

Non-covalent force fields computed *ab initio*

- Supermolecule calculations
- Symmetry-adapted perturbation theory (SAPT)

Supermolecule calculations

$$\Delta E = E_{AB} - E_A - E_B$$

Requirements:

1. Include electron correlation, intra- and inter-molecular (dispersion energy = intermolecular correlation)
2. Choose good basis, with diffuse orbitals (and “bond functions”) especially to converge the dispersion energy
3. Size consistency. Currently best method: CCSD(T)
4. Correct for basis set superposition error (BSSE) by computing E_A and E_B in dimer basis

Symmetry-adapted perturbation theory (SAPT)

Combine perturbation theory with antisymmetrization \mathcal{A} (Pauli) to include short-range exchange effects.

Advantages:

1. ΔE calculated directly.
2. Contributions (electrostatic, induction, dispersion, exchange) computed individually. Useful in analytic fits of potential surface.

Advantage of supermolecule method:

Easy, use any black-box molecular electronic structure program

Problems in SAPT:

1. Pauli: $\mathcal{A}H = H\mathcal{A}$.

Antisymmetrizer commutes with total Hamiltonian $H = H^{(0)} + H^{(1)}$, but not with $H^{(0)}$ and $H^{(1)}$ separately.

Has led to different definitions of second (and higher) order energies.

2. Free monomer wavefunctions $\Phi_{k_1}^A$ and $\Phi_{k_2}^B$ not exactly known. Use Hartree-Fock wave functions and apply double perturbation theory to include intra-molecular correlation, or use CCSD wave functions of monomers \Rightarrow **Many-body SAPT**.

Program packages:

- SAPT2 for pair potentials
- SAPT3 for 3-body interactions

Most difficult: dispersion interactions

First *ab initio* calculation of He–He binding curve:

Phys. Rev. Letters, **25** (1970)

- H.F. Schaefer, D.R. McLaughlin, F.E. Harris, and B.J. Alder
page 988: $D_e = 12.0$ K
- P. Bertoncini and A. C. Wahl
page 991: $D_e = 11.4$ K

Present value:

$$D_e = 11.01 \text{ K} = 7.65 \text{ cm}^{-1}$$

$$\approx 0.1 \text{ kJ/mol} \approx 10^{-3} \text{ eV} \approx 3.5 \times 10^{-5} \text{ Hartree}$$

Can one use DFT methods?

Reviews by Johnson & DiLabio, Zhao & Truhlar

Many different functionals tested with different basis sets

type	dimer	mean error in D_e
Van der Waals	Rg ₂ , (CH ₄) ₂ , (C ₂ H ₂) ₂ , (benzene) ₂	40 - 200 %
dipole-induced dipole	CH ₄ -HF, H ₂ O-benzene, etc.	15 - 100 %
dipole-dipole	(H ₂ CO) ₂ , etc.	10 - 40 %
hydrogen bonded	(NH ₃) ₂ , (H ₂ O) ₂ , (HCOOH) ₂ , etc.	3 - 20%

- Some VdW dimers, (benzene)₂ for example, not bound
- B971 best, B3LYP worst
- Often best results without BSSE correction, or smaller basis sets
⇒ Right for wrong reason

Basic problems with DFT

1. Exchange repulsion

- Incorrect asymptotic behavior of one-electron potential:
 $v(r) \rightarrow \exp(-\alpha r)$ instead of $-1/r$
- In intermolecular Coulomb energy no self-term present
self-exchange \Rightarrow spurious attraction

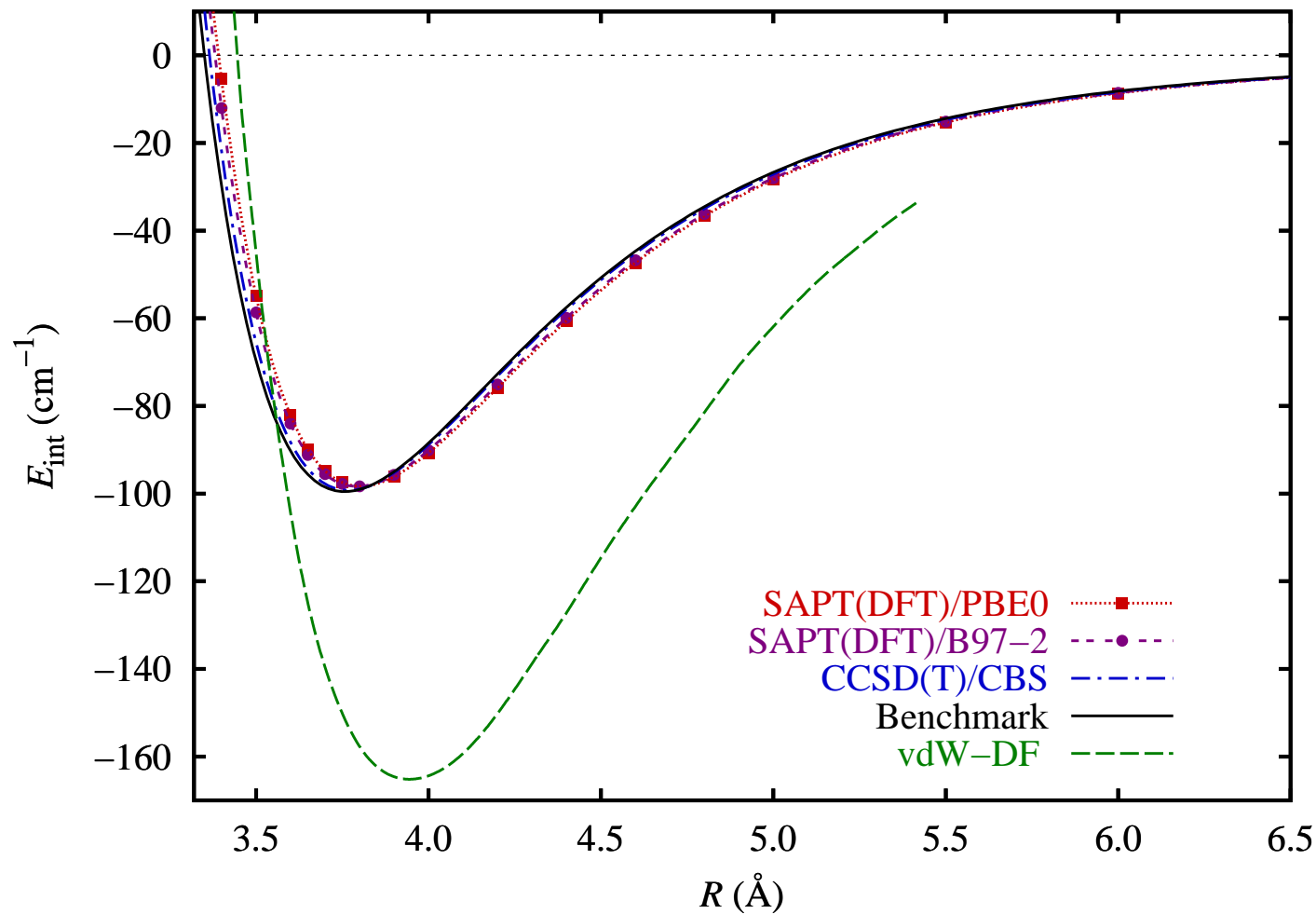
2. Dispersion

- Intrinsically non-local:
cannot be described by local LDA or semi-local GGA methods

DFT with dispersion explicitly included

vdW-DF: M. Dion, H. Rydberg, E. Schroder, D.C. Langreth, B.I. Lundqvist,
Phys. Rev. Lett. **92** (2004) 246401

Ar–Ar interaction



From: R. Podeszwa and K. Szalewicz, Chem. Phys. Lett. **412** (2005) 488

DFT with dispersion included semi-empirically

Becke, Johnson, and others:

- Include atom-atom $-C_6R^{-6} - C_8R^{-8} - C_{10}R^{-10}$ term
in addition to the semi-local correlation energy
- Approximate C_6, C_8, C_{10} from atomic squared multipole moment
expectation values and (empirical) static polarizabilities
- Empirically optimized damping parameters

Alternative: SAPT-DFT

Implemented by G. Jansen *et al.* (Essen) and K. Szalewicz *et al.* (Delaware)

- First order SAPT energy (electrostatic + exchange) computed with monomer densities and density matrices from Kohn-Sham DFT
- Second-order SAPT energy (induction, dispersion + exchange) from (time-dependent) coupled perturbed Kohn-Sham response functions

Only Hartree-Fock like expressions from Many-Body SAPT needed
⇒ better scaling

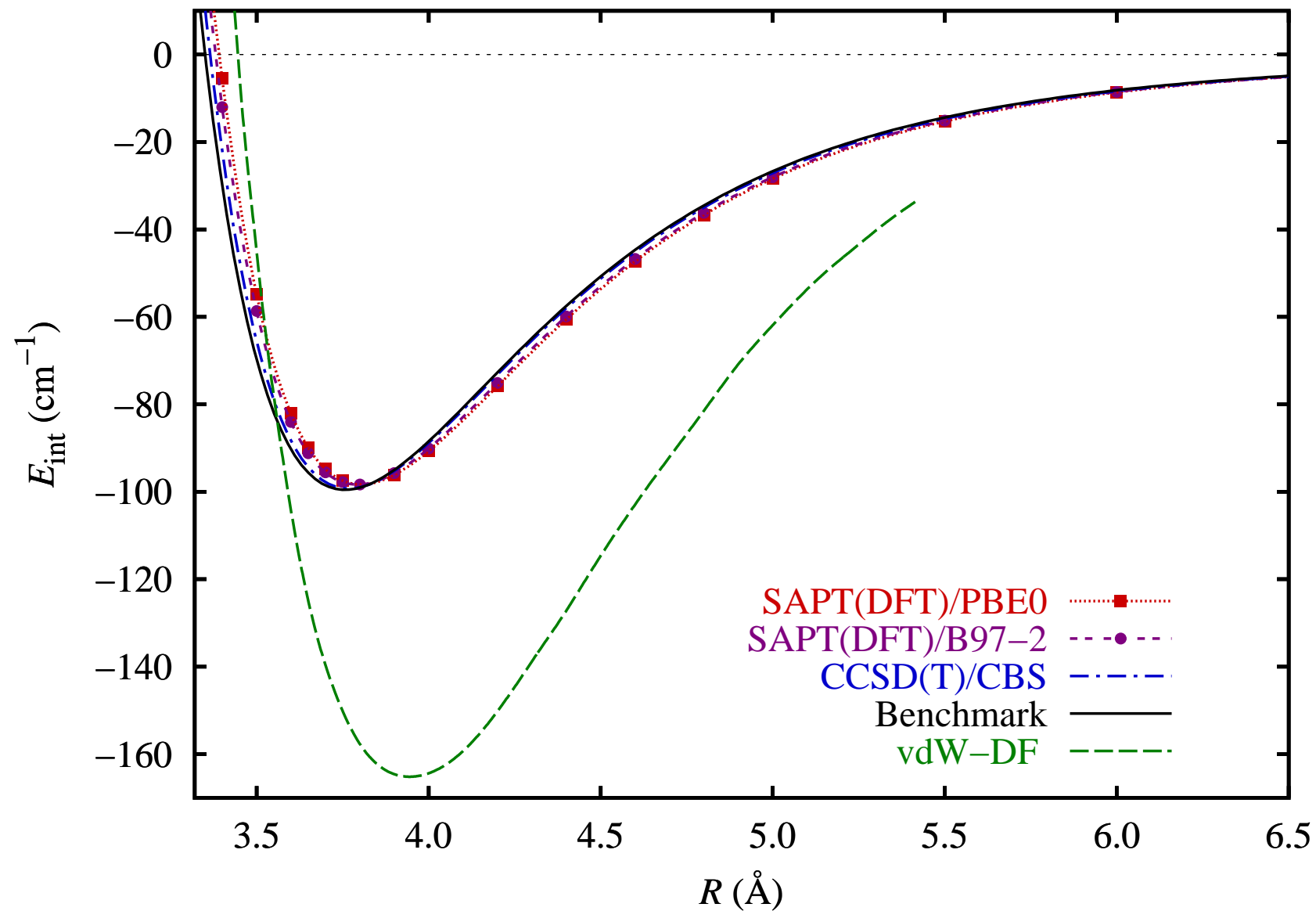
Caution !

- SAPT-DFT requires XC potential that is **good in inner region** and has **correct $-1/r$ behavior for $r \rightarrow \infty$**
- **Coupled** time-dependent DFT must be used for (frequency-dependent) density-density polarizabilities $\alpha(\mathbf{r}, \mathbf{r}', \omega)$

Both groups, K. Szalewicz (Delaware) and G. Jansen (Essen), further improved efficiency by implementation of density fitting.

