Potential energy surfaces and predicted infrared spectra for van der Waals complexes

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Outline

• Introduction

• Rg—(linear molecule) vdW complexes

• H₂—(linear molecule) vdW complexes

• Path integral Monte Carlo Study for He₉-N₂O

• Summary
Introduction

Van der Waals interactions

Collections of molecules

Biochemical reactions

Stability of molecular complexes

The spectroscopy provides very useful information for the intermolecular potential energy surface (IPES) and dynamics.

Theoretical study of the ro-vibrational spectra provide complete description of the spectra.
Rigid monomer molecule

Separate the inter- and intra- molecular vibrations and fix the geometry of the linear molecule.

The rovibrational Hamiltonian:

\[
\hat{H}(R, \theta, \hat{j}_x, \hat{j}_y, \hat{j}_z) = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \left(\frac{\hbar^2}{2\mu R^2} + \frac{\hbar^2}{2I}\right) \left( -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{\hat{j}_z^2}{\sin^2 \theta} \right) + \frac{1}{2\mu R^2} \left( \hat{j}_x^2 - 2\hat{j}_z^2 \right) \\
+ \cot \theta \left[ \frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial \theta} \left( \hat{j}_x + i\hat{j}_y \right) + \frac{\hbar}{2\mu R^2} \frac{\partial}{\partial \theta} \left[ \left( \hat{j}_x + i\hat{j}_y \right) \right] + V(R, \theta) \right]
\]

\[V(R, \theta)\] : potential energy of intermolecular interaction
\[\mu\] : reduced mass of the vdW molecule
\[I\] : moment of inertia of the linear molecule
This strategy is usually good for microwave spectra. But not enough for infrared spectra, which involves excitation of the intermolecule vibrations.

For example, for the infrared spectra of He-N_2O,

\textit{Band origin shift: Calculated: } -0.019 \text{ cm}^{-1}, \text{ Observed: } 0.253 \text{ cm}^{-1}


\textbf{An improved way is to include the dependence of intramolecular modes}
The observed infrared spectra usually involve excitation of only one intermolecule vibrations.

(Linear molecule)

\[ \hat{H} = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial Q^2} + B_1 \hat{j}_1^2 + \frac{\hat{j}_2^2}{2I_Q} + \frac{(\hat{j} - \hat{j}_1 - \hat{j}_2)^2}{2\mu_1 R^2} + V(R, \varphi, \theta_1, \theta_2, Q) \]

Rg—(linear molecule) vdW complexes

\[
\hat{H} = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial Q^2} + \left(\frac{1}{2I_Q} + \frac{1}{2\mu_1 R^2}\right) \left(-\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{\hat{J}_z^2}{\sin^2 \theta}\right) \\
+ \frac{1}{2\mu_1 R^2} \left(\hat{J}_x^2 - 2\hat{J}_z^2\right) + \frac{\cot \theta}{2\mu_1 R^2} \left[\left(\hat{J}_x + i\hat{J}_y\right) + \left(\hat{J}_x - i\hat{J}_y\right)\right] \cdot \hat{J}_z \\
+ \frac{1}{2\mu_1 R^2} \frac{\partial}{\partial \theta} \left[\left(\hat{J}_x + i\hat{J}_y\right) - \left(\hat{J}_x - i\hat{J}_y\right)\right] + V(R, \theta, Q)
\]

(in the Body-Fixed frame)
The three-dimensional PES can be divided as:

\[
V(R, \theta, Q) = V_{\text{mon}}(Q) + \Delta V(R, \theta, Q)
\]

\(V_{\text{mon}}(Q)\): PES for isolated linear molecule.
\(\Delta V(R, \theta, Q)\): IPES at fixed \(Q\)

Total wavefunction (in FBR):

**FBR: finite basis representation**

\[
\Psi_{n}^{J_{M}p}(R, \theta, Q, \alpha, \beta, \gamma) = \sum_{j,K,v_{1},v_{2}} c_{j,K,v_{1},v_{2}}^{n,J_{M}p} \psi_{v_{1}}(R) \psi_{v_{2}}(Q) P_{j}^{K}(\cos \theta) C_{KM}^{J_{M}p}(\alpha, \beta, \gamma)
\]

\[
C_{KM}^{J_{M}p}(\alpha, \beta, \gamma) = [2(1 + \delta_{K0})]^{-1/2} \left[ D_{MK}^{J^*} + (-1)^{J+K+p} D_{M-K}^{J^*} \right], \quad p = 0,1
\]

(total parity is given by \((-1)^{J+p}\))

\[
\left[ -\frac{1}{2\mu_{2}} \frac{d^2}{dQ^2} + V_{\text{mon}}(Q) \right] \psi_{v_{2}}(Q) = E_{v_{2}} \psi_{v_{2}}(Q)
\]
For example of Rg-CO\textsubscript{2} complex:

The one-dimensional energy curve for the $Q_3$ coordinate of CO\textsubscript{2}

\[
\psi_v(Q_3) = E_v \psi_v(Q_3)
\]

\[
Q_3 = \frac{r_{\text{CO}_1} - r_{\text{CO}_2}}{\sqrt{2}}
\]

$E_{0\text{obs.}} = 2349.149\text{cm}^{-1}$

$E_{0\text{cal.}} = 2418.759\text{cm}^{-1}$ (without scale)

$E_{0\text{cal.}} = 2349.1483\text{cm}^{-1}$ (scaled)

\textbf{Scale factor} = 0.971449

\textsuperscript{1} J. Mol. Spec. 76, 430 (1979)
Then the PODVR grid points for Q can be determined by

*(PODVR: potential optimized discrete variable representation)*

\[
X_{mn} = \langle \psi_m \mid x \mid \psi_n \rangle
\]

Vibrationally averaged intermolecular PES:

\[
V_v(R, \theta) = \int_{-\infty}^{\infty} \psi_v(Q) \Delta V(R, \theta, Q) \psi_v(Q) dQ = \sum_k T_{kv}^2 \Delta V(R, \theta, Q_k)
\]

Only a few PODVR grid points for Q are sufficient!

