A simultaneous fit of $v_t = 0$ and 1 torsion-wagging-rotational levels of CH$_3$NH$_2$ using a hybrid (tunneling-and-non-tunneling) Hamiltonian formalism

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Hybrid program for CH$_3$-NH$_2$ type molecules

What is a “methylamine-type molecule”? = a molecule with 2 Large Amplitude Motions:
1 internal-rotation motion (rotatory)
1 back-and-forth motion (oscillatory)

What is the form of a “hybrid” H matrix?

\[
\begin{pmatrix}
H_{\text{rot-torsion}} & H_{\text{tunneling}} \\ \\
H_{\text{tunneling}} & H_{\text{rot-torsion}}
\end{pmatrix}
\]

Up
\(\text{H}_3\text{C}-\text{N}\)
\(\text{H}\)

Down
\(\text{H}_3\text{C}-\text{N}\)
\(\text{H}\)
Why do we need a hybrid program?

Rotational levels of methylamine-like molecules can be fit nearly to measurement error by a pure tunneling Hamiltonian formalism. (Ohashi & Hougen, J. Mol. Spectrosc. 121 (1987) 474-501.)

The two main deficiencies of the tunneling formalism (which the hybrid program partially fixes) are:

(i) It cannot (can) treat the tunneling components of two different vibrational (torsional) states at the same time.

(ii) It cannot (can) treat vibrational (torsional) states near or above the (torsional) barrier to any tunneling motion.
Today’s application of the hybrid program:
Fit two torsional states simultaneously, but both are below the top of the torsional barrier.

The fitted MW and FIR data are in the 1980 – 2016 literature (~10 papers). Two recent papers are:
Gulaczyk, Kręglewski, Horneman, JMS 342 (2016) 25

Data: ~ 14 760 lines ≈ ~ 2630 MW ⊕ ~ 12 040 IR
Quantum numbers: ν_t = 0, 1;  J ≤ 36;  K ≤ 17
Symmetry species: A_1, A_2, B_1, B_2, E_1, E_2
Fitting parameters: 75, so ~197 lines/parameter
Weighted standard deviation = 1.60 = 😞 & 😊.
Comparison of our present best fit with Gulaczyk et al. Green = Good for hybrid program. Red = Bad for hybrid.

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td># of parameters:</td>
<td>75 (~ half of 88+55)</td>
</tr>
<tr>
<td>( J_{\text{max}} ) = 40</td>
<td>( J_{\text{max}} ) = 36 (tech. diff.)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( v_t = 0-0 ) FIR [1]</td>
<td>670 0.00060 cm(^{-1})</td>
</tr>
<tr>
<td>(one-state fit)</td>
<td></td>
</tr>
<tr>
<td>( v_t = 1-1 ) FIR [1]</td>
<td>86 0.00091 cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( v_t = 1-0 ) FIR [3]</td>
<td>11371 0.00063 cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( v_t = 0-0 ) MW [2]</td>
<td>2487 0.20 MHz</td>
</tr>
<tr>
<td>(one-state fit)</td>
<td></td>
</tr>
<tr>
<td>( v_t = 1-1 ) MW [2]</td>
<td>212 0.31 MHz</td>
</tr>
<tr>
<td></td>
<td>206 0.41 MHz</td>
</tr>
</tbody>
</table>

Meaning of a weighted standard deviation $\sigma = 1.6$ is shown to the right $\rightarrow$

$\therefore \sigma = 1.6$ is good enough to apply hybrid program to higher $\nu_t$ states. **BUT** may need help in choosing fitting parameters.
Summary and examples of new ordering scheme


Old and New order

<table>
<thead>
<tr>
<th>Torsional motion:</th>
<th>Rotational motion:</th>
<th>Inversion motion:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_\alpha^k$, $\cos 3m\alpha$</td>
<td>$J_x^p, J_y^q, J_z^r$</td>
<td>$P_\gamma$, $\gamma$</td>
</tr>
<tr>
<td>$k, 2m$</td>
<td>$p, q, r$</td>
<td>$0, 0$</td>
</tr>
</tbody>
</table>

LR, RL adds 2 to order 2, 2

<table>
<thead>
<tr>
<th>ntrw</th>
<th>Expression</th>
<th>LL, RR</th>
<th>LR, RL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>$\frac{1}{2}(1 - \gamma \cos 3\alpha)$</td>
<td>LL, RR</td>
<td>1 (inv. tunneling)</td>
</tr>
<tr>
<td>2110</td>
<td>$P_\alpha J_z$</td>
<td>LL, RR</td>
<td>3012</td>
</tr>
<tr>
<td>2020</td>
<td>$J_x^2, J_y^2, J_z^2$</td>
<td>LL, RR</td>
<td>4022</td>
</tr>
</tbody>
</table>

$\gamma = \{J_x J_z\}$

$\text{LL: } H_{\text{rot-torsion}}$

$\text{LR: } H_{\text{tunneling}}$

$\text{RL: } H_{\text{tunneling}}$

$\text{RR: } H_{\text{rot-torsion}}$
Conclusions

The hybrid model seems to be useful to treat two torsional states simultaneously in a 2-D large amplitude motion problem.