Ar–Ar interaction

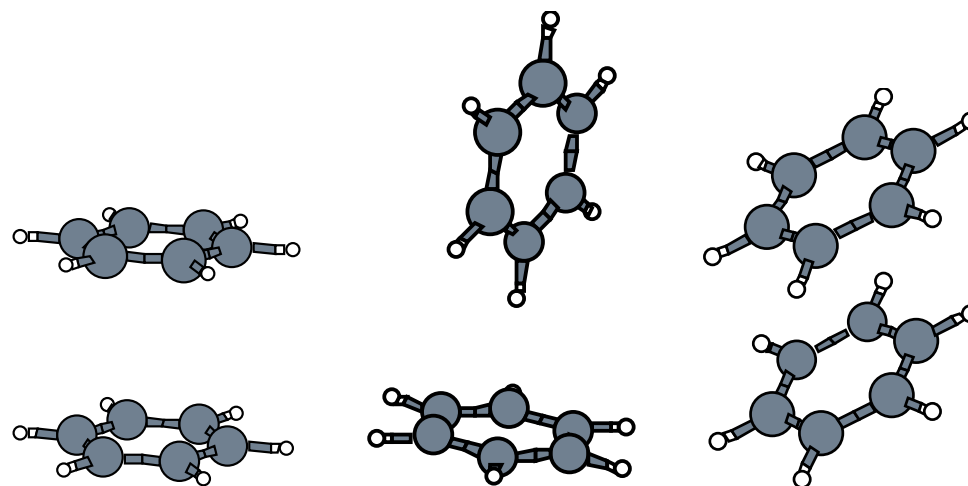
From: R. Podeszwa and K. Szalewicz, Chem. Phys. Lett. **412** (2005) 488



A. Heßelmann, G. Jansen, M. Schütz, J. Chem. Phys. **122** (2005) 014103

(benzene)₂

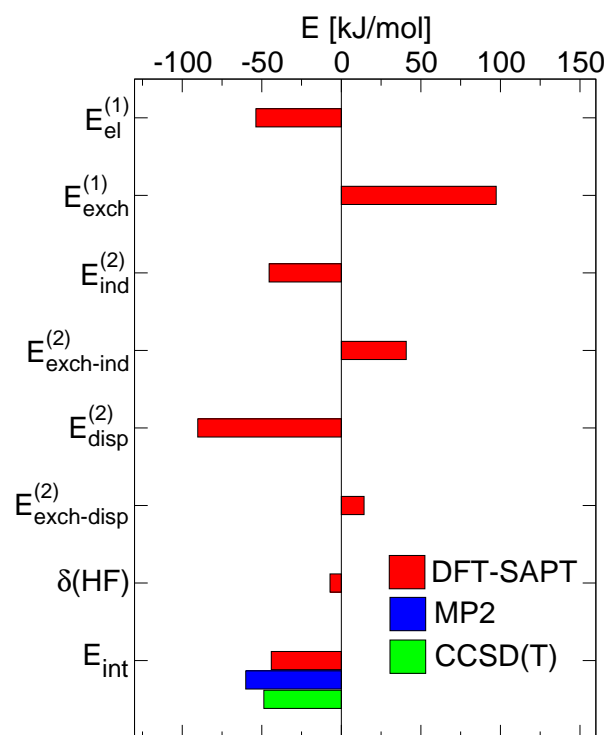
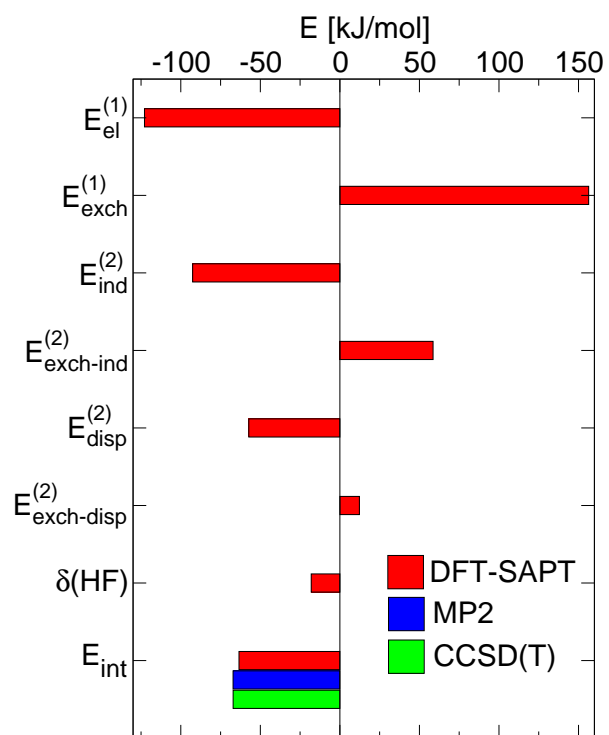
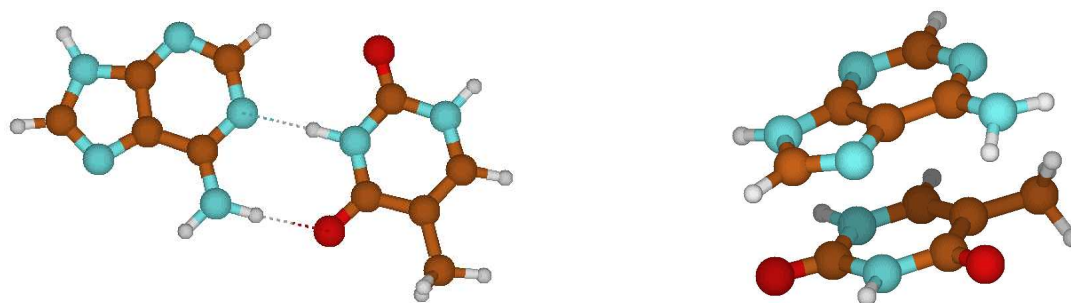
1512 GTOs (aug-cc-pVQZ), extrapolation to basis set limit



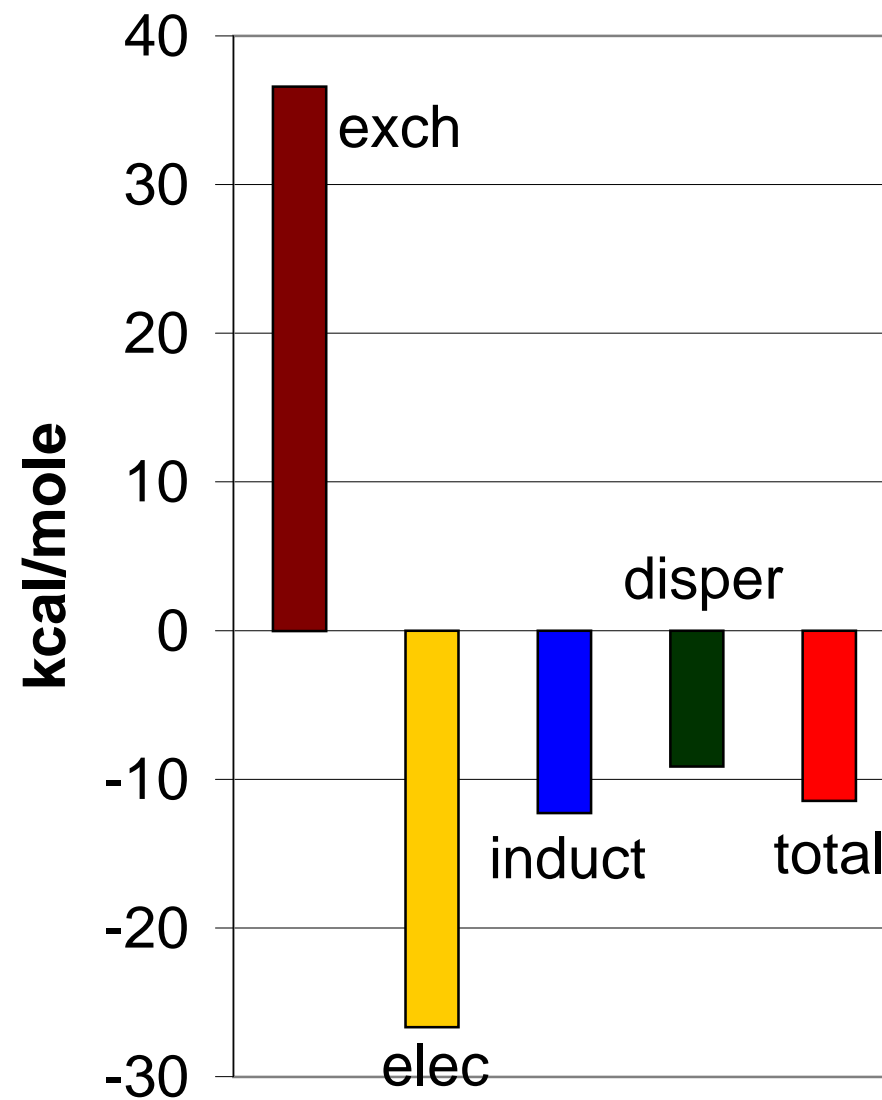
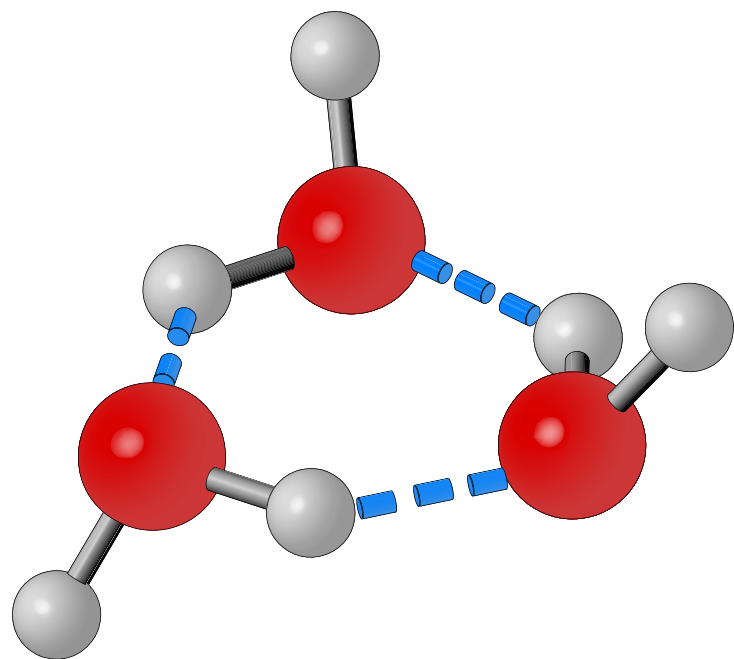
MP2	-14.4	-15.1	-20.3	kJ/mol
CCSD(T)	-6.7	-11.8	-11.4	
DF-SAPT-DFT	-7.6	-11.9	-12.7	
standard DFT	unbound	metastable	unbound	

Adenine-Thymine (G. Jansen *et al.*)

DF-SAPT-DFT up to aug-cc-pVQZ level



Pair interactions in water trimer



Many-body interactions (per hydrogen bond)

