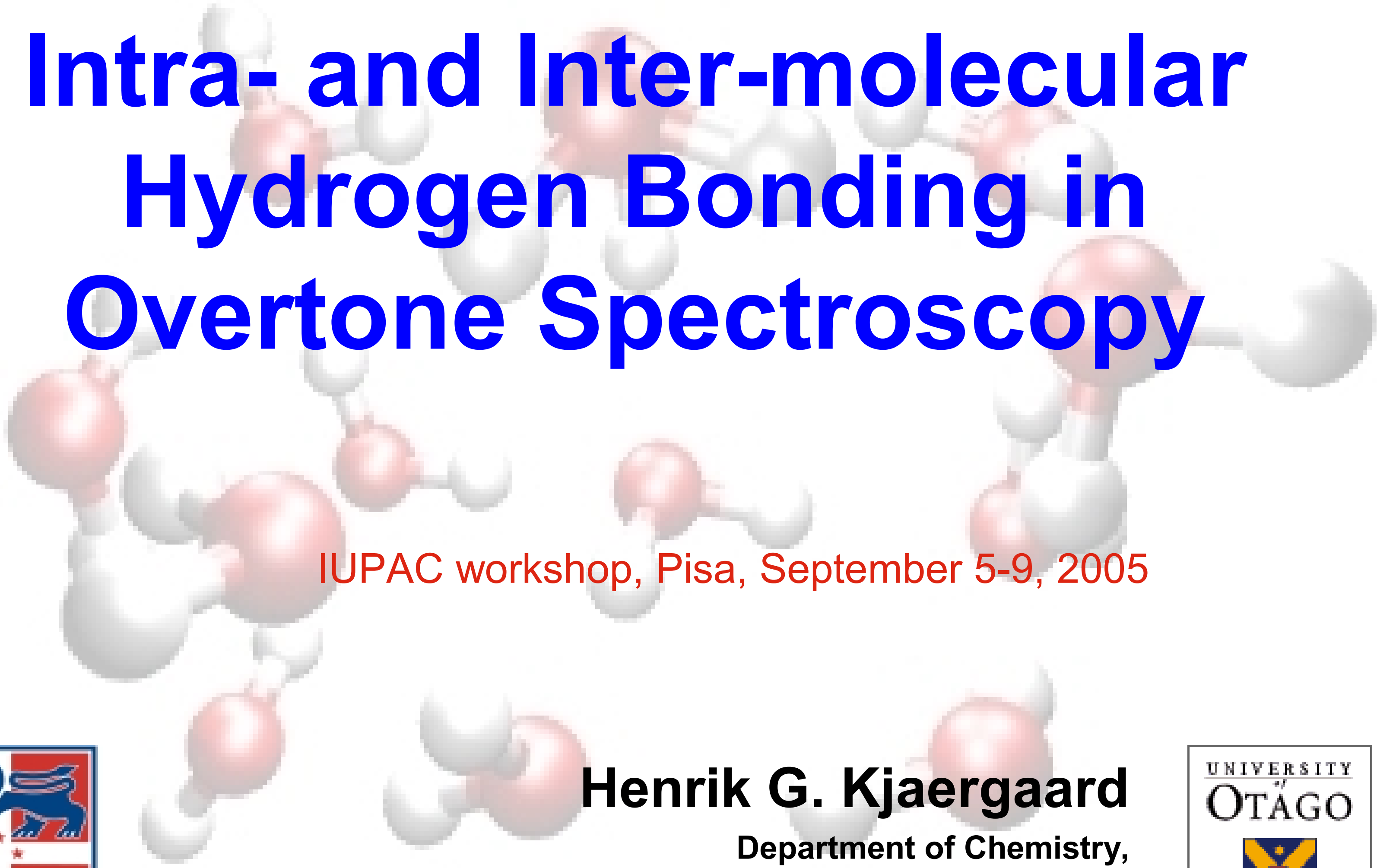

Intra- and Inter-molecular Hydrogen Bonding in Overtone Spectroscopy

IUPAC workshop, Pisa, September 5-9, 2005

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University of Otago,
Dunedin, New Zealand.

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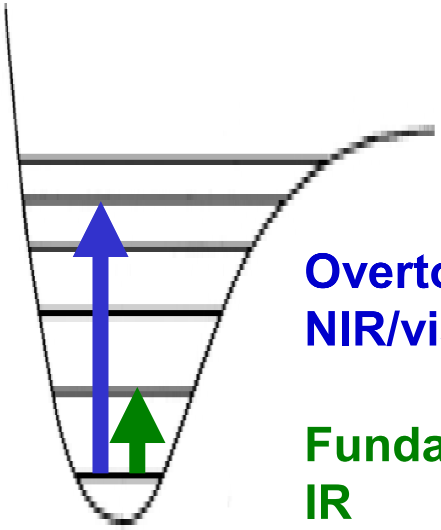
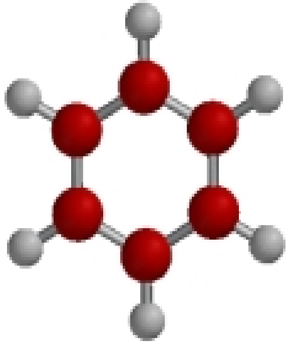
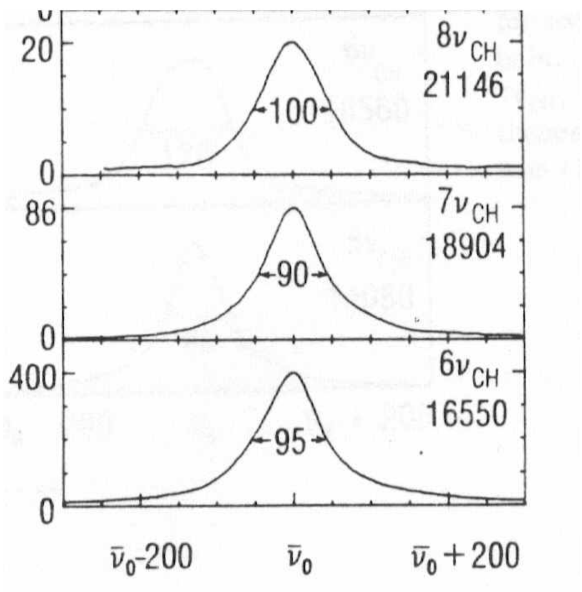
Vibrational Overtones



Overtone
NIR/vis

Fundamental
IR





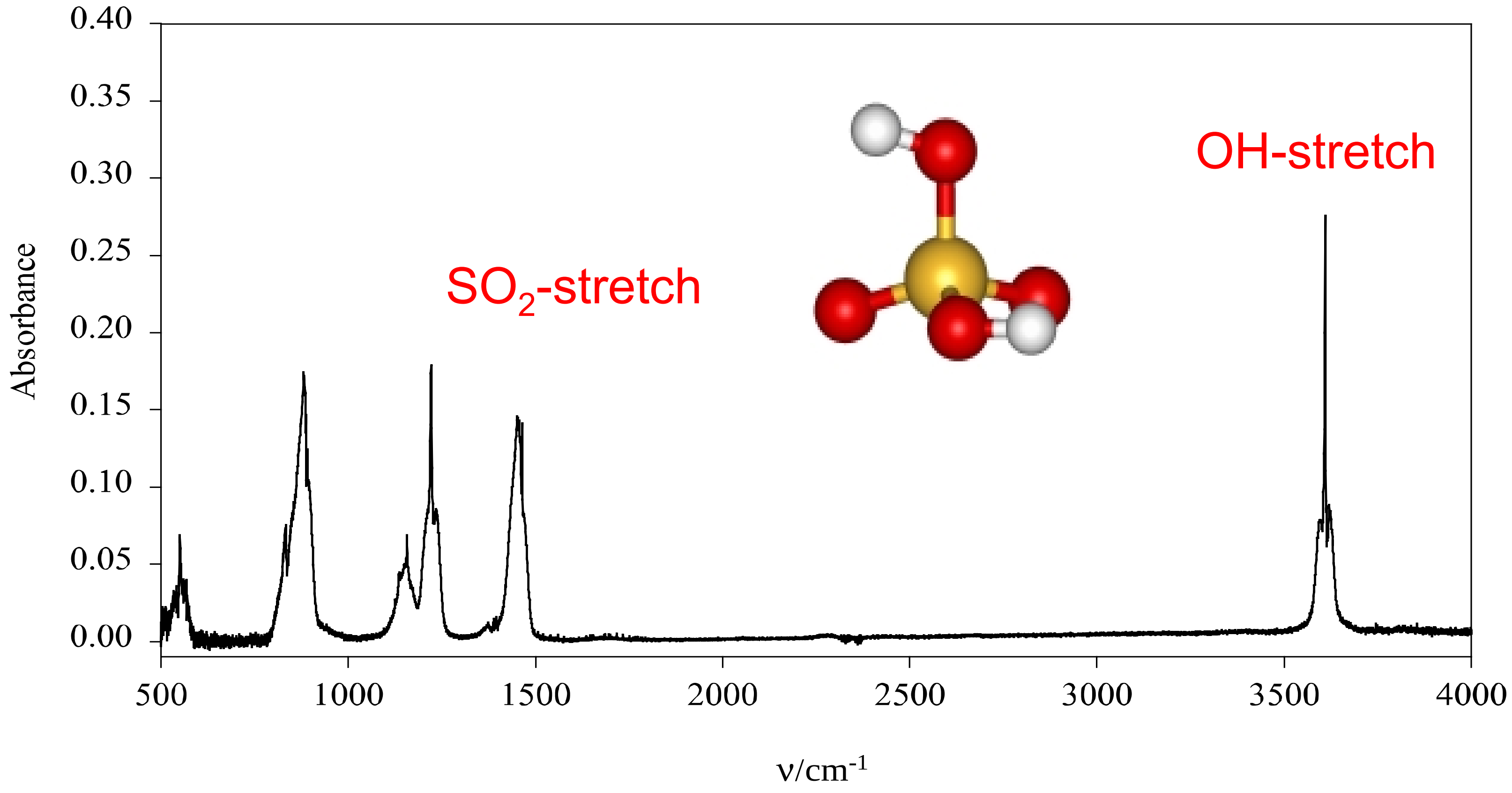
Reddy *et al*, J. Chem.Phys. **76**, 2814 (1982).

Overtone spectra are dominated by XH-stretching vibrations.

Described well by Local modes.

Vibrational energy is localized in a single bond or in a linear combination of equivalent bonds.