The FBR can be conveniently transformed to the DVR.
Any local functions are assumed to be diagonal in the DVR.
The matrix elements of the Hamiltonian in the DVR are given by

\[
\langle \alpha' \beta' q' K' | \hat{H} | \alpha \beta q K \rangle =
\]

\[
\langle \alpha' | - \frac{1}{2 \mu_1} \frac{\partial^2}{\partial R^2} | \alpha \rangle \cdot \delta_{\beta' \beta} \cdot \delta_{K K} \cdot \delta_{q' q} + \langle q' | - \frac{1}{2 \mu_2} \frac{\partial^2}{\partial Q^2} | q \rangle \cdot \delta_{\alpha' \alpha} \cdot \delta_{\beta' \beta} \cdot \delta_{K K} +
\]

\[
\left( \frac{1}{2 \mu_1 R_\alpha^2} + \frac{1}{I_{Q_q}} \right) \langle \beta' | \hat{J}^2 | \beta \rangle \cdot \delta_{\alpha' \alpha} \cdot \delta_{K K} \cdot \delta_{q' q} + \frac{1}{2 \mu_1 R_\alpha^2} \left\{ \left[ J (J + 1) - 2 K^2 \right] \cdot \delta_{\beta' \beta} \cdot \delta_{K K} \right. \\
- \left(1 + \delta_{K K} \right)^{1/2} \Lambda_{j K}^+ \cdot \langle \beta' | \hat{j}_+ | \beta \rangle \cdot \delta_{K K + 1} - \left(1 + \delta_{K K} \right)^{1/2} \Lambda_{j K}^- \cdot \langle \beta' | \hat{j}_- | \beta \rangle \cdot \delta_{K K - 1} \left\} \cdot \delta_{\alpha' \alpha} \cdot \delta_{q' q}
\]

\[
+ V(R_a, \theta_{\beta'}, Q_q) \cdot \delta_{\alpha' \alpha} \cdot \delta_{\beta' \beta} \cdot \delta_{K K} \cdot \delta_{q' q}
\]

\[
\Lambda_{j K}^\pm = \sqrt{J (J + 1) - K (K \pm 1)}
\]

The IPES can be constructed at a few PODVR points of \( Q \), so that the possible interpolation error could be avoided.
How many PODVR points are enough for the $r$ coordinate?

For Example:

![Diagram of H$_2$ molecule with Kr atom showing distance of 3.38 Å]

The vibrational energy levels (in cm$^{-1}$) of H$_2$ at a fixed Kr-H distance of 3.38 Å.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>6 DVR points</th>
<th>5 DVR points</th>
<th>4 DVR points</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>4157.6683</td>
<td>4157.6618</td>
<td>4157.6379</td>
</tr>
<tr>
<td>2</td>
<td>8079.4942</td>
<td>8079.4714</td>
<td>8079.4976</td>
</tr>
<tr>
<td>3</td>
<td>11769.4622</td>
<td>11769.5329</td>
<td>11768.7091</td>
</tr>
</tbody>
</table>

Five PODVR grid points are enough

0.6050, 0.7332, 0.8607, 1.0000, 1.1694 Å
Lanczos algorithm: (Lanczos 1950)

• Three term recursion:

\[
\psi_k = \left[ \left( \mathbf{H} - \alpha_{k-1} \right) \psi_{k-1} - \beta_{k-1} \psi_{k-2} \right] / \beta_k
\]

where

\[
\alpha_k = \psi_k^T \mathbf{H} \psi_k
\]

\[
\beta_k = \left\| \left( \mathbf{H} - \alpha_{k-1} \right) \psi_{k-1} - \beta_{k-1} \psi_{k-2} \right\|
\]
• Reduction of $H$:

$$T_{K \times K} = \begin{bmatrix} \alpha_1 & \beta_2 & \cdots & 0 \\ \beta_2 & \alpha_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \alpha_K \end{bmatrix} = Q_{N \times K}^T H_{N \times N} Q_{N \times K}$$

$$H_{N \times N} \xrightarrow{\text{Lanczos}} T_{K \times K} \xrightarrow{\text{diagonalization}} D_{K \times K}$$
• Diagonalization (QL or inverse iteration):

\[ T^{(K)} z_i^{(K)} = E_i^{(K)} z_i^{(K)} \]

- Lanczos eigenvectors:

\[ z_i^{(K)} = \begin{pmatrix} z_{1i}^{(K)} \\ z_{2i}^{(K)} \\ \vdots \\ z_{Ki}^{(K)} \end{pmatrix} \]

- Lanczos eigenstates:

\[ \phi_i^{(K)} = \sum_{k=1}^{K} z_{ki}^{(K)} \psi_k \]
• Convergence:

\[ H\phi_i^{(K)} = E_i^{(K)}\phi_i^{(K)} + \beta_K z_{Ki}^{(K)} \psi_{K+1} \]

If \( |z_{Ki}^{(K)}| \to 0 \), \( \phi_i^{(K)} \) converges!