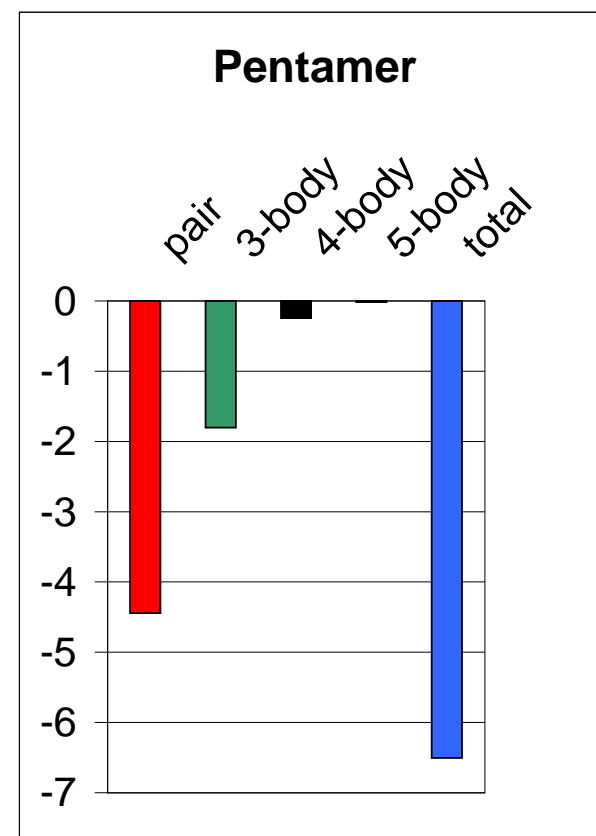
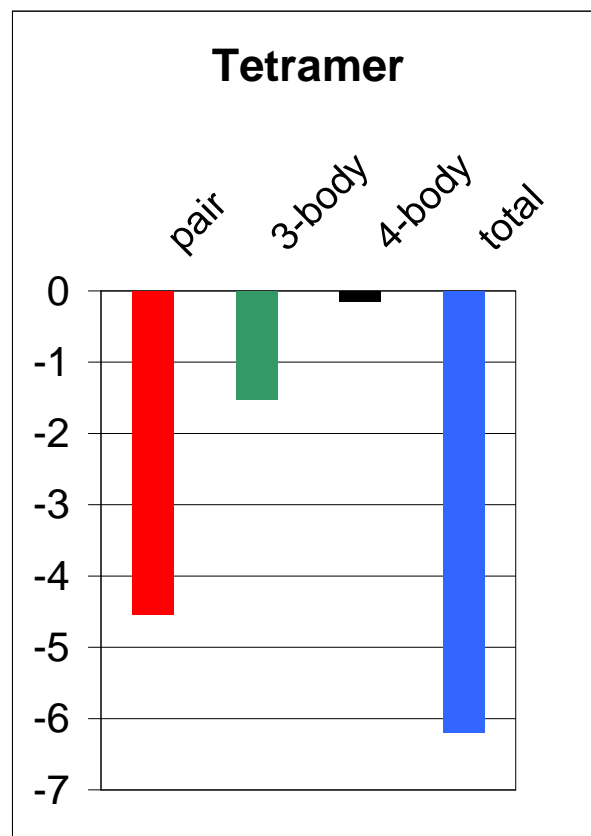
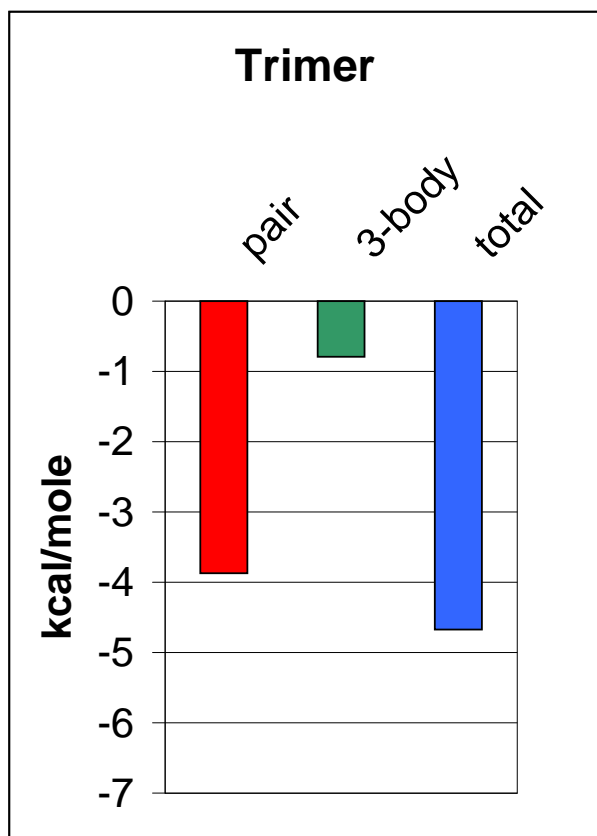
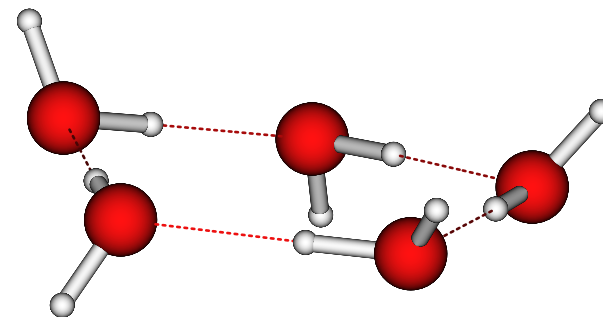
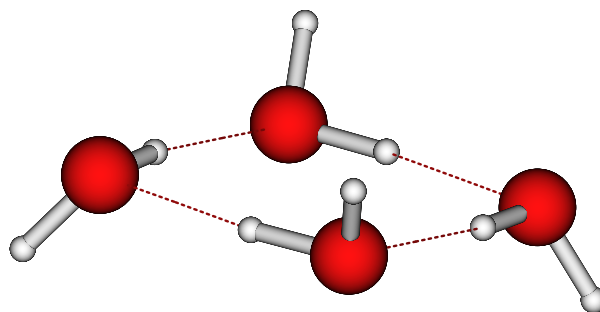
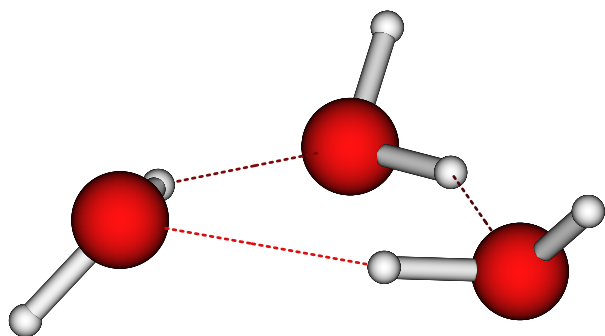


Illustration:

New water potential

- Tested by spectroscopy on dimer and trimer
- Used in MD simulations for liquid water

R. Bukowski, K. Szalewicz, G.C. Groenenboom, and A. van der Avoird,
Science, **315**, 1249 (2007)

New polarizable water pair potential: CC-pol

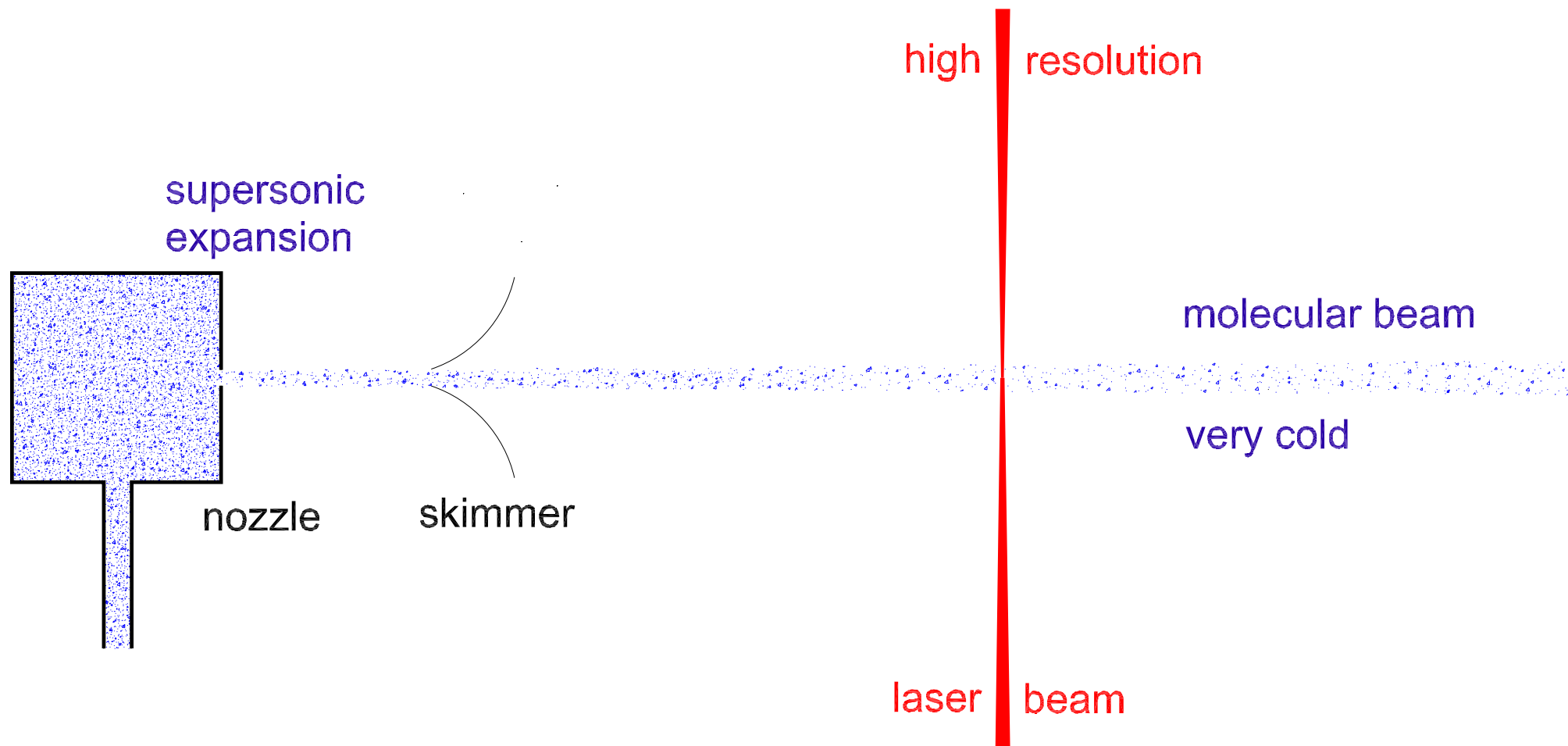
- From CCSD(T) calculations in aug-cc-pVTZ + bond function basis
- Extrapolated to complete basis set (CBS) limit at MP2 level
- 2510 carefully selected water dimer geometries
- Estimated uncertainty < 0.07 kcal/mol
(same as best single-point calculations published)

CC-pol: Analytic representation

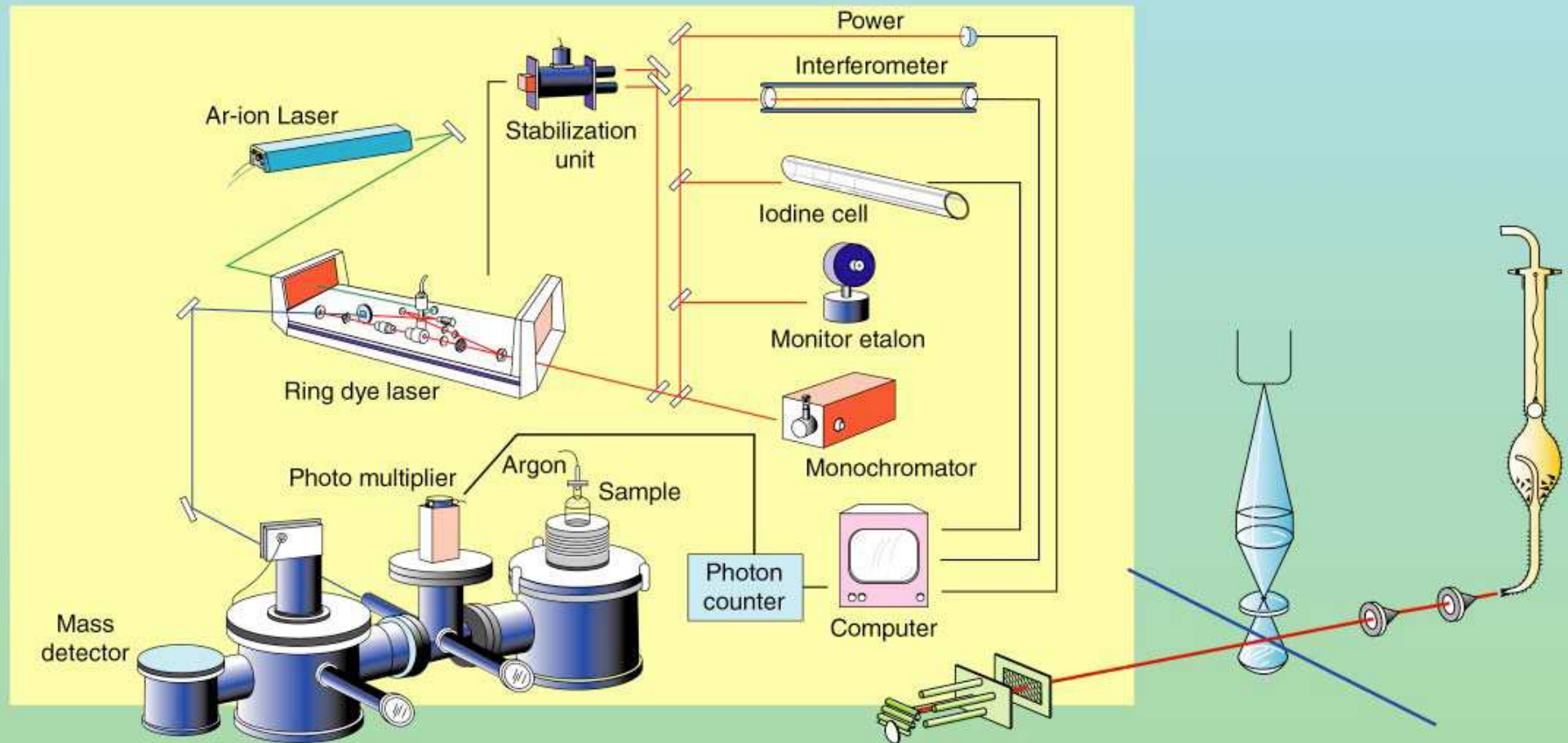
- Site-site model with 8 sites (5 symmetry distinct) per molecule
 - Coulomb interaction,
 - dispersion interaction,
 - exponential ‘overlap’ terms: first-order exchange repulsion, second-order exchange induction + dispersion
- Extra polarizability site for induction interaction
- Long range R^{-n} contributions computed by perturbation theory, subtracted before fit of short range terms
- Good compromise between accuracy of reproducing computed points (rmsd of 0.09 kcal/mol for $\Delta E < 0$) and simplicity needed for molecular simulations

How to test non-covalent force fields?

