How to use the spectra of Van der Waals and hydrogen bonded clusters to improve (ab initio) intermolecular force fields;

**Theoretical tools**

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Molecular beam spectroscopy of Van der Waals molecules
Experimental Set-Up

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

Preamble: Born-Oppenheimer approximation

1. electronic structure calculations
   \[\Rightarrow\] potential energy surface

2. “dynamics” \(=\) nuclear motion problem
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

Fix rotating frame to the (vibrating) molecule by Eckart conditions

$\implies$ Eckart/Watson Hamiltonian

Neglect of Coriolis coupling, linearized vibrations, quadratic
approximation of potential $V$

$\implies$ rigid rotor/harmonic oscillator model

- Wilson $GF$-matrix method
- normal coordinates
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 $q = \{\ldots, q_k, \ldots\}$ $\Rightarrow$ complicated kinetic energy operator $T$
Kinetic energy operator $T$ for curvilinear coordinates
—An exercise in mechanics

Overall/internal rotations, tunneling, etc.

$\Rightarrow$ curvilinear coordinates $\mathbf{q} = \left( \begin{array}{c} q_1 \\ \vdots \\ q_k \\ \vdots \\ \end{array} \right)$

and conjugate momenta $\mathbf{p}$.

Start from Cartesian coordinates of all nuclei, with mass $m_i$

$x_i = \left( \begin{array}{c} x_i \\ y_i \\ z_i \end{array} \right)$

momenta

$p_i = m_i \dot{x}_i$
1\textsuperscript{st} route

Quantize: \[ p_i \rightarrow \frac{\hbar}{i} \left( \frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right) \]

kinetic energy

\[ T = \sum_i \frac{p_i^2}{2m_i} \rightarrow \sum_i -\hbar^2 \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \]

Use chain rule

\[ \frac{\partial}{\partial x_i} = \sum_k \frac{\partial q_k}{\partial x_i} \frac{\partial}{\partial q_k} = \sum_k (J^{-1})_{ik} \frac{\partial}{\partial q_k} \]

\( J \) is the Jacobian \( J_{ik} = \frac{\partial x_i}{\partial q_k} \) of the transformation from \( x_i \) to \( q \)

N.B. \( J = J(q) \) for non-linear transformations!

\[ \Rightarrow \text{kinetic energy operator } T \text{ in terms of } q_k \text{ and } p_k = \frac{\hbar}{i} \frac{\partial}{\partial q_k} \]
2nd route

\[ \dot{x}_i = \frac{dx_i}{dt} = \sum_k \frac{\partial x_i}{\partial q_k} \frac{dq_k}{dt} = \sum_k J_{ik} \dot{q}_k \]

\[ T = \frac{1}{2} \sum_i m_i |\dot{x}_i|^2 = \frac{1}{2} \dot{q}^T J^T M J \dot{q} \]

Metric tensor \( G = J^T M J \), where \( M \) is a diagonal matrix with masses \( m_i \) on the diagonal

\[ \Rightarrow T = \frac{1}{2} \dot{q}^T G \dot{q} \quad \text{(Lagrange)} \]

Conjugate momenta

\[ p_k = \frac{\partial T}{\partial \dot{q}_k} = \sum_{k'} G_{kk'} \dot{q}_{k'} \]

\[ \Rightarrow \dot{q} = G^{-1} p \]

\[ T = \frac{1}{2} p^T G^{-1} p \quad \text{(Hamilton)} \]
Quantize:

\[ p_k = \frac{\hbar}{i} \frac{\partial}{\partial q_k} \]

\[ T = \frac{1}{2} g^{-1/2} p^T g^{1/2} G^{-1} p \] (Podolsky)

with \( g = \text{det}(G) \)

Symmetric form:

\[ T = \frac{1}{2} g^{-1/4} p^T g^{1/2} G^{-1} p g^{-1/4} \]

Since \( p \) is non-Hermitian and \( p^\dagger = g^{-1/2} p^T g^{1/2} \) one may also write

\[ T = \frac{1}{2} p^\dagger G^{-1} p \]

Convenient in basis set and DVR calculations!
In practice:

- The 2nd route is usually more convenient.

- For constrained motions, i.e., when the number of $q_k$ is smaller than the number of $x_i$, $y_i$, $z_i$: only the 2nd route is guaranteed to work!

**Observation regarding the potential $V$**

It is not sufficient to use only the second derivatives of $V$ (the force constants) at the equilibrium structure, as in the harmonic oscillator model of semi-rigid molecules.