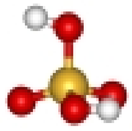
IR Spectrum of Sulfuric Acid Vapor



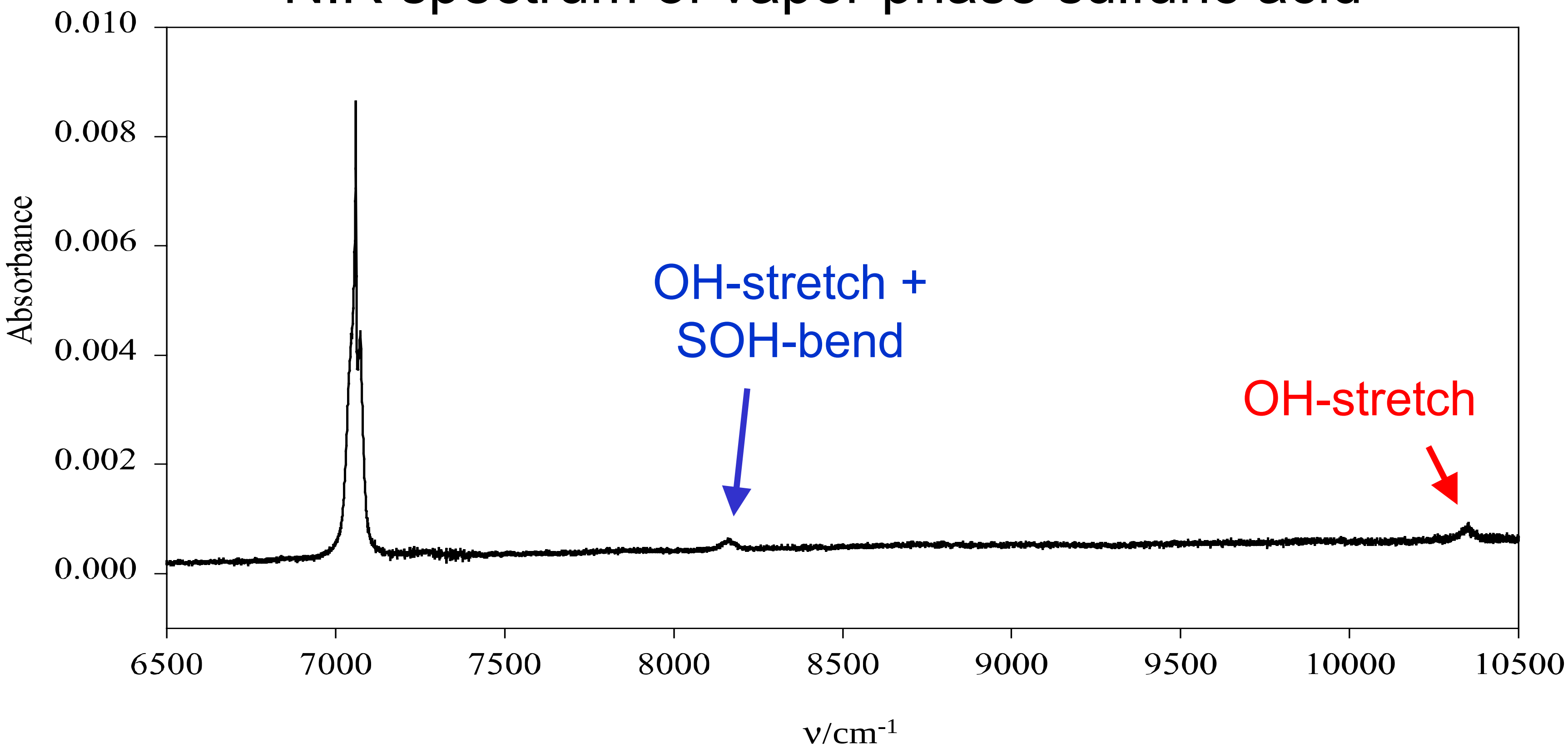
Several normal modes of vibration seen in the fundamental region.

Hintze, Kjaergaard, Vaida, Burkholder, JPC A 2003.

Normal versus Local modes



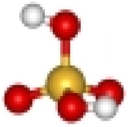
NIR spectrum of vapor phase sulfuric acid



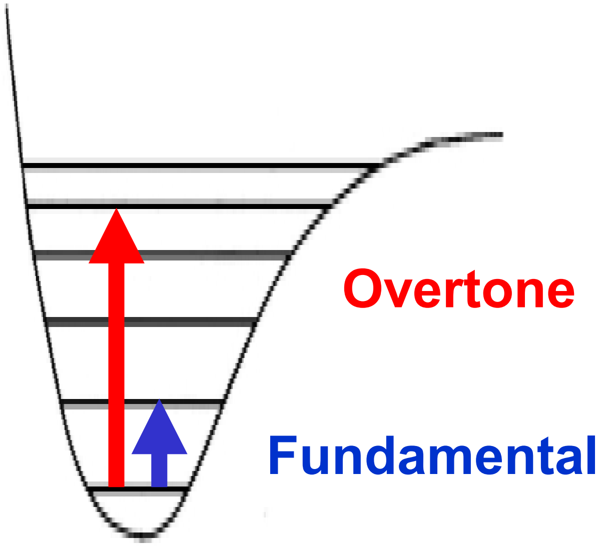
Overtone spectra dominated by OH-stretching vibrations

Described well by anharmonic local modes.

OH-stretching frequencies



Vibrational energies described well by isolated OH bond.



Δv_{OH}	Freq. (cm^{-1})	
	Obs.	Calc.
1	3609.2	3609.2
2	7060.7	7059.4
3	10350.3	10350.6
4		13483

Best fit Morse parameters $\tilde{\omega} = 3768.2\ \text{cm}^{-1}$ $\tilde{\omega}x = 79.5\ \text{cm}^{-1}$

Vibrational local modes

OH-stretch as anharmonic (Morse) oscillator:

$$(H - E_{|0>})/hc = \mathrm{v}\tilde{\omega} - (\mathrm{v}^2 + \mathrm{v})\tilde{\omega}x \quad \Rightarrow E_{vib} \text{ and } \psi_{vib}$$

$\tilde{\omega}$ and $\tilde{\omega}x$ from observed peak positions

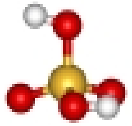
Dimensionless oscillator strength: $f_{eg} \propto \tilde{\nu}_{eg} \left| \langle e | \vec{\mu} | g \rangle \right|^2$

Dipole moment function of single OH bond

$$\vec{\mu}(q) = \sum_i \vec{\mu}_i q^i$$

From *ab initio* calculated dipole grid

OH-stretching intensities



Use 1D Morse oscillator model with:

Δv_{OH}	Int. (km/mol)	
	Obs.	Calc.
1	180	205
2	6.3	7.0
3	0.23	0.29
4		0.014

$$\tilde{\omega} = 3768.2\ \text{cm}^{-1}$$

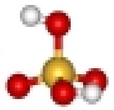
$$\tilde{\omega}x = 79.5\ \text{cm}^{-1}$$

B3LYP/6-311++G(2d,2p)
Dipole Moment Function

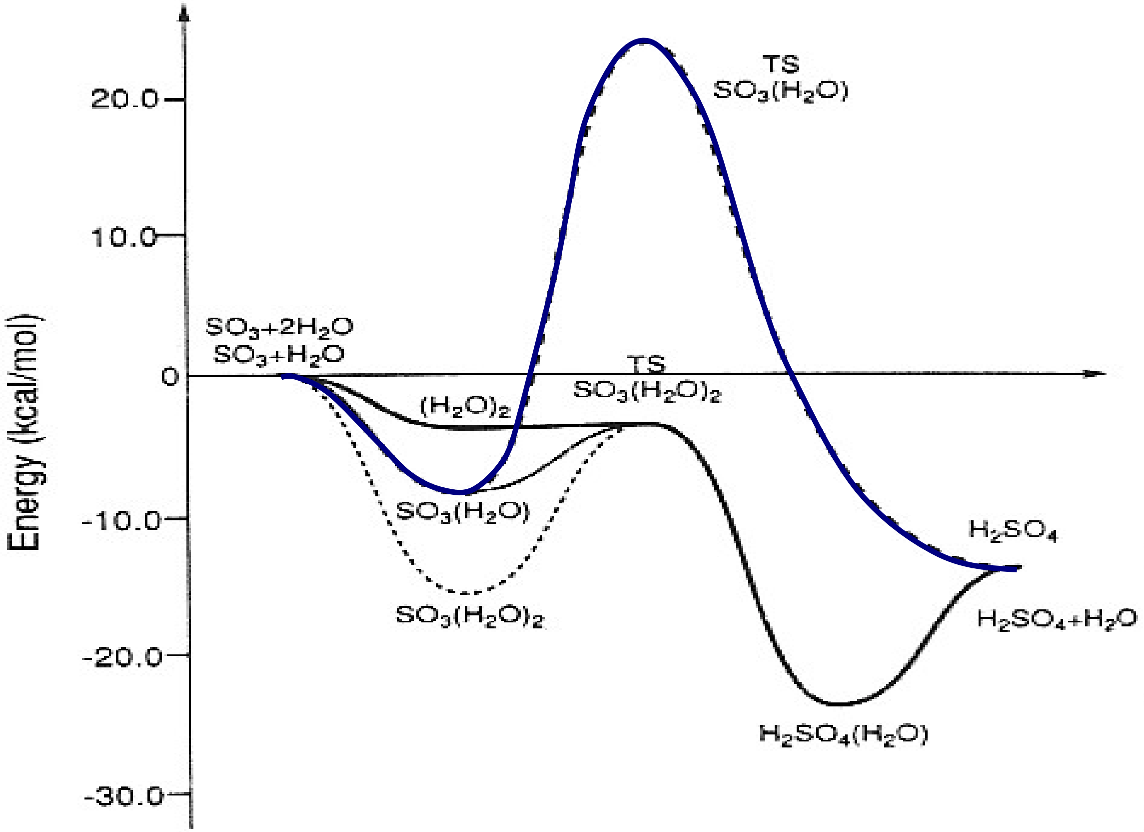
Adding SOH-bending mode
has little effect on OH-stretch

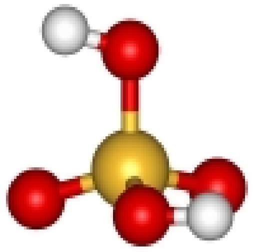
G98 FREQ Calculation with B3LYP/6-311++G(2d,2p)
Harmonic Oscillator Linear Dipole calculation ⇒ 252 km/mol

Photolysis of H_2SO_4



$H_2SO_4 \leftrightarrows SO_3 + H_2O$ $\Delta H \approx 40$ kcal/mol (~ 715 nm)





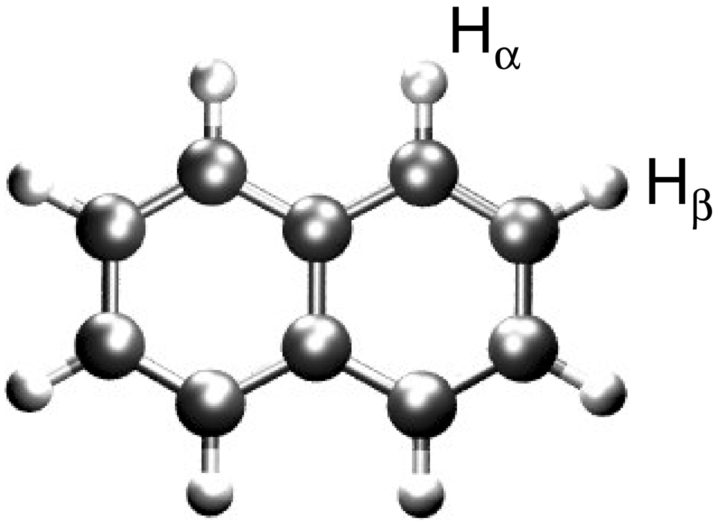
Thus H_2SO_4 photolysis can proceed via overtone excitations.

Morokuma, Mugurama, JACS (1994).