Future Work

Predict and fit $v_t=2,3$ FIR (Poznań) and $v_t=1,2$ MW data (Kharkov & Lille) for methylamine. Find determinable parameters by doing a contact-transformation reduction of $H$ with new ordering scheme.
Diagram of Frameworks for the Pure Tunneling Formalism

Diagram of Frameworks for the Hybrid Formalism
The only previous application of the hybrid program successfully resolved a specific 2-methylmalonaldehyde problem. (Kleiner & Hougen, J.Phys.Chem. A 119 (2015) 10664)

But, this previous work was not really a good test of the hybrid model because:

(i) Only one vibrational level was fitted.
(ii) The level was deep in the well.
New ordering scheme used for hybrid program

Interaction terms are products of powers of basic operators that are allowed in the PI group $G_{12}$:

Old ordering is from Nakagawa, Tsunekawa, Kojima, JMS 126 (1987) 329-340. $n = t + r \rightarrow ntr$

New ordering recognizes that operators occur in tunnelling or non-tunneling blocks of $H$ matrix.

$P_{\alpha^2}, \cos6\alpha, J_x^2, J_y^2, J_z^2$ in LL, RR, LR, RL
$\gamma\cos3\alpha, \gamma(J_xJ_z+J_zJ_x)$ in LL, RR
$P_\gamma J_y$ in LR, RL

LR, RL adds 2 to new order index $w$. 

\[
\begin{array}{c|c|c|c}
\text{LL} & H_{\text{rot-torsion}} & \text{LR} & H_{\text{tunneling}} \\
\text{RL} & H_{\text{tunneling}} & \text{RR} & H_{\text{rot-torsion}} \\
\end{array}
\]
**Theoretical Model: the global approach**

\[ H_{\text{RAM}} = H_{\text{rot}} + H_{\text{tor}} + H_{\text{int}} + H_{\text{d.c.}} \]

**Torsional operators and potential function \( V(\alpha) \)**

<table>
<thead>
<tr>
<th>Constants</th>
<th>1</th>
<th>1-cos3(\alpha) (p^2_\alpha)</th>
<th>(J_a p_\alpha)</th>
<th>1-cos6(\alpha) (p^4_\alpha)</th>
<th>(J_a p^3_\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J^2)</td>
<td></td>
<td>(V_3/2)</td>
<td>(F)</td>
<td>(V_6/2)</td>
<td>(k_4)</td>
</tr>
<tr>
<td>(J_a^2)</td>
<td></td>
<td>(F_v)</td>
<td>(G_v)</td>
<td>(L_v)</td>
<td>(N_v)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(M_v)</td>
<td></td>
<td>(k_3J)</td>
<td></td>
</tr>
<tr>
<td>(J_b^2 - J_c^2)</td>
<td></td>
<td>(k_5)</td>
<td>(k_2)</td>
<td>(k_1)</td>
<td>(K_2)</td>
</tr>
<tr>
<td>(J_a J_b + J_b J_a)</td>
<td></td>
<td>(K_1)</td>
<td>(k_{3K})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha) = angle of torsion, (\rho) = couples internal rotation and global rotation, ratio of the moment of inertia of the top and the moment of inertia of the whole molecule</td>
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Kirtman et al 1962  
Lees and Baker, 1968  
Herbst et al 1986  
Hougen, Kleiner, Godefroid JMS 1994
Theoretical approach of the “hybrid” program

For internal rotation RAM Hamiltonian of Herbst et al (1984):
\[ F(P_\alpha - \rho J_z)^2 + \frac{1}{2} V_3 (1 - \cos 3\alpha), \]
+ higher order torsion-rotation terms as found in the BELGI code.

For the motion in a double-well potential (-NH\(_2\) inversion or H transfer motion),
a tunneling formalism, where \( H = T + V \) is replaced with one tunneling splitting parameter +
higher-order torsion-rotation corrections.