One must know the full potential surface!
Exercise 1:
Kinetic energy operator of point mass in polar coordinates

Polar coordinates: \( q = \begin{pmatrix} R \\ \vartheta \\ \varphi \end{pmatrix} \)

\( x = R \sin \vartheta \cos \varphi \)
\( y = R \sin \vartheta \sin \varphi \)
\( z = R \cos \vartheta \)

Jacobian

\( J = \begin{pmatrix} \sin \vartheta \cos \varphi & R \cos \vartheta \cos \varphi & -R \sin \vartheta \sin \varphi \\ \sin \vartheta \sin \varphi & R \cos \vartheta \sin \varphi & R \sin \vartheta \cos \varphi \\ \cos \vartheta & -R \sin \vartheta & 0 \end{pmatrix} \)

Metric tensor

\( G = mJ^T J = m \begin{pmatrix} 1 & 0 & 0 \\ 0 & R^2 & 0 \\ 0 & 0 & R^2 \sin^2 \vartheta \end{pmatrix} \)

\( g = \det(G) = m^3 R^4 \sin^2 \vartheta \)
\[ T = \frac{1}{2} g^{-1/2} p^T g^{1/2} G^{-1} p \quad \text{with} \quad p = \frac{\hbar}{i} \left( \begin{array}{c} \partial/\partial R \\ \partial/\partial \vartheta \\ \partial/\partial \varphi \end{array} \right) \]

yields

\[ T = -\frac{\hbar^2}{2m} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{R^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \sin \vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{R^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right] \]

Introduce angular momentum \( l = x \times p \) (Cartesian)

\[ l = \begin{pmatrix} l_x \\ l_y \\ l_z \end{pmatrix} = \frac{\hbar}{i} \left( \begin{array}{ccc} -\sin \varphi & -\cot \vartheta \cos \varphi \\ \cos \varphi & -\cot \vartheta \sin \varphi \\ 0 & -1 \end{array} \right) \left( \begin{array}{c} \partial/\partial \vartheta \\ \partial/\partial \varphi \end{array} \right) \]

gives

\[ T = -\frac{\hbar^2}{2mR^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{l^2}{2mR^2} \]
Exercise 2:

The rigid rotor Hamiltonian

Rigid rotor: a set of particles with masses $m_i$ and fixed positions $a_i$ with respect to a rotating frame.

Coordinates are the Euler angles $q = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$ that relate the positions of the particles

$$x_i[t] = R(\alpha, \beta, \gamma) a_i \equiv R(\alpha[t], \beta[t], \gamma[t]) a_i$$

to the fixed coordinates $a_i$ by the Euler rotation

$$R(\alpha, \beta, \gamma) = R_z(\alpha) R_y(\beta) R_z(\gamma)$$
Rewrite the classical expression for the kinetic energy

\[ T = \frac{1}{2} \sum_i m_i \dot{x}_i T \dot{x}_i \]

as

\[ T = \frac{1}{2} \omega^T I \omega \]

where \( \omega \) is the angular velocity of the rotating frame and \( I \) the inertia tensor of the rigid rotor.

\( I \) contains the fixed particle coordinates \( a_i \) and masses \( m_i \). Its eigenvalues are the moments of inertia \( I_a, I_b, I_c \). \( a, b, c \) are the principal axes.
From the properties of rotation matrices it follows that $\omega$ is related to the time derivatives of the Euler angles as

$$\omega = U \dot{q} = \begin{pmatrix} -\sin \beta \cos \gamma & \sin \gamma & 0 \\ \sin \beta \sin \gamma & \cos \gamma & 0 \\ \cos \beta & 0 & 1 \end{pmatrix} \begin{pmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{pmatrix}$$

From the general expression

$$T = \frac{1}{2} \dot{q}^T G \dot{q}$$

for the kinetic energy we then find that the metric tensor is

$$G = U^T I U$$

For a symmetric top with $I_a = I_b$

$$G = \begin{pmatrix} I_a \sin^2 \beta + I_c \cos^2 \beta & 0 & I_c \cos \beta \\ 0 & I_a & 0 \\ I_c \cos \beta & 0 & I_c \end{pmatrix}$$

$$g = \det(G) = I_a^2 I_c \sin^2 \beta$$
Substitution of $G$ into the Podolsky formula with

$$p = \frac{\hbar}{i} \begin{pmatrix} \partial / \partial \alpha \\ \partial / \partial \beta \\ \partial / \partial \gamma \end{pmatrix}$$

