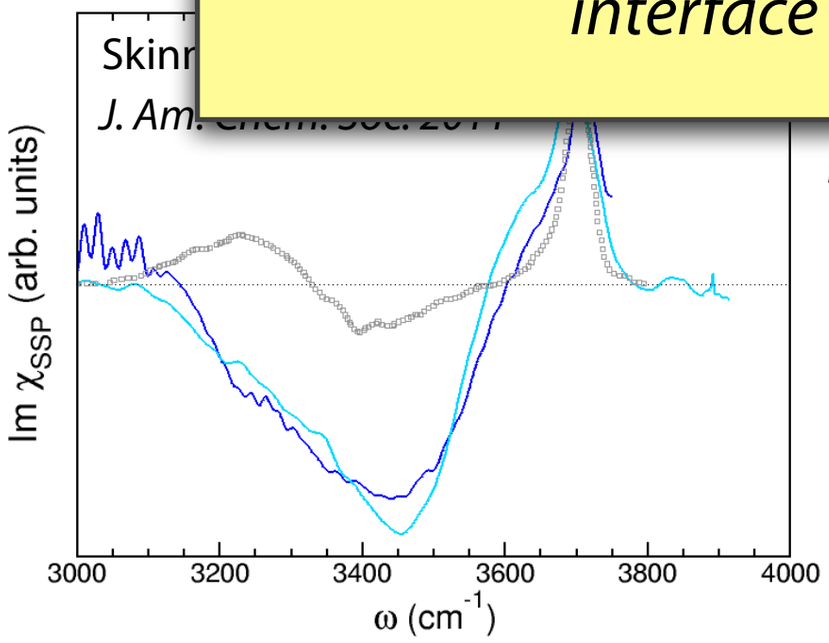


Nihonyanagi, Kusaka, Inoue, Adhikari, Yamaguchi & Tahara



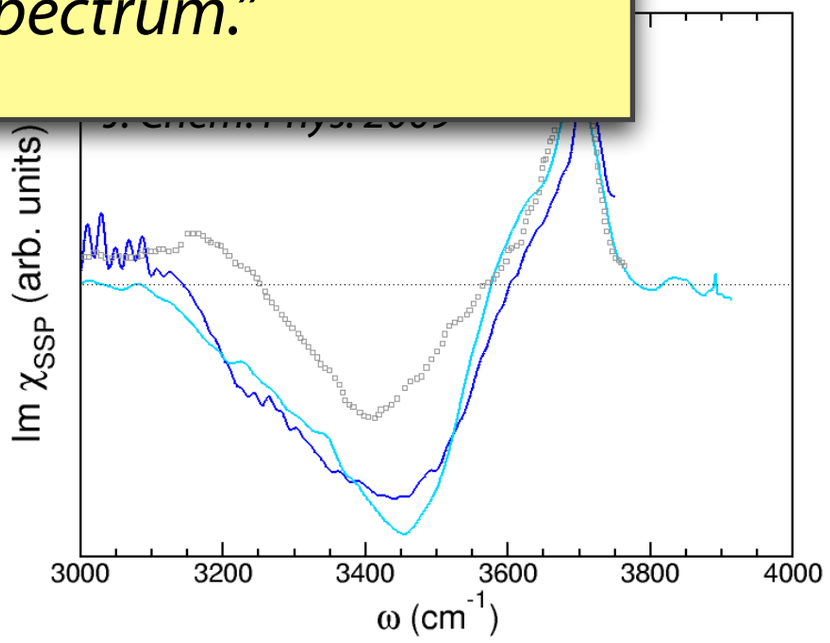
Nihonyanagi, Ishiyama, Lee, Yamaguchi, Bonn, Morita & Tahara
5 (2011)

"This result urges us to reconsider the structure of the air/water interface based on the accurate $\chi^{(2)}$ spectrum."



E3B model
↓
3B effects

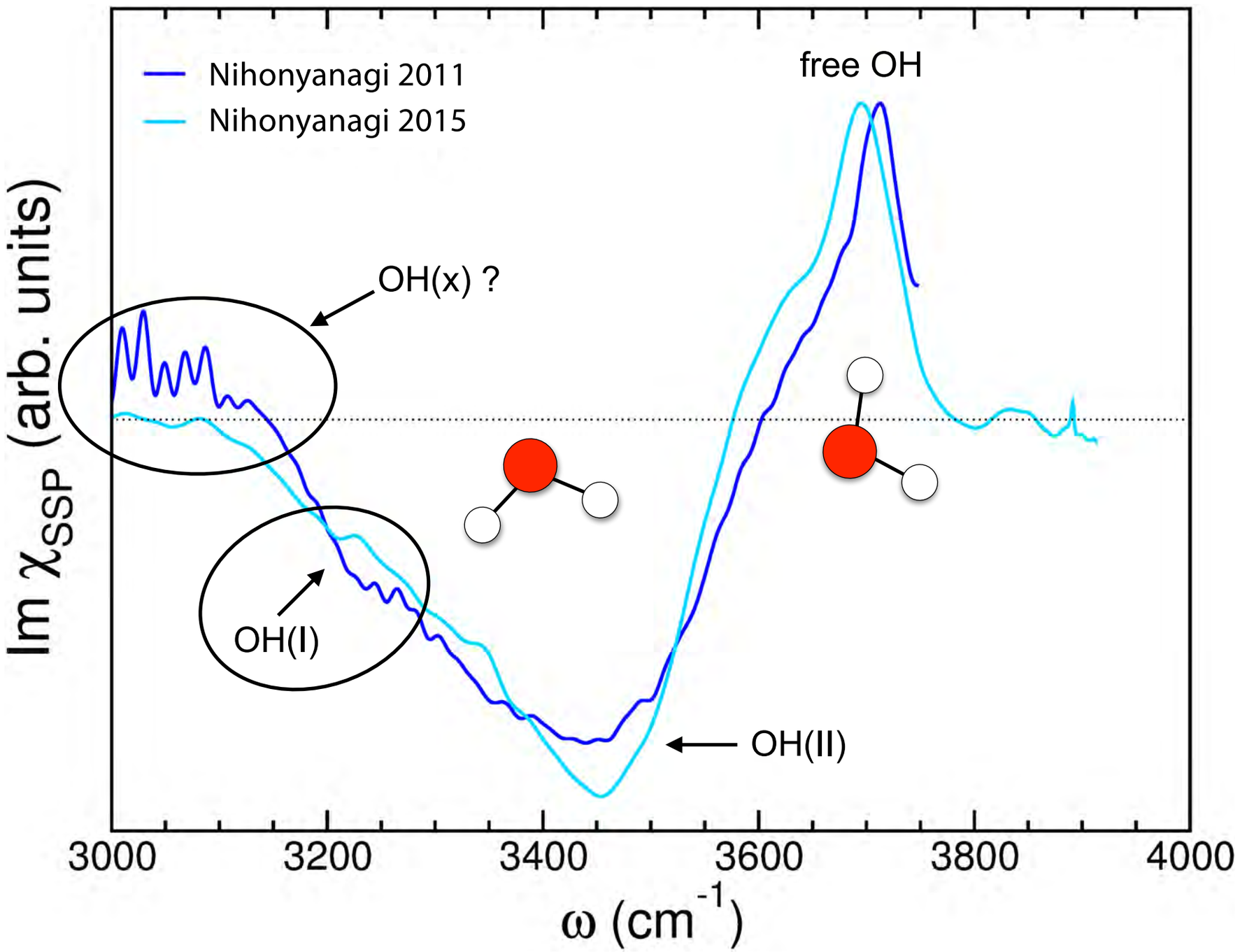
PD model
↓
anisotropic local field



Medders & FP, J. Am. Chem. Soc. 138, 3912 (2016)