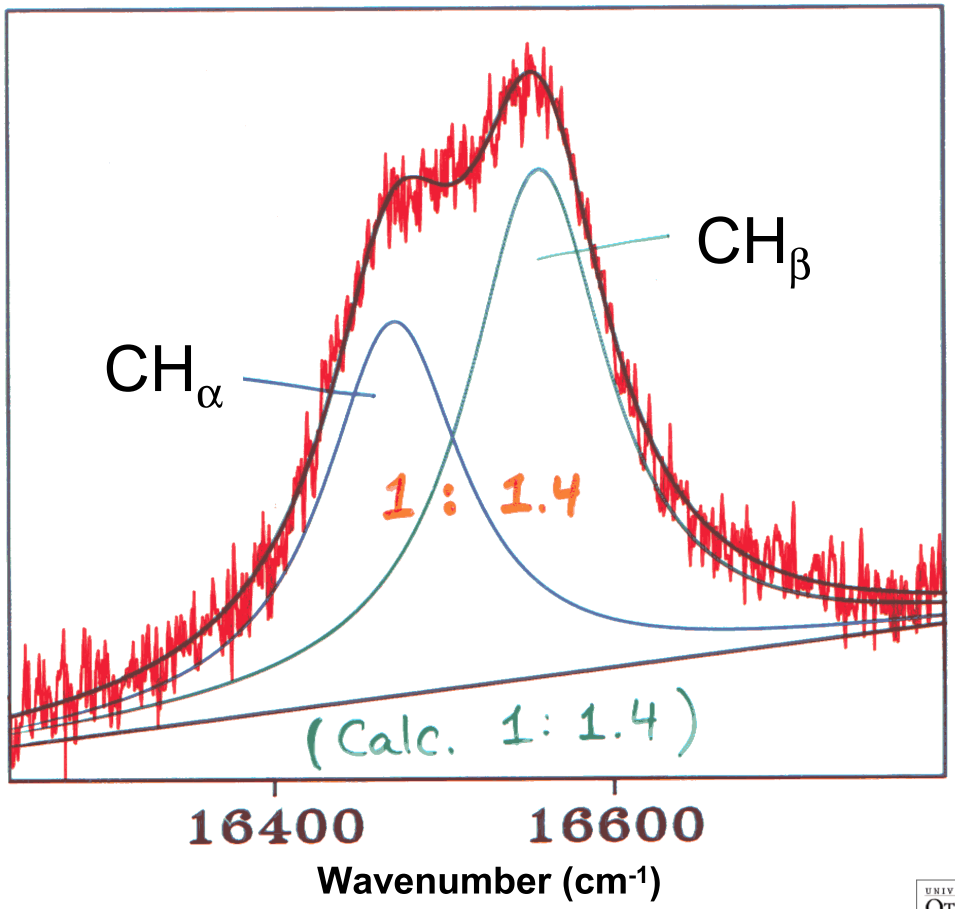
Vaida, Kjaergaard, Hintze, Donaldson, Science (2003).

Relative intensities

Naphthalene



Vapor phase $\Delta v_{CH} = 6$ spectrum



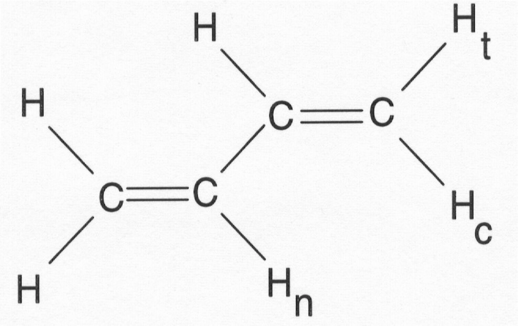
HF/6-311+G(d,p)
calculated bond lengths:

CH_α = 1.085 Å

CH_β = 1.084 Å

Relative intensities

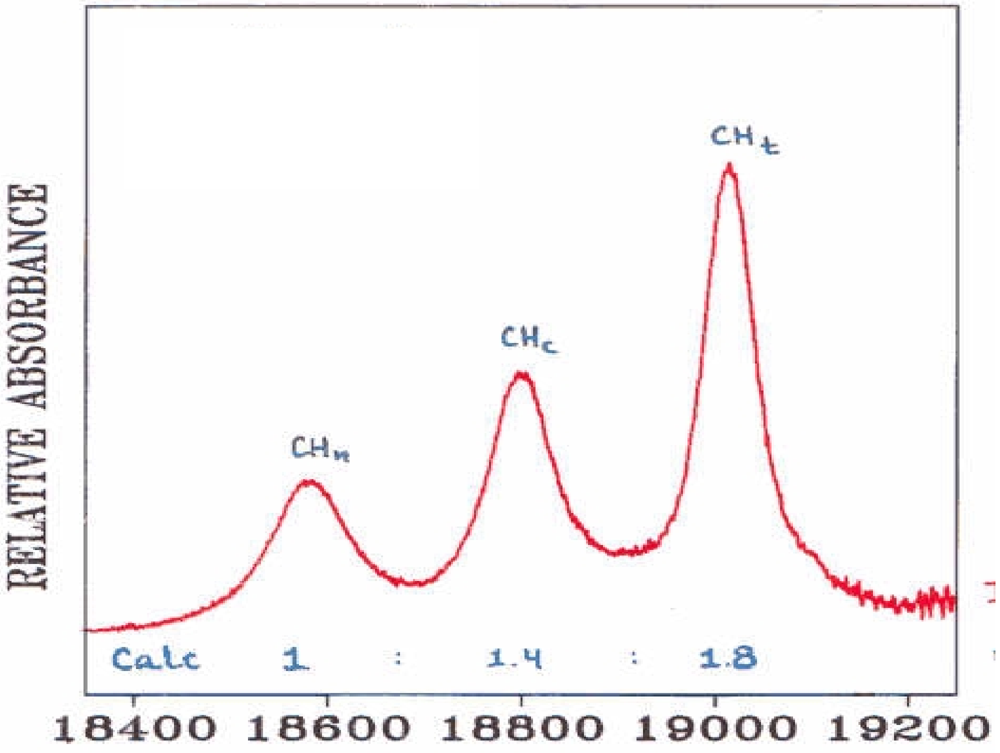
1,3-butadiene



Calculate *ab initio* DMF for each of the three non-equivalent CH bonds.

HF/6-31G(d) method.

Vapor phase $\Delta v_{CH} = 7$ spectrum



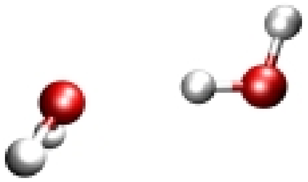
Wavenumber (cm^{-1})

Kjaergaard, Turnbull, Henry, JPC 1993.

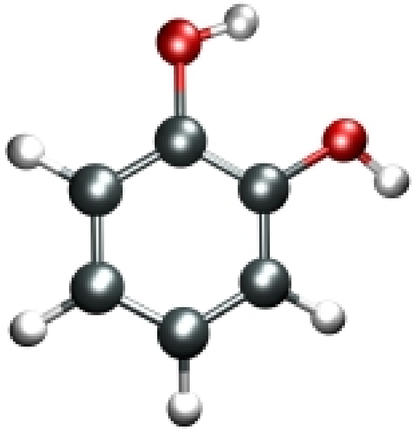
Inter- vs Intra-molecular interaction

How are overtone spectra effected by small change from weak molecular interactions?

Weak van der Waals interaction (including hydrogen bonding) can occur both inter-molecular as in complexes and intra-molecular.



Water dimer

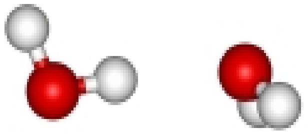


Catechol

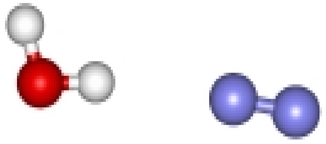
Complexes in the Atmosphere

O_2•O_2 and O_2•N_2 complexes have been shown to absorb about 1 W/m^2 of incoming solar radiation.

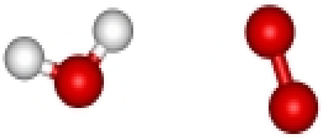
Hydrated complexes, H_2O•X, are likely to contribute.



H_2O•H_2O



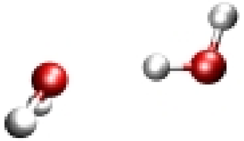
H_2O•N_2



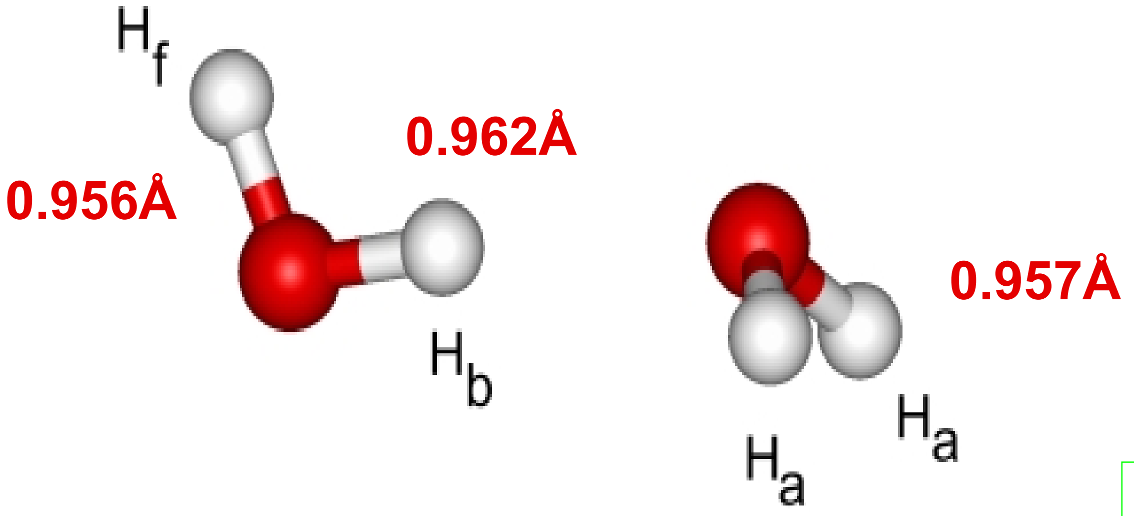
H_2O•O_2

Contribution depends on position, intensity and shape of spectroscopic transitions as well as atmospheric abundance.

Water dimer, $H_2O \bullet H_2O$



QCISD/6-311++G(2d,2p) optimized geometry



H donor

H acceptor

Water monomer,
R_{OH} = 0.958Å

OH bond involved in hydrogen bonding is significantly longer $\Rightarrow$ frequency red shift

Water dimer, $H_2O \bullet H_2O$

Simple vibrational model for water dimer

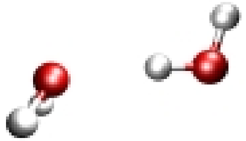
$$\hat{H} = \hat{H}_{acceptor} + \hat{H}_{donor}$$

Each H_2O unit is modeled by two OH-stretching and one HOH-bending local mode oscillator.

We use the Harmonically Coupled Anharmonic Oscillators (HCAO) local mode model for each of the H_2O units.

Not sufficient experimental data to determine local mode parameters. Obtain these from ab initio calculations.

