Calculation of Cold Infrared Spectra of Water Dimer

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Background

The spectroscopy of water dimer has been studied for more than half a century, and its OH–O hydrogen bond is considered by many to be the archetype of hydrogen bonds. A range of experimental jet-cooled spectra have been published of the water dimer OH-stretching region (fundamental and first overtone), but a firm assignment of the observed transitions has not yet been possible due to the lack of accurate calculations. The water dimer is a deceptively simple molecule (only six nuclei and 20 electrons) with eight versions of its equilibrium structure connected by low-energy barriers. The light molecular frame and the highly anharmonic potential energy surface result in large amplitude motion, making conventional vibrational models unreliable. We calculate the spectrum of water dimer in the OH-stretching region with a finite basis representation of an effective Hamiltonian.

Figure 1: Definition of the intermolecular coordinates of the water dimer and the numbering of the atoms of the two H2O units. The two centers of mass are used to define the last internal coordinate, \( \mu = [c_\mu R_\mu - c_\mu R_\mu] \).

The Vibrational Model

Podolsky Hamiltonian with CCSD(T)-F12a/cc-pVTZ-F12 potential energy surface:

\[
H = \frac{1}{2} \sum_{ij} \left( \frac{\partial^2}{\partial q_i \partial q_j} + V \right), \text{ where } p_i = -i \frac{\partial}{\partial q_i}
\]

\[
g = \text{det}(g), g_{ij} = \sum_m a_m \delta_{q_i, q_m} \delta_{q_j, q_m}, G_{ij} = \sum_k a_k \delta_{q_i, q_k} \delta_{q_j, q_k}
\]

Many-mode expansion of \( G, V \), and \( \mu \), the (dipole moment function), shown here for \( V' \):

\[
V(q_1, q_2, ..., q_{12}) = V_0 + \sum_i V_{1i}^{1D}(q_i) + \sum_{i<j} V_{ij}^{2D}(q_i, q_j) + \sum_{i<j<k} V_{ijk}^{3D}(q_i, q_j, q_k)
\]

1D basis functions expressed as symmetrized products of 1D eigenvectors:

\[
\Psi_{\chi_1\chi_2}(q_1, q_2) = \frac{1}{\sqrt{2}} \left( \Psi_{\chi_1}(q_1) \Psi_{\chi_2}(q_2) + \Psi_{\chi_2}(q_1) \Psi_{\chi_1}(q_2) \right)
\]

1D eigenvectors (at reference value of all other coordinates) are obtained from:

\[
\mathcal{H}(q_i) \Psi_{\chi_i}(q_i) = \epsilon_i \Psi_{\chi_i}(q_i)
\]

Energy ceilings and polyad truncations are used to control the size of the 1D basis.1

OH-stretching Fundamental Region

Table 2: Calculated \( v \) and experimental \( v \) transition wavenumbers (\( \nu \), in cm\(^{-1}\)) and relative oscillator strengths (\( f \), in parentheses) for the OH-stretching fundamental transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>( \nu ) cm(^{-1})</th>
<th>( f ) x 10(^{-8})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_{OH} )</td>
<td>3555.1 (100)</td>
<td>3601</td>
</tr>
<tr>
<td>( v_{OH} )</td>
<td>3651.5 (2.5)</td>
<td>3650.6 (3.4)</td>
</tr>
<tr>
<td>( v_{OH} )</td>
<td>3769.6 (24)</td>
<td>3726.7 (54)</td>
</tr>
<tr>
<td>( v_{OH} )</td>
<td>3746.0 (22)</td>
<td>3742.6 (33)</td>
</tr>
</tbody>
</table>

*The model includes the four OH-stretching modes and the two OH-bending modes.

OH-stretching First Overtone Region

Table 3: Calculated \( v \) transition wavenumbers (\( \nu \)), oscillator strengths (\( f \)), and rotational band types for selected OH-stretching transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>( \nu ) cm(^{-1})</th>
<th>( f ) x 10(^{-8})</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2v_{OH} )</td>
<td>7045.9</td>
<td>5.5</td>
<td>A/C</td>
</tr>
<tr>
<td>( 2v_{OH} )</td>
<td>7187.6</td>
<td>9.3</td>
<td>A/C</td>
</tr>
<tr>
<td>( 2v_{OH} )</td>
<td>7221.2</td>
<td>25</td>
<td>A/C</td>
</tr>
<tr>
<td>( 2v_{OH} )</td>
<td>7231.1</td>
<td>44</td>
<td>B</td>
</tr>
</tbody>
</table>

Figure 4: Infrared-ultraviolet vibrationally mediated dissociation spectrum of water dimer.10 Reprinted from [J. Chem. Phys. 122, 194316 (2005)], with the permission of AIP Publishing.

Acknowledgements

We are grateful to José Fernández, Andrei Vilesov, Martin Suhm and Ling Jiang for sharing their experimental data. We also thank José Fernández and Keith Shine for helpful discussions on the water dimer. We acknowledge funding from the Independent Research Fund Denmark (Grant No. 9040-001428), and the Novo Nordisk Foundation Interdisciplinary Synergy Program (Grant No. NNFI05C007374).

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Figure 5: PGOPHER11 simulated vibrational-rotational band profiles at 10 K.