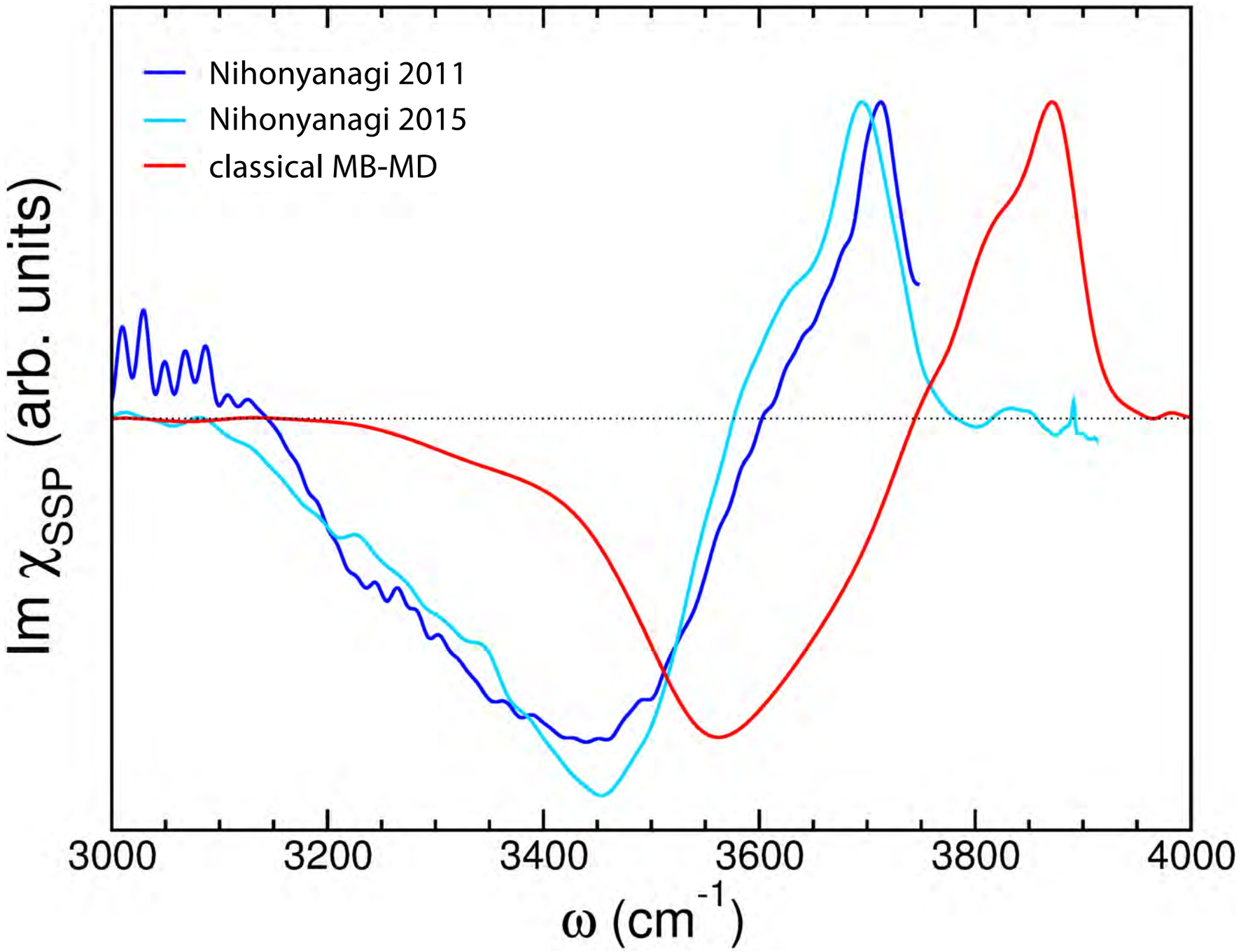
A New Look at the Air/Water Interface

Experiments



Dissecting the SFG Spectrum: Classical Response

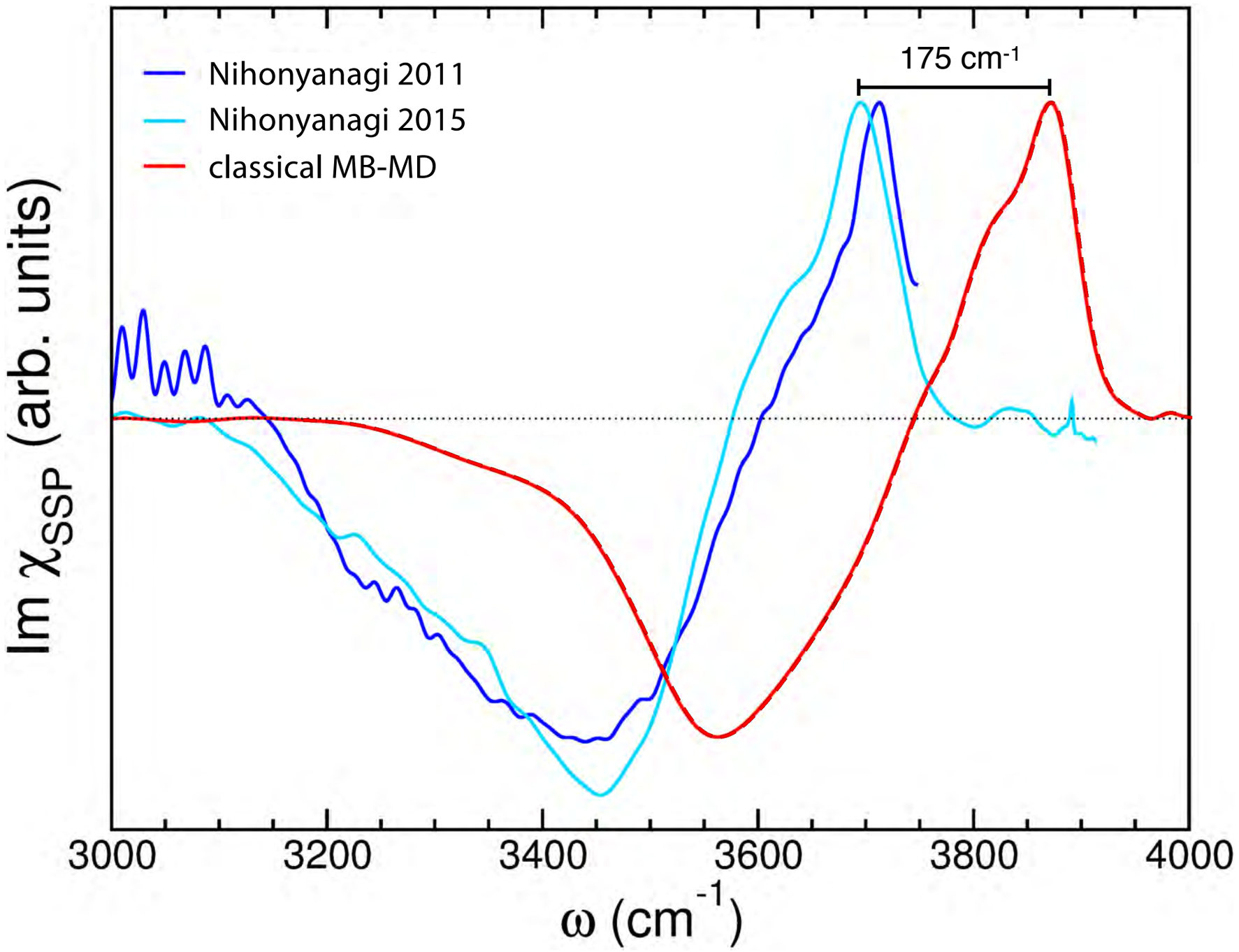
Classical MB-MD



Medders & FP, J. Am. Chem. Soc. 138, 3912 (2016)

Dissecting the SFG Spectrum: Classical Response

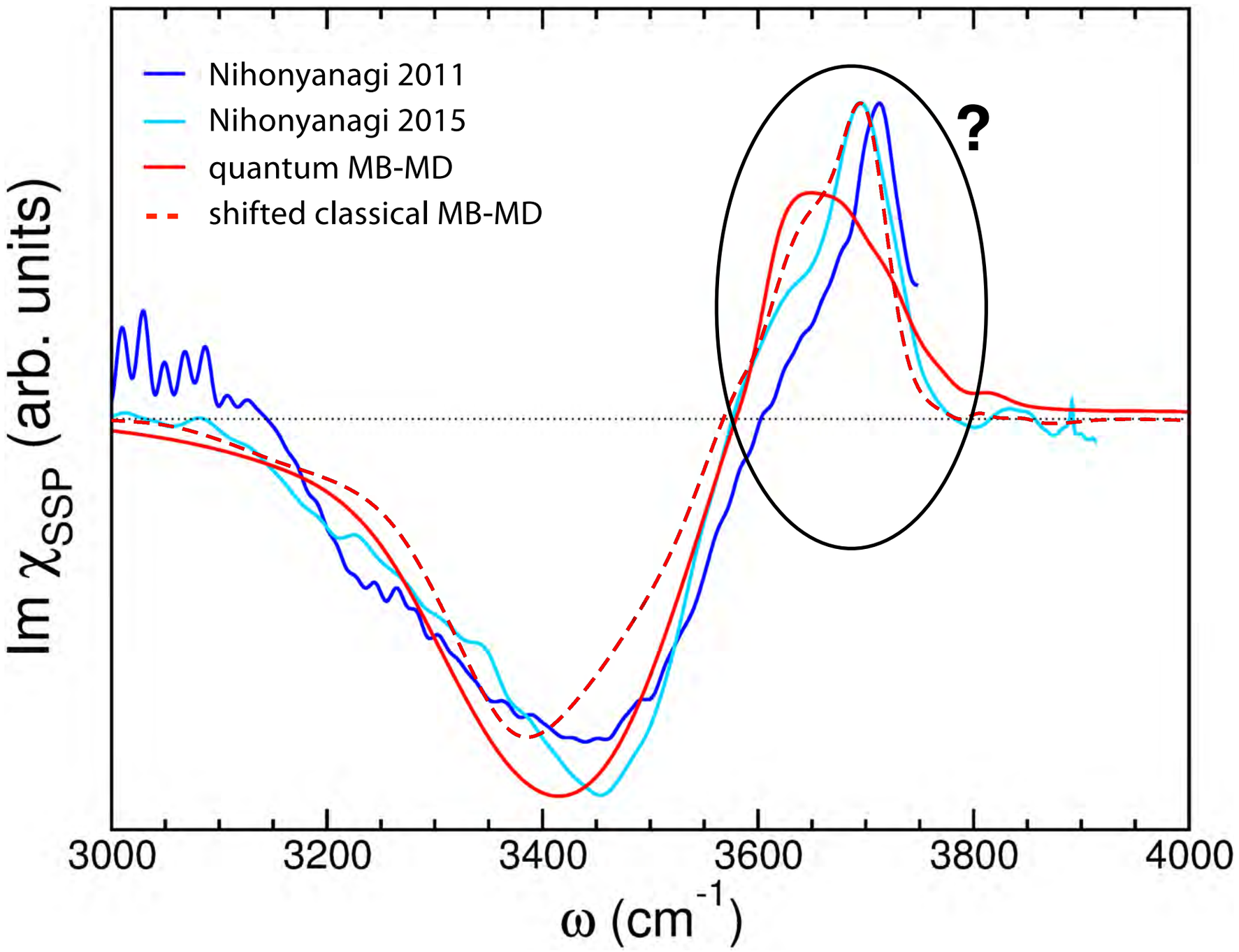
Classical MB-MD



Medders & FP, J. Am. Chem. Soc. 138, 3912 (2016)

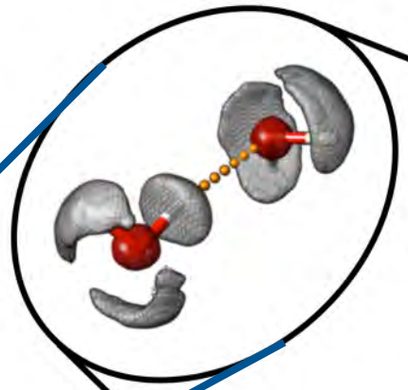
Dissecting the SFG Spectrum: Quantum Effects

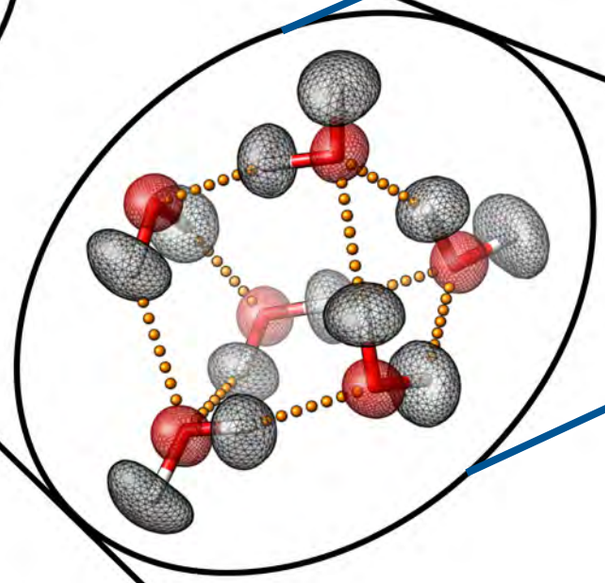
Classical vs. Quantum MB-MD

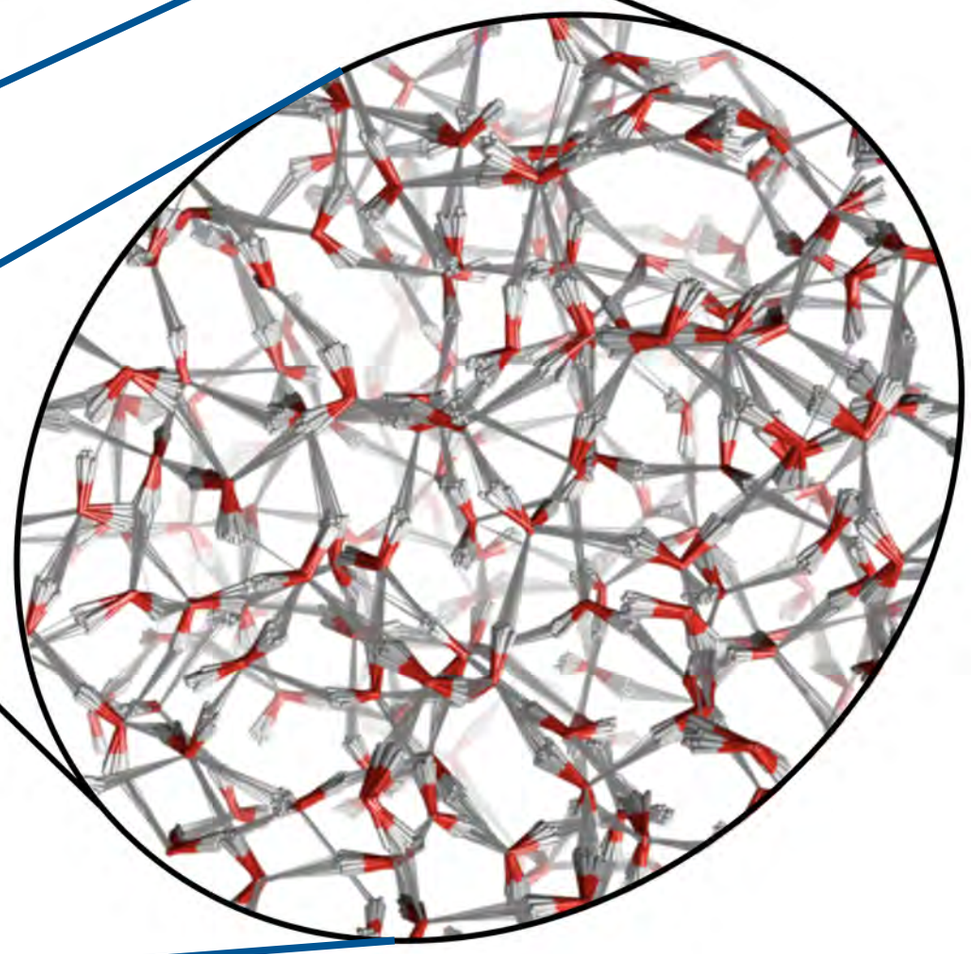


Medders & FP, J. Am. Chem. Soc. 138, 3912 (2016)