and use of the angular momentum operator

$$J = \begin{pmatrix} J_a \\ J_b \\ J_c \end{pmatrix} = \begin{pmatrix} -\frac{\cos \gamma}{\sin \beta} & \sin \gamma & \cot \beta \cos \gamma \\ \frac{\sin \beta}{\sin \gamma} & \cos \gamma & -\cot \beta \sin \gamma \\ \frac{\sin \beta}{\sin \gamma} & 0 & 1 \end{pmatrix} p$$

gives the (general) result

$$T = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

This looks identical to the classical result for $T$, but the simplification of the Podolsky expression for $T$ is not trivial because the momentum operator $p$ is not Hermitian.
Exercise:

- Prove, by partial integration, that

\[ p^\dagger = \frac{1}{\sin \beta} p^T \sin \beta \]

Hence, \( p \) is not Hermitian, but \( \frac{1}{\sin \beta} p \) is Hermitian.

- Prove also that the angular momentum operators

\[
J = \begin{pmatrix}
J_a \\
J_b \\
J_c
\end{pmatrix} = \begin{pmatrix}
\frac{-\cos \gamma}{\sin \beta} & \sin \gamma & \cot \beta \cos \gamma \\
\frac{\sin \beta}{\sin \gamma} & \cos \gamma & -\cot \beta \sin \gamma \\
\frac{\sin \beta}{\sin \gamma} & 0 & 0 & 1
\end{pmatrix} p
\]

are Hermitian.
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 \( E^* \).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Point group</th>
<th>PI group</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Molecule 1" /></td>
<td>( C_{2v} )</td>
<td>( {E, E^<em>, (12), (12)^</em>} )</td>
</tr>
<tr>
<td><img src="image2.png" alt="Molecule 2" /></td>
<td>( C_{3v} )</td>
<td>( {E, (123), (132), (12)^<em>, (13)^</em>, (23)^*} )</td>
</tr>
</tbody>
</table>
Proof:

Every feasible $PI$ operation corresponds to a rotation of the reference (equilibrium) structure, and a point-group operation on the internal (vibrational) coordinates.

J. D. Louck and H. W. Galbraith

*Eckart vectors, Eckart frames, and polyatomic molecules*

Example: $H_2O$

<table>
<thead>
<tr>
<th>PI operation</th>
<th>frame rotation</th>
<th>point group operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12)</td>
<td>$R_z(\pi) = C_{2z}$</td>
<td>$C_{2z}$</td>
</tr>
<tr>
<td>$E^*$</td>
<td>$R_y(\pi) = C_{2y}$</td>
<td>$\sigma_{xz}$ reflection</td>
</tr>
<tr>
<td>(12)*</td>
<td>$R_x(\pi) = C_{2x}$</td>
<td>$\sigma_{yz}$ reflection</td>
</tr>
</tbody>
</table>

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”.

$\Rightarrow$ additional “feasible” $PI$-operations

**Example**  
$NH_3$

<table>
<thead>
<tr>
<th>Semi-rigid $NH_3$</th>
<th>$PI(C_{3v}) = {E, (123), (132), (12)^<em>, (13)^</em>, (23)^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inversion + tunneling (umbrella up ↔ down)</td>
<td>$PI(D_{3h}) = PI(C_{3v}) \otimes {E, E^<em>}$ Also $(12), (13), (23)$ and $E^</em>$ are feasible</td>
</tr>
</tbody>
</table>

Additional feasible $PI$-operations $\iff$ observable tunneling splittings in spectrum
Applications

*Atom-molecule dimers*

Example: Ar-CH$_4$
Ar–CH₄ infrared spectrum ($\nu_3$ mode) measured by Roger Miller
Ar–CH$_4$ ab initio SAPT potential ($\phi = 0^\circ$)

Computed for 34 points, $T_d$ symmetry of CH$_4$ $\Rightarrow$ 736 geometries
Second virial coefficient

\[ B_2(T) = B_2^{(0)}(T) + B_2^{(1)}(T) \]

Classical

\[ B_2^{(0)}(T) = \frac{N_A}{2} \int \left( 1 - \exp \left[ -\beta V(R) \right] \right) dR \]