• Scaling laws:

  – Memory \( \propto N \), CPU \( \propto N^2 \).
  – Capable of handling problems with \( N \) up to \( 10^8 \).
• Finite precision arithmetic
  
  – Loss of orthonormality among Lanczos states:
    \[ \langle \psi_k | \psi_{k'} \rangle \neq \delta_{kk'}, \quad |k - k'| >> 0 \]
  
  – Unnormalized Lanczos eigenstates
    \[ \langle \phi_i^{(K)} | \phi_i^{(K)} \rangle = \sum_{k,k'} z_{ki}^{(K)} z_{k'i}^{(K)} \langle \psi_k | \psi_{k'} \rangle \neq 1 \]

  Observation: sum of norms of converged copies in a cluster = # of copies:

  \[ \sum_i \langle \phi_i^{(K)} | \phi_i^{(K)} \rangle = M \]

  – Arithmetic average

    \[ \langle \chi_m | \phi_n \rangle^2 = \frac{\sum_{i=1}^M \langle \chi_m | \phi_i^{(K)} \rangle^2}{M} \]

Calculation of the transition intensity

The line intensity of a transition at a temperature \( T \):

\[
I_{J_{jpn} \rightarrow J'_{jpn'}} \propto (E_{J'_{jpn'}} - E_{J_{jpn}}) \left[ e^{-E_{J_{jpn}}/kT} - e^{-E_{J'_{jpn'}}/kT} \right] \sum_{M, M'} \sum_{A=X', Y', Z'} \left| \langle \Psi_{n}^{JMp} | \mu_{A} | \Psi_{n'}^{J'Mp'} \rangle \right|^2
\]

The calculated dipole moment in BF frame is rewritten as:

\[
\mu_{+1} = -\frac{1}{\sqrt{2}}(\mu_{x} + i\mu_{y}), \quad \mu_{-1} = \frac{1}{\sqrt{2}}(\mu_{x} - i\mu_{y}), \quad \mu_{0} = \mu_{z}
\]

Transformation between BF and SF frames:

\[
\mu'_{g} = \sum_{h=-1}^{1} \mu_{h} D_{gh}^{1}(\alpha, \beta, \gamma)
\]

(component of the dipole moment along \( A \) axis of the space-fixed (SF) frame)
The rovibrational wave function can be rewritten as:

\[
\Psi_n^{JMp}(R, \theta, Q, \alpha, \beta, \gamma) = \sum_K \Psi_{K}^{Jnp}(R, \theta, Q)C_{KM}^{Jp}(\alpha, \beta, \gamma)
\]

The transition intensity:

\[
I_{Jm \rightarrow J'_{m'}} \propto (2J + 1)(2J' + 1)(E_{J'_{m'}} - E_{Jm})[e^{-E_{Jm}/kT} - e^{-E_{J'_{m'}/kT}}]
\]

\[
\sum_{K} \sum_{K'} [(1 + \delta_{K0})(1 + \delta_{K'0})] \frac{1}{2} \sum_{h} \left\{ (-1)^{K} \begin{pmatrix} J & J' & 1 \\ -K & K' & h \end{pmatrix} + (-1)^{J+p} \begin{pmatrix} J & J' & 1 \\ K & K' & h \end{pmatrix} \right\}
\]

\[
+ (-1)^{K+J'+p+K'} \begin{pmatrix} J & J' & 1 \\ -K & -K' & h \end{pmatrix} + (-1)^{J+p+J'+p'+K'} \begin{pmatrix} J & J' & 1 \\ K & -K' & h \end{pmatrix} \int \psi_{Km}^{Jnp} \psi_{K'm'}^{J'n'p'} d\tau
\]

(Winger 3-j symbol)
He-N$_2$O: rovibraional spectra in the $v_3$ region of N$_2$O


- Consider the $Q_3$ normal mode for the antisymmetric vibrational stretching of N$_2$O molecule

\[ Q_3 = 8.834062(r_1-r_{1e}) - 4.056573(r_2-r_{2e}) \]
• **CCSD(T)** method with **aug-cc-pVTZ** basis set

• **Bond function** (3s 3p 2d1f 1g) (for 3s and 3p, $\alpha =0.9,0.3,0.1$; for 2d, $\alpha =0.6,0.2$, for f, g, $\alpha =0.3$)

• The **supermolecular** approach

• Full CP was used to correct **BSSE**

\[
V_{\text{int}} = V_{\text{vdW}}(\chi_A + \chi_B) - (V_A(\chi_A + \chi_B) + V_B(\chi_A + \chi_B))
\]

• **5 PODVR points** for $Q_3$ coordinate:
  -2.0202, -0.9586, 0.0, 0.9586, 2.0202
  and **250 geometries** for each IPES
Contour plot of the intermolecular potential energy of He–N₂O. Contours are labeled in cm⁻¹.
Vibrational energy levels (in cm$^{-1}$) for $^4$He-N$_2$O and $^3$He-N$_2$O

<table>
<thead>
<tr>
<th>Ground state</th>
<th>$^4$He-N$_2$O</th>
<th>$^3$He-N$_2$O</th>
<th>$^4$He-N$_2$O</th>
<th>$^3$He-N$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 1</td>
<td>-9.3540</td>
<td>-7.5059</td>
<td>-9.3467</td>
<td>-7.4957</td>
</tr>
<tr>
<td>0 2</td>
<td>-7.2367</td>
<td>-5.4854</td>
<td>-7.2031</td>
<td>-5.4566</td>
</tr>
<tr>
<td>0 3</td>
<td>-4.1228</td>
<td>-1.5844</td>
<td>-4.0833</td>
<td>-1.5431</td>
</tr>
<tr>
<td>1 0</td>
<td>-2.2008</td>
<td>-1.5844</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Frequency of $\nu_3$ band of N$_2$O: 2223.7567 cm$^{-1}$

Band shift in $^4$He: 0.2532 cm$^{-1}$ (obs), 0.1704 cm$^{-1}$ (cal)

in $^3$He: 0.2170 cm$^{-1}$ (obs), 0.1551 cm$^{-1}$ (cal)
The calculated line intensities of $^3\text{He}-\text{N}_2\text{O}$ and $^4\text{He}-\text{N}_2\text{O}$ at a rotational temperature of 2K.
He-CO$_2$: Assignment of the hot band in the infrared spectra