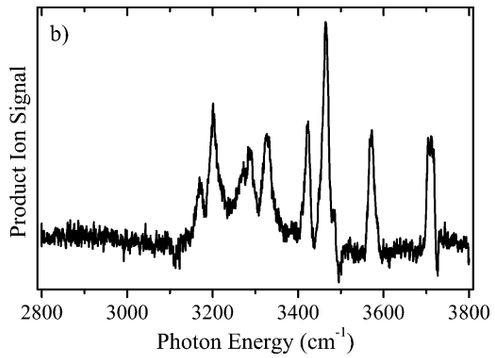
Chemical and Spectroscopic Accuracy Across Phases







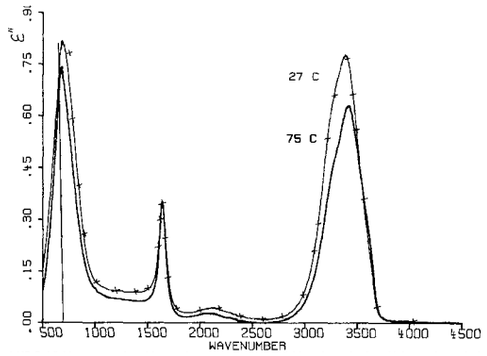
$(H_2O)_6$



Diken, Robertson & Johnson, J. Phys. Chem. A 108, 64 (2005)

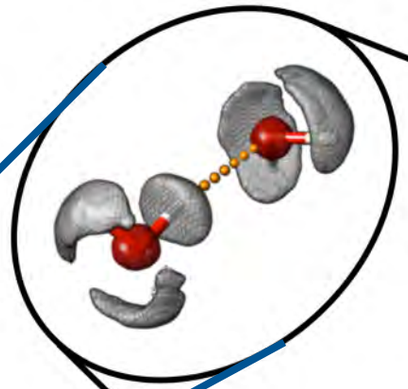
Experiment (cm^{-1})	MB-pol (cm^{-1})
153.62	154.77
	149.05
	129.49
120.19	119.23
108.89	109.14
107.93	108.76
	113.18
64.52	61.24
11.18	11.88
0	0

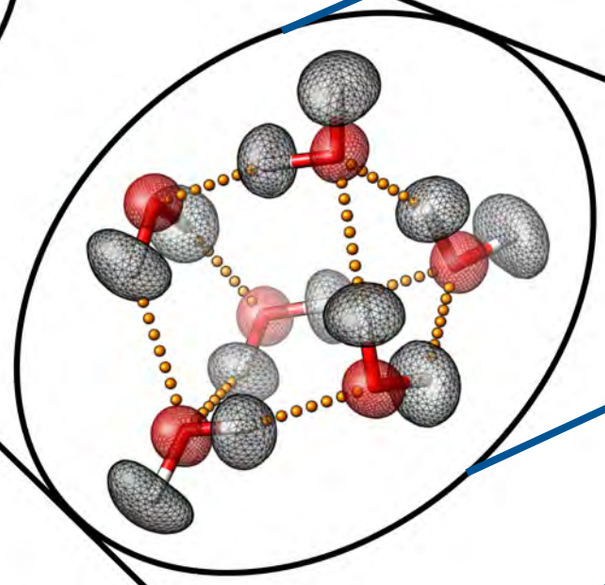
bulk water

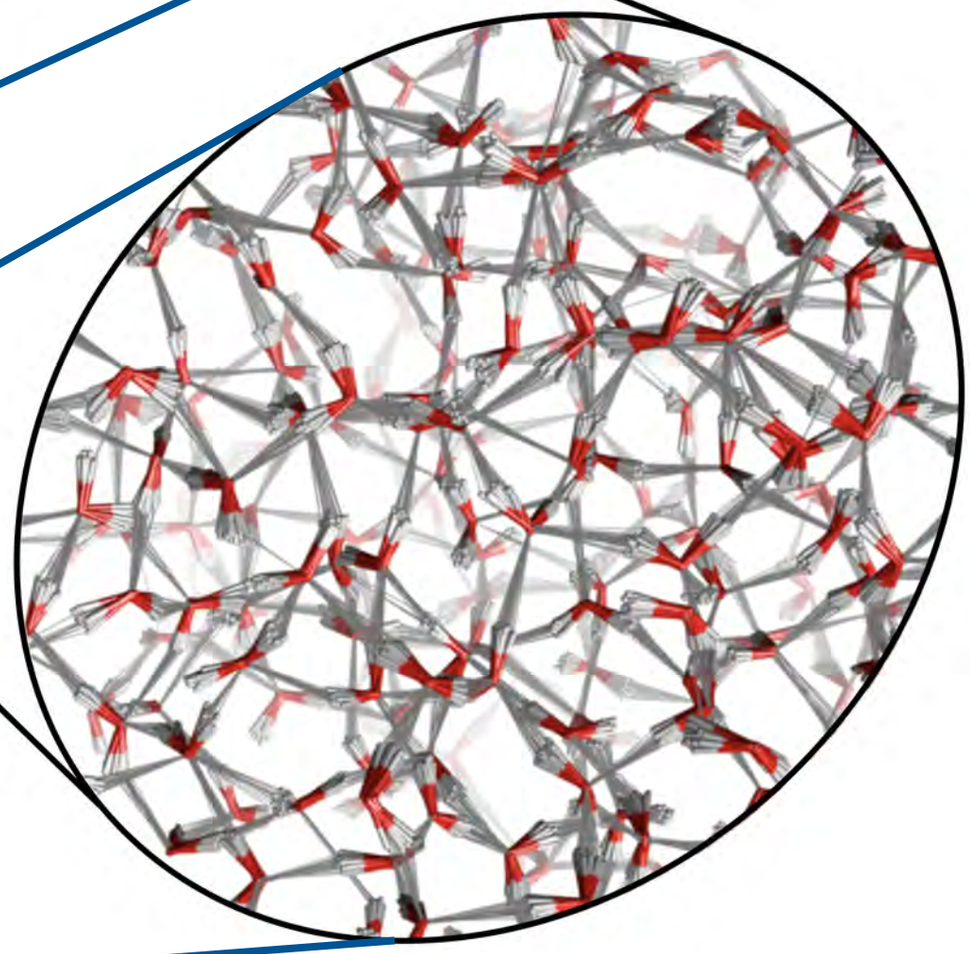


Marechal J. Chem. Phys. 95, 5565 (1991)

Chemical and Spectroscopic Accuracy Across Phases

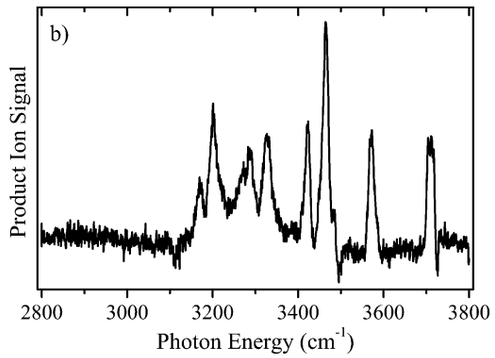






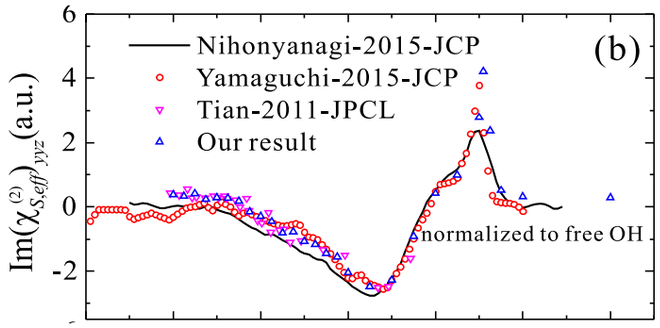
Experiment (cm^{-1})	MB-pol (cm^{-1})
153.62	154.77
	149.05
	129.49
120.19	119.23
108.89	109.14
107.93	108.76
	113.18
64.52	61.24
11.18	11.88
0	0

