Intra- and Inter-molecular Hydrogen Bonding in Overtone Spectroscopy

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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.

Normal versus Local modes

NIR spectrum of vapor phase sulfuric acid

Overtone spectra dominated by OH-stretching vibrations

Described well by anharmonic local modes.
Vibrational energies described well by isolated OH bond.

<table>
<thead>
<tr>
<th>$\Delta v_{OH}$</th>
<th>Freq. (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs.</td>
<td>Calc.</td>
</tr>
<tr>
<td>1</td>
<td>3609.2</td>
</tr>
<tr>
<td>2</td>
<td>7060.7</td>
</tr>
<tr>
<td>3</td>
<td>10350.3</td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

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

OH-stretch as anharmonic (Morse) oscillator:

\[
\frac{(H - E_0)}{\hbar c} = \nu \tilde{\omega} - (\nu^2 + \nu) \tilde{\alpha} \chi \quad \Rightarrow \quad E_{\text{vib}} \quad \text{and} \quad \psi_{\text{vib}}
\]

\(\tilde{\omega}\) and \(\tilde{\alpha} \chi\) from observed peak positions

Dimensionless oscillator strength:

\[
f_{eg} \propto \tilde{V}_{eg} \left| \langle e | \tilde{\mu} | g \rangle \right|^2
\]

Dipole moment function of single OH bond

\[
\tilde{\mu}(q) = \sum_i \tilde{\mu}_i q^i
\]

From \textit{ab initio} calculated dipole grid
### OH-stretching intensities

Use 1D Morse oscillator model with:

<table>
<thead>
<tr>
<th>$\Delta v_{\text{OH}}$</th>
<th>Int. (km/mol)</th>
<th>$\tilde{\omega}$ = 3768.2 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
<td>Calc.</td>
</tr>
<tr>
<td>1</td>
<td>180</td>
<td>205</td>
</tr>
<tr>
<td>2</td>
<td>6.3</td>
<td>7.0</td>
</tr>
<tr>
<td>3</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.014</td>
</tr>
</tbody>
</table>

G98 FREQ Calculation with B3LYP/6-311++G(2d,2p)

Harmonic Oscillator Linear Dipole calculation $\Rightarrow$ 252 km/mol

Dipole Moment Function

Adding SOH-bending mode has little effect on OH-stretch
Photolysis of $\text{H}_2\text{SO}_4$

$\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}$ \hspace{1cm} $\Delta H \approx 40 \text{kcal/mol} (~ 715 \text{ nm})$


Thus $\text{H}_2\text{SO}_4$ photolysis can proceed via overtone excitations.

Morokuma, Mugurama, JACS (1994).
Relative intensities

Naphthalene

\begin{align*}
\text{HF/6-311+G(d,p)} \\
\text{calculated bond lengths:} \\
\text{CH}_\alpha &= 1.085 \text{ Å} \\
\text{CH}_\beta &= 1.084 \text{ Å}
\end{align*}

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

\begin{align*}
\text{CH}_\alpha \\
\text{CH}_\beta
\end{align*}
Calculate *ab initio* DMF for each of the three non-equivalent CH bonds.

HF/6-31G(d) method.

**Kjaergaard, Turnbull, Henry, JPC 1993.**
Weak van der Waals interaction (including hydrogen bonding) can occur both inter-molecular as in complexes and intra-molecular.

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

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$_2$O•X, are likely to contribute.**

![Molecules](image)

H$_2$O•H$_2$O  
H$_2$O•N$_2$  
H$_2$O•O$_2$

Contribution depends on position, intensity and shape of spectroscopic transitions as well as atmospheric abundance.
Water dimer, H$_2$O•H$_2$O

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

OH bond involved in hydrogen bonding is significantly longer $\Rightarrow$ frequency red shift
Water dimer, H$_2$O•H$_2$O

Simple vibrational model for water dimer

\[ \hat{H} = \hat{H}_\text{acceptor} + \hat{H}_\text{donor} \]

Each H$_2$O 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$_2$O units.

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

Local mode parameters for water

<table>
<thead>
<tr>
<th></th>
<th>QCISD</th>
<th>Expt.</th>
<th>Scaling factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{\omega}$</td>
<td>3934</td>
<td>3870</td>
<td>0.9836</td>
</tr>
<tr>
<td>$\tilde{\omega}_x$</td>
<td>96.5</td>
<td>82.1</td>
<td>0.851</td>
</tr>
</tbody>
</table>

QCISD calculated Local mode parameters for water dimer after scaling

<table>
<thead>
<tr>
<th></th>
<th>OH$_a$</th>
<th>OH$_f$</th>
<th>OH$_b$</th>
<th>H$_2$O expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{\omega}$</td>
<td>3863</td>
<td>3878</td>
<td>3781</td>
<td>3870</td>
</tr>
<tr>
<td>$\tilde{\omega}_x$</td>
<td>81.7</td>
<td>82.3</td>
<td>85.4</td>
<td>82.1</td>
</tr>
</tbody>
</table>

Low, Kjaergaard, JCP 1999.
Ab initio methods

OH-stretching fundamental transitions in H$_2$O•H$_2$O

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

Huang, Miller, JCP 1989.

Low, Kjaergaard, JCP 1999.

Huisken, Kaloudis, Kulcke, JCP 1996.
Water dimer, OH-stretching

First overtone of OH\textsubscript{b}-stretching transition is very weak, only recently observed in Ne matrix.