Experimental researches:


Theoretical researches:


![Absorbance spectrum](image)

TABLE III. List of observed HeCO$_2$ $\nu_3$ hot band transitions.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Peak absorbance ($\times 10^{-4}$)</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Absorbance ($\times 10^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2347.9305</td>
<td>3</td>
<td>2349.7367</td>
<td>3</td>
</tr>
<tr>
<td>2348.0022</td>
<td>3</td>
<td>2350.1536</td>
<td>6</td>
</tr>
<tr>
<td>2348.2619</td>
<td>4</td>
<td>2350.1869</td>
<td>5</td>
</tr>
<tr>
<td>2348.3179</td>
<td>2</td>
<td>2350.5311</td>
<td>6</td>
</tr>
<tr>
<td>2348.3966</td>
<td>5</td>
<td>2350.5444</td>
<td>5</td>
</tr>
<tr>
<td>2348.4457</td>
<td>5</td>
<td>2350.7978</td>
<td>4</td>
</tr>
<tr>
<td>2348.5263</td>
<td>3</td>
<td>2351.0401</td>
<td>3</td>
</tr>
<tr>
<td>2348.9434</td>
<td>7</td>
<td>2351.4294</td>
<td>...b</td>
</tr>
<tr>
<td>2349.5298</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Absorbance is at a jet temperature of 4.6 K. All intensities have an uncertainty of $\pm 2 \times 10^{-4}$.

bPartially overlapped with (CO$_2$)$_2$ monomer transition.
TABLE IV. Theoretical infrared transitions in the frequency range of 2347.7–2351.4 cm⁻¹ in the ν₅ band of He–CO₂ and a tentative assignment of the observed ν₅ transitions.

<table>
<thead>
<tr>
<th>Transition $J'<em>{K_a'K_c'} - J''</em>{K_a''K_c''}$</th>
<th>Frequency (cm⁻¹)</th>
<th>$\Delta$ (cm⁻¹) Expt.–theor</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4_{04} - 3_{13}$</td>
<td>2347.7449</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>$1_{01} - 1_{10}$</td>
<td>2347.8199</td>
<td>2347.9305</td>
<td>0.1106</td>
</tr>
<tr>
<td>$2_{21} - 3_{12}$</td>
<td>2347.8699</td>
<td></td>
<td>0.9</td>
</tr>
<tr>
<td>$3_{21} - 3_{12}$</td>
<td>2348.0819</td>
<td>2348.0022</td>
<td>-0.0797</td>
</tr>
<tr>
<td>$2_{02} - 1_{11}$</td>
<td>2348.1149</td>
<td>2348.2619</td>
<td>0.1470</td>
</tr>
<tr>
<td>$2_{21} - 2_{12}$</td>
<td>2348.3619</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>$4_{22} - 4_{13}$</td>
<td>2348.4129</td>
<td>2348.3179</td>
<td>-0.0950</td>
</tr>
<tr>
<td>$4_{22} - 3_{31}$</td>
<td>2348.4399</td>
<td>2348.3966</td>
<td>-0.0433</td>
</tr>
<tr>
<td>$3_{21} - 2_{12}$</td>
<td>2348.5739</td>
<td>2348.4457</td>
<td>-0.1282</td>
</tr>
<tr>
<td>$3_{22} - 3_{13}$</td>
<td>2348.7689</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>$2_{20} - 2_{11}$</td>
<td>2348.7849</td>
<td>2348.5263</td>
<td>-0.2586</td>
</tr>
<tr>
<td>$5_{05} - 4_{14}$</td>
<td>2348.8769</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>$2_{20} - 1_{11}$</td>
<td>2349.2649</td>
<td>2349.9434</td>
<td>0.3215</td>
</tr>
<tr>
<td>$4_{23} - 3_{10}$</td>
<td>2349.4239</td>
<td>2349.5298</td>
<td>0.1052</td>
</tr>
</tbody>
</table>

The wave number is not surprising. Except for seven lines the theoretical intensity pattern closely follows the experimental one. However, a few noticeable exceptions are observed. Thus, the assignment reported in Table IV should definitely be considered as tentative and more work should be done to produce a definite assignment of the observed transitions.
New \textit{ab initio} potential calculation:

- Jacobi coordinate \( (R, \theta, Q_3) \);
- about \textbf{700} symmetry unique points;
- aVQZ basis set plus bond functions;
- CCSD(T) level

Five PODVR grid points, \(-0.21715, -0.10325, 0.0, 0.10325, \text{ and } 0.21715 \) \( \text{a}_0 \), for the \( Q_3 \) coordinate.
Energy levels (cm\(^{-1}\)) of bound vibrational states

<table>
<thead>
<tr>
<th>((n_s, n_b))</th>
<th>Ground state</th>
<th>(\nu_4) state</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 0)</td>
<td>-16.979</td>
<td>-16.875</td>
</tr>
<tr>
<td>(0, 1)</td>
<td>-8.687</td>
<td>-8.700</td>
</tr>
<tr>
<td>(0, 2)</td>
<td>-7.593</td>
<td>-7.599</td>
</tr>
<tr>
<td>(0, 3)</td>
<td>-3.954</td>
<td>-3.974</td>
</tr>
<tr>
<td>(0, 4)</td>
<td>-1.268</td>
<td>-1.235</td>
</tr>
</tbody>
</table>

8.292 \(\nu_s\) 9±2 cm\(^{-1}\)

No bound states with the stretching excitation
## New Assignment of ‘hot band’ transitions:

<table>
<thead>
<tr>
<th></th>
<th>Obs.</th>
<th>Our work</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν(cm(^{-1}))</td>
<td>I</td>
<td>ν(obs.-cal.)</td>
</tr>
<tr>
<td>1</td>
<td>2347.9305</td>
<td>3±2</td>
<td>0.0096</td>
</tr>
<tr>
<td>2</td>
<td>2348.0022</td>
<td>3±2</td>
<td>0.0026</td>
</tr>
<tr>
<td>3</td>
<td>2348.2619</td>
<td>4±2</td>
<td>-0.0663</td>
</tr>
<tr>
<td>4</td>
<td>2348.3179</td>
<td>2±2</td>
<td>-0.0041</td>
</tr>
<tr>
<td>5</td>
<td>2348.3966</td>
<td>5±2</td>
<td>0.0418</td>
</tr>
<tr>
<td>6</td>
<td>2348.4457</td>
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<tr>
<td>16</td>
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<td>3±2</td>
<td>0.0254</td>
</tr>
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</table>

Transitions from $v_3=0$ to $v_3=1$ state of CO$_2$ with the complex at the van der Waals ground state at T=4.1 K.

Calculated shift of band origin: 0.101 cm$^{-1}$; Observed value: 0.094 cm$^{-1}$

Journal of Chemical Physics, 128, 124323(2008)
H$_2$—(linear molecule) vdW complexes

\[ \hat{H} = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial Q^2} + B \hat{j}_1^2 + \frac{\hat{j}_2^2}{2I_0} + \frac{(\hat{\mathbf{j}} - \hat{j}_1 - \hat{j}_2)^2}{2\mu R^2} + V(R, \varphi, \theta_1, \theta_2, Q) \]
Radial DVR/Angular FBR

Sin-DVR for $R$ coordinate

PODVR for $Q$ coordinate

The basis set for angular coordinate $(\theta_1, \theta_2, \phi)$:

$$|j_1,j_2,m,K;JMP\rangle = (2 + 2\delta_{K0}\delta_{m0})^{-1} 2 [D^J_{MK}Y_{j_1m}(\theta_1,\phi)\Theta_{j_2,K-m}(\theta_2)$$
$$+ (-1)^{J+P} D^J_{M-K}Y_{j_1-m}(\theta_1,\phi)\Theta_{j_2,m-K}(\theta_2)]$$

Vibrationally averaged intermolecular PES:

$$V_v(\vec{R}) = \int_{-\infty}^{\infty} \psi_v(Q) \Delta V(\vec{R},Q) \psi_v(Q)dQ = \sum_k T_{kv}^2 \Delta V(\vec{R},Q_k)$$

Transition dipole moments:

$$\bar{d}_\alpha(\vec{R}) = \int_{-\infty}^{\infty} \psi_{v=1}(Q)d_\alpha(\vec{R},Q)\psi_{v=0}(Q)dQ = \sum_k T_{k1}\mu_\alpha(\vec{R},Q_k)T_{k0}$$
In the angular FBR, the angular kinetic energy matrix elements:

$$\langle j_1', j_2', m', K'; J M p | \hat{J}_1^2 | j_1, j_2, m, K; J M p \rangle = j_1(j_1 + 1)\delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K)\delta(m', m)$$

$$\langle j_1', j_2', m', K'; J M p | \hat{J}_2^2 | j_1, j_2, m, K; J M p \rangle = j_2(j_2 + 1)\delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K)\delta(m', m)$$

$$\langle j_1', j_2', m', K'; J M p | (\hat{J} - \hat{J}_1 - \hat{J}_2)^2 | j_1, j_2, m, K; J M p \rangle$$

$$= \langle j_1', j_2', m', K'; J M p | \hat{J}^2 - \hat{J} (\hat{J}_1 + \hat{J}_2) - (\hat{J}_1 + \hat{J}_2)\hat{J} + (\hat{J}_1 + \hat{J}_2)^2 | j_1, j_2, m, K; J M p \rangle$$

$$= [J(J + 1) - 2K^2 + 2m(K - m) + j_1(j_1 + 1) + j_2(j_2 + 1)]\delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K)\delta(m', m)$$

$$- (1 + \delta(K', 0)\delta(m', 0))^{1/2} \Lambda_{j K}^- \Lambda_{j_1 m}^- \delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K - 1)\delta(m', m - 1)$$

$$- (1 + \delta(K, 0)\delta(m, 0))^{1/2} \Lambda_{j K}^+ \Lambda_{j_1 m}^+ \delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K + 1)\delta(m', m + 1)$$

$$- (1 + \delta(K', 0)\delta(m, 0))^{1/2} \Lambda_{j K}^- \Lambda_{j_2 K - m}^- \delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K - 1)\delta(m', m)$$

$$- (1 + \delta(K, 0)\delta(m, 0))^{1/2} \Lambda_{j K}^+ \Lambda_{j_2 K - m}^+ \delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K + 1)\delta(m', m)$$

$$+ (1 + \delta(K, 0)\delta(m, 0))^{1/2} \Lambda_{j_1 m}^+ \Lambda_{j_2 K - m}^- \delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K)\delta(m', m + 1)$$

$$+ (1 + \delta(K, 0)\delta(m', 0))^{1/2} \Lambda_{j_1 m}^- \Lambda_{j_2 K - m}^+ \delta(j_1'j_1)\delta(j_2'j_2)\delta(K', K)\delta(m', m - 1)$$
Fitting of the potential energy surface

\[ \Delta V(R, \varphi, \theta_1, \theta_2, Q) = \left[ \sum_{l_1 l_2 l} g_{l_1 l_2 l}(R, Q) A_{l_1 l_2 l}(\theta_1, \theta_2, \varphi) \right] \exp \left[ \sum_{l_1 l_2 l} d_{l_1 l_2 l}(R, Q) A_{l_1 l_2 l}(\theta_1, \theta_2, \varphi) \right] \]