$(H_2O)_6$



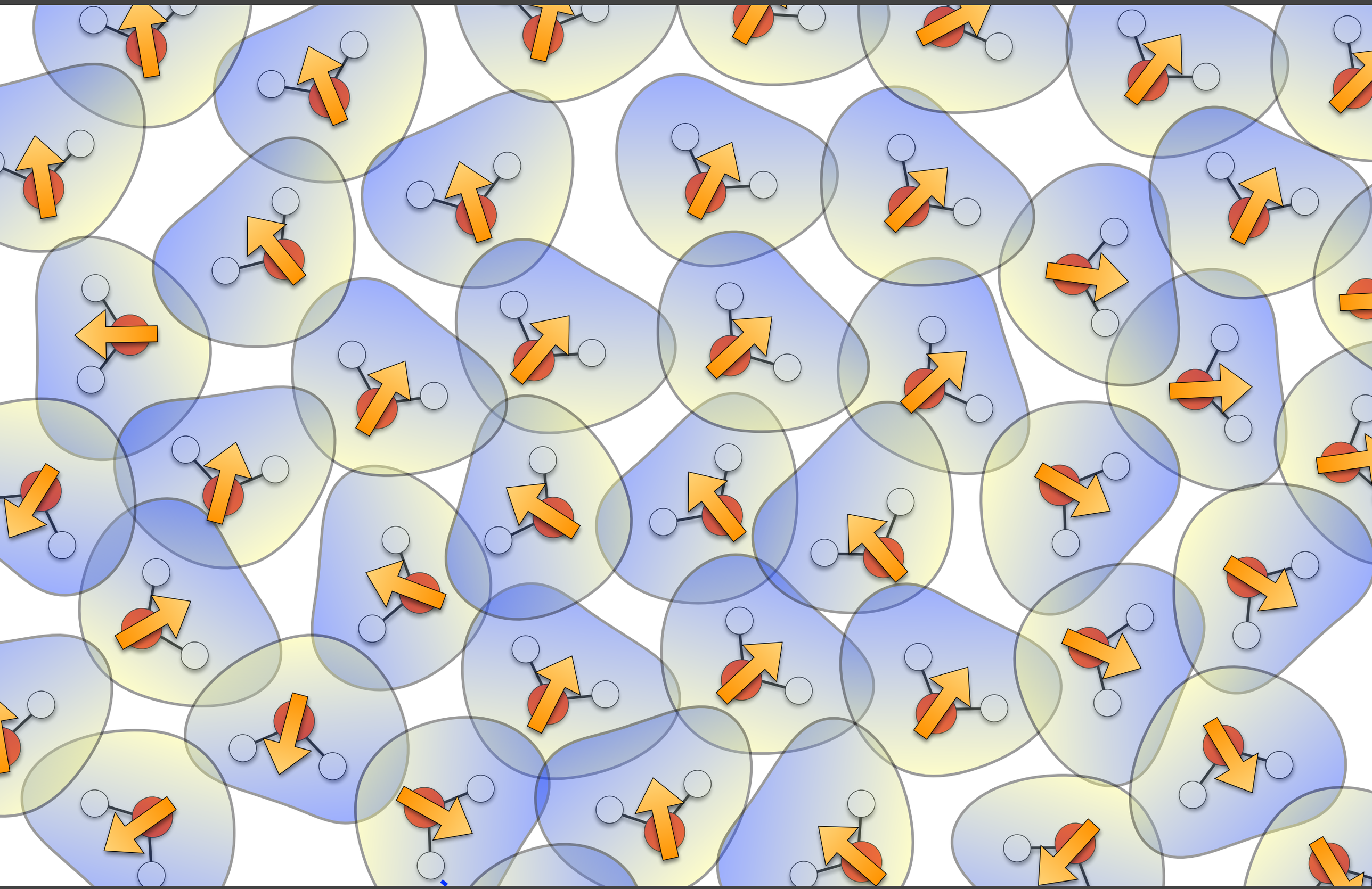
Diken, Robertson & Johnson, J. Phys. Chem. A 108, 64 (2005)

air/water interface

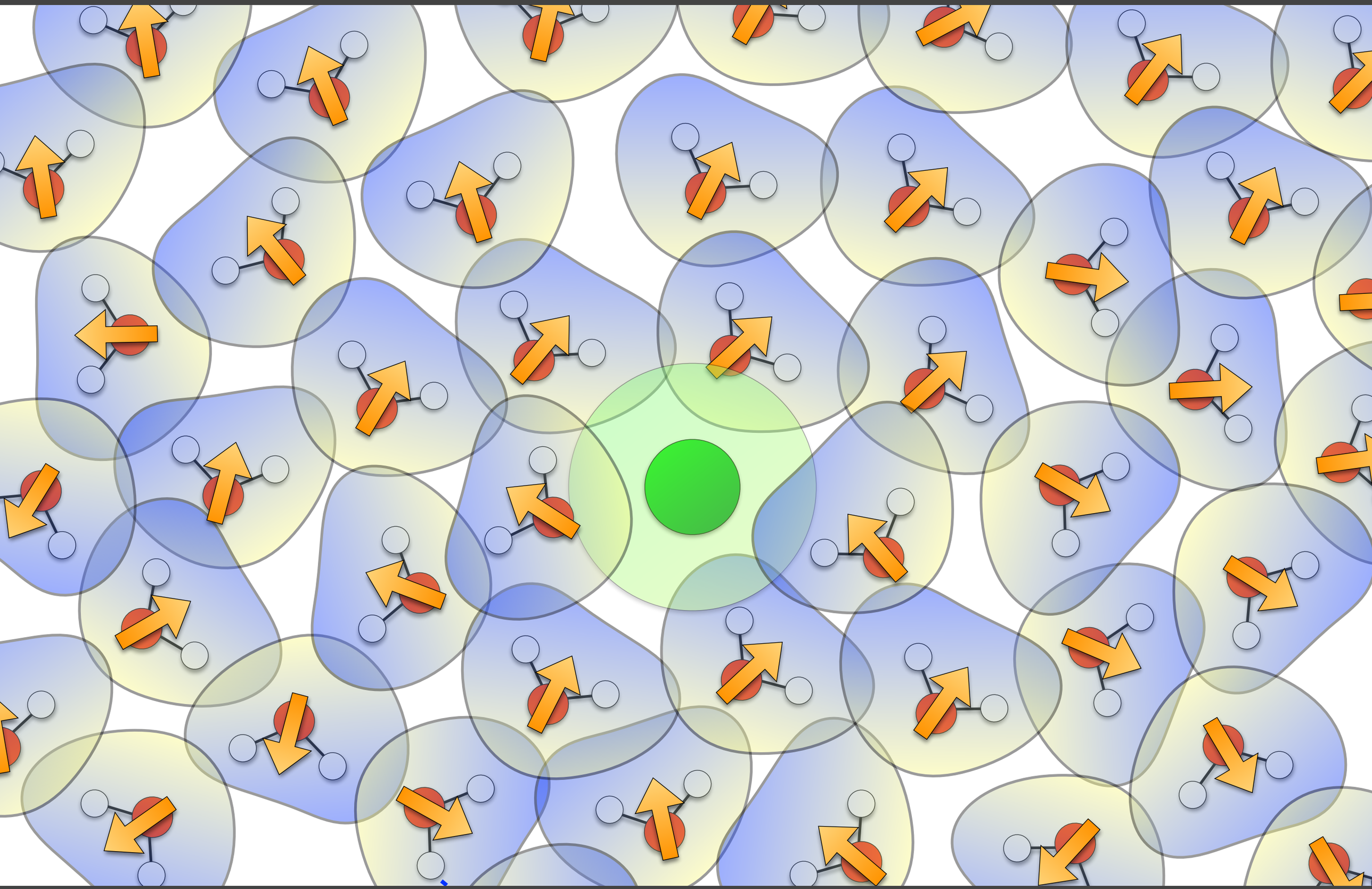


Sun, Liang, Xu, Zhu, Shen, Tian,
J. Chem. Phys. 144, 244711 (2016)

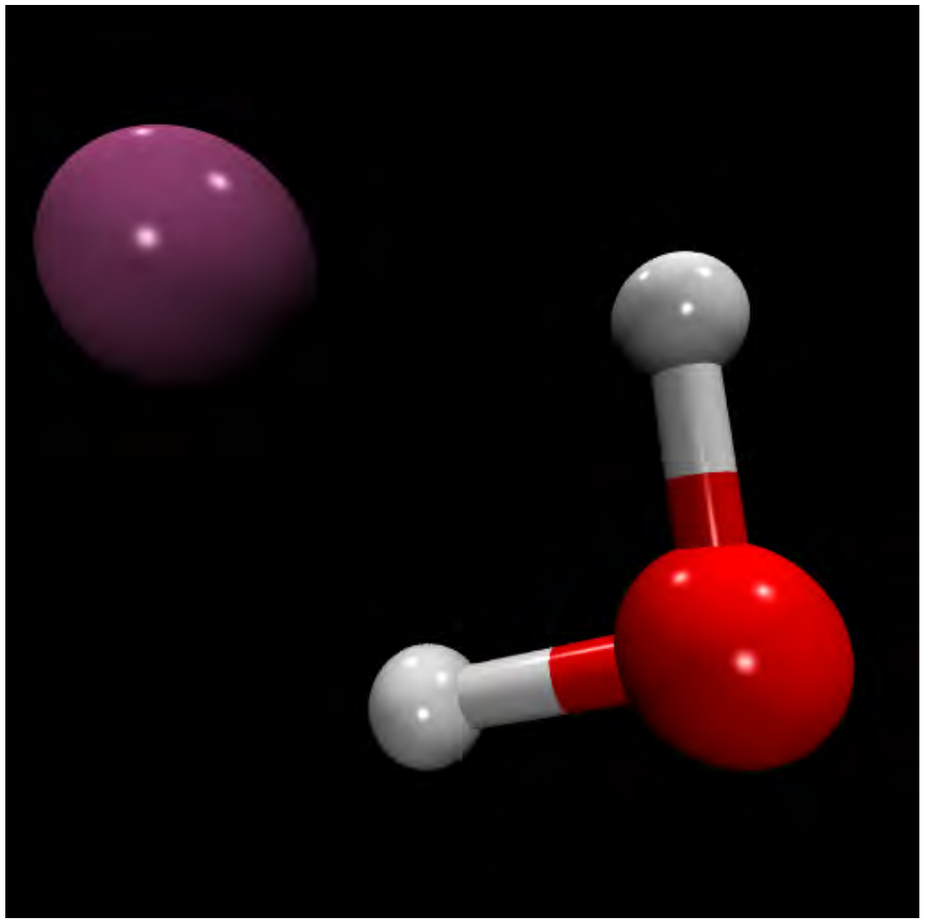
MB-MD: Quo Vadis?



From Water to Electrolyte Solutions



From Water to Electrolyte Solutions



$X^-(H_2O)$ explicit many-body potentials

permanent electrostatics

$$V^{2B} = \sum_i V_i^{rep} + V_{elect}^{2B} + V_{ind}^{2B} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R_{ij}^6}$$

pairwise short-range interactions

2B dispersion

V_{ind}^{3B}

NB induction

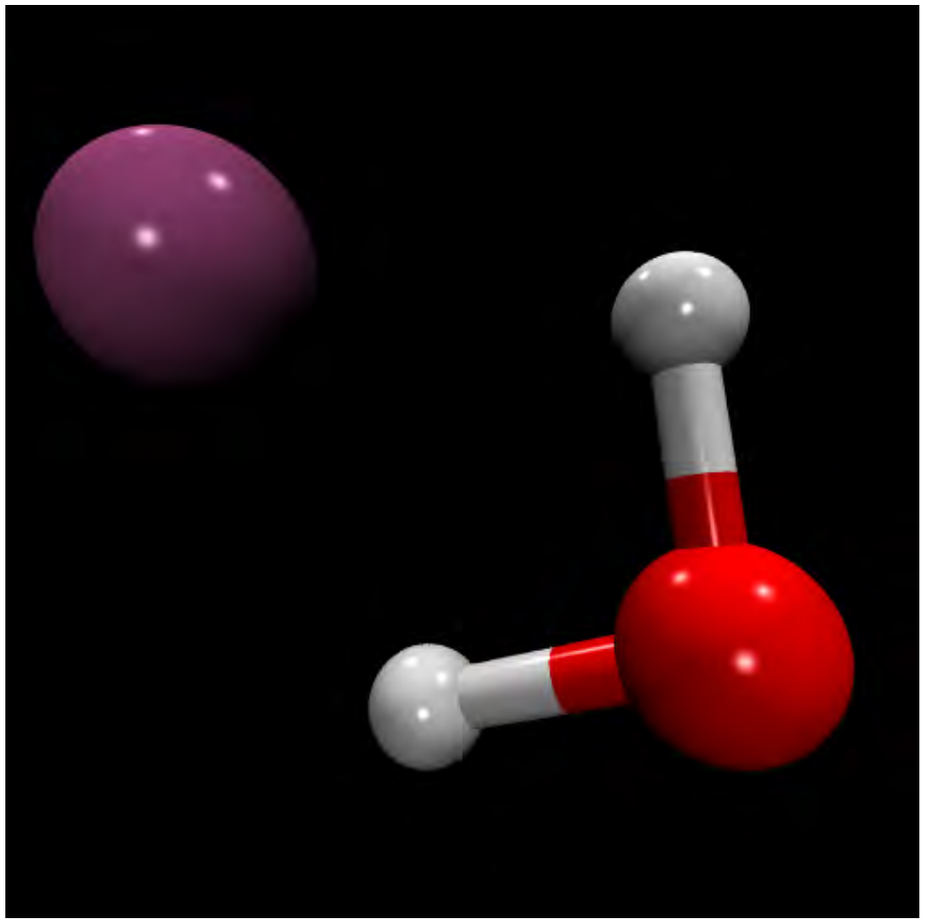
$$V^{>3B} = V_{ind}^{>3B}(1, \ldots, N)$$

$$V^{i-TTM} = V^{TTM,elec} + V^{TTM,ind} + \sum_{i=1}^{n} \left(V_i^{rep} + V_i^{disp} \right)$$

$$\sum_i V_i^{rep} = A_{OX} e^{-b_{OX} R_{OX}} + A_{H_1X} e^{-b_{H_1X} R_{H_1X}} + A_{H_2X} e^{-b_{H_2X} R_{H_2X}}$$