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:** \[ \langle 1 | q | 0 \rangle \approx 0.07 \quad \langle 1 | q^2 | 0 \rangle \approx 0.0035 \]

**1st overtone:** \[ \langle 2 | q | 0 \rangle \approx -0.0072 \quad \langle 2 | q^2 | 0 \rangle \approx 0.0062 \]

Ab initio dipole expansion coefficients

**OH bond in H\(_2\)O:** \[ \mu_1 \approx 0.76 \quad \mu_2 \approx -0.60 \]

**OH\(_b\) bond in (H\(_2\)O)\(_2\):** \[ \mu_1 \approx 2.53 \quad \mu_2 \approx 2.66 \]
# Water dimer, OH-stretching

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

<table>
<thead>
<tr>
<th>Mode</th>
<th>Ne Matrix</th>
<th>Jet-cooled</th>
<th>HCAO calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>0\rangle_f</td>
<td>2\rangle_b$</td>
<td>7018</td>
</tr>
<tr>
<td>$</td>
<td>20\rangle_+$</td>
<td>7207</td>
<td>7193</td>
</tr>
<tr>
<td>$</td>
<td>2\rangle_f</td>
<td>0\rangle_b$</td>
<td>7237</td>
</tr>
<tr>
<td>$</td>
<td>20\rangle_-$</td>
<td>7245</td>
<td>7250</td>
</tr>
<tr>
<td>$</td>
<td>1\rangle_f</td>
<td>1\rangle_b$</td>
<td>7362</td>
</tr>
</tbody>
</table>

Nizkorodov, Ziemkiewicz, Nesbitt, Knight, JCP (2005)  
HCAO calculation at QCISD/6-311++G(2d,2p)
Water dimer, stretch-bend

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

\[ |0\rangle_f |1\rangle_b |1\rangle_\beta \quad |10\rangle_f |1\rangle_\beta \]

Water dimer in the atmosphere

$\Delta v_{\text{OH}} = 3\frac{1}{2}$  $|0\rangle_f |4\rangle_b$  $\Delta v_{\text{OH}} = 4$

H$_2$O$\cdot$H$_2$O (calc)

H$_2$O (observed)

Atmos. observation of water dimer.

Abundance $\sim$1/1000 of water monomer.

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

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 $\Delta v_{OH} = 3$ region

Bond lengths:
$OH_b = 0.964 \text{ Å}$
$OH_f = 0.961 \text{ Å}$

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

Rotational isomers

cis- and trans-m-aminophenol.

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

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

NID-NIR spectroscopy

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

The CCSD(T)/aug'-cc-pVTZ calculated frequencies, with no scaling, are close to experimental values.

$\Delta f_1 = +2 \text{cm}^{-1}$, $\Delta f_2 = +25 \text{cm}^{-1}$, $\Delta b_1 = +56 \text{ cm}^{-1}$, $\Delta f_2 = +43 \text{ cm}^{-1}$

Conf. 3 predicted in gap $\sim 13666 \text{ cm}^{-1}$. Supported by temperature study.

Geometric position of bonds 1b and 2b similar to bond 3. Both 1b and 2b shifted relative to 3 $\Rightarrow$ Hydrogen bonding!
Overtone spectroscopy is a very sensitive probe for inter- and intra-molecular interactions.

We can calculate quite accurate absolute overtone intensities \textit{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 \textit{ab initio} method for systems with weak inter- or intra-molecular forces.
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Hydrated complexes

Total absorption of solar radiation

Large dependence on linewidth and shape of the transitions.

Kjaergaard, Robinson, Howard, Daniel, Headrick, Vaida, JPCA 2003
Empirical continuum used to explain discrepancy in models

Seems likely that these hydrated complexes, $\text{H}_2\text{O} \cdot X$, are the explanation for this continuum.
Oscillator strengths of $|v0\rangle$-$|0\rangle$ states for H$_2$O

Effect of basis set size

QCISD level of theory & 3D HCAO local mode model

Effect of level of theory

Oscillator strengths of $|v0>\cdot|0>$ states for H$_2$O

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:

\[
\left( \hat{H} - E_{00} \right)/\hbar c = \left( v_1 + v_2 \right) \tilde{\omega} - \left( v_1^2 + v_1 + v_2^2 + v_2 \right) \tilde{\omega} x - \gamma' \left( a_1^+ a_2 + a_1 a_2^+ \right)
\]

\(\tilde{\omega}, \tilde{\omega} x,\) and \(\gamma'\) from observed peak positions \(\Rightarrow E_{\text{vib}}\) and \(\psi_{\text{vib}}\)

Dipole moment function of two XH bonds

\[
\tilde{\mu}(q_1, q_2) = \sum_{i,j} \tilde{\mu}_{ij} q_i^i q_j^j
\]

Coefficients calculated from 2D \textit{ab initio} dipole moment grid

Intensity calculation reduced to 1D integrals like \(\langle v | q^n | 0 \rangle\)
Electronic spectrum of H$_2$SO$_4$

Lowest energy transition at $\lambda = 144$ nm
$f_{\text{calc}} = 0.03$

Solar photons
$\lambda > 179$ nm
$\sim 55800$ cm$^{-1}$

Burkholder, Mills, McKeen, GRL (2000)