(For a set value of R and Q)

with

\[ A_{l_1 l_2 l}(\theta_1, \theta_2, \varphi) = \sum_{m=-l}^{l} \left( \begin{array}{ccc} l_1 & l_2 & l \\ m & -m & 0 \end{array} \right) Y_{l_1 m}(\theta_1, \varphi_1) Y_{l_2, -m}(\theta_2, \varphi_2) \]

where

\[ \varphi = \varphi_1 - \varphi_2 \quad \quad l_\leq = \min(l_1, l_2) \]

(both \( l_1 \) and \( l + l_1 + l_2 \) must be even)
Fitting of the dipole moment surface

\[ \mu_\alpha(R, \varphi, \theta_1, \theta_2, Q) = \sum_{l_1l_2l} g_{l_1l_2l; \alpha}(R, Q) A_{l_1l_2l; \alpha}(\theta_1, \theta_2, \varphi), \ \alpha = x, y, \text{ or } z. \]

The angular form of \( \mu_z \) is the same as that for the potential energy.

\[ A_{l_1l_2l; \alpha}(\theta_1, \theta_2, \varphi) = \sum_m \left( \begin{array}{ccc} l_1 & l_2 & l \\ m & -m+1 & -1 \end{array} \right) \Theta_{l_1m}(\theta_1) \Theta_{l_2-m+1}(\theta_2) \cos(m\varphi) \]

\[ A_{l_1l_2l; \alpha}(\theta_1, \theta_2, \varphi) = \sum_m \left( \begin{array}{ccc} l_1 & l_2 & l \\ m & -m+1 & -1 \end{array} \right) \Theta_{l_1m}(\theta_1) \Theta_{l_2-m+1}(\theta_2) \sin(m\varphi) \]
Calculation of the transition intensity

\[
\Psi_{n}^{JMP}(R, \varphi, \theta_{1}, \theta_{2}, Q, \alpha, \beta, \gamma) = \sum_{K} \left[ \Psi_{K+}^{Jnp}(R, \varphi, \theta_{1}, \theta_{2}, Q) D_{MK}^{J^*}(\alpha, \beta, \gamma) + \right.
\]
\[
(-1)^{J+p} \Psi_{K-}^{Jnp}(R, \varphi, \theta_{1}, \theta_{2}, Q) D_{M-K}^{J^*}(\alpha, \beta, \gamma) \right]
\]

\[
I_{J_{pn} \rightarrow J'_{p'n'}} \propto (2J + 1)(2J' + 1) (E_{J_{pn}} - E_{J_{pn}'}) [e^{-E_{J_{pn}}/kT} - e^{-E_{J_{pn}'}/kT}]
\]
\[
\left| \sum_{K} \sum_{K'} \sum_{h} (-1)^{K} \left( \begin{array}{cc} J & J' \\ -K & h \end{array} \right) \int \Psi_{K+}^{Jnp} \mu_h \Psi_{K'+}^{J'n'p'} d\tau + (-1)^{J+p} \left( \begin{array}{cc} J & J' \\ K & h \end{array} \right) \int \Psi_{K-}^{Jnp} \mu_h \Psi_{K'+}^{J'n'p'} d\tau \right.
\]
\[
+ (-1)^{J'+p'} \left( \begin{array}{cc} J & J' \\ -K & -K' \end{array} \right) \int \Psi_{K+}^{Jnp} \mu_h \Psi_{K'-}^{J'n'p'} d\tau + (-1)^{J+p+J'+p'} \left( \begin{array}{cc} J & J' \\ K & -K' \end{array} \right) \int \Psi_{K-}^{Jnp} \mu_h \Psi_{K'-}^{J'n'p'} d\tau \right) \right|^{2}
\]
\( \text{H}_2-\text{N}_2\text{O}: \) rovibraional spectra in the \( \nu_3 \) region of \( \text{N}_2\text{O} \)


\( \text{H}_2: \) possibly the most abundant molecule in the universe

\( p\text{H}_2: \) indistinguishable boson

superfluid behavior

Nuclear spin state: \( I = 0 \) for \( p\text{H}_2 \), \( I = 0, 2 \) for \( o\text{D}_2 \)

\( I = 1 \) for \( o\text{H}_2 \) and \( p\text{D}_2 \)

At low temperature: \( j_H = 0 \) for \( p\text{H}_2 \) and \( o\text{D}_2 \)

\( j_H = 1 \) for \( o\text{H}_2 \) and \( p\text{D}_2 \)
• CCSD(T) method

• aug-cc-pVTZ basis set for H atom
  cc-pVTZ plus diffuse functions (1s1p1d) for O and N atoms

• Bond function (3s 3p 2d1f) (for 3s and 3p, \( \alpha = 0.9, 0.3, 0.1 \); for 2d, \( \alpha = 0.6, 0.2 \), for f, \( \alpha = 0.3 \))

• 4 PODVR points for \( Q_3 \) coordinate:
  -1.6507, -0.5246, 0.5246, 1.6507
  and about 5000 geometries in total

  \( R: [4.5a_0, 15.0a_0] \) with 12 points

  \( \theta_1, \theta_2, \phi \) in increments of 30°
Contour plots of potential energy surface for $\text{N}_2\text{O-H}_2$ at $R = 5.43\ a_0$ for $Q_3 = -0.5246$. (a) $\varphi = 0^\circ$ (b) $\varphi = 90^\circ$ (c) $\theta_2 = 93.6^\circ$. The contour spacing is 30 cm$^{-1}$.
Pure vibrational energy levels (in cm\(^{-1}\)) for first ten bound states of four species of N\(_2\)O–hydrogen complexes.