Local mode parameters



Local mode parameters for water

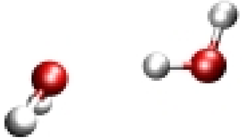
	QCISD	Expt.	Scaling factor
$\tilde{\omega}$	3934	3870	0.9836
$\tilde{\omega}x$	96.5	82.1	0.851

QCISD calculated Local mode parameters for water dimer after scaling

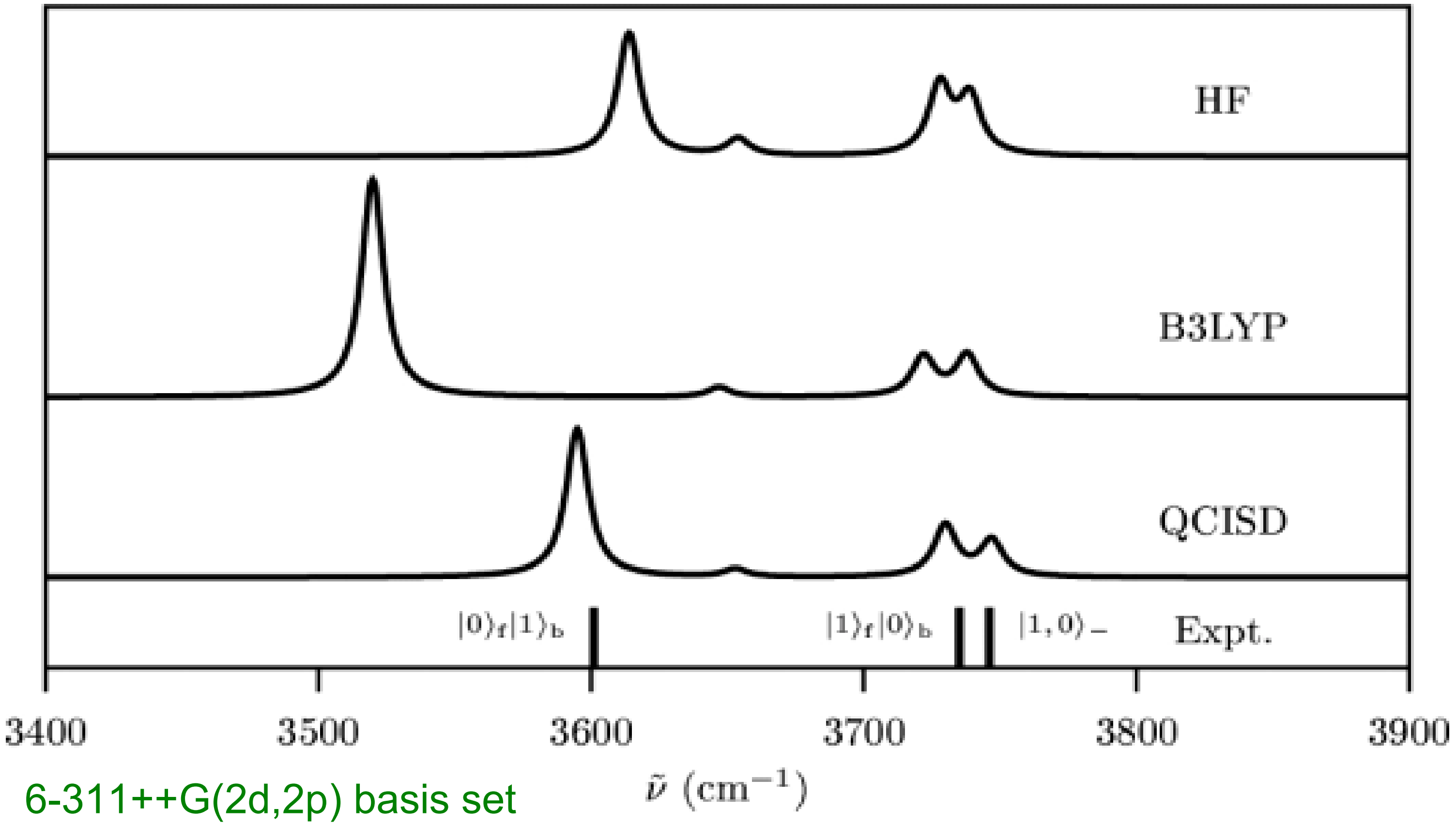
	OH_a	OH_f	OH_b	H_2O expt.
$\tilde{\omega}$	3863	3878	3781	3870
$\tilde{\omega}x$	81.7	82.3	85.4	82.1

Low, Kjaergaard, JCP 1999.

Ab initio methods



OH-stretching fundamental transitions in $H_2O•H_2O$



6-311++G(2d,2p) basis set

Low, Kjaergaard, JCP 1999.

Huang, Miller, JCP 1989.

Huisken, Kaloudis, Kulcke, JCP 1996.

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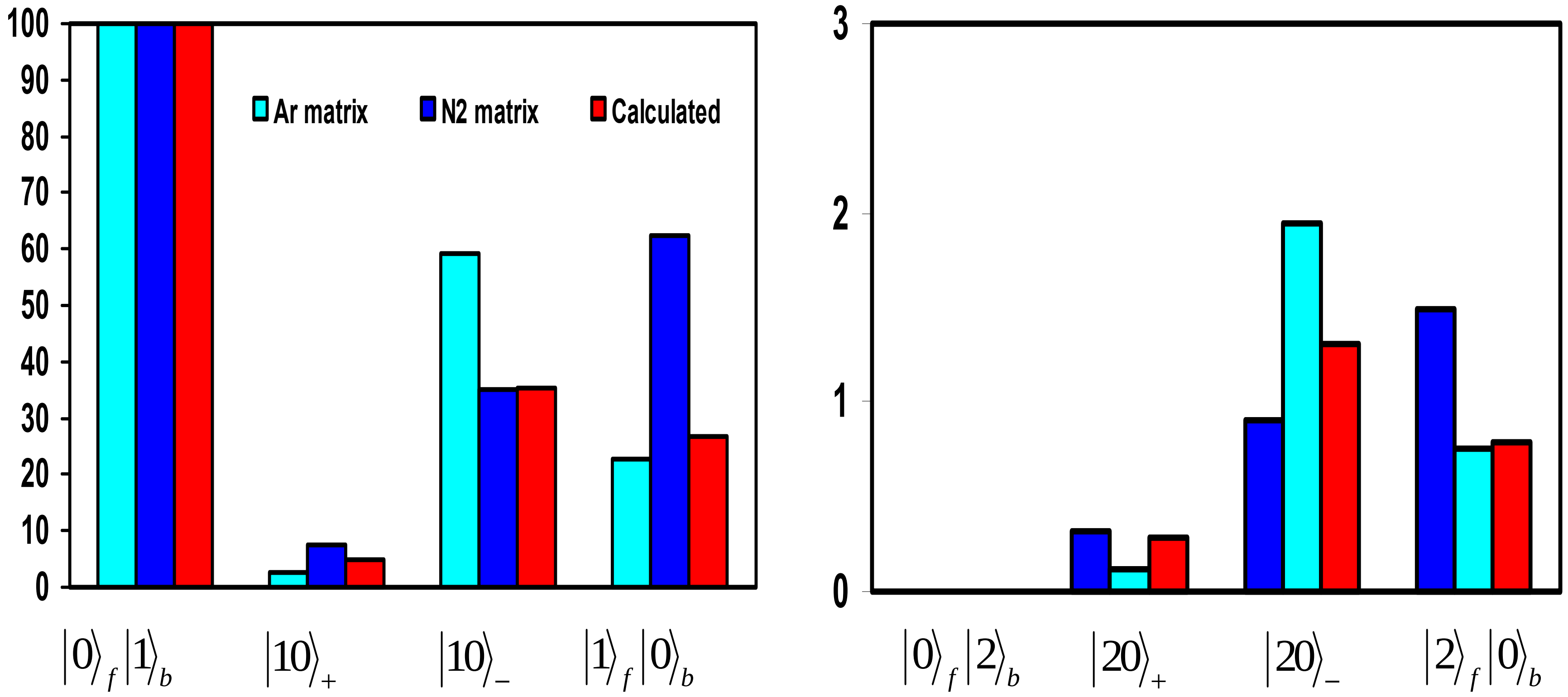
Water dimer, OH-stretching



First overtone of OH_b-stretching transition is very weak, only recently observed in Ne matrix.

Perchard, Chem. Phys. (2001)   Schofield, Kjaergaard, PCCP 2003.

Cancellation of terms

Expansion: $\langle v|\mu|0\rangle \approx \mu_1 \langle v|q|0\rangle + \mu_2 \langle v|q^2|0\rangle + \cdots$

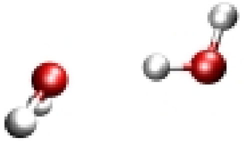
Matrix elements for a typical OH-stretching Morse oscillator

Fundamental:	$\langle 1|q|0\rangle \approx 0.07$	$\langle 1|q^2|0\rangle \approx 0.0035$
1st overtone:	$\langle 2|q|0\rangle \approx -0.0072$	$\langle 2|q^2|0\rangle \approx 0.0062$

Ab initio dipole expansion coefficients

OH bond in H_2O:	$\mu_1 \approx 0.76$	$\mu_2 \approx -0.60$
OH_b bond in $(H_2O)_2$:	$\mu_1 \approx 2.53$	$\mu_2 \approx 2.66$

Water dimer, OH-stretching



OH-stretching frequencies in the $\Delta v_{OH} = 2$ region (in cm^{-1})

Mode	Ne Matrix	Jet-cooled	HCAO calc.
$\lvert 0\rangle_f \lvert 2\rangle_b$	7018	-	7044
$\lvert 20\rangle_+$	7207	7193	7198
$\lvert 2\rangle_f \lvert 0\rangle_b$	7237	7240	7236
$\lvert 20\rangle_-$	7245	7250	7238
$\lvert 1\rangle_f \lvert 1\rangle_b$	7362	-	7370

Bouteiller, Perchard, Chem. Phys. (2004)

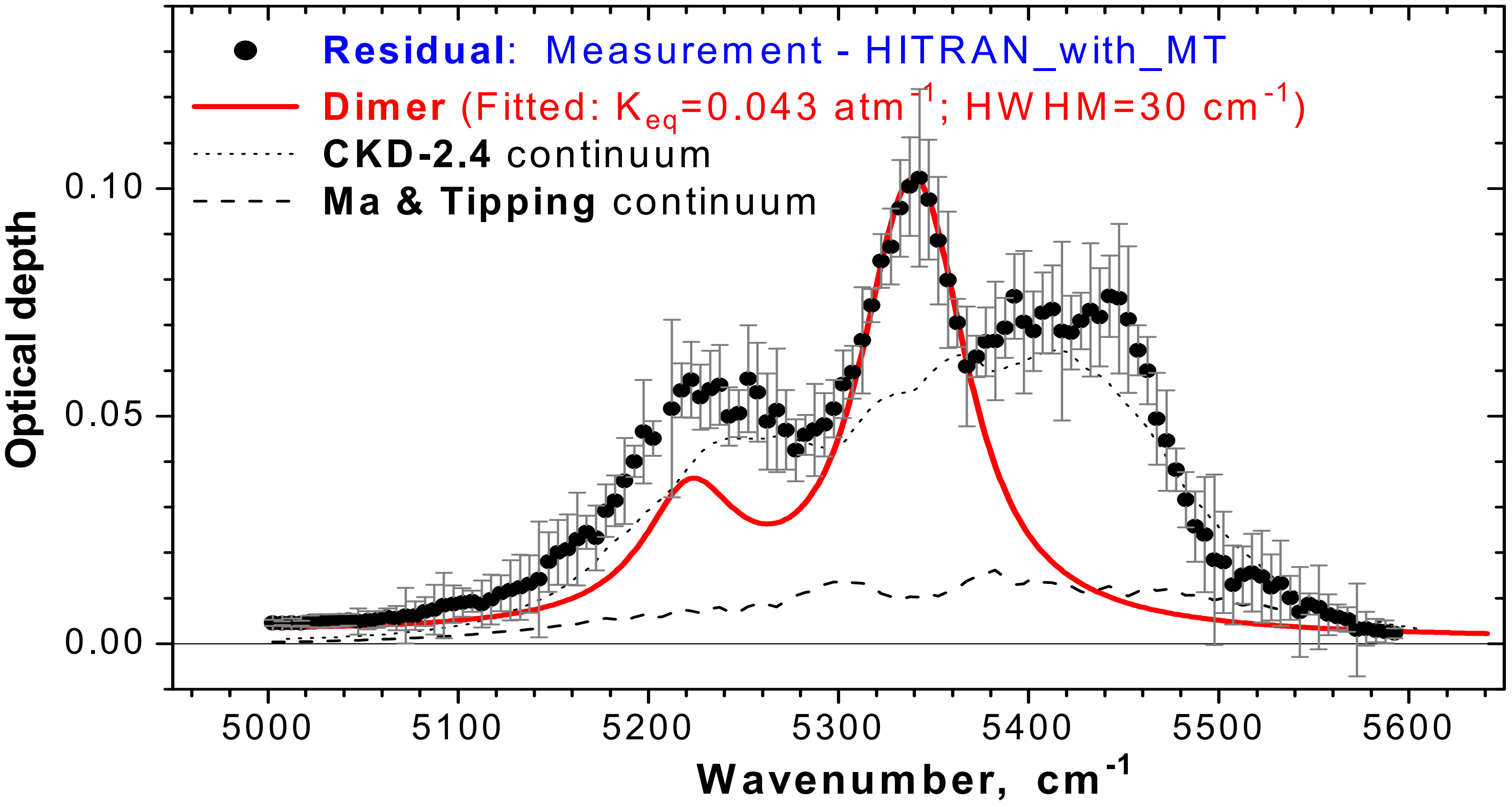
Nizkorodov, Ziemkiewicz, Nesbitt, Knight, JCP (2005)

Schofield, Kjaergaard, PCCP 2003.

