Vibrational Conical Intersections in CH$_3$SH:
Implications for Spectroscopy and Dynamics in the CH Stretch Region

David S. Perry, Bishnu P. Thapaliya, Mahesh B. Dawadi, and Ram Bhatta
The University of Akron
**CH stretch vibrations in CH$_3$SH**

- Asymmetric CH stretches are quasi-degenerate (TF05 – Ron Lees, et al.)
- Degeneracy is required at $C_{3v}$ ($\rho = 0$), not at $\rho_{eq} = 83^\circ$.
- In CH$_3$OH the two asymmetric CH stretches are $\nu_2$ and $\nu_9$.
  - 42 cm$^{-1}$ apart
  - Split by Jahn-Teller coupling
- Extend the Jahn-Teller model to very large $\rho$. 
**CH stretch vibrations in CH₃SH**

- Asymmetric CH stretches are quasi-degenerate (TF05 – Ron Lees, *et al.*)
- Degeneracy is required at $C_{3v}$ ($\rho = 0$), not at $\rho_{eq} = 83^\circ$.
- In CH₃OH the two asymmetric CH stretches are $\nu_2$ and $\nu_9$.
  - 42 cm⁻¹ apart
  - Split by Jahn-Teller coupling
- Extend the Jahn-Teller model to very large $\rho$. 

Electronic potential energy, $U$

- 24,000 cm⁻¹

- $\rho_{eq} = 83^\circ$
- $\gamma = 24,000$ cm⁻¹
An $E \otimes e$ Jahn-Teller Model for Large-Amplitude Motion

- Use the Cartesian basis for the 2 asymmetric CH stretches

$$H_f = \begin{bmatrix} H_{f}^{a_1} & 0 \\ 0 & H_{f}^{a_1} \end{bmatrix} + \begin{bmatrix} H^{e}_{fxx} & H^{e}_{fxy} \\ H^{e}_{fxy} & -H^{e}_{fxx} \end{bmatrix}$$

- Expand coupling terms in the real spherical harmonics

$$H_{fi}^{\Gamma} (\rho, \gamma) = \sum_{l,m} c_{l,m}^{\Gamma} Y_{lm} (\rho, \gamma)$$

- Only symmetry-allowed terms appear ($l \geq |m|$):
  - $A_1$ terms $H_{f}^{a_1}$: $m = 0, 3, 6, ...$
  - $E$ terms $H^{e}_{fxx}$: $m = 1, 2, 4, 5, ...$ (cosine forms)
  - $H^{e}_{fxy}$: $m = -1, -2, -4, -5, ...$ (sine forms)

- The $E$ terms are Jahn-Teller coupling of order $|m|$.
An E⊗e Jahn-Teller Model for Large-Amplitude Motion

- Eigenvalues are adiabatic CH stretch energies.
- Keep Jahn-Teller coupling up to 4th order:

\[
E_{\pm} = (V^{0\gamma} + U^{0\gamma}) + (V^{3\gamma} + U^{3\gamma}) \cos 3\gamma + (V^{6\gamma} + U^{6\gamma}) \cos 6\gamma \\
\pm \left\{ (W^{1\gamma})^2 + (W^{2\gamma})^2 + (W^{4\gamma})^2 + 2W^{1\gamma}(W^{2\gamma} + W^{4\gamma}) \cos 3\gamma + 2W^{2\gamma}W^{4\gamma} \cos 6\gamma \right\}^{1/2}
\]

with

\[
U^{m\gamma}(\rho) = \sum_{l=m, m+1, \ldots} a_{lm} \frac{Y_{lm}(\rho, \gamma)}{\cos m\gamma}
\]

Electronic potential

\[
V^{m\gamma}(\rho) = \sum_{l=m, m+1, \ldots} c_{lm} \frac{Y_{lm}(\rho, \gamma)}{\cos m\gamma}
\]