<table>
<thead>
<tr>
<th>(n)</th>
<th>N(_2)O–pH(_2)</th>
<th>N(_2)O–oH(_2)</th>
<th>N(_2)O–oD(_2)</th>
<th>N(_2)O–pD(_2)</th>
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<tr>
<td>1</td>
<td>-64.7179</td>
<td>31.4662</td>
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<tr>
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</tr>
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<td>29.8419</td>
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</table>

\(V_{\text{min}} = -242.43\) cm\(^{-1}\)

The ground state energies for oH\(_2\) and pD\(_2\) are 118.48675 cm\(^{-1}\) and 59.78042 cm\(^{-1}\)
Band origin shift:

$N_2O-pH_2$: 0.2219 cm$^{-1}$(cal); 0.2261 cm$^{-1}$(obs)

$N_2O-oH_2$: 0.4236 cm$^{-1}$(cal); 0.6238 cm$^{-1}$(obs)

$N_2O-oD_2$: 0.3585 cm$^{-1}$(cal); 0.4534 cm$^{-1}$(obs)

$N_2O-pD_2$: 0.5437 cm$^{-1}$(cal); 0.7900 cm$^{-1}$(obs)
The contour plots of probability density integrated over two angular variables \( \theta_1 \) and \( \varphi \) for some vibration states of \( \text{N}_2\text{O-}p\text{H}_2 \) at \( Q_3 = -0.5246 \).
The contour plots of probability density integrated over two angular variables $\theta_1$ and $\varphi$ for some vibration states of $N_2O-oD_2$ at $Q_3 = -0.5246$. 
The calculated line intensities at a rotational temperature of $T = 1.5K$. The transition frequencies are relative to the band origin.

\textsuperscript{a} J. Tang and A. R. W. McKellar, JCP 117, 8308 (2002)
The calculated line intensities for $\text{N}_2\text{O-D}_2$ at a rotational temperature of $T = 1.5\text{K}$. The transition frequencies are relative to the band origin.
Spectroscopic studies offer insights into dynamical and structural information.
Superfluidity Within a Small Helium-4 Cluster


In $^4$He, sharp rotational lines, absent Q branch $\rightarrow$ free linear rotor

In $^3$He, broad line $\rightarrow$ conventional rotation diffusion in viscous solution
High resolution infrared spectra of CO$_2$ solvated with helium atoms


Turnaround at critical point $\Rightarrow$ decoupling from environment, i.e the rotor is no longer dragged by $^4$He.

Due to microscopic superfluidity
For quantum solvents such as $^4\text{He}$ and *para-*H$_2$, microscopic superfluidity and transition from vdw complexes to quantum solvation have been established.

Theoretical description requires both QM approach to the finite temperature dynamics and accurate intermolecular PES.
Path integral Monte Carlo Study for He$_N$-N$_2$O

Hamiltonian for a $^4$He cluster doped with a N$_2$O molecule:

$$\hat{H}^\nu = \hat{H}^{N_2O}_\nu + \hat{H}_{\text{He}} + V^{\nu}_{\text{He-N}_2\text{O}}$$

$$\hat{H}^{N_2O}_\nu = \frac{p_0^2}{2m_{N_2O}} + B^{\nu}_{N_2O}L^2$$

$$V^{\nu}_{\text{He-N}_2\text{O}} = \sum_{i=1}^{N} V^{\nu}_{\text{He-N}_2\text{O}}$$

$$B^{\nu}_{N_2O} = \langle \varphi_\nu | 2I^{-1}_{Q_i} | \varphi_\nu \rangle$$

$$\hat{H}_{\text{He}} = \sum_{i=1}^{N} \frac{p_i^2}{2m_{\text{He}}} + \sum_{i<j} u(|r_i - r_j|)$$

$\{p_i ; r_i\}$: the momenta and positions of the helium atoms
$\{p_0; r_0\}$: the momenta and position of the N$_2$O molecule
Any physical observable \( \langle O \rangle \) can be evaluated as

\[
\langle \hat{O} \rangle_\beta = \frac{1}{Z} \text{Tr} \{ \hat{O} \hat{\rho}(\beta) \}
\]

\[
= \frac{1}{Z} \int dq dq' d\Omega d\Omega' \langle q\Omega | \hat{O} | q'\Omega' \rangle \langle q'\Omega' | \hat{\rho}(\beta) | q\Omega \rangle
\]

\( \hat{\rho}(\beta) = e^{-\beta \hat{H}} \)  \hspace{1cm} \text{(Density operator)}

\( Z = \text{Tr} \{ \hat{\rho}(\beta) \} \)  \hspace{1cm} \text{(Partition function)}

\( \beta = 1/k_B T \)

\( q = (r_0, \{ r_i | i > 0 \}) \)

\text{imaginary time}
In the path integral picture with a finite number \((K)\) of discretization of the imaginary time, the density matrix can be written as

\[
\left< q'\Omega' \right| e^{-\beta \hat{H}} \left| q\Omega \right> = \int \cdots \int \prod_{k=2}^{K} dq_k d\Omega_k \prod_{k=1}^{K} \left< \Omega_k \left| e^{-\tau \hat{T}_{N2O}} \right| \Omega_{k+1} \right> \left< q_k \left| e^{-\tau \hat{H}^{\text{vir}}(\Omega_k)} \right| q_{k+1} \right> = \tau = \beta / K
\]

\[
\sum_{l=0}^{\infty} \frac{2l + 1}{4\pi} e^{-\tau B_{0}^{N2O} l (l+1)} p_l(\cos \gamma)
\]

\[
\left( \frac{1}{4\pi \Lambda \tau} \right)^{3/2} \left( \frac{1}{4\pi \lambda \tau} \right)^{3N/2} e^{-0.5 \tau [V(R_k) + V(R_{k+1})]}
\]

\[
\times e^{-\left( R_k - R_{k+1} \right)^2 / 4 \Lambda \tau} e^{-\sum_{i}^N \left( \eta_i^k - \eta_i^{k+1} \right)^2 / 4 \lambda \tau}
\]

