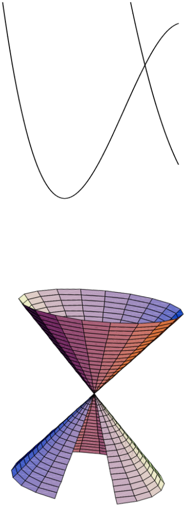
Rotational Parameters from Vibronic Eigenfunctions of Jahn-Teller Active Molecules

Scottt Garner and Terry A. Miller

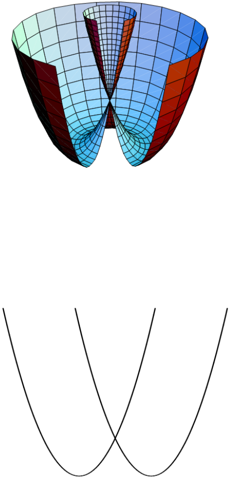
The Ohio State University

June 19, 2017

Conical Intersections

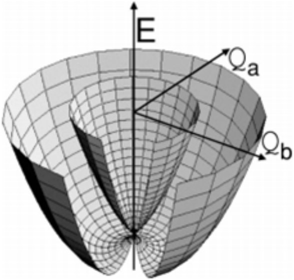


- Advances in theory allow for greater insight into the role conical intersections play in determining molecular properties



Jahn-Teller Effect

- The Jahn-Teller effect distorts molecular geometry to lower symmetry and break degeneracies
- Breaking symmetry creates conical intersections on potential energy surfaces



Rotational Hamiltonian

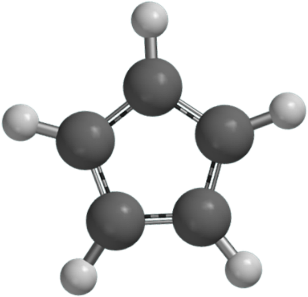
$$H = H_R + H_{COR} + H_{CD} + H_{JT}$$

$$H_R = CN_z^2 + B\left(N_x^2 + N_y^2\right)$$
$$H_{COR} = -C\xi_t N_z$$

$$H_{CD} = -D_N\mathbf{N}^4 - D_{NK}\mathbf{N}^2N_z^2 - D_K N_z^4 - \eta_N\xi_t\mathbf{N}^2N_z\mathcal{L}_z - \eta_k\xi_k N_z^3\mathcal{L}_z$$

$$H_{JT} = h_1\left[\mathcal{L}_-^2N_+^2 + \mathcal{L}_+^2N_-^2\right] + h_2\left[\mathcal{L}_-^2\left(N_zN_- + N_-N_z\right) + \mathcal{L}_+^2\left(N_zN_+ + N_+N_z\right)\right]$$

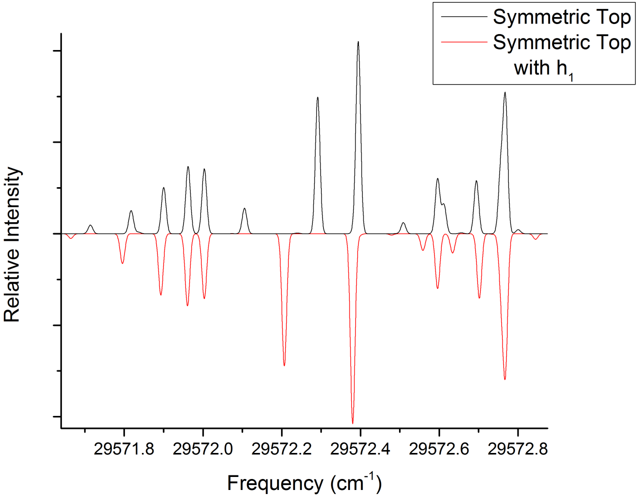
h_1 Parameter from H_{JT}



- Cyclopentadienyl radical (CP): A Great Candidate!

- 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

Simulations of Cyclopentadienyl $\tilde{A}^2A_2'' \leftarrow \tilde{X}^2E_1''\ 0_0^0$



h_1 Fundamental Definition

- An element of the rovibronic Hamiltonian

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

$$\left|E_j^k, \pm\right\rangle \equiv \left|\pm j, n_j, E_j^k, \Sigma\right\rangle = \sum_i \left(c_{i,n_j,\Sigma} \left|\pm\Lambda_i\right\rangle \prod_{k=1}^{p} \left|v_{k,i}, \pm l_{k,i}\right\rangle \right. \\ \left. \times \prod_{n=1}^{3N-6-2p} \left|v_{n,i}\right\rangle \left|\pm\Sigma_i\right\rangle \right)$$

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

---

J.T. Hougen, *J. Mol. Spectrosc.* **81,** 73-92 (1980).