Arismendi-Arrieta, Riera, Bajaj, Prosmiti & FP, J. Phys. Chem. B 120, 1822 (2016); Riera, Götz & FP, Phys. Chem. Chem. Phys. ASAP (2016)

From Water to Electrolyte Solutions



$X^-(H_2O)$ explicit many-body potentials

permanent electrostatics

$$V^{2B} = s_2 V^{2B}_{poly} - V^{2B}_{elect} + V^{2B}_{ind} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R^6_{ij}}$$

short-range interactions

2B dispersion

$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

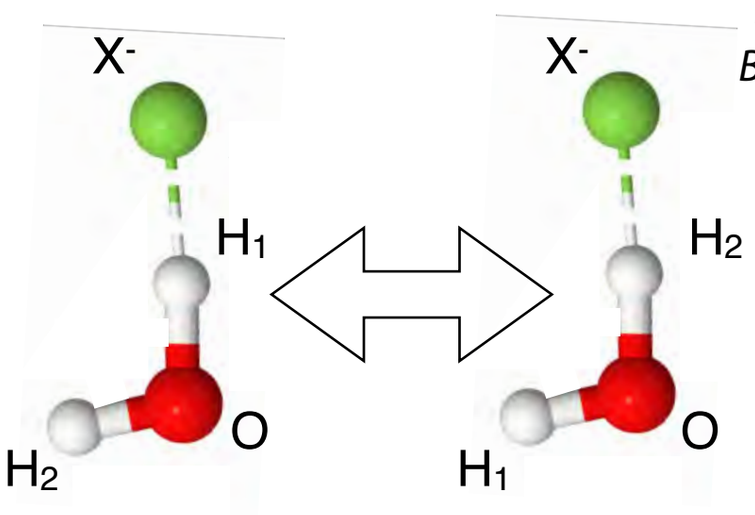
NB induction

$$V^{>3B} = V^{>3B}_{ind}(1, \ldots, N)$$

Permutationally invariant polynomials

Marquardt & Quack, J. Chem. Phys. 109, 10628 (1998)

Braams & Bowman, Int. Rev. Phys. Chem. 28, 577 (2009)



$$V = \sum_{m=a+b+c=0}^{M} D_{abc} \left\{ y_{12}^a \left[y_{13}^b y_{23}^c + y_{13}^c y_{23}^b \right] \right\}$$

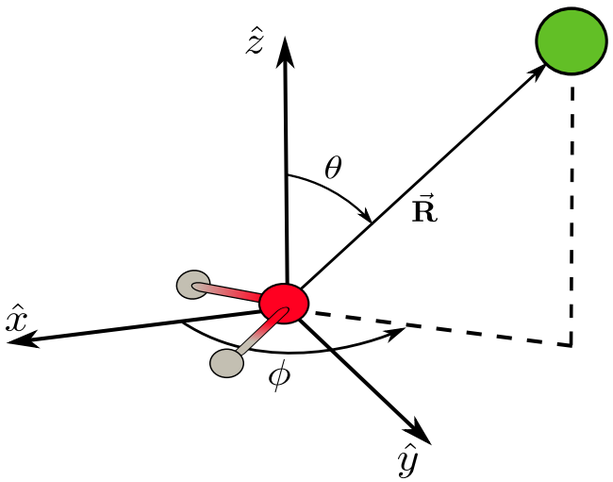
Morse variables

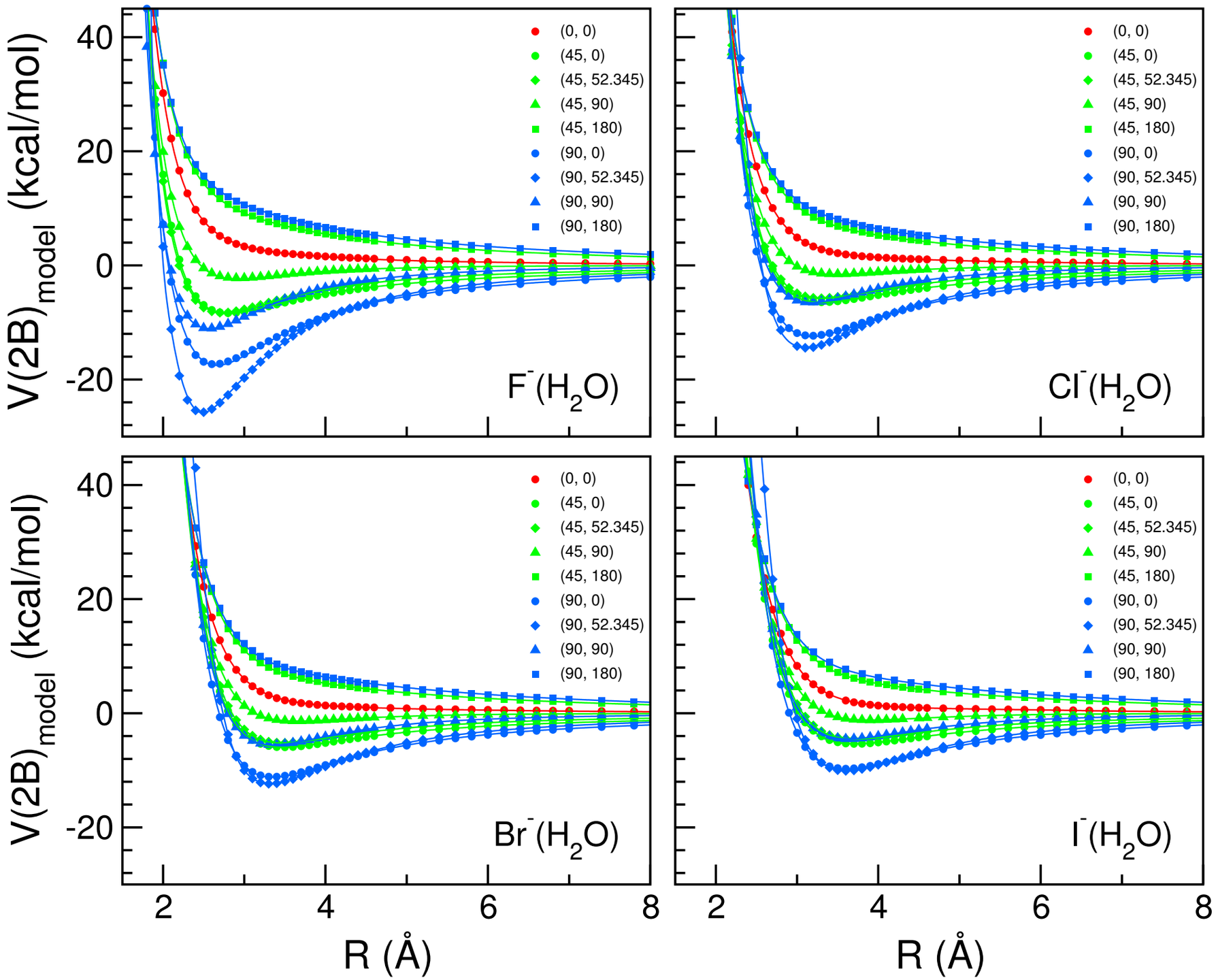
$$y_{ij} = e^{-k r_{ij}} \qquad y_{ij} = \frac{e^{-k r_{ij}}}{r_{ij}}$$

Bajaj, Götz & FP, J. Chem. Theory Comput. 12, 2698 (2016)