The **Bosonic exchange effect** was incorporated into PIMC by including permutation sampling.
The “raw” PIMC data were extrapolated to the limit of $\tau \to 0$, 

$$\langle E \rangle_{\beta}^{PIMC} = a + b\tau^2$$

**Distance distribution** of the $i$th He atom,

$$\langle R_i \rangle = \frac{1}{K} \left\langle \sum_{k=1}^{K} |r_{ik} - r_{0k}| \right\rangle_{\beta}$$

**Orientation estimator:**

$$\langle \cos \theta_i \rangle = \frac{\langle n \cdot R_i \rangle}{R_i}$$
Vibrational band origin shift:

\[ \Delta \nu = \left\langle E^{\nu=1} \right\rangle_{\beta} - \left\langle E^{\nu=0} \right\rangle_{\beta} \]

Effective rotational and centrifugal distortion constants:

\[ E(J) = B_{\text{eff}} J(J + 1) - D_{\text{eff}} J^2 (J + 1)^2 \]

\[
\left\langle n(\tau) \cdot n(0) \right\rangle = \frac{1}{Z} \text{Tr}\left\{ e^{-\beta H} e^{\tau H} n e^{-\tau H} \cdot n \right\} \\
= \frac{1}{Z} \left( \exp(-2B\tau + 4D\tau) + \sum_{J>0} \exp[-\beta B J (J + 1) + \beta D J^2 (J + 1)^2] \times \right.
\left. \left\{ J \exp(2BJ\tau - 4DJ^3\tau) + (J + 1) \exp[-2B(J + 1)\tau + 4D(J + 1)^3\tau] \right\} \right)
\]

(Orientational correlation function)
Refitting for He-N$_2$O PES

The formula for analytic potential energy surface:

$$V(R, \theta) = A(R, \theta) \times \exp[B(R, \theta)] + \sum_{i=6}^{12} \left( \frac{f_i[D(\theta)R]}{R^{i-2}} \right) \times \sum_{l=0}^{l_{\text{max}}} C_i \frac{P_i(\cos \theta)}{\sqrt{2l + 1}}$$

**Short-range term**

**Long-range term**

$P_l(\cos \theta)$ is Legendre polynomial

$A(R, \theta)$ is short range linear term:

$$A(R, \theta) = \exp(d^0) R^{-2} \sum_{i=0}^{4} R_i \sum_{l=0}^{5} g_i \frac{P_i(\cos \theta)}{\sqrt{2l + 1}}$$

$B(R, \theta)$ is short range exponential term:

$$B(R, \theta) = \sum_{l=1}^{4} d^l \frac{P_l(\cos \theta)}{\sqrt{2l + 1}} + (-R) \sum_{l=0}^{4} b^l \frac{P_l(\cos \theta)}{\sqrt{2l + 1}}$$

$f_i[D(\theta)R]$ is dumping factor which is defined as

$$f_n(x) = 1 - e^{-3} \sum_{k=0}^{n} x^k / k!$$

where

$$D(\theta) = \sum_{l=0}^{4} b^l \frac{P_l(\cos \theta)}{\sqrt{2l + 1}}$$
Contour plot in Jacobi coordinates of the He–$\text{N}_2\text{O}$ PES

\[ V = -62.27 \text{ cm}^{-1} \]

\[ V = -32.88 \text{ cm}^{-1} \]
PIMC simulation parameters

◆ Effective rotational temperature,
  \[ T = 0.37K \]


◆ Rotational constant

  \[ B = 0.4190 \text{ cm}^{-1} \], for ground state of \( \text{N}_2\text{O} \)

  0.4156 \text{ cm}^{-1} \], for ground state of \( \text{N}_2\text{O} \)
• **Accept ratio**
  0.3-0.6, to enhance the efficiency of PIMC sampling.

• **Number of time slices of transitional freedom:**
  N=256, 384,512.

• **Number of time slices of rotation freedom:**
  N= 32, 64, 128

• **Sampling steps**
  More than 2,000,000 sampling steps to reach quasi-ergodicity
Benchmark calculation: He-N$_2$O dimer of different time slices

<table>
<thead>
<tr>
<th>Number of time slices</th>
<th>Translation</th>
<th>Rotation</th>
<th>$E_{\nu=0}$(cm$^{-1}$)</th>
<th>$E_{\nu=1}$(cm$^{-1}$)</th>
<th>$\Delta \nu$(cm$^{-1}$)</th>
</tr>
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<td>64</td>
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<td>-21.295</td>
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</table>
Angular distribution of helium atoms around the N$_2$O probe molecule in the $^4$He$_N$−N$_2$O complexes. The density is normalized.
$^4\text{He}$ density $\rho(r, \theta)$ and averaged positions of the $^4\text{He}$ atoms around the $\text{N}_2\text{O}$ molecule. The ‘bond’ only shows the configurations of rings.
Vibrational band origin shift for the $^4\text{He}_N\text{N}_2\text{O}$ clusters
Effective rotational constant $B_{\text{eff}}$
Summary

1. It now becomes possible to **include the explicit dependence of the intramolecular degrees of freedom** in the studies of the rovibrational spectra of the complex.

2. With the explicit involvement of one intramolecular vibrational coordinate that is related to the transition in the infrared spectra, **full prediction of the infrared spectra including the shift of band origin can be achieved**.

3. The **vibrationally averaged potentials** are essential to simulate the spectroscopic properties of the related **vdW clusters**.
Further developments:

- complexes with a non-linear molecule
- complexes with an open-shell linear molecule.
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