Molecular beam spectroscopy of Van der Waals molecules

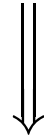


Experimental Set-Up

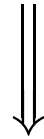


W.L. Meerts, Molecular and Laser Physics, Nijmegen

Intermolecular potential



**Cluster (Van der Waals molecule)
quantum levels,
i.e.,
eigenstates of
nuclear motion Hamiltonian**



Van der Waals spectra

Nuclear motion Hamiltonian $H = T + V$ for “normal” (= semi-rigid) molecules

- single equilibrium structure
- small amplitude vibrations

Use rigid rotor/harmonic oscillator model

For (harmonic) vibrations

- Wilson GF -matrix method \Rightarrow frequencies, normal coordinates

Rigid rotor model \Rightarrow fine structure (high resolution spectra)

Nuclear motion Hamiltonian $H = T + V$ for weakly bound complexes (Van der Waals or hydrogen bonded)

- multiple equivalent equilibrium structures
(= global minima in the potential surface V)
- small barriers \Rightarrow tunneling between minima
- large amplitude (VRT) motions:
vibrations, internal rotations, tunneling
(more or less rigid monomers)
- curvilinear coordinates
 \Rightarrow complicated kinetic energy operator T

Method for molecule-molecule dimers

$\text{H}_2\text{O}-\text{H}_2\text{O}$, NH_3-NH_3 , etc.

Hamiltonian

$$H = T_A + T_B - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{(\mathbf{J} - \mathbf{j}_A - \mathbf{j}_B)^2}{2\mu R^2} + V(R, \omega_A, \omega_B)$$

Monomer Hamiltonians ($X = A, B$):

$$T_X = A_X (j_X)_a^2 + B_X (j_X)_b^2 + C_X (j_X)_c^2$$

Basis for bound level calculations

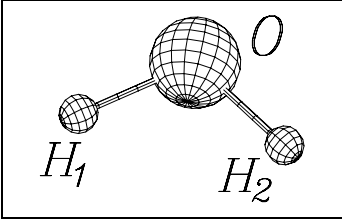
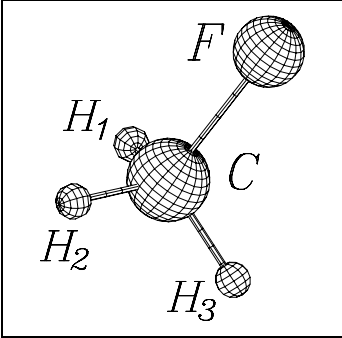
$$\chi_n(R) D_{MK}^{(J)}(\alpha, \beta, 0)^* \sum_{m_A, m_B} D_{m_A k_A}^{(j_A)}(\omega_A)^* D_{m_B k_B}^{(j_B)}(\omega_B)^* \langle j_A, m_A; j_B, m_B | j_{AB}, K \rangle$$

The permutation-inversion (PI) symmetry group

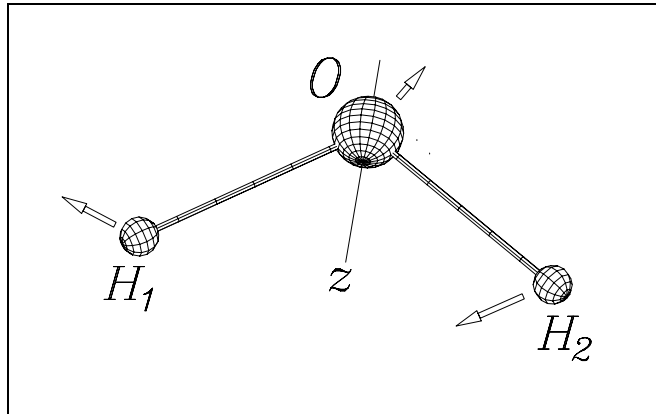
For semi-rigid molecules

Use *Point Group of Equilibrium Geometry* to describe the (normal coordinate) vibrations

N.B. This point group is isomorphic to the *PI* group, which contains all “feasible” permutations of identical nuclei, combined with inversion E^* .

Molecule	Point group	<i>PI</i> group
	C_{2v}	$\{E, E^*, (12), (12)^*\}$
	C_{3v}	$\{E, (123), (132), (12)^*, (13)^*, (23)^*\}$

Example: H₂O



<i>PI</i> operation	frame rotation	point group operation
(12)	$R_z(\pi) = C_{2z}$	C_{2z}
E^*	$R_y(\pi) = C_{2y}$	σ_{xz} reflection
(12)*	$R_x(\pi) = C_{2x}$	σ_{yz} reflection

permutation \Rightarrow frame rotation + point group rotation

permutation-inversion \Rightarrow frame rotation + reflection

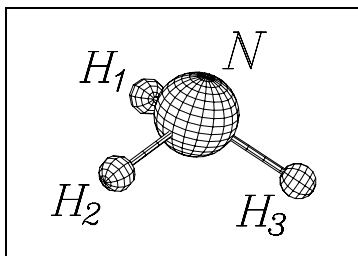
Hence: *PI*-group \simeq point group

For “floppy” molecules/complexes

- multiple equivalent minima in V
- low barriers: tunneling between these minima is “feasible”.

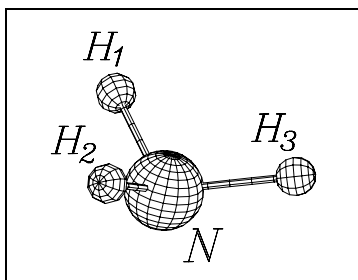
⇒ additional “feasible” PI -operations

Example NH_3



semi-rigid NH_3

$$PI(C_{3v}) = \{E, (123), (132), (12)^*, (13)^*, (23)^*\}$$



+ inversion
tunneling
(umbrella
up \leftrightarrow down)

$$PI(D_{3h}) = PI(C_{3v}) \otimes \{E, E^*\}$$

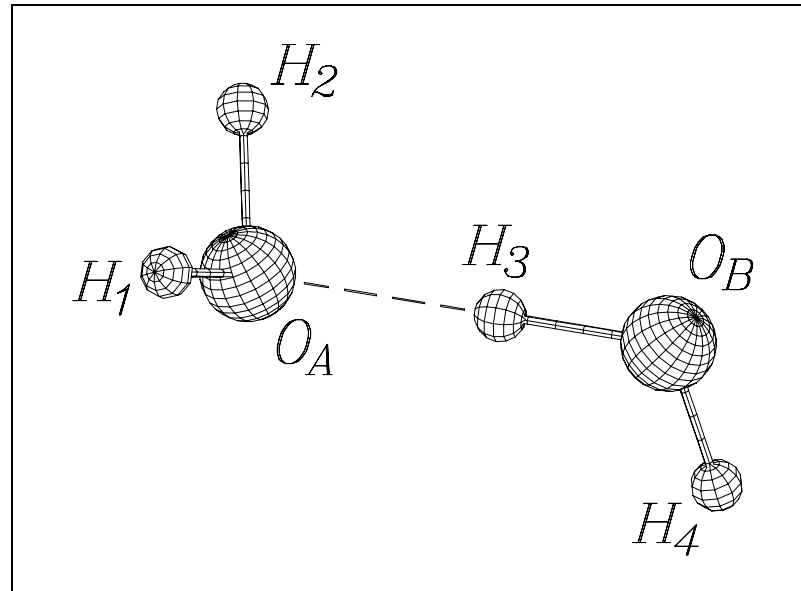
Also (12), (13), (23)
and E^* are feasible

Additional feasible PI -operations



observable tunneling
splittings in spectrum

For $\text{H}_2\text{O}-\text{H}_2\text{O}$



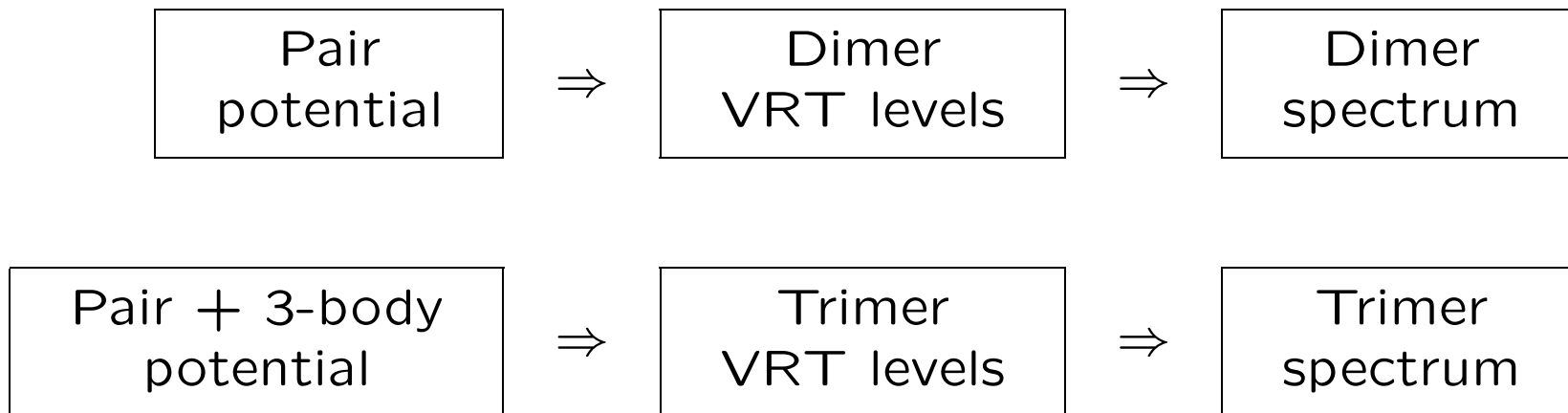
PI group $G_{16} = \{E, P_{12}\} \otimes \{E, P_{34}\} \otimes \{E, P_{AB}\} \otimes \{E, E^*\}$

Equilibrium geometry has C_s symmetry

\Rightarrow 8-fold tunneling splitting of rovib levels

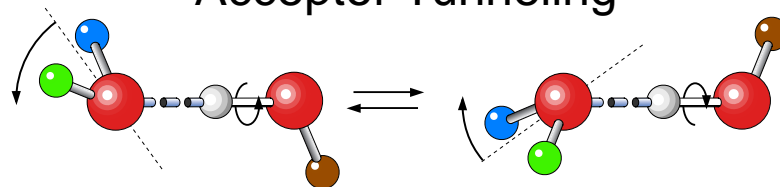
Water cluster spectra (far-infrared, high-resolution) from Saykally group (UC Berkeley)

Used for test of potential:

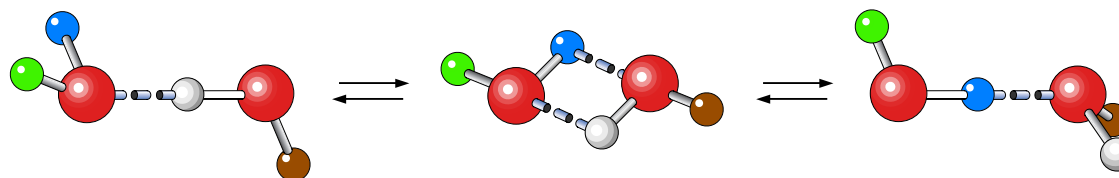


Water dimer tunneling pathways

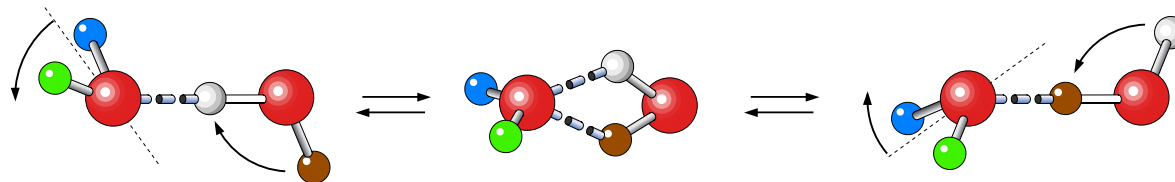
Acceptor Tunneling



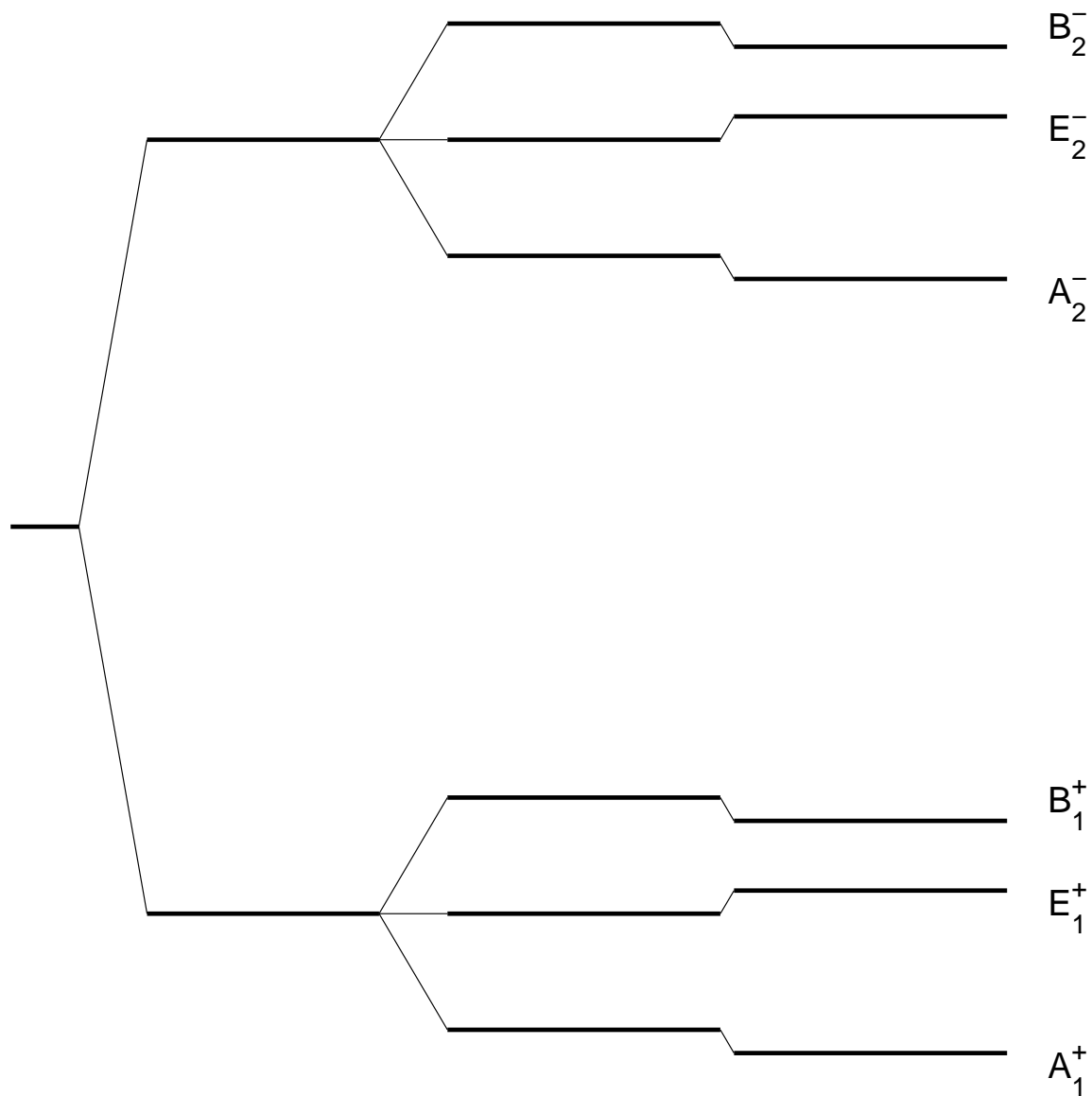
Donor-Acceptor Interchange Tunneling



Donor (Bifurcation) Tunneling



**Water dimer
tunneling
levels**
 $(J = K = 0)$



Acceptor
tunneling



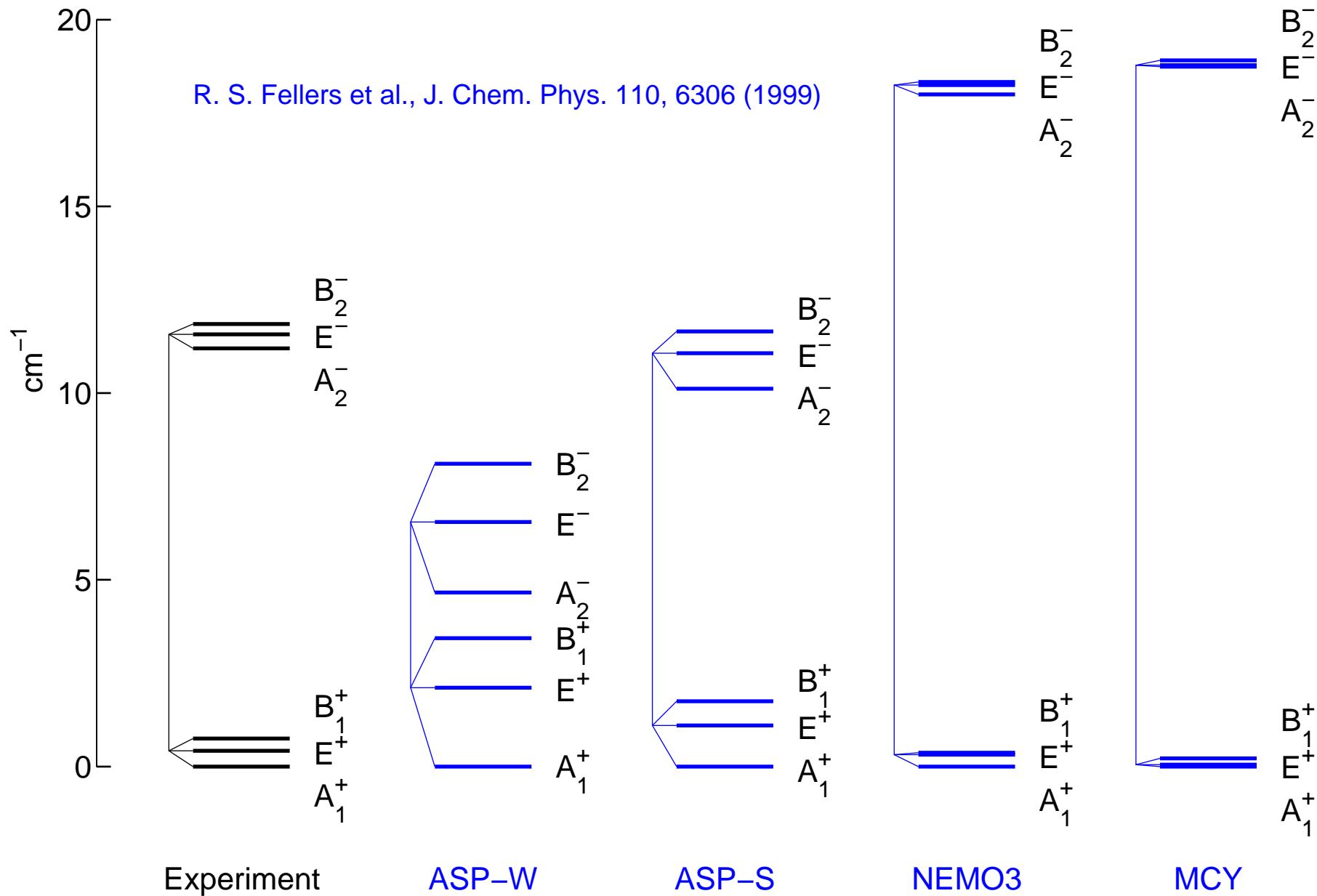
Interchange
tunneling



Bifurcation
tunneling

$(\text{H}_2\text{O})_2$ levels computed from various potentials ($J=K=0$)

R. S. Fellers et al., J. Chem. Phys. 110, 6306 (1999)



H₂O dimer

tunneling levels

from CC-pol (red)

experiment (black)

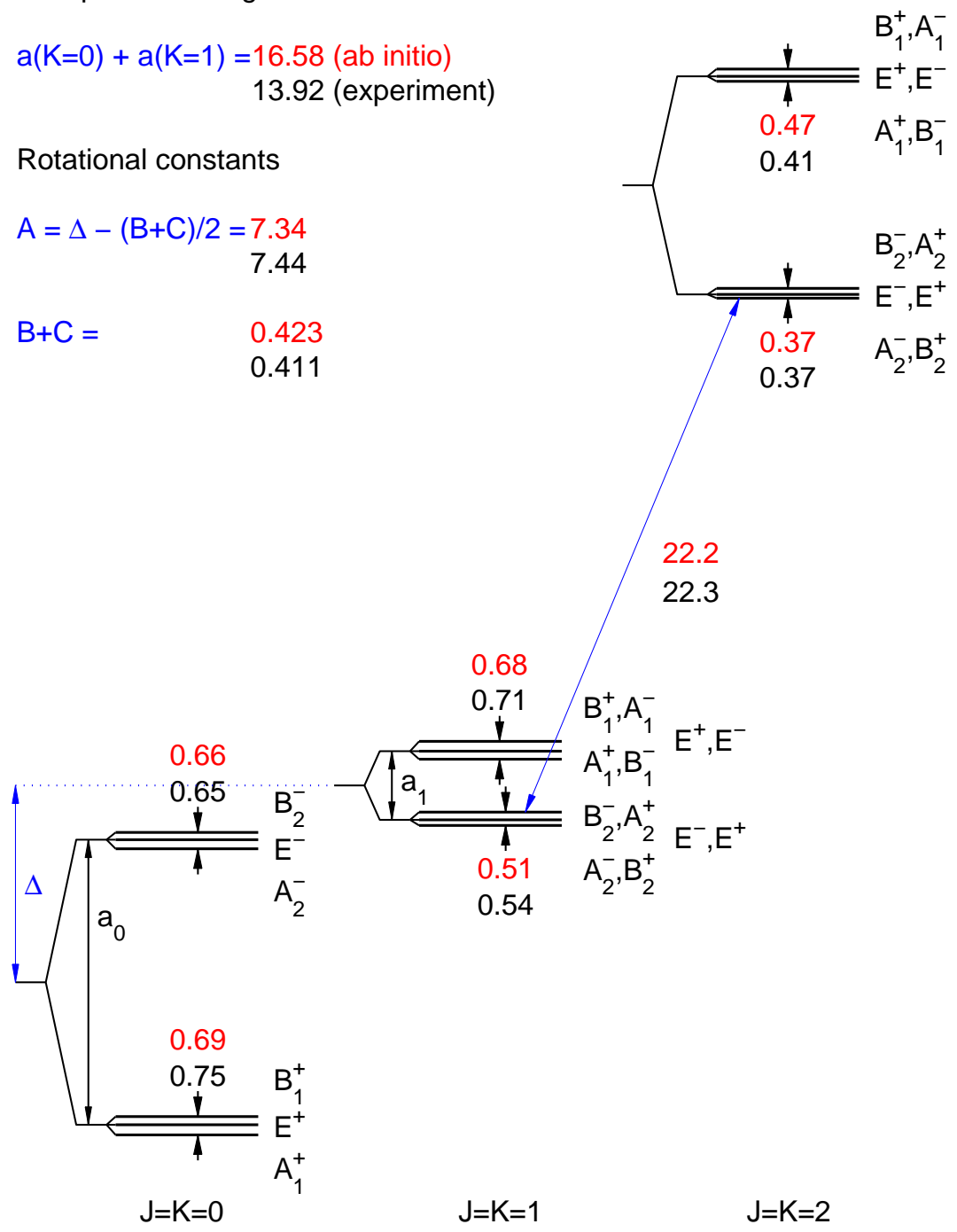
Acceptor tunneling

$$a(K=0) + a(K=1) = 16.58 \text{ (ab initio)}$$
$$13.92 \text{ (experiment)}$$

Rotational constants

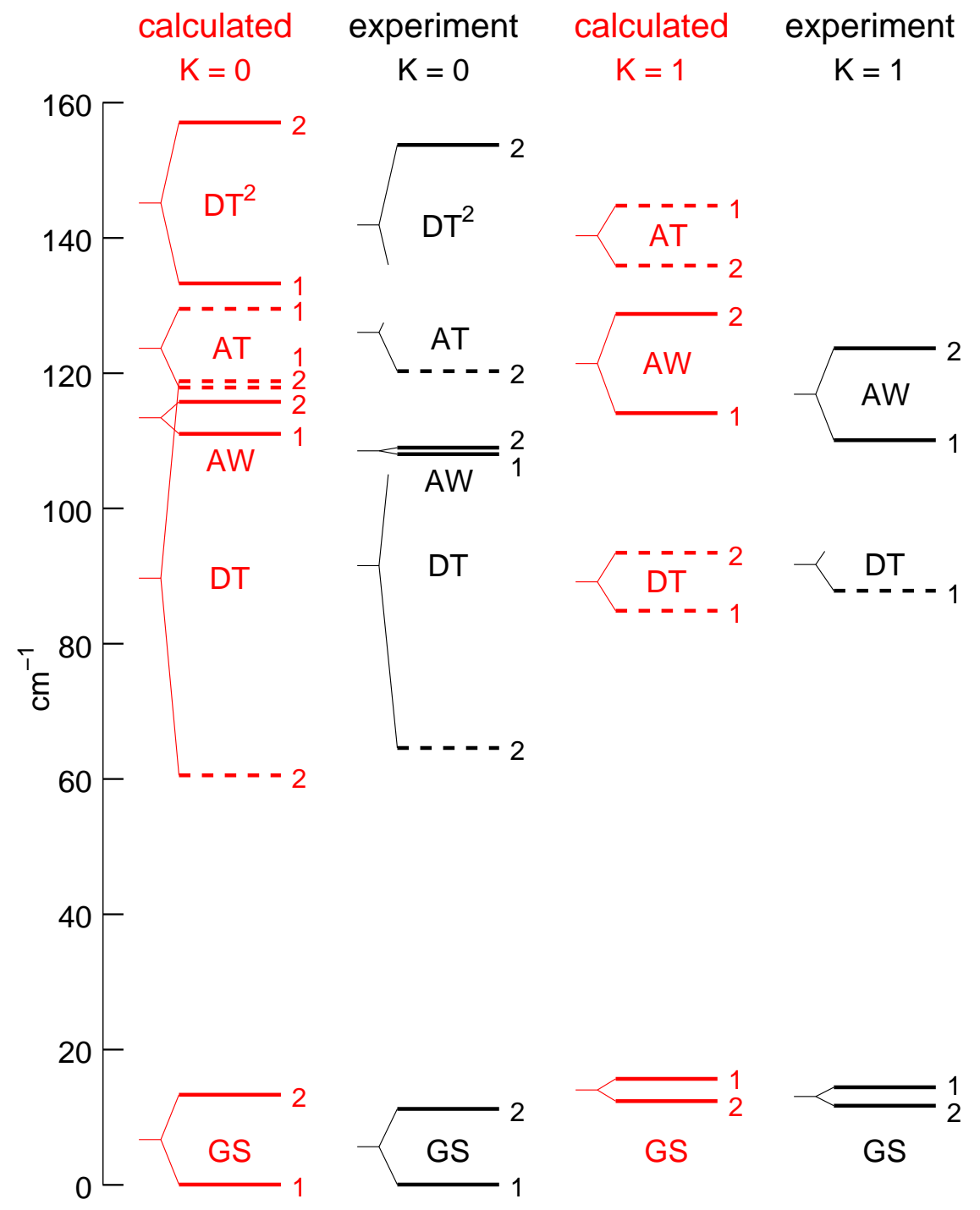
$$A = \Delta - (B+C)/2 = 7.34$$
$$7.44$$

$$B+C = 0.423$$
$$0.411$$



H₂O dimer
intermolecular
vibrations

from CC-pol (red)
experiment (black)