MB-nrg: Halide-Water Interactions

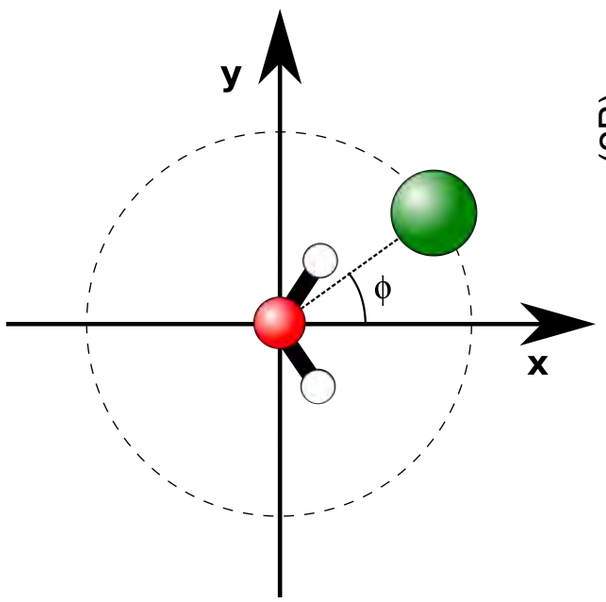
Dimer potential energy surfaces



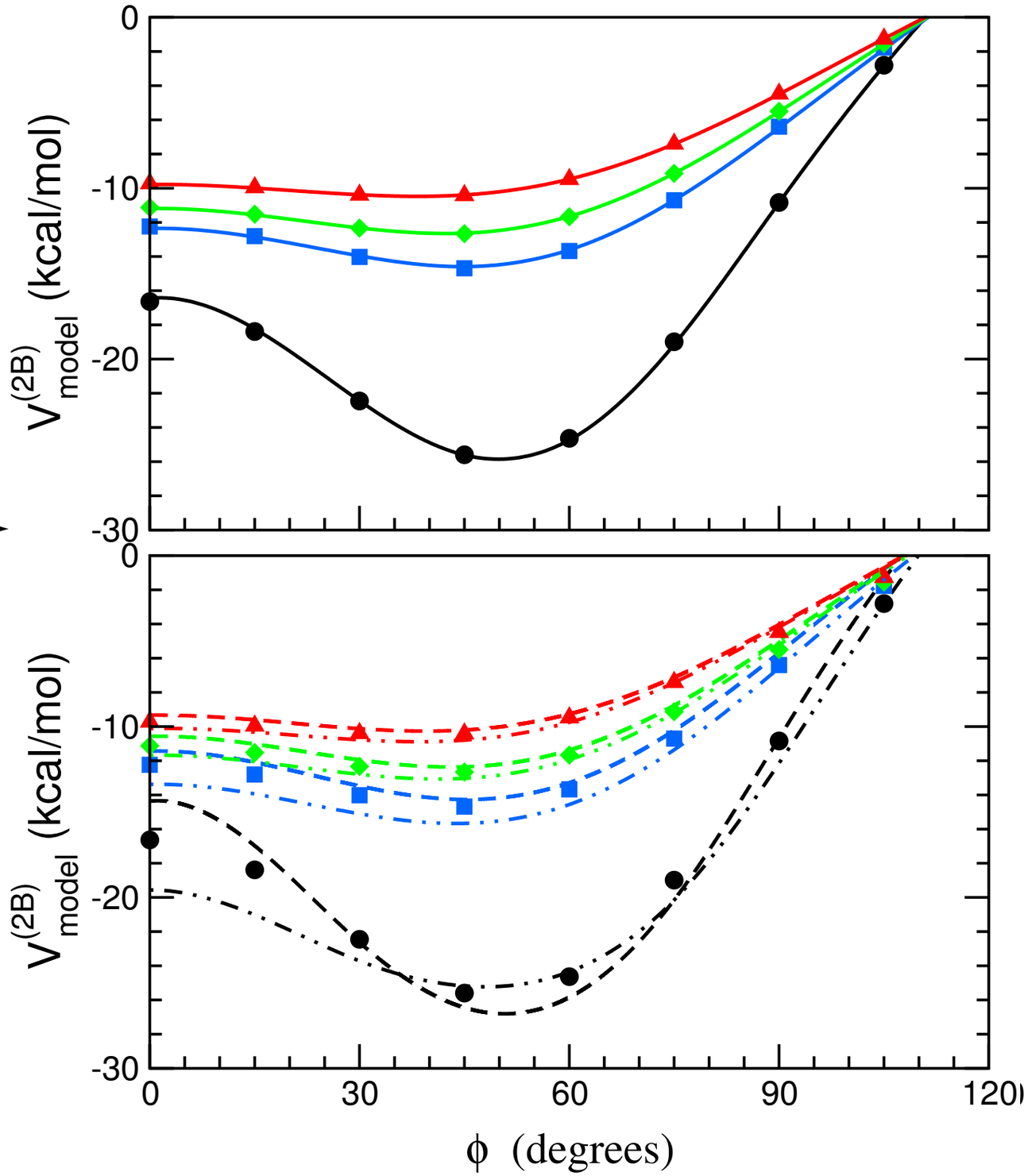


Bajaj, Götz & FP, J. Chem. Theory Comput. 12, 2698 (2016)

MB-nrg vs. Polarizable Models



Dimer potential energy surfaces



H_2O-F^-

H_2O-Cl^-

H_2O-Br^-

H_2O-I^-

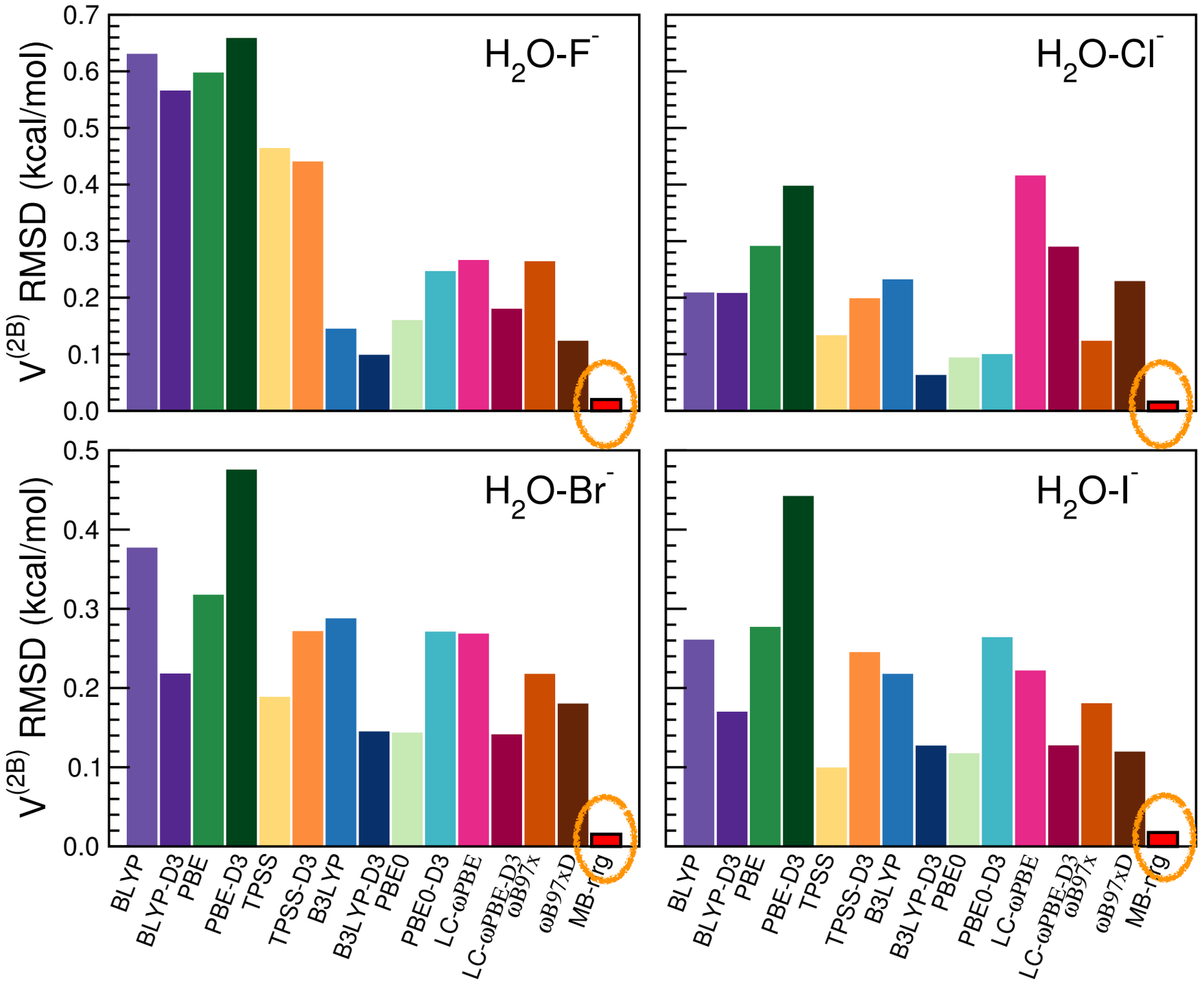
—— MB-nrg

– – i-TTM

-·-·- AMOEBA

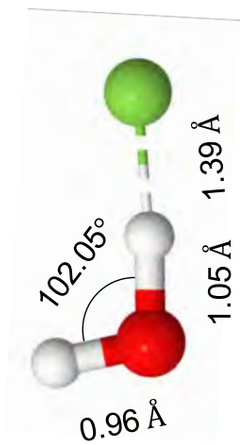
Putting Things in Perspective: MB-nrg vs. DFT

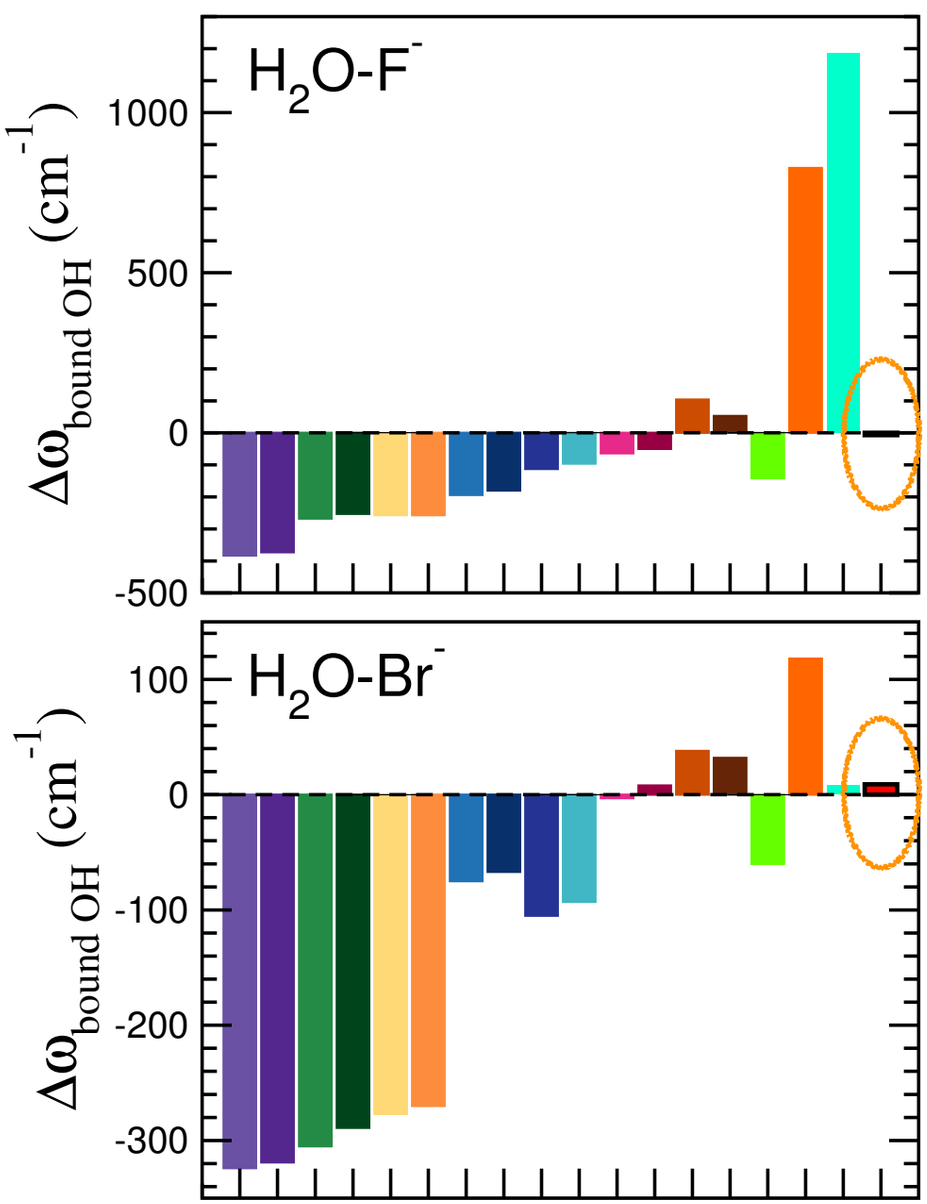
RMSD for more than 2000 dimers relative to CCSD(T)-F12

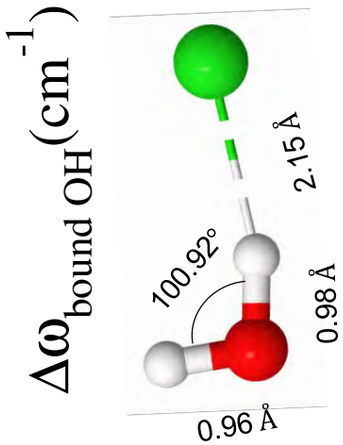


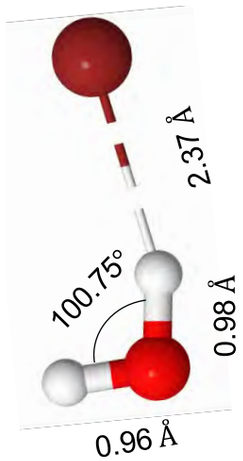
Putting Things in Perspective: MB-nrg vs. DFT