Diagonal vibrational energies

\[
W^{m\gamma}(\rho) = \sum_{l=m, m+1, \ldots} c_{lm}^e \frac{Y_{lm}(\rho, \gamma)}{\cos m\gamma}
\]

Jahn-Teller coupling terms of order \( m = 1, 2, 4 \).
Asymmetric CH stretch vibrations

CCSD(T)/aug-cc-pVTZ – nearly level-independent

- Dominant effect: Variation of the single-bond CH force constant
Asymmetric CH stretch vibrations

CCSD(T)/aug-cc-pVTZ – nearly level-independent

\[ C_3v \]

Staggered

Eclipsed

Experimental Splitting 1.5 cm\(^{-1}\)

1.48 cm\(^{-1}\)

\[ \rho_{eq} = 83^\circ \]
**Fit to the Jahn-Teller Hamiltonian**

- Conical intersections occur where even and odd coupling orders cancel.
- RMS of fit = 0.2 cm\(^{-1}\)
Asymmetric CH stretch vibrations in CH$_3$SH

CCSD(T)/aug-cc-pVTZ

- $V^{0y}$ is suppressed
Comparison to Methanol

$\text{CH}_3\text{SH}$

$\text{CH}_3\text{OH}$
CH$_3$SH Diabatization


Diabatic Surfaces
Jahn-Teller $1^{\text{st}}$-order
Jahn-Teller $2^{\text{nd}}$-order
1$^{\text{st}}$- and 2$^{\text{nd}}$-orders equal

Coupling
Methanol Diabatization

3 diabatization schemes correspond to Xu, Hougen, Lees' 3 limiting cases.