HCAO calculation at QCISD/6-311++G(2d,2p)

Water dimer, stretch-bend

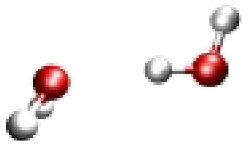
Ptashnik, Smith, Shine, Newnham, QJRMS (2004)

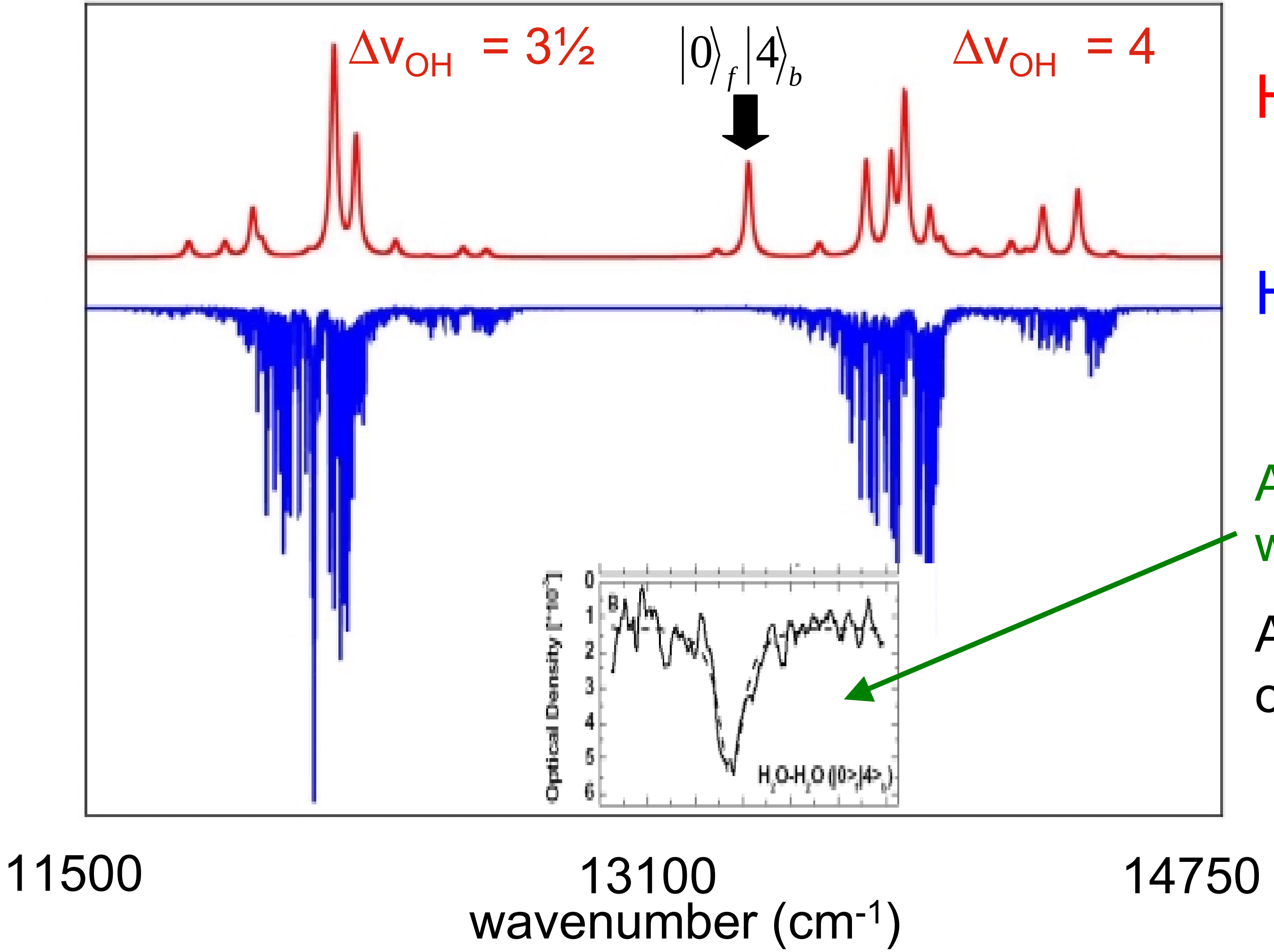


$|0\rangle_f |1\rangle_b |1\rangle_\beta$ $|10\rangle_- |1\rangle_\beta$

Schofield, Kjaergaard, PCCP 2003.

Water dimer in the atmosphere





$H_2O•H_2O$ (calc)

H_2O (observed)

Atmos. observation of water dimer.

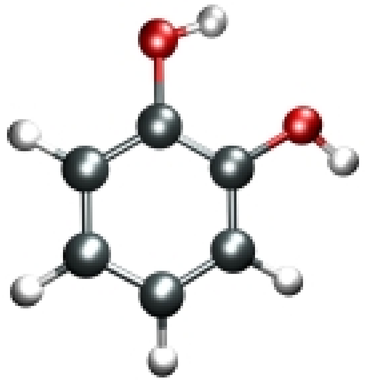
Abundance ~1/1000 of water monomer.

Schofield, Kjaergaard, PCCP 2003.

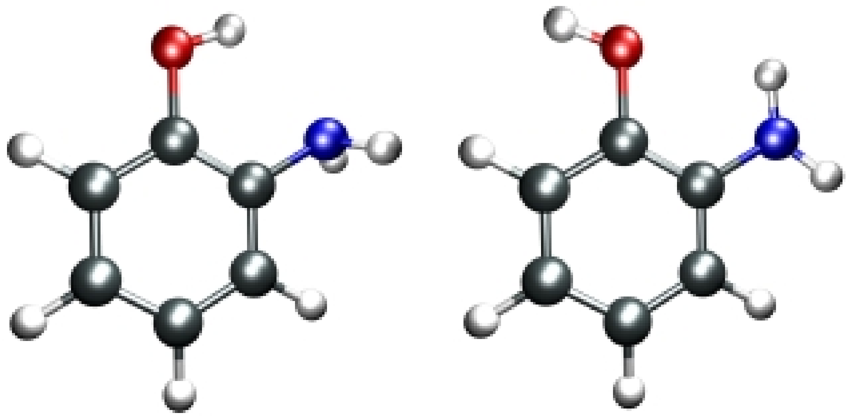
Pfeilsticker, Lotter, Peters, Bösch , Science 2003.

Intra-molecular interaction

Intra-molecular interaction seen in overtone spectra of a few molecules.



Catechol

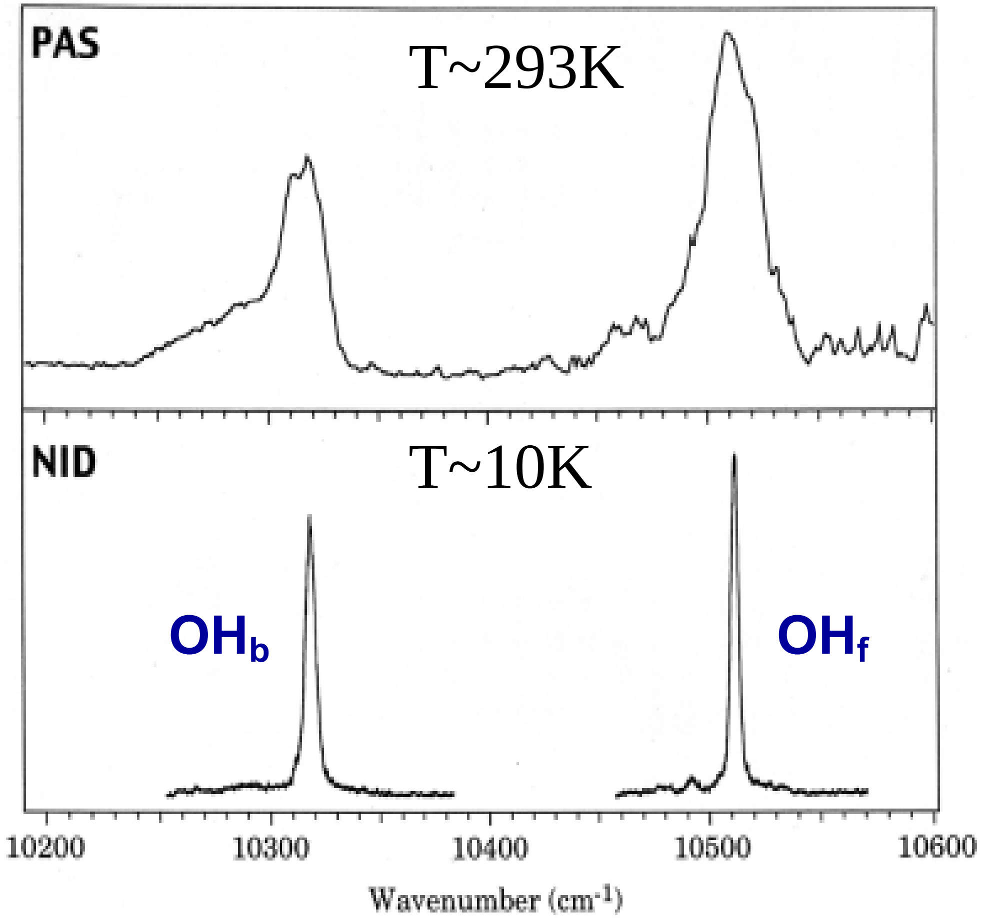


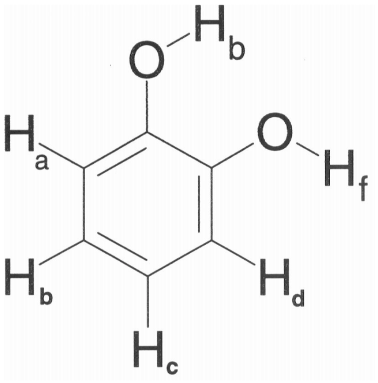
cis- and *trans*-*o*-aminophenol

Vapor pressure often low and the overtones are inherently weak, so a sensitive technique is necessary.

Catechol

ICL-PAS and NID spectrum of catechol in the Δv_{OH} = 3 region





Bond lengths:

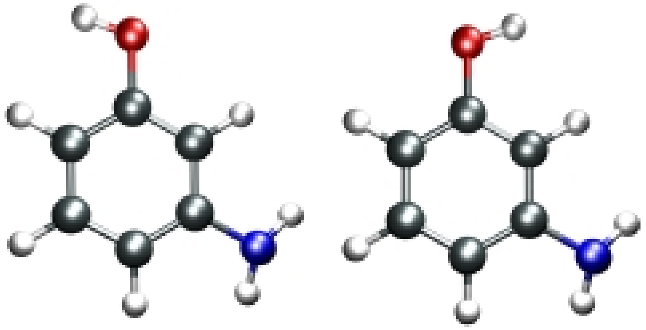
OH_b = 0.964 Å

OH_f = 0.961 Å

B3LYP/6-311++G(2d,2p)

Kjaergaard, Howard, Schofield, Robinson, Ishiuchi, Fujii, JPC A 2002.