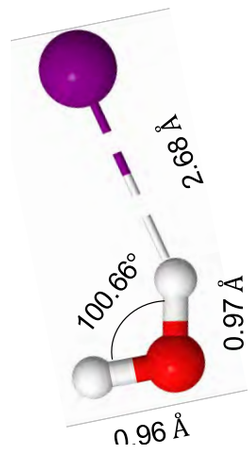
Vibrational frequencies











Bajaj, Götz & FP, J. Chem. Theory Comput. 12, 2698 (2016)

$X^-(H_2O)$: Vibrational Spectra

		bound OH	free OH
$F^-(H_2O)$	*Experiment*	1523	3687
	MB-nrg	1586	3731
$Cl^-(H_2O)$	*Experiment*	3146	3123
	MB-nrg	3697	3704
$Br^-(H_2O)$	*Experiment*	3296	3297
	MB-nrg	3695	3698
$I^-(H_2O)$	*Experiment*	3393 / 3422	3440
	MB-nrg	3392 / 3406	3452

Collaboration : Tucker Carrington and Xiaogang Wang, Queen's University

Experiment: Horvath et al., J. Phys. Chem. A 114, 1556 (2010); Sarka et al. Phys. Chem. Chem. Phys. 18, 1768 (2016)

$X^-(D_2O)$: Vibrational Spectra

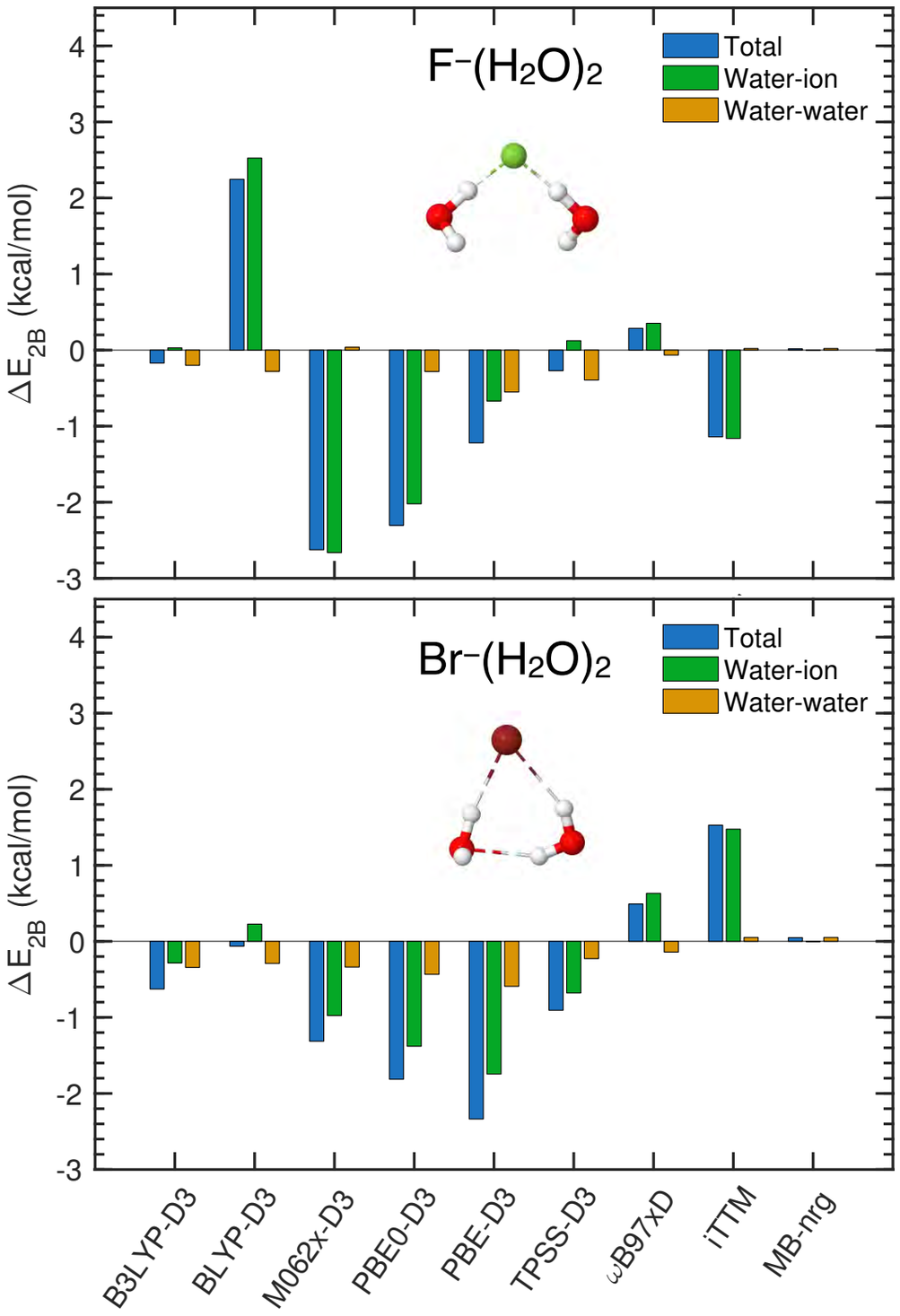
		bound OD	free OD
F^- (D_2O)	*Experiment*	—	—
	MB-nrg	1274	2730
Cl^- (D_2O)	*Experiment*	2341	2737
	MB-nrg	2328	2729
Br^- (D_2O)	*Experiment*	2451	2726
	MB-nrg	2441	2737
I^- (D_2O)	*Experiment*	2511 / 2527	2728
	MB-nrg	2531	2725

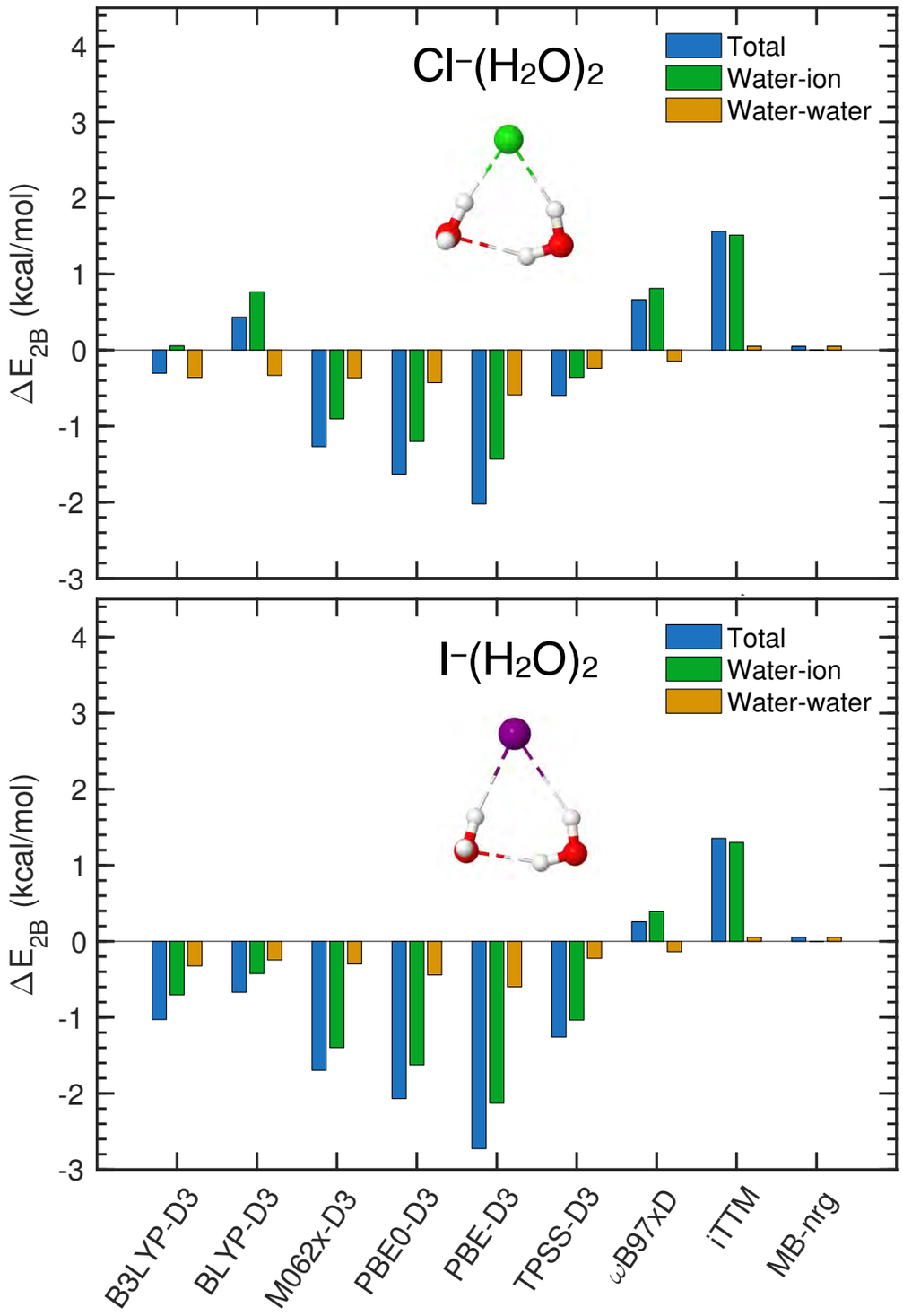
Collaboration : Tucker Carrington and Xiaogang Wang, Queen's University

Experiment: Horvath et al., J. Phys. Chem. A 114, 1556 (2010); Sarka et al. Phys. Chem. Chem. Phys. 18, 1768 (2016)