Diabatic Surfaces
Jahn-Teller 1\textsuperscript{st}-order

Jahn-Teller 2\textsuperscript{nd}-order

1\textsuperscript{st}- and 2\textsuperscript{nd}-orders equal

Coupling
CH$_3$SH and CH$_3$OH Comparison

**Adiabatic**, CH$_3$SH

**Diabatic**, Jahn-Teller 1$^{\text{st}}$-order, CH$_3$SH

**Coupling**, 1$^{\text{st}}$- and 2$^{\text{nd}}$-orders equal, CH$_3$SH

**Adiabatic**, CH$_3$OH

**Diabatic**, Jahn-Teller 1$^{\text{st}}$-order, CH$_3$OH

**Coupling**, 1$^{\text{st}}$- and 2$^{\text{nd}}$-orders equal, CH$_3$OH
<table>
<thead>
<tr>
<th>Fourier term $U^{\gamma_1}$</th>
<th>Parameter $^{a,b,c}$</th>
<th>Value $^{d,e,f}$</th>
<th>Fourier term $W^{\gamma_1}$</th>
<th>Parameter $^{g,h,i}$</th>
<th>Value $^{j,k,l}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0^{(0)}$</td>
<td>3.30095E4 (4.E1)</td>
<td>$b_0^{(0)}$</td>
<td>1.12453E4 (5.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_1^{(0)}$</td>
<td>-1.50622E4 (5.E1)</td>
<td>$b_1^{(0)}$</td>
<td>-2.42011E1 (6.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_2^{(0)}$</td>
<td>3.0758E4 (4.E1)</td>
<td>$b_2^{(0)}$</td>
<td>7.08361E1 (3.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_3^{(0)}$</td>
<td>-2.04977E3 (2.E1)</td>
<td>$b_3^{(0)}$</td>
<td>1.05213E1 (1.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_4^{(0)}$</td>
<td>3.42375E3 (1.E1)</td>
<td>$b_4^{(0)}$</td>
<td>-5.95254E-1 (9.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_6^{(0)}$</td>
<td>8.42112E2 (1.E0)</td>
<td>$b_{10}^{(0)}$</td>
<td>-1.19588E0 (9.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_8^{(0)}$</td>
<td>2.79798E2 (3.E-1)</td>
<td>$b_{12}^{(0)}$</td>
<td>-5.04997E-1 (9.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{10}^{(0)}$</td>
<td>1.05715E2 (2.E-1)</td>
<td>$b_{14}^{(0)}$</td>
<td>2.28496E-1 (8.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{12}^{(0)}$</td>
<td>4.05045E1 (2.E-1)</td>
<td>$V^{\gamma_1}$</td>
<td>7.88918E0 (2.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{14}^{(0)}$</td>
<td>1.63229E1 (1.E-1)</td>
<td>$b_3^{(3)}$</td>
<td>1.16344E1 (2.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{16}^{(0)}$</td>
<td>7.09012E0 (1.E-1)</td>
<td>$b_5^{(3)}$</td>
<td>3.78829E0 (2.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{18}^{(0)}$</td>
<td>2.04663E0 (9.E-2)</td>
<td>$b_7^{(3)}$</td>
<td>1.73914E0 (1.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_3^{(3)}$</td>
<td>5.98817E2 (2.E0)</td>
<td>$b_9^{(3)}$</td>
<td>6.10201E-1 (9.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_4^{(3)}$</td>
<td>-1.95957E2 (3.E0)</td>
<td>$b_{11}^{(3)}$</td>
<td>1.29995E-1 (2.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_5^{(3)}$</td>
<td>2.90249E2 (2.E0)</td>
<td>$b_6^{(6)}$</td>
<td>6.69021E2 (3.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_7^{(3)}$</td>
<td>3.02098E1 (2.E0)</td>
<td>$b_7^{(6)}$</td>
<td>2.3168E-2 (2.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_8^{(3)}$</td>
<td>1.36379E1 (2.E0)</td>
<td>$W^{\gamma_1}$</td>
<td>9.24198E0 (2.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_9^{(3)}$</td>
<td>1.76821E1 (8.E-1)</td>
<td>$c_1^{(1)}$</td>
<td>-1.97897E1 (3.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{10}^{(3)}$</td>
<td>2.53787E0 (7.E-2)</td>
<td>$c_2^{(1)}$</td>
<td>-2.87824E0 (6.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{11}^{(3)}$</td>
<td>3.6708E0 (1.E-1)</td>
<td>$c_3^{(1)}$</td>
<td>-6.37778E0 (9.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{13}^{(3)}$</td>
<td>4.89657E-1 (4.E-2)</td>
<td>$c_7^{(1)}$</td>
<td>-2.91523E0 (8.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{15}^{(3)}$</td>
<td>6.46955E-1 (1.E-1)</td>
<td>$c_9^{(1)}$</td>
<td>-1.14541E0 (7.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{17}^{(3)}$</td>
<td>-1.19922E1 (3.E-2)</td>
<td>$c_{11}^{(1)}$</td>
<td>-2.17707E-1 (2.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{19}^{(3)}$</td>
<td>-5.66397E-1 (3.E-2)</td>
<td>$c_5^{(4)}$</td>
<td>-6.54657E-1 (1.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_2^{(2)}$</td>
<td>3.97752E0 (1.E-1)</td>
<td>$c_6^{(4)}$</td>
<td>-7.48121E-1 (2.E-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_4^{(2)}$</td>
<td>-4.1412E0 (2.E-1)</td>
<td>$c_{10}^{(4)}$</td>
<td>2.40606E-1 (9.E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_5^{(2)}$</td>
<td>2.58245E0 (1.E-1)</td>
<td>Calculation method</td>
<td>CCSD(T)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{10}^{(2)}$</td>
<td>6.90844E-1 (9.E-2)</td>
<td>Basis set</td>
<td>aug-cc-pVTZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{12}^{(2)}$</td>
<td>2.68789E-1 (8.E-2)</td>
<td>RMS (vibrational part) $^{i}$</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMS (overall) $^{i}$</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_{data}^{u}$</td>
<td>114</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>