First quantum correction

\[
B_2^{(1)}(T) = \frac{N_A \hbar^2 \beta^3}{48 \mu} \int \exp \left[ -\beta V(R) \right] \left( \frac{\partial V}{\partial R} \right)^2 dR \\
- \frac{N_A \beta^2}{24} \int \exp \left[ -\beta V(R) \right] \left[ \left( b_0 \hat{l}^2 + \frac{\hat{l}^2}{2 \mu R^2} \right) V(R) \right] dR
\]

with \( R = (R, \theta, \phi) \), the associated angular momentum operator \( l \), and \( dR = R^2 \sin \theta \, dR \, d\theta \, d\phi \)
Second virial coefficient of Ar-methane
 Calculation of (quasi-)bound states of \( \text{Ar--CH}_4 \)

**Hamiltonian** (for vibrational state \( v \))

\[
H_v = B_v j^2 + \frac{1}{2\mu R^2} \left[ -\hbar^2 \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + J^2 + j^2 - 2 j \cdot J \right] + V_v(R, \theta, \phi)
\]

**Basis**

\[
| n, j, k, K \rangle = \chi_n(R) D^{(j)}_{KK'}(0, \theta, \phi)^* D^{(J)}_{MK}(\alpha, \beta, \gamma)^*
\]

\( \nu_3 \) excited state is 3-fold degenerate \( \Rightarrow \) basis \( | v_{3x} \rangle, | v_{3y} \rangle, | v_{3z} \rangle \)

Vibrational angular momentum \( l_3 = 1 \) \( \Rightarrow \) extra term \( -2 \zeta_3 B l_3 \cdot j \) in Hamiltonian

**Permutation-inversion symmetry group** \( PI(T_d) \)

- Van der Waals “vibrations” \( A_1, A_2, E, F_1, F_2 \)
- \( \nu_3 \) mode has \( F_2 \) symmetry
- Nuclear spin species \( A, F \) and \( E \)
Ar–CH$_4$ bound levels (ground state)

<table>
<thead>
<tr>
<th></th>
<th>free</th>
<th>Ar–CH$_4$</th>
<th>Ar–CH$_4$</th>
<th>Ar–CH$_4$</th>
<th>Ar–CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>J=K=0</td>
<td>J=</td>
<td>K</td>
<td>=1</td>
<td>J=</td>
</tr>
</tbody>
</table>

$cm^{-1}$
Monomer P(1)  
Monomer Q(1)  
Monomer R(0)  
Monomer R(1)

Measured

Calculated

![Graphs showing measured and calculated monomer peaks.](Image)
IR spectrum ($\nu_3$ mode of CH$_4$ at 3020 cm$^{-1}$)  
⇒ vibrational predissociation

Hamiltonian must be extended to include $\nu_3$ and $\nu_1$ (harmonic) modes of CH$_4$.

Ar–CH$_4$ potential must depend on $\nu_3$ and $\nu_1$ normal coordinates.

Same basis except for radial functions $\chi_n(R)$.

Solve coupled-channel equations by propagation from $R = 0 \rightarrow \infty$
⇒ Photodissociation cross sections
  Spectral linewidths (excited state lifetimes)
  Product distribution
Ar–CH₄ photodissociation cross sections

\[ J, K = 1, 0 \rightarrow 0, 0 \]

\[ J, K = 0, 0 \rightarrow 1, 1 \]

Energy (cm\(^{-1}\))

\[ \sigma(E) \]

x \(10^6\)

x \(10^7\)
Molecule-molecule dimers

Examples: HF–HF, HCl–HCl, H₂O–H₂O, NH₃–NH₃

Hamiltonian

\[ H = T_A + T_B - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{J^2 + j_{AB}^2 - 2j_{AB} \cdot J}{2\mu R^2} + V(R, \omega_A, \omega_B) \]

where \( j_{AB} = j_A + j_B \)

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

\[ | n j_A k_A j_B k_B j_{AB} K \rangle^{J,M} = \chi_n(R) \ D^{(J)}_{MK}(\alpha, \beta, 0)^* \]

\[ \times \sum_{m_A, m_B} D^{(j_A)}_{m_A k_A} (\omega_A)^* D^{(j_B)}_{m_B k_B} (\omega_B)^* \langle j_A, m_A; j_B, m_B | j_{AB}, K \rangle \]
PI group $G_4 = \{E, P_{AB}\} \otimes \{E, E^*\}$

Equilibrium geometry has $C_s$ symmetry

$\Rightarrow$ 2-fold tunneling splitting of rovib levels
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
NH$_3$–NH$_3$

**PI group** $G_{36}$ for rigid NH$_3$ monomers,
$G_{144}$ for inverting NH$_3$ monomers

Equilibrium geometry has $C_s$ symmetry

$\Rightarrow$ 18 × 4 fold tunneling splitting of rovib levels

Some of the levels are Pauli-forbidden for NH$_3$, but allowed for ND$_3$
Water trimer