Acceptor tunneling

$a(K=0)$	$a(K=1)$	$a(K=2)$	
2.41	0.79	1.71	(ab initio)
1.77	0.62	1.31	(experiment)

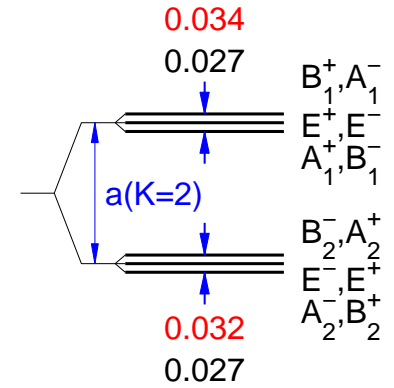
Rotational constants

$$A = \Delta - (B+C)/2 = 4.17$$

4.17

$$B+C = 0.380$$

0.362

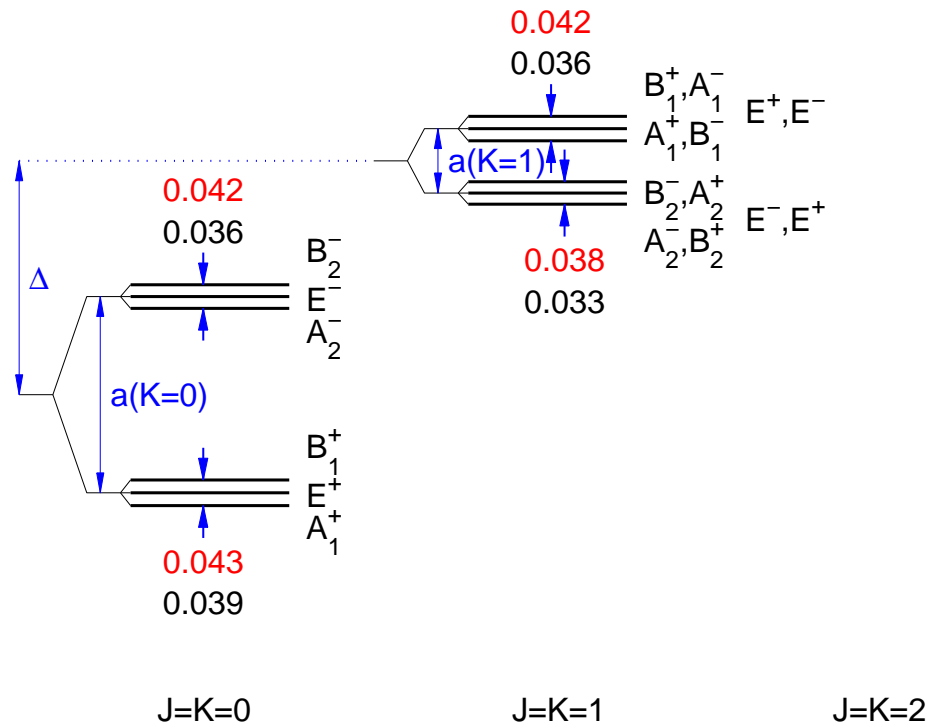


D₂O dimer

tunneling levels

from CC-pol (red)

experiment (black)



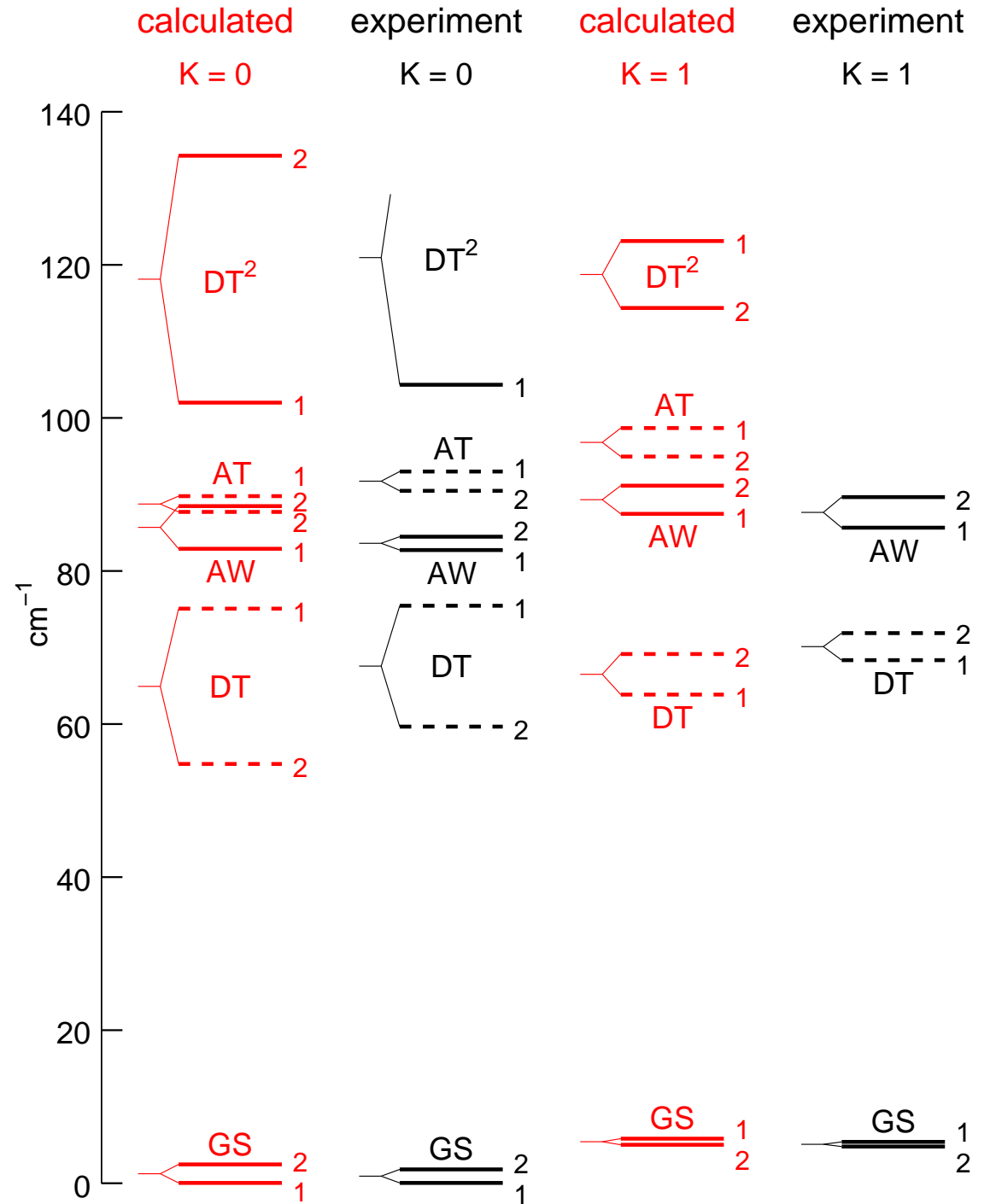
D₂O dimer

intermolecular

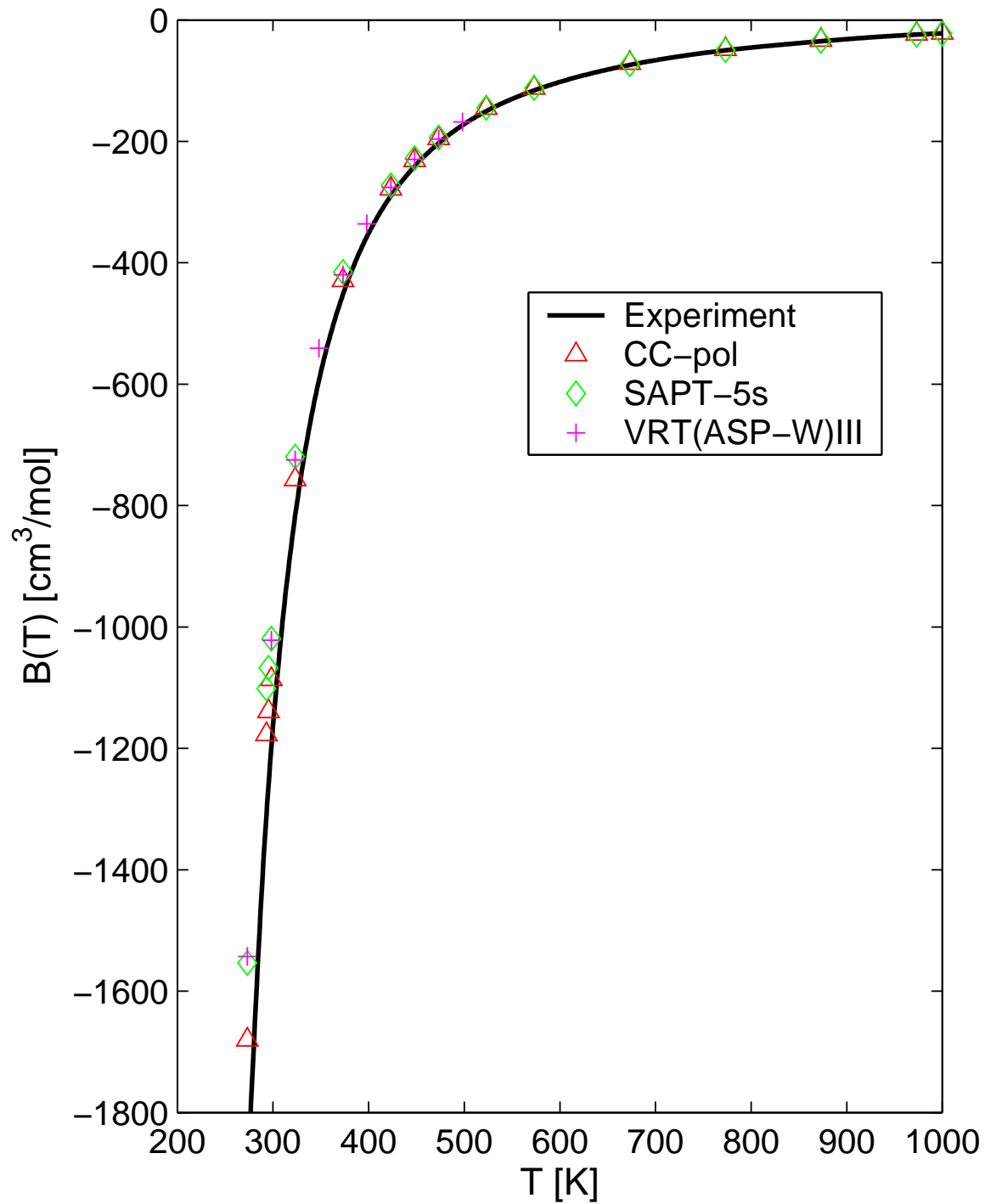
vibrations

from CC-pol (red)

experiment (black)

