Rotational Parameters from Vibronic Eigenfunctions of Jahn-Teller Active Molecules

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Advances in theory allow for greater insight into the role conical intersections play in determining molecular properties.
The Jahn-Teller effect distorts molecular geometry to lower symmetry and break degeneracies.

Breaking symmetry creates conical intersections on potential energy surfaces.
Rotational Hamiltonian

\[ H = H_R + H_{COR} + H_{CD} + H_{JT} \]

\[ H_R = C N_z^2 + B (N_x^2 + N_y^2) \]
\[ H_{COR} = -C \xi_t N_z \]

\[ H_{CD} = -D_N N^4 - D_{NK} N^2 N_z^2 - D_K N_z^4 - \]
\[ \eta N_z \xi_t N_z L_z - \eta_k \xi_k N_z^3 L_z \]

\[ H_{JT} = h_1 \left[ L_-^2 N_+^2 + L_+^2 N_+^2 \right] \]
\[ + h_2 \left[ L_-^2 (N_z N_+ + N_+ N_z) + L_+^2 (N_z N_+ + N_+ N_z) \right] \]
$h_1$ Parameter from $H_{JT}$

- Experimental value for vibrationless state $h_1$ is well known
- We want to predict $h_1$ for various vibrationally excited states using electronic structure calculations

- Cyclopentadienyl radical (CP): A Great Candidate!
Simulations of Cyclopentadienyl $\tilde{A}^2A'' \leftarrow \tilde{X}^2E''$ $0^0_0$
$h_1$ Fundamental Definition

- An element of the rovibronic Hamiltonian

\[
h_1 = \frac{1}{2} \left[ \langle E_j^k, + | \left| B_{++} \right| E_j^k, - \rangle + \langle E_j^k, - | \left| B_{--} \right| E_j^k, + \rangle \right]
\]

\[
| E_j^k, \pm \rangle \equiv | \pm j, n_j, E_j^k, \Sigma \rangle = \sum_i \left( c_{i,n_j,\Sigma} | \pm \Lambda_i \rangle \prod_{k=1}^{p} | v_{k,i}, \pm l_{k,i} \rangle \right)
\]

\[
\times \prod_{n=1}^{3N-6-2p} | v_{n,i} \rangle \left| \pm \Sigma_i \right\rangle
\]

- A measure of geometric distortions due to Jahn-Teller effects

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An Expression for $h_1$

- Watson derived $h_1$ through a perturbation type analysis

\[ q^{JT} = 2 \sum_t k_t \omega_t C_{ta}^{xx} = 2 \sum_t k_t \frac{\partial B_{xx}}{\partial q_{ta}} \]

\[ h_1 = \frac{1}{2} q^{JT} = \sum_t k_t \frac{\partial B_{xx}}{\partial q_{ta}} \]

\[ D_t \equiv \frac{1}{2} k_t^2 \]

Results from Perturbation Analysis on CP

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<tr>
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Perturbation type analyses works best only in cases of small distortions. Limited to cases of linear Jahn-Teller effects.

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- Limited to cases of linear Jahn-Teller effects.

Our Approach

We treat the operator as a Taylor series expansion about the conical intersection with respect to normal mode vibrations

\[ h_1 = \frac{1}{2} \left[ \langle E_j^k, + | B_{++} | E_j^k, - \rangle + \langle E_j^k, - | B_{--} | E_j^k, + \rangle \right] \]

\[ B_{\pm \pm} \approx B_{\pm \pm}^{CI} + \sum_k \sum_{m=+, -} \left( \frac{\partial B_{\pm \pm}}{\partial q_{km}} \right)_{CI} q_{km} + \ldots \]
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\[
B_{\pm\pm} \approx B_{\pm\pm}^{\text{CI}} + \sum_k \sum_{m=\pm} p \left( \frac{\partial B_{\pm\pm}}{\partial q_{km}} \right)_{\text{CI}} q_{km} + \ldots
\]

- To simply this operator we express it in Cartesian coordinates

\[
B_{\pm\pm} = \frac{1}{4} \left( B_{xx} - B_{yy} \mp 2iB_{xy} \right) \quad B_{\pm\pm}^{\text{CI}} = 0
\]

\[
B_{\pm\pm} \approx B_{\pm\pm}^{\text{CI}} + \frac{1}{4} \sum_k \sum_{m=\pm} p \left( \frac{\partial B_{xx}}{\partial q_{km}} - \frac{\partial B_{yy}}{\partial q_{km}} \mp 2i \frac{\partial B_{xy}}{\partial q_{km}} \right)_{\text{CI}} q_{km}
\]
We have treated $q$ as the complex combination of the degenerate components

$$q_{k\pm} = q_{ka} \pm i q_{kb}$$

$$\frac{\partial B_{\pm\pm}}{\partial q_{k\pm}} = \frac{1}{8} \left( \frac{\partial B_{xx}}{\partial q_{ka}} - \frac{\partial B_{yy}}{\partial q_{ka}} \mp 2 \frac{\partial B_{xy}}{\partial q_{kb}} \right)$$
With Respect to Complex Combinations