PI group $G_{48} = G_6 \otimes G_8$

$G_6$ from torsional tunneling flips

$G_8 = G_2 \otimes G_2 \otimes G_2$ from bifurcation tunneling

Equilibrium geometry has no symmetry

$\Rightarrow 6 \times 8$ fold tunneling splitting of rovib levels
Hamiltonian for torsional motion in water trimer

Fixed-axis monomer rotations + overall rotation

Coordinates: - torsional angles $\chi_A, \chi_B, \chi_C$
- Euler angles $\alpha, \beta, \gamma$

From the Podolsky formula one obtains

$$H = \frac{1}{2} \left( J^\dagger - j^\dagger \right) \mu^{-1} (J - j) + \frac{1}{2} \sum_{\nu=A,B,C} \Lambda^{-1}_{\nu} p^\dagger_{\nu} p_{\nu} + V(\chi_A, \chi_B, \chi_C)$$

with

$$p_{\nu} = \frac{\hbar}{i} \frac{\partial}{\partial \chi_{\nu}}$$

and torsional angular momentum

$$j = \sum_{\nu=A,B,C} j_{\nu}$$
The operators

\[ \dot{j}_\nu = \Lambda_{\nu}^{-1} b_\nu(\chi_\nu) p_\nu \]

are non-Hermitian because they contain functions \( b_\nu(\chi_\nu) \) depending on the torsional angles \( \chi_\nu \).

\( \Lambda_\nu \) is the moment of inertia of monomer \( \nu \) about the fixed rotation axis.

The trimer inertia tensor \( \mu \) is nearly independent of the torsional angles \( \chi_\nu \). When \( \mu \) is diagonalized the Hamiltonian can be separated

\[ H = H^{\text{rot}} + H^{\text{Cor}} + H^{\text{int}} \]
Overall rotation

\[ H^{\text{rot}} = A(J_x^2 + J_y^2) + CJ_z^2 \]

with rotational constants

\[ A = B = (2\mu_{xx})^{-1} = (2\mu_{yy})^{-1} \quad C = (2\mu_{zz})^{-1} \]

Coriolis coupling

\[ H^{\text{Cor}} = -\frac{1}{2}A [(J_+ + J_\uparrow)J_+ + (J_- + J_\uparrow)J_-] - C(J_z + J_\uparrow)J_z \]

Internal motions:

torsions and tunneling flips hindered by potential \( V(\chi_A, \chi_B, \chi_C) \)

\[ H^{\text{int}} = -\frac{\hbar^2}{2\Lambda} \sum_\nu \frac{\partial^2}{\partial \chi_\nu^2} + \frac{1}{2}A \left( J_+^\dagger J_+ + J_-^\dagger J_- \right) + Cj_z^\dagger j_z + V(\chi_A, \chi_B, \chi_C) \]
Quantitative calculations

- Three-dimensional DVR for $\chi_A, \chi_B, \chi_C$ with sinc-functions

$$\xi_n(\chi) = \Delta^{-1/2} \frac{\sin \pi (\frac{\chi}{\Delta} - n)}{\pi (\frac{\chi}{\Delta} - n)}.$$ 

- Multiplied by symmetric rotor functions

$$D_{MK}^J(\alpha, \beta, \gamma)^*$$

for the overall rotation.

- Construct $H$-matrix and diagonalize to obtain the torsional states of the trimer. Use PI symmetry group $G_6$.

- Include bifurcation tunneling splittings with parameterized model and application of the PI group $G_{48}$. 
Rotational structure in trimer spectra

Could not be represented by semi-rigid rotor model: too many parameters needed, bad fit!

Van Vleck perturbation theory:

\[ H^{\text{rot}} + H^{\text{Cor}} \rightarrow H^{\text{rot}}_{\text{effective}} \]

\( H^{\text{rot}}_{\text{effective}} \) contains

- Linear (diagonal) Coriolis terms \( \pm 2 \zeta CK \) for degenerate torsional levels with \( k = \pm 1 \) and \( k = \pm 2 \)

- Interference between unusual Coriolis coupling and bifurcation tunneling explains irregular rotational structure.

⇒ Perfect fit of all measured \((\text{H}_2\text{O})_3\) and \((\text{D}_2\text{O})_3\) bands in high-resolution FIR spectra!

(with R.J. Saykally’s group at U.C. Berkeley)