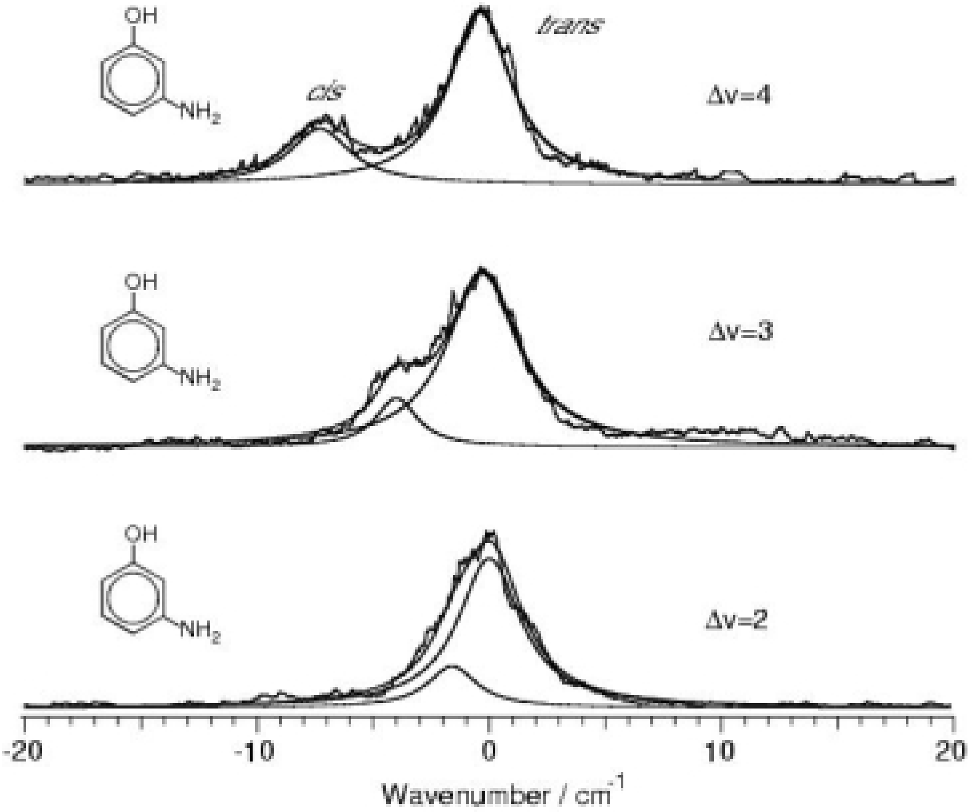
Rotational isomers



cis- and *trans*-*m*-aminophenol.

B3LYP/6-311++G(2d,2p)
Calculated OH bond length difference is only 0.0002Ǻ

In *o*-aminophenol, the *trans* isomer is observed, as little shift in OH-stretch vs phenol is observed.



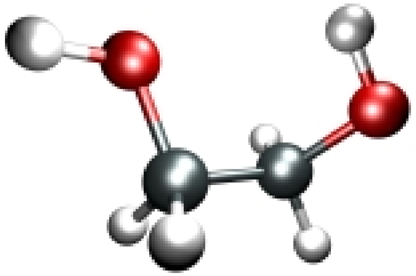
NID-NIR spectroscopy

Robinson, Kjaergaard, Ishiuchi, Shinozaki, Fujii, JPC A 2004.

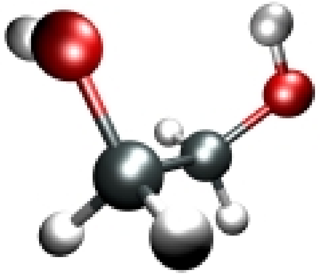
Ethylene Glycol

Different conformers present at room temperature and seen in the overtone spectra.

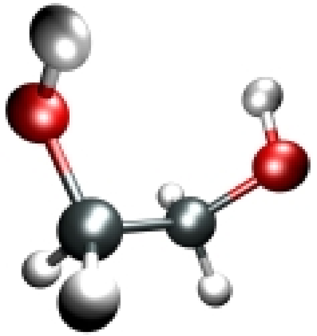
Hydrogen bonding



(~58%)



(~26%)

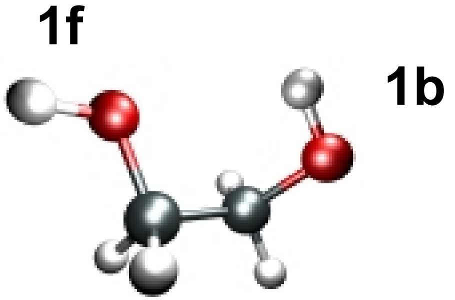


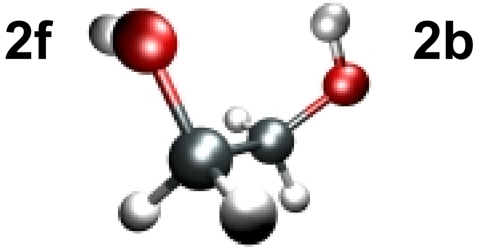
(~10%)

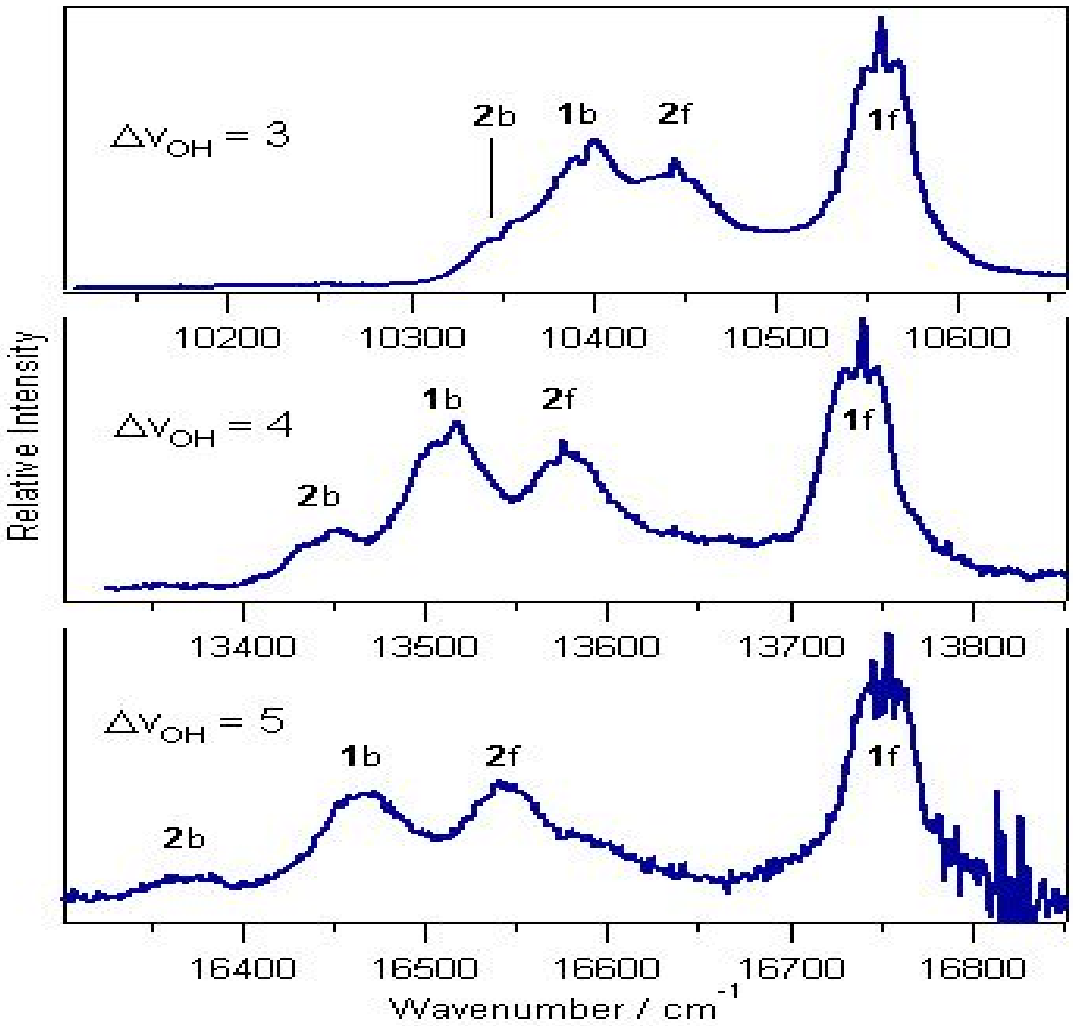
Small molecule, so high level ab initio calculations are possible: CCSD(T)/aug’-cc-pVTZ.

Howard, Jørgensen, Kjaergaard, submitted Aug 05.

Ethylene Glycol

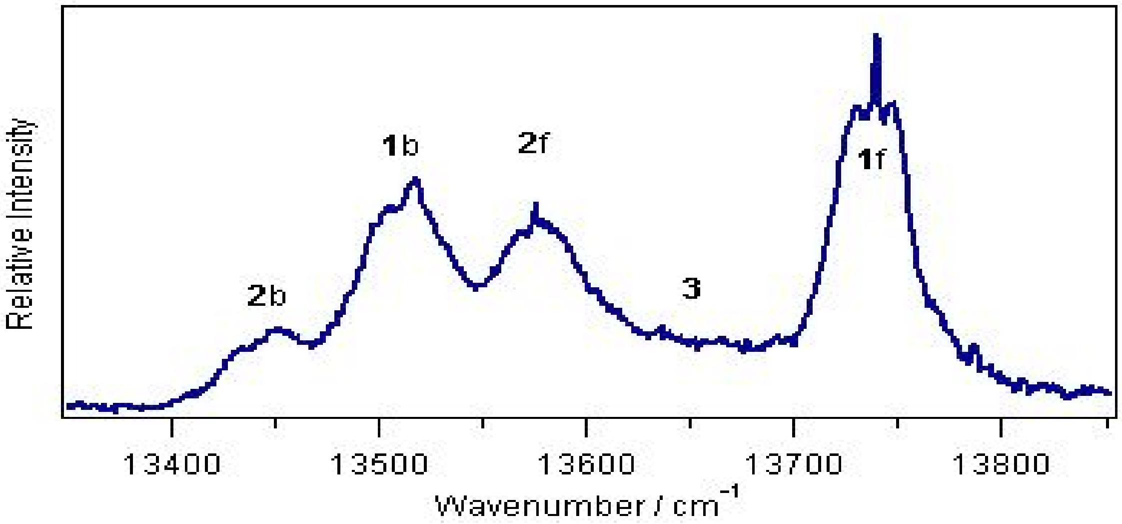






Higher overtones better but also more difficult!

Ethylene Glycol



Conf. 3 predicted in gap ~13666 cm^{-1}. Supported by temperature study.

The CCSD(T)/aug'-cc-pVTZ calculated frequencies, with no scaling, are close to experimental values.
Δ1f = +2cm^{-1}, Δ2f = +25cm^{-1}, Δ1b = +56 cm^{-1}, Δ2f = +43cm^{-1}

Geometric position of bonds 1b and 2b similar to bond 3. Both 1b and 2b shifted relative to 3 ⇒ Hydrogen bonding!