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$$\frac{\partial B_{xx}}{\partial q_a} = -\frac{\partial B_{yy}}{\partial q_a} = \frac{\partial B_{xy}}{\partial q_b} \quad \frac{\partial B_{xx}}{\partial q_b} = \frac{\partial B_{yy}}{\partial q_b} = \frac{\partial B_{xy}}{\partial q_a} = 0$$
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$$\begin{align*} 
\frac{\partial B_{xx}}{\partial q_a} &= -\frac{\partial B_{yy}}{\partial q_a} = \frac{\partial B_{xy}}{\partial q_b} \\
\frac{\partial B_{xx}}{\partial q_b} &= \frac{\partial B_{yy}}{\partial q_b} = \frac{\partial B_{xy}}{\partial q_a} = 0 \\
\frac{\partial B_{-\pm}}{\partial q_{k+}} &= \frac{\partial B_{++}}{\partial q_{k-}} = \frac{1}{2} \frac{\partial B_{xx}}{\partial q_a} \\
\frac{\partial B_{++}}{\partial q_{k+}} &= \frac{\partial B_{--}}{\partial q_{k-}} = 0
\end{align*}$$
A Simple Expression

\[ h_1 = \frac{1}{2} \left[ \langle E_j^k, + \mid B_{++} \mid E_j^k, - \rangle + \langle E_j^k, - \mid B_{--} \mid E_j^k, + \rangle \right] \]

\[ h_1 = \frac{1}{4} \sum_k \frac{\partial B_{xx}}{\partial q_a} \left( \langle E_j^k, + \mid q_{k-} \mid E_j^k, - \rangle + \langle E_j^k, - \mid q_{k+} \mid E_j^k, + \rangle \right) \]

\[ < q > \equiv \langle E_j^k, + \mid q_{k-} \mid E_j^k, - \rangle + \langle E_j^k, - \mid q_{k+} \mid E_j^k, + \rangle \]
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\[ \langle q \rangle \equiv \langle E_j^k, + | q_{k-} | E_j^k, - \rangle + \langle E_j^k, - | q_{k+} | E_j^k, + \rangle \]

\[ h_1 = \frac{1}{4} \sum_k \frac{\partial B_{xx}}{\partial q_a} \langle q \rangle \]

This relatively simple expression only requires two components:
- Derivatives of rotational constants
- Matrix elements of the ladder operators
Derivatives of $B$

Derivatives taken by uniform grid central finite differentiation in Cartesian coordinates

$$\frac{\partial B_{xx}}{\partial q_a} \approx \frac{B_{xx}(\omega + \delta q_a) - B_{xx}(\omega - \delta q_a)}{2\delta}$$

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Cartesian coordinates provided courtesy of Dr. John Stanton
Rotational Parameters from Vibronic Eigenfunctions of Jahn-Teller Active Molecules

**B(q) for Degenerate 1072.7 cm$^{-1}$ Vibration**
Calculating $< q >$

- SOCJT 2 calculates spin vibronic eigenfunctions and eigenvalues
- $q_{k\pm}$ are the ladder operators on the polar harmonic oscillator

$$
\langle v + 1, l + 1 | q_+ | v, l \rangle = \sqrt{(v + l + 2)/(2\gamma)}
$$

$$
\langle v + 1, l - 1 | q_- | v, l \rangle = \sqrt{(v - l + 2)/(2\gamma)}
$$

$$
\langle v - 1, l + 1 | q_+ | v, l \rangle = \sqrt{(v - l)/(2\gamma)}
$$

$$
\langle v - 1, l - 1 | q_- | v, l \rangle = \sqrt{(v + l)/(2\gamma)}
$$

- For reduced normal coordinates

$$\gamma = 1$$

## Results from Cyclopentadienyl Vibrationless State

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<thead>
<tr>
<th>Vibrational Frequency</th>
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<tr>
<td>853.9</td>
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<td>-0.00726066</td>
</tr>
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<td>1133.9</td>
<td>-1.943826112</td>
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<td>1512.2</td>
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<td>0.00175759</td>
</tr>
<tr>
<td>3371.8</td>
<td>0.029440343</td>
<td>0.000909696</td>
</tr>
</tbody>
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| Calculated $h_1$      | -0.00691 cm$^{-1}$       |
| Magnitude Experimental $h_1$ | 0.00706$^a$ cm$^{-1}$   |

Extension to Vibrationally Excited States

- SOCJT 2 produces eigenvalues and eigenvectors for all vibrational states
- Predicting $h_1$ requires a calculation of $\langle q \rangle$
Conclusions

Accomplishments

- A simple formulation and code to predict $h_1$ for vibrational states using electronic structure parameters
- Determining $h_1$ helps benchmark potential energy surfaces for JT distorted molecules

Upcoming

- Extension to high order terms in the Taylor expansion for increasingly accurate calculations
- Use the calculated values for $h_1$ to determine rotational structure and verify assignments of vibrational bands
- Apply methodology to other parameters in rovibronic Hamiltonian
Acknowledgments

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  - Dr. Terry A. Miller
  - Dr. Ketan Sharma
  - Meng Huang
  - Yi Yan
- Dr. John Stanton at The University of Florida