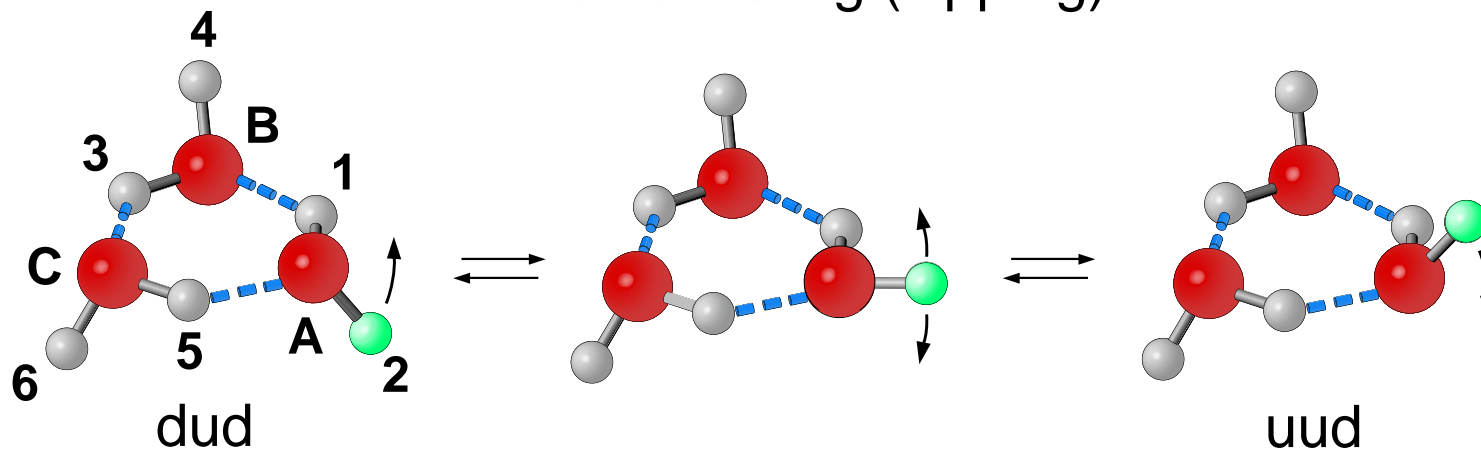


Second virial
coefficient
of water vapor

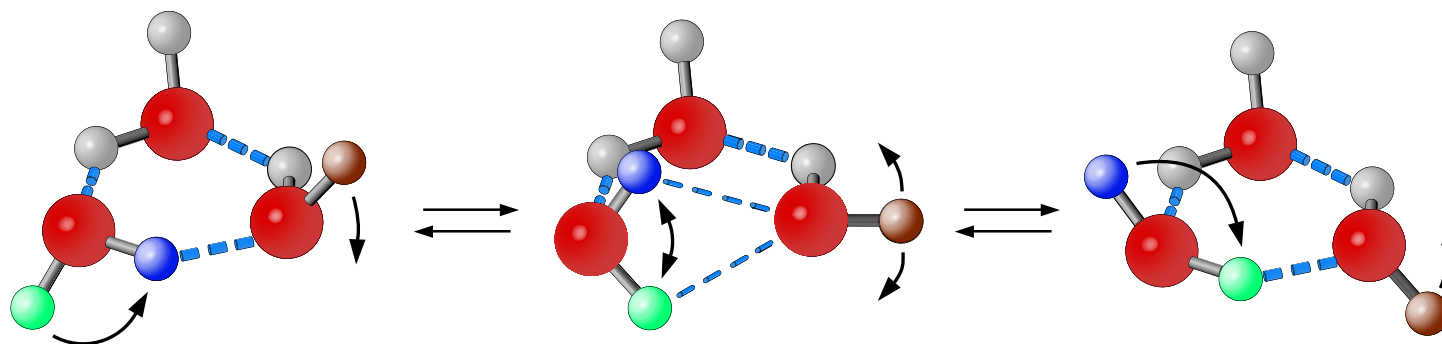


Water trimer tunneling pathways

Torsional tunneling (flipping)

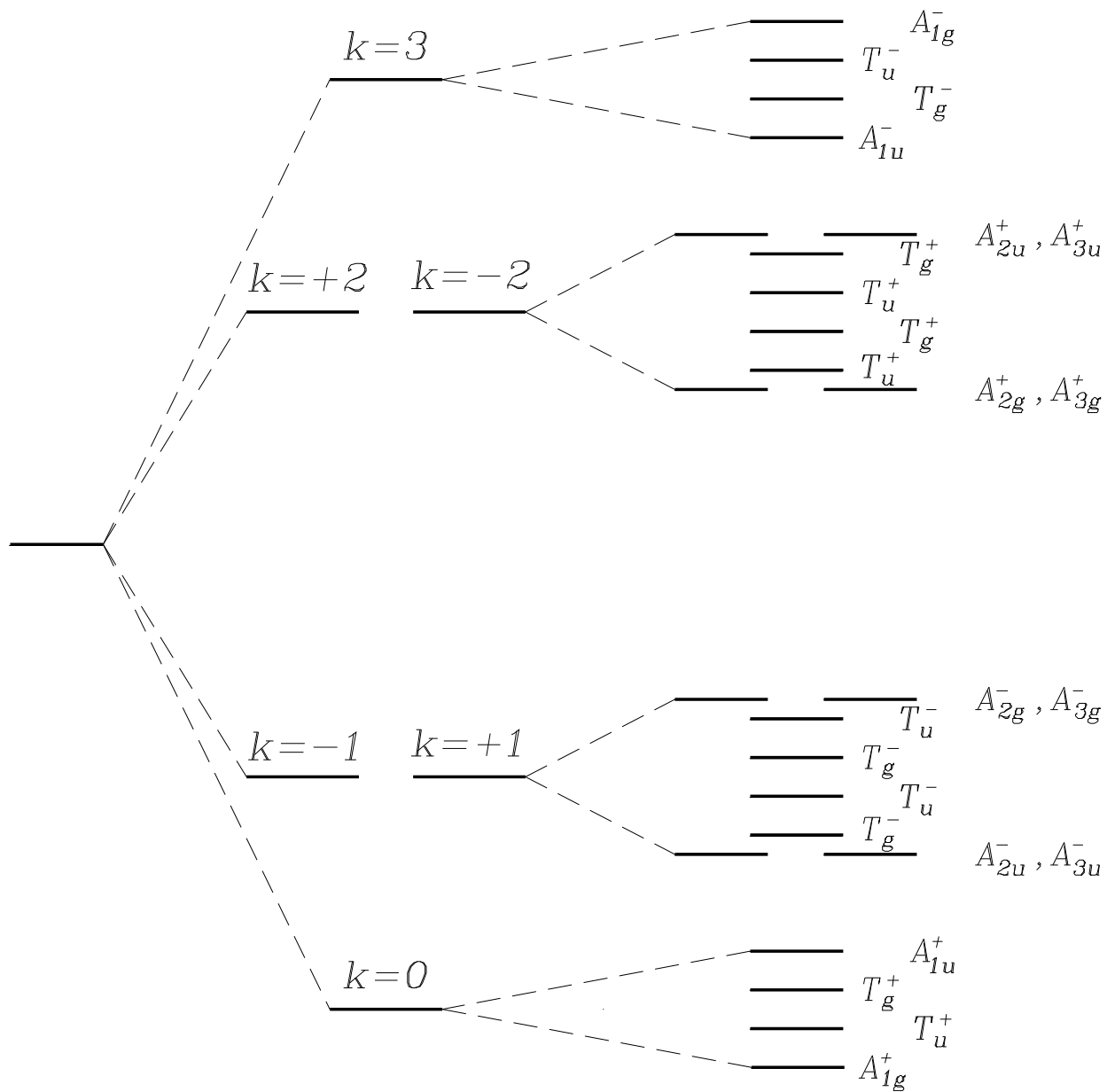


Bifurcation (donor) tunneling

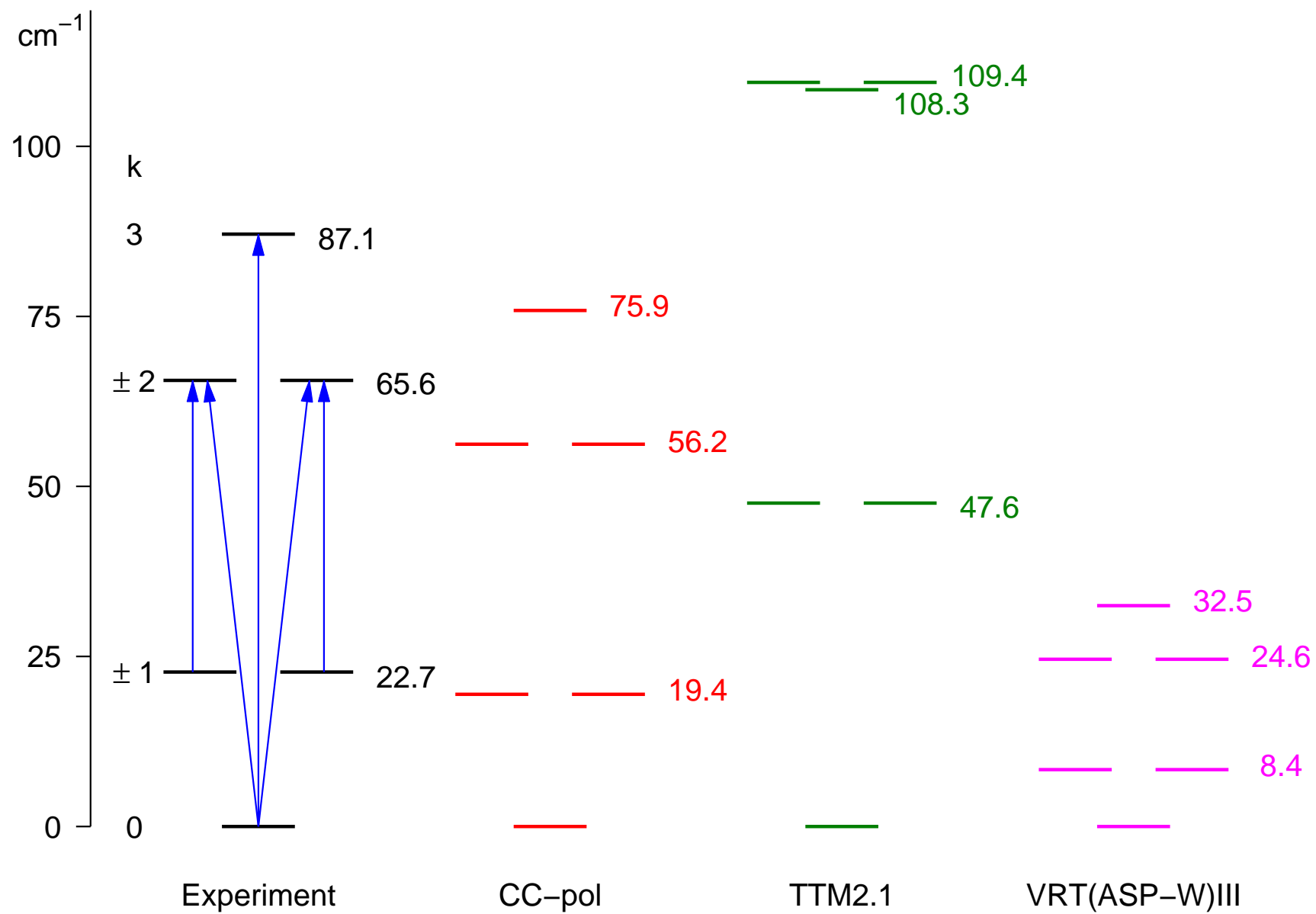


flipping (G_6) + bifurcation tunneling (G_{48})

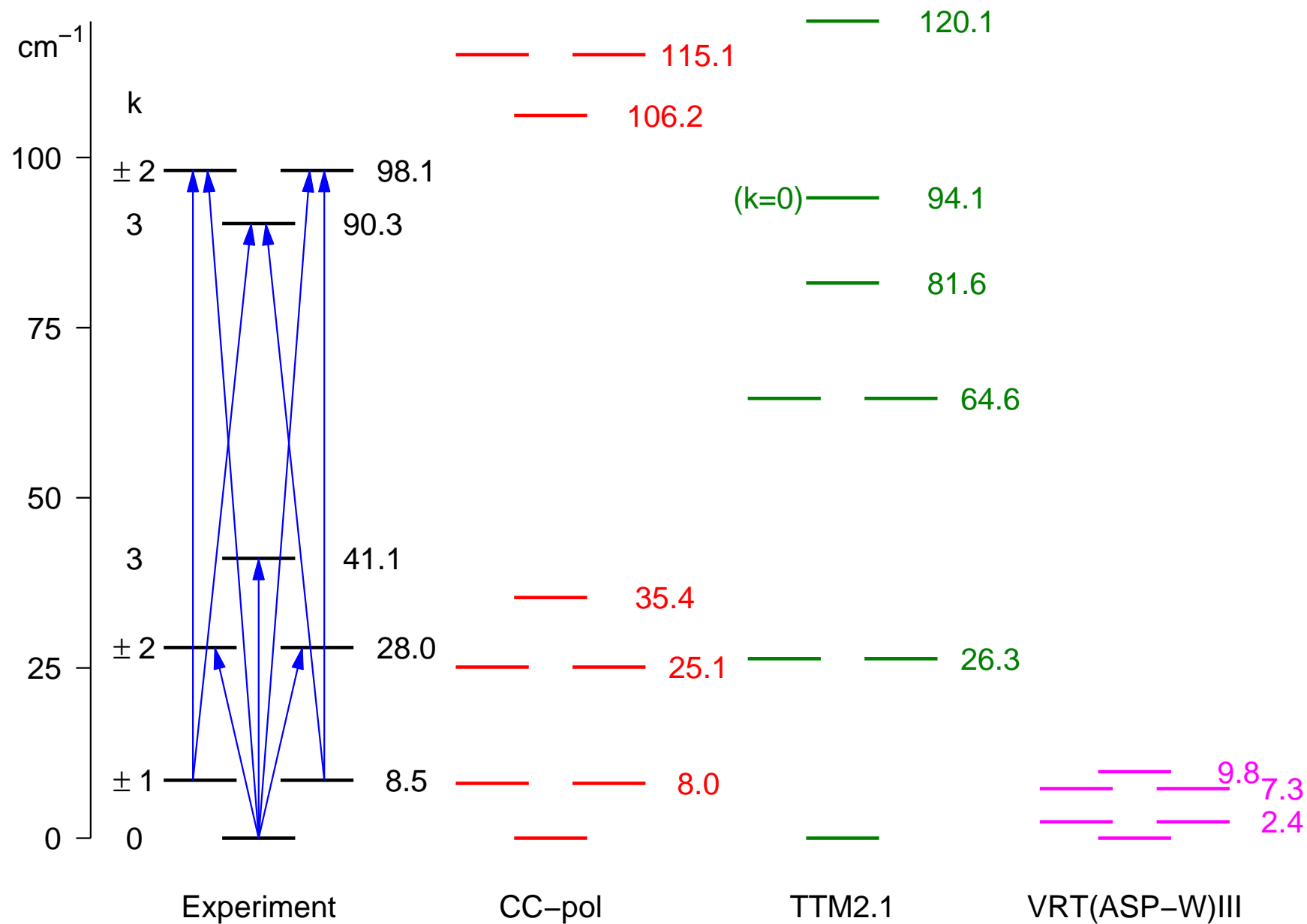
**Water trimer
tunneling
levels
($J = 0$)**