Conclusion

- ☺ Overtone spectroscopy is a very sensitive probe for inter- and intra-molecular interactions.
- ☺ We can calculate quite accurate absolute overtone intensities *ab initio* for species that have not been observed.
  - ☺ Guide experimental efforts to observe these species.
  - ☺ Provide input for atmospheric impact studies.
- ☺ The HCAO local mode model give good absolute overtone intensities in neutral molecules. However, care is required with the choice of *ab initio* method for systems with weak inter- or intra-molecular forces

Acknowledgements

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Masaaki Fujii, Tokyo
Terrence Quickenden, Perth
Jean-Pierre Perchard, Paris
Poul Jørgensen, Aarhus

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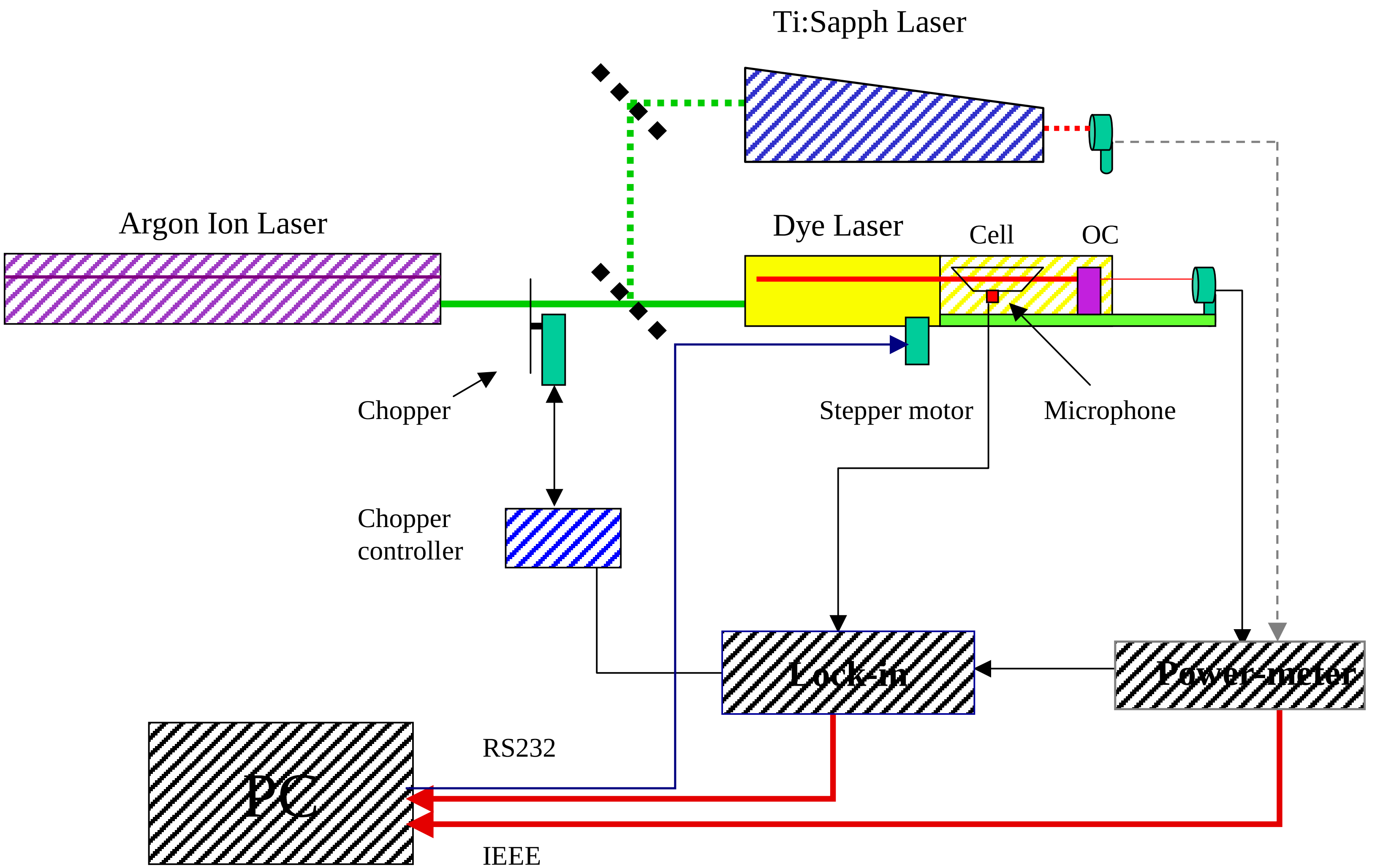
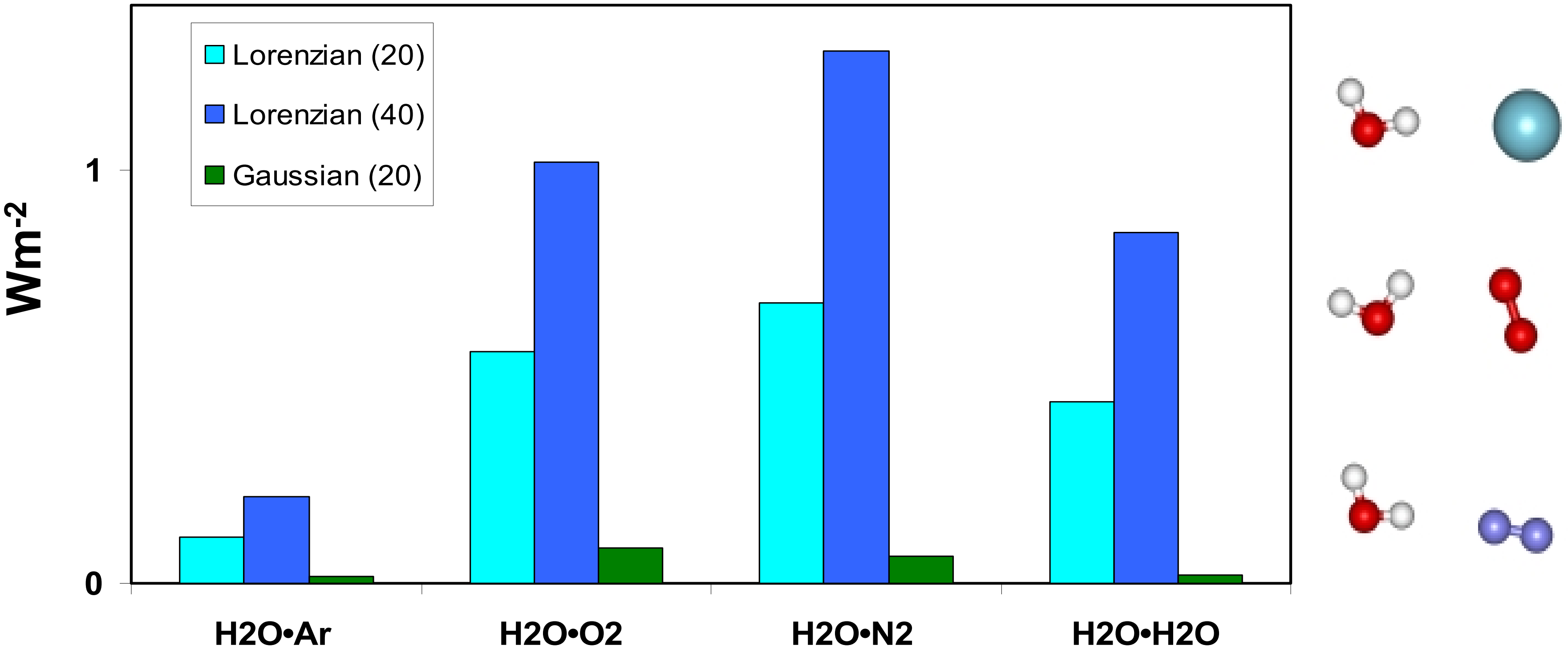
Dunedin

ICL-PAS at Otago



Hydrated complexes

Total absorption of solar radiation

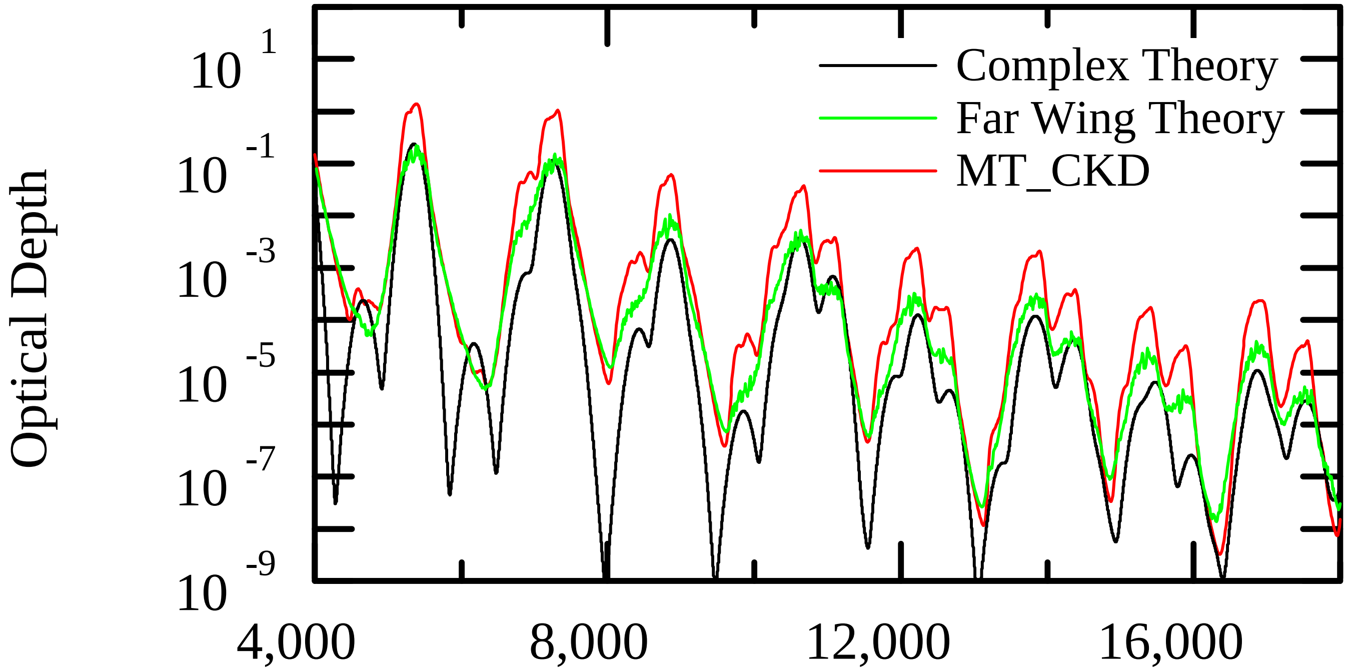


Large dependence on linewidth and shape of the transitions.