$X^-(H_2O)_2$: Many-Body Contributions

2B interactions

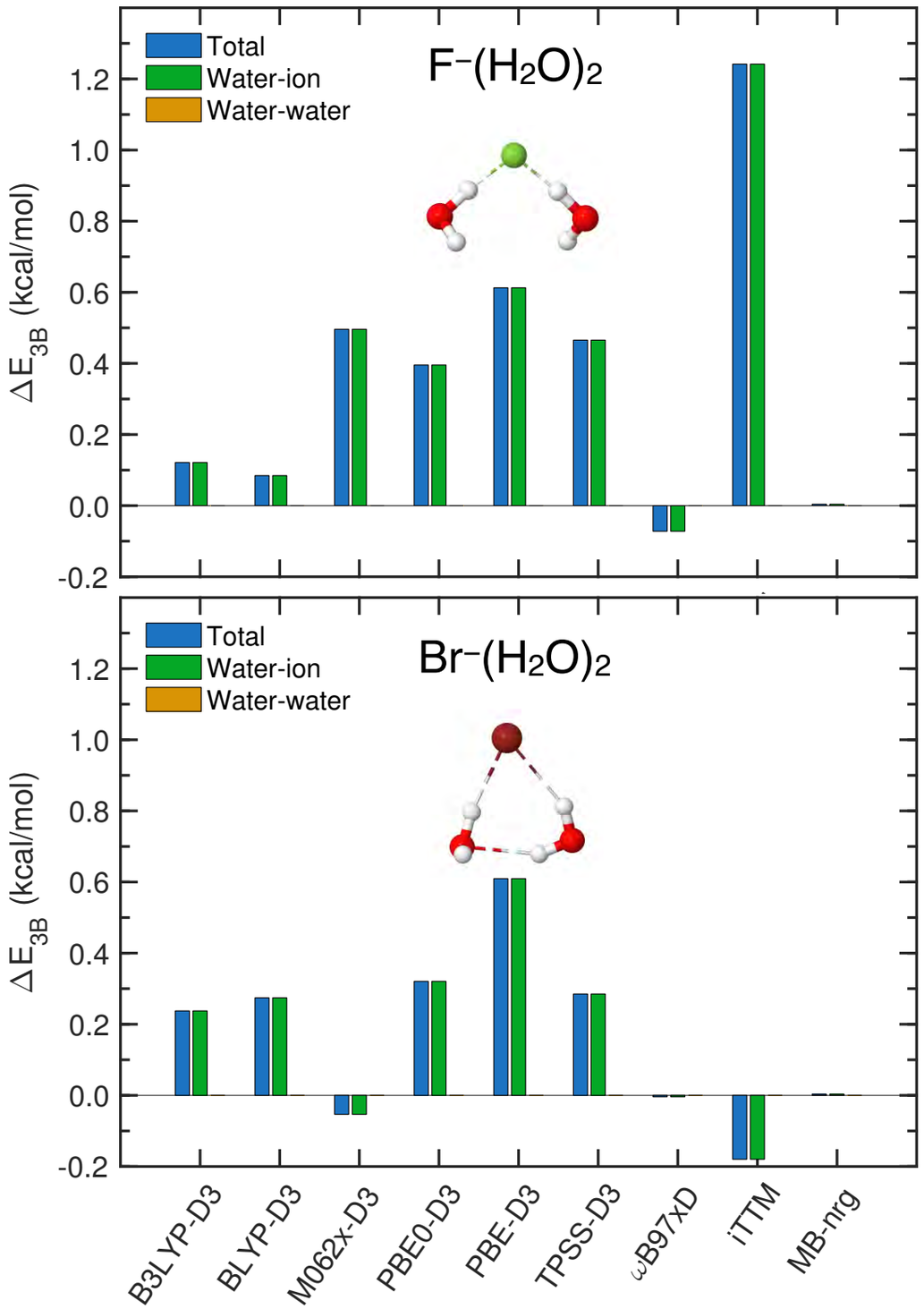




Bajaj, Götz & FP, to be submitted

$X^-(H_2O)_2$: Many-Body Contributions

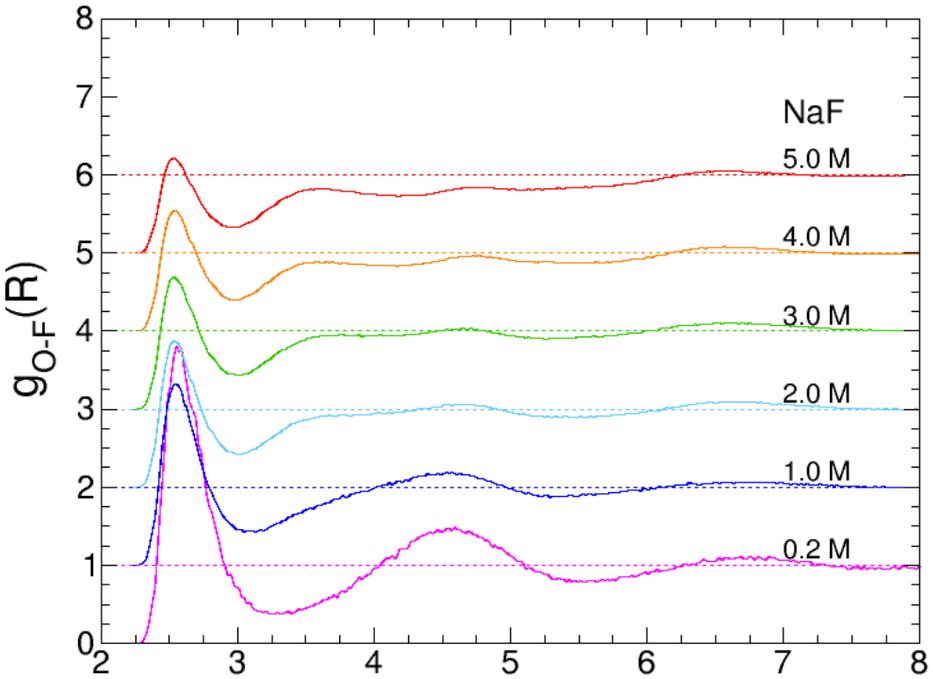
3B interactions

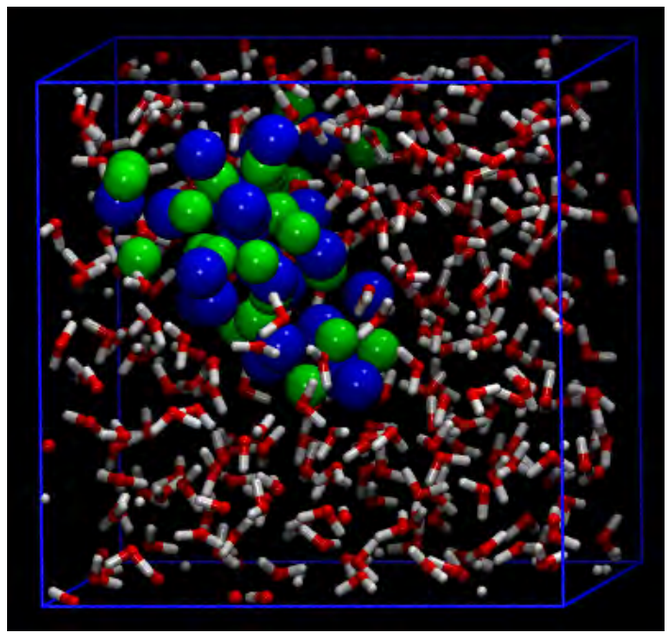


Bajaj, Götz & FP, to be submitted

From Water to Electrolyte Solutions

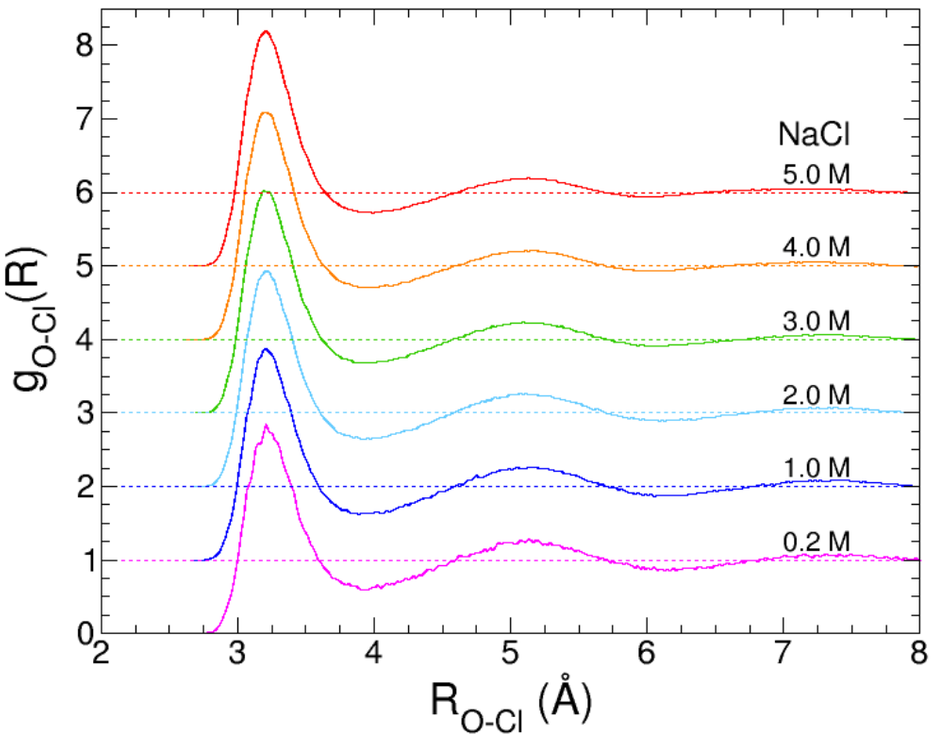
X-O radial distribution functions

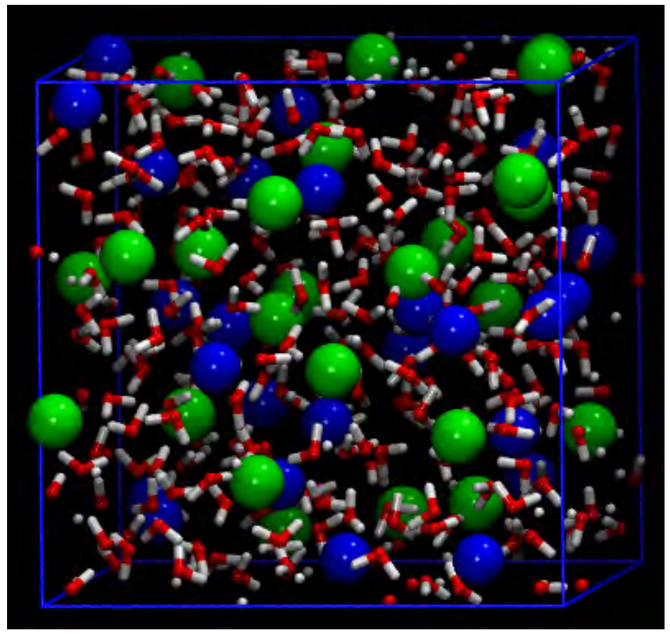




low solubility

(~1 M)





high solubility

(~6 M)

Arismendi-Arrieta, Riera, Bajaj, Prosmiti & FP, J. Phys. Chem. B 120, 1822 (2016); Bajaj, Götz & FP, J. Chem. Theory Comput. 12, 2698 (2016)

Summary

- **MB-pol = TAP water aka: Would you drink MB-pol water?**
  - No! MB-pol (currently) provides an accurate and physically correct representation of the interactions in water in the limit of $pK_w \longrightarrow \infty$
  - MB-pol is systematically improvable (e.g., explicit higher-order terms)
  - Work to include autoionization is ongoing

- **What is needed to accurately represent the water interactions?**
  - An accurate description of many-body effects (i.e., CCSD(T) work!)
  - MB-pol provides an accurate reference for both force fields and DFT models

    see Fritz, Fernandez-Serra, Soler, J. Chem. Phys. 144, 224101 (2016)

- **Can MB-pol be extended to generic aqueous solutions?**
  - Yes! Studies of electrolyte solutions are underway
  - More complex systems? Likely, but it will require a "community effort" and synergistic collaborations with computer scientists

- **Better quantum dynamics methods for the condensed phase are needed!**

MB-pol is interfaced with:
OpenMM: http://paesanigroup.ucsd.edu/software/mbpol_openmm.html
i-PI: http://paesanigroup.ucsd.edu/software/mbpol_ipi.html