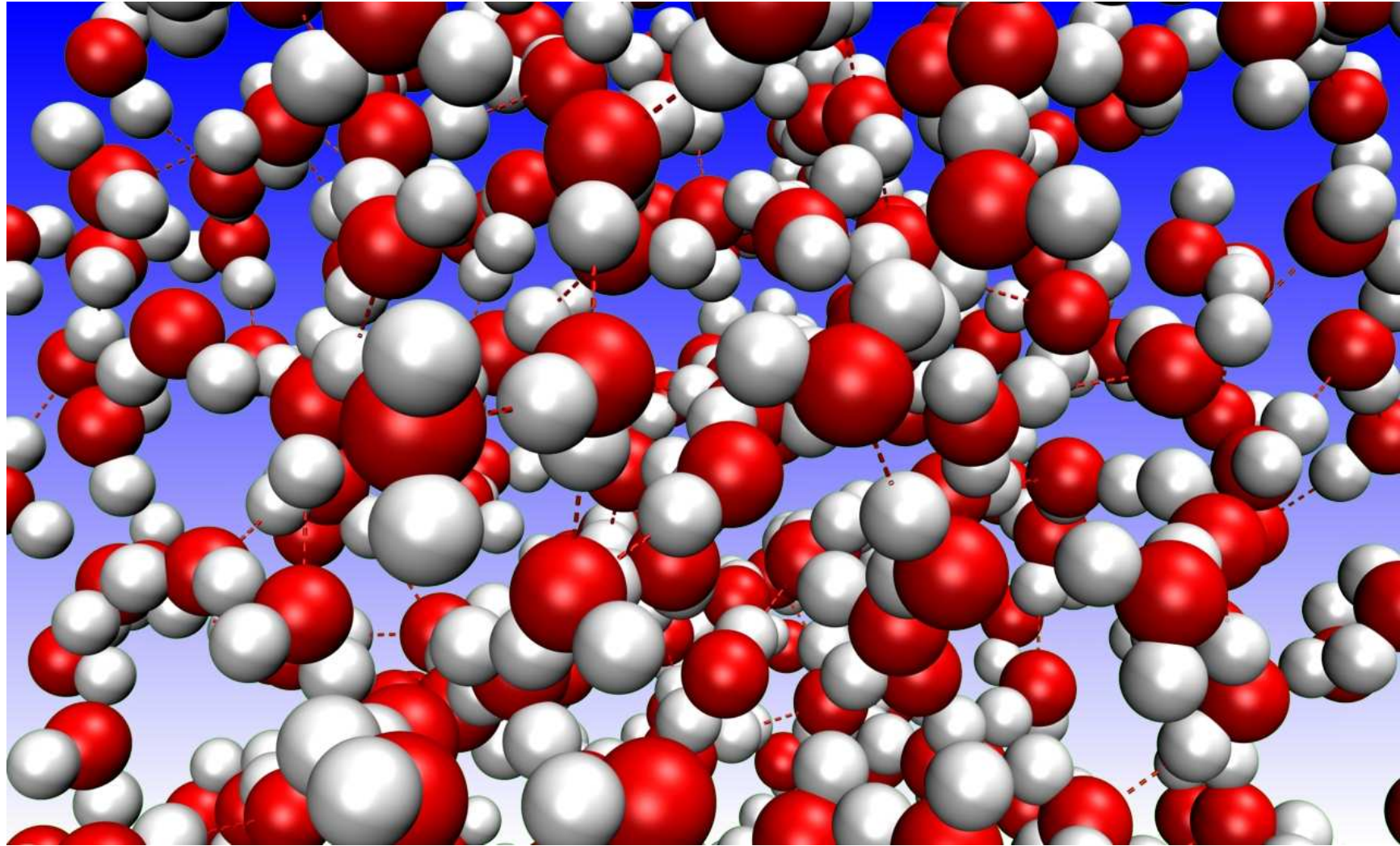
H₂O trimer torsional levels

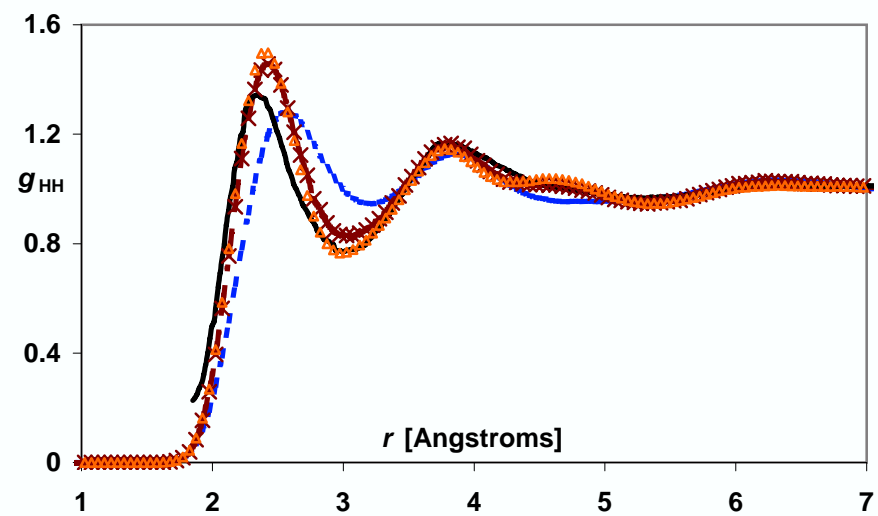
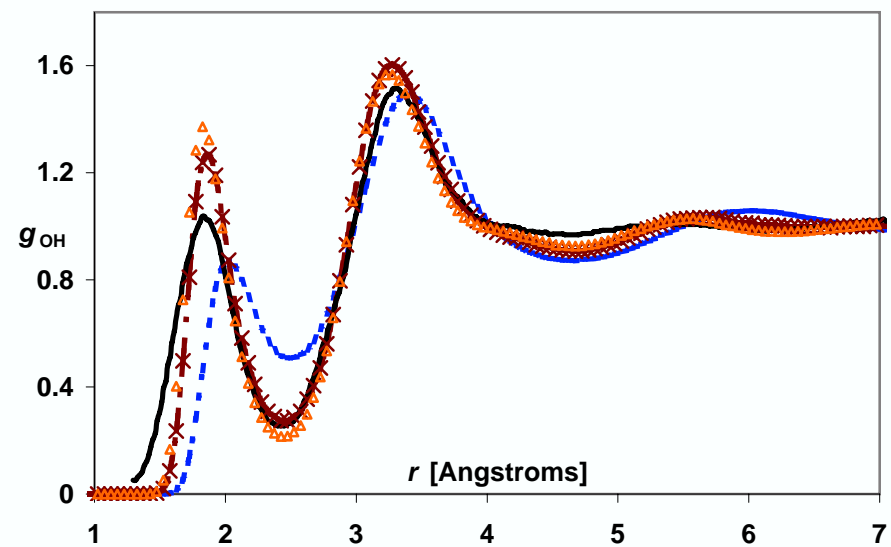
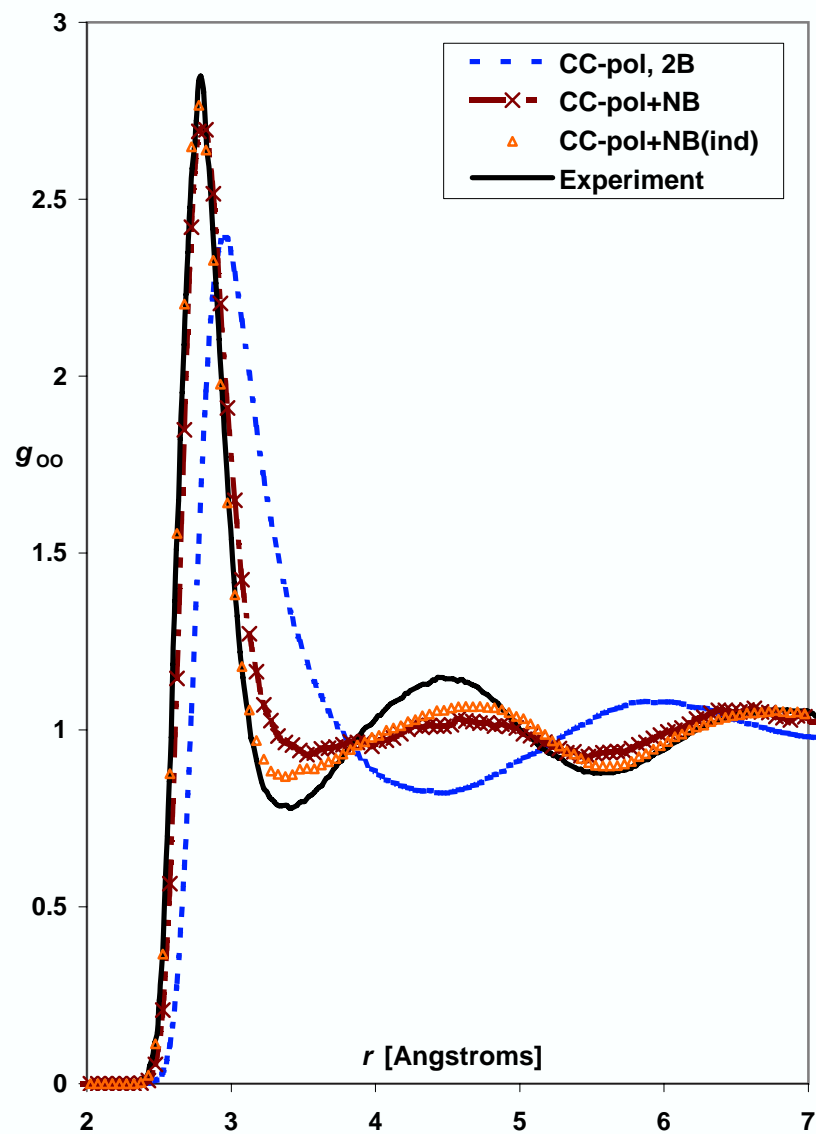


D₂O trimer torsional levels



MD simulations of liquid water, $T = 298 \text{ K}$





Atom-atom radial distribution functions

Conclusions

- CC-pol pure *ab initio*
- Predicts dimer spectra better than semi-empirical potentials fitted to these spectra
- Second virial coefficients in excellent agreement with experiment
- CC-pol + 3-body potential gives good trimer spectrum
- Simulations of liquid water with CC-pol + N-body forces predict the neutron and X-ray diffraction data equally well as the best empirical potentials fitted to these data
- Important role of many-body forces in liquid water
 - Nearly tetrahedral coordination:
 - 3.8 hydrogen bonds, only 2.8 with pure pair potential

General conclusion

CC-pol, with the accompanying many-body interaction model, provides the first water force field that recovers the dimer, trimer, and liquid properties well

Latest development

Water pair potential with flexible monomers: 12-dimensional

X. Huang, B. J. Braams, and J. M. Bowman, J. Phys. Chem. A **110** (2006) 445
Improved version (J. Chem. Phys., accepted)

- From CCSD(T) calculations in aug-cc-pVTZ basis.
- 20 000 \Rightarrow 30 000 water dimer geometries.
- Accurate fit in terms of symmetry-adapted polynomials of scaled atom-atom distances.
- Produces even more accurate VRT levels of $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$. Also acceptor splitting $a_0 + a_1$ accurate in 12d calculations.
- Good VRT levels of $(\text{H}_2\text{O})_3$ and $(\text{D}_2\text{O})_3$ when 3-body interactions added.