Kjaergaard, Robinson, Howard, Daniel, Headrick, Vaida, JPCA 2003

Continuum

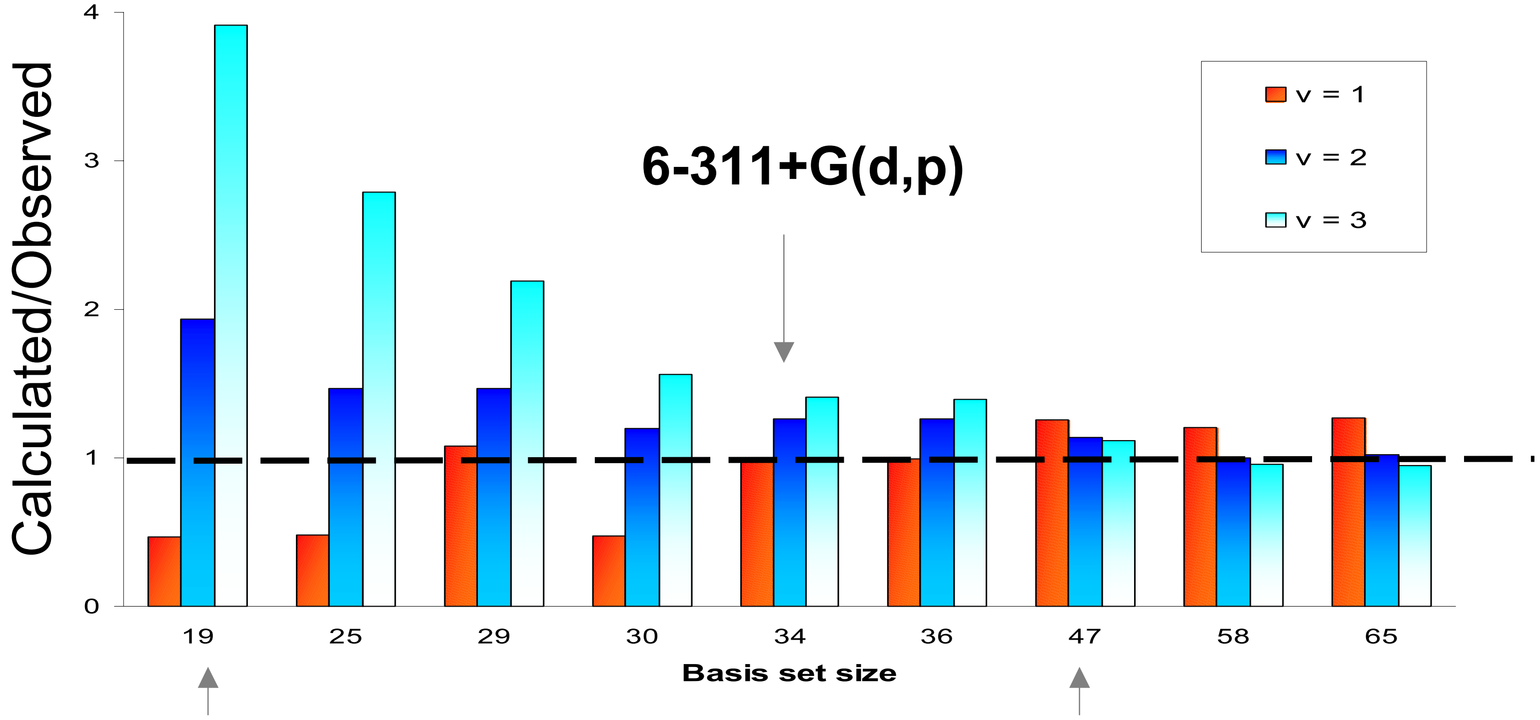
Empirical continuum used to explain discrepancy in models



Seems likely that these hydrated complexes, H_2O•X, are the explanation for this continuum

Effect of basis set size

Oscillator strengths of $|v0\rangle_-|0\rangle$ states for H_2O



6-311+G(d,p)

6-31G(d)

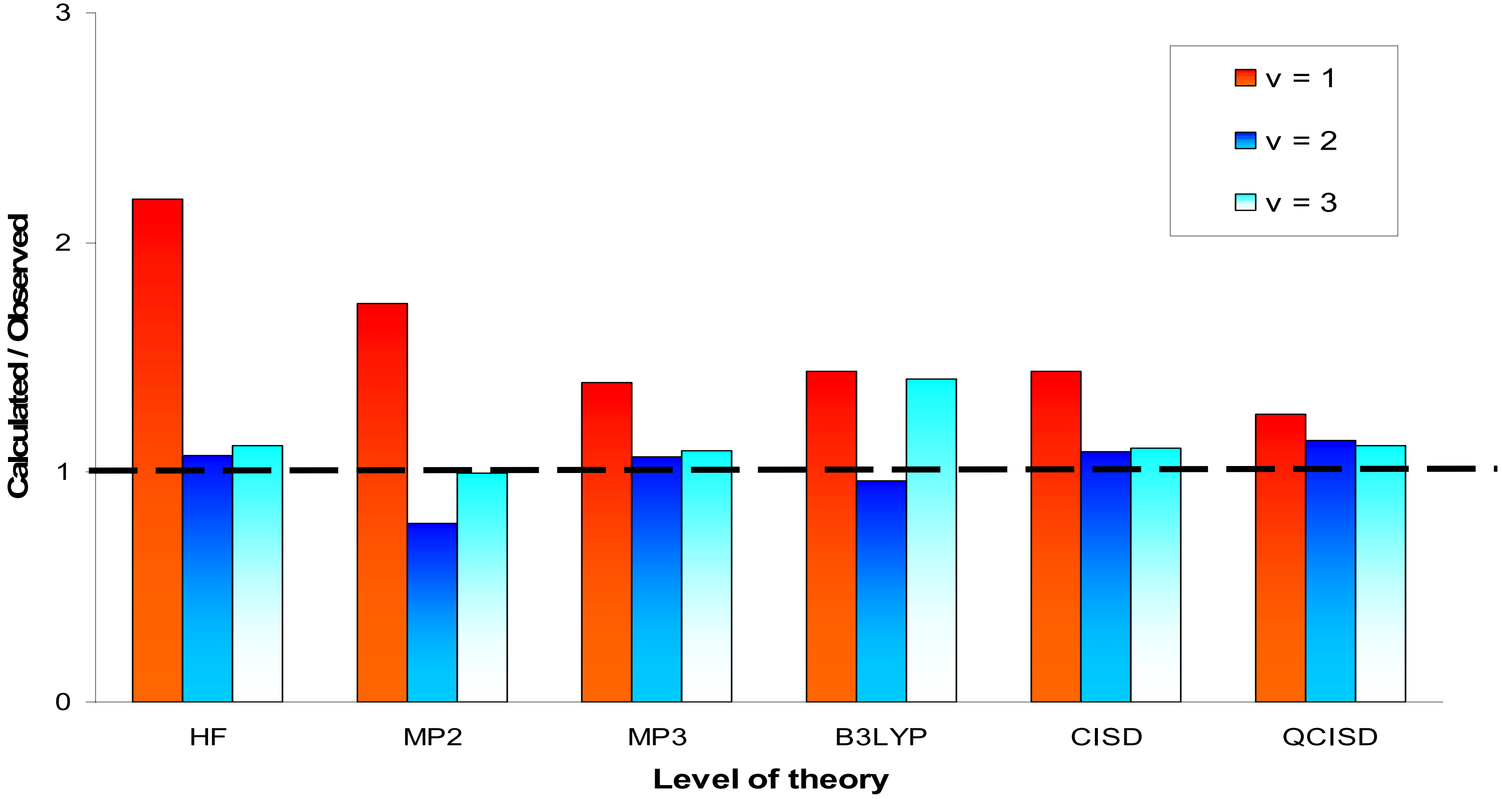
6-311++G(2d,2p)

QCISD level of theory & 3D HCAO local mode model

Kjaergaard, Henry, Mol. Phys. 1994.

Effect of level of theory

Oscillator strengths of $|v0\rangle_{-}|0\rangle$ states for H_2O



6-311++G(2d,2p) basis set & 3D HCAO local mode model

HCAO local mode model

Harmonically Coupled Anharmonic Oscillators (HCAO) local mode model. Two equivalent oscillators:

$$\left(\hat{H}-E_{|00\rangle}\right)/hc=\left(\mathrm{v}_1+\mathrm{v}_2\right)\tilde{\omega}-\left(\mathrm{v}_1^2+\mathrm{v}_1+\mathrm{v}_2^2+\mathrm{v}_2\right)\tilde{\omega}x$$
$$-\gamma'\left(a_1^+a_2+a_1a_2^+\right)$$

$\tilde{\omega}$, $\tilde{\omega}x$, and γ' from observed peak positions $\Rightarrow E_{vib}$ and ψ_{vib}

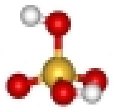
Dipole moment function of two XH bonds

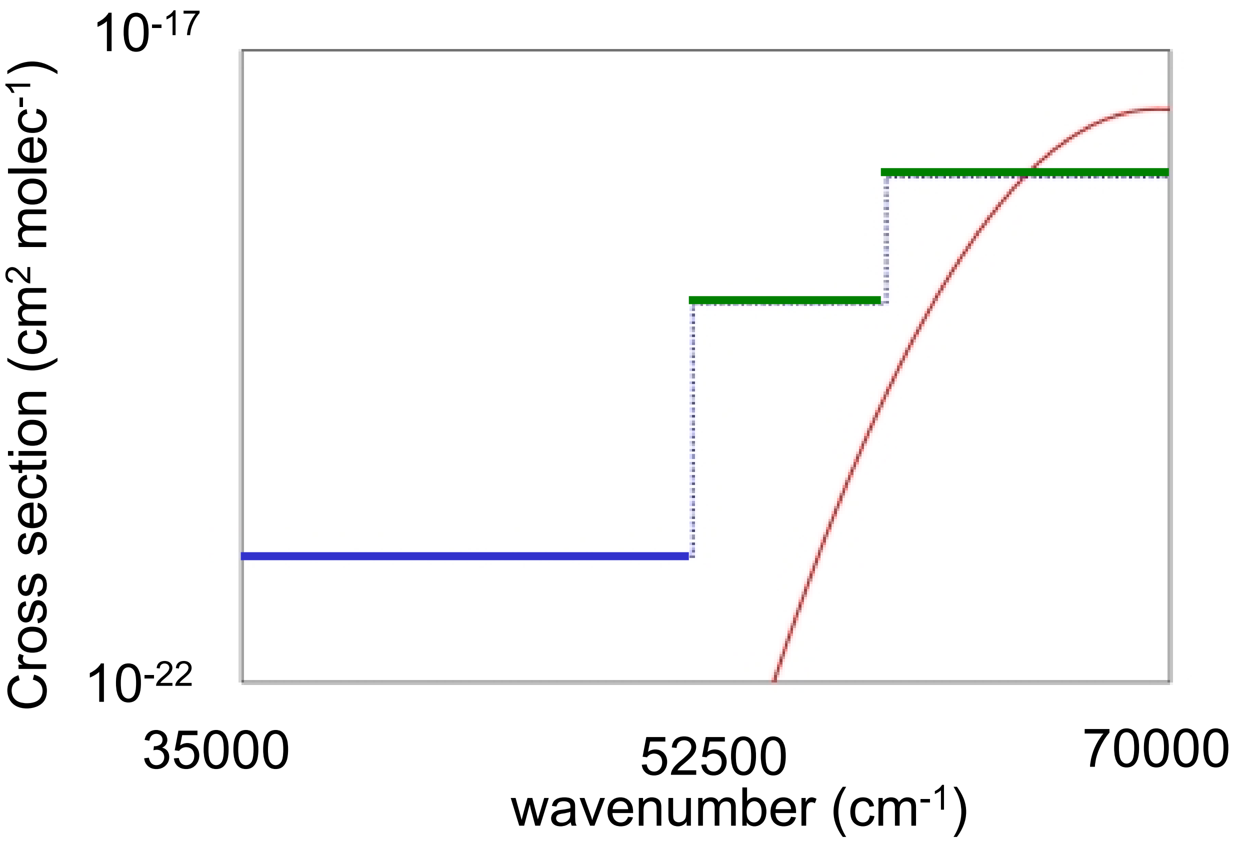
$$\vec{\mu}\left(q_1,q_2\right)=\sum_{i,j}\vec{\mu}_{ij}q_1^iq_2^j$$

Coefficients calculated from 2D *ab initio* dipole moment grid

Intensity calculation reduced to 1D integrals like $\langle \mathrm{v}|q^n|0\rangle$

Electronic spectrum of H_2SO_4





Lowest energy transition at
λ =144 nm
f_{calc}= 0.03

Solar photons
λ > 179 nm
~55800 cm^{-1}

Burkholder, Mills, McKean, GRL (2000)

Hintze, Kjaergaard, Vaida, Burkholder, JPC A (2003)

Robinson, Schofield, Kjaergaard, JCP (2003)