An Expression for h_1

- Watson derived h_1 through a perturbation type analysis

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

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

$$D_t \equiv \frac{1}{2} k_t^2$$

J. K. G. Watson, *J. Molec. Spectrosc.* **103** 125-146, (1984)

Results from Perturbation Analysis on CP

Vibrational Mode Frequency	D$\equiv \frac{1}{2}k_t^2$ (unitless)	$\frac{\partial B_{xx}}{\partial q_a}$ (cm^{-1})
846.7	0.184852507	-0.00726066
1072.7	0.358097239	0.006906353
1421	0.634506116	0.00175759
3165.9	8.09396E-05	0.000909696
Calculated h_1	0.003398 cm^{-1}	
Magnitude Experimental h_1	0.00706 cm^{-1}	

Lian Yu et al. *Chem. Phys. Letters* **162,** 431, (1989)

Results from Perturbation Analysis on CP

Vibrational Mode Frequency	D$\equiv \frac{1}{2}k_t^2$ (unitless)	$\frac{\partial B_{xx}}{\partial q_a}$ (cm^{-1})
846.7	0.184852507	-0.00726066
1072.7	0.358097239	0.006906353
1421	0.634506116	0.00175759
3165.9	8.09396E-05	0.000909696
Calculated h_1	0.003398 cm^{-1}	
Magnitude Experimental h_1	0.00706 cm^{-1}	

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

Lian Yu et al. *Chem. Phys. Letters* **162,** 431, (1989)

Our Approach

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

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

$$B_{\pm\pm} \approx B_{\pm\pm}^{\mathrm{CI}} + \sum_{k}^{p} \sum_{m=+,-} \left(\frac{\partial B_{\pm\pm}}{\partial q_{km}}\right)_{\mathrm{CI}} q_{km} + \dots$$

Our Approach

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

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

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

- To simply this operator we express it in Cartesian coordinates

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

$$B_{\pm\pm} \approx B_{\pm\pm}^{\text{CI}} + \frac{1}{4}\sum_k^p \sum_{m=+,-} \left(\frac{\partial B_{xx}}{\partial q_{km}} - \frac{\partial B_{yy}}{\partial q_{km}} \mp 2i\frac{\partial B_{xy}}{\partial q_{km}}\right)_{\text{CI}} q_{km}$$

With Respect to Complex Combinations

- 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

- We have treated q as the complex combination of the degenerate components

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

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

$$\frac{\partial B_{xx}}{\partial q_a} = -\frac{\partial B_{yy}}{\partial q_a} = \frac{\partial B_{xy}}{\partial q_b} \qquad \frac{\partial B_{xx}}{\partial q_b} = \frac{\partial B_{yy}}{\partial q_b} = \frac{\partial B_{xy}}{\partial q_a} = 0$$

With Respect to Complex Combinations

- We have treated q as the complex combination of the degenerate components

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

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

$$\frac{\partial B_{xx}}{\partial q_a} = -\frac{\partial B_{yy}}{\partial q_a} = \frac{\partial B_{xy}}{\partial q_b} \qquad \frac{\partial B_{xx}}{\partial q_b} = \frac{\partial B_{yy}}{\partial q_b} = \frac{\partial B_{xy}}{\partial q_a} = 0$$

$$\frac{\partial B_{--}}{\partial q_{k+}} = \frac{\partial B_{++}}{\partial q_{k-}} = \frac{1}{2}\frac{\partial B_{xx}}{\partial q_a} \qquad \frac{\partial B_{++}}{\partial q_{k+}} = \frac{\partial B_{--}}{\partial q_{k-}} = 0$$

A Simple Expression

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

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

$$< q > \equiv \left\langle E_j^k,+\right| q_{k-}\left|E_j^k,-\right\rangle + \left\langle E_j^k,-\right| q_{k+}\left|E_j^k,+\right\rangle$$

A Simple Expression

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

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

$$< q > \equiv \left\langle E_j^k, +\right| q_{k-} \left|E_j^k, -\right\rangle + \left\langle E_j^k, -\right| q_{k+} \left|E_j^k, +\right\rangle$$

$$h_1 = \frac{1}{4}\sum_k^p \frac{\partial B_{xx}}{\partial q_a} < q >$$

This relatively simple expression only requires two components

- Derivatives of rotational constants
- Matrix elements of the ladder operators

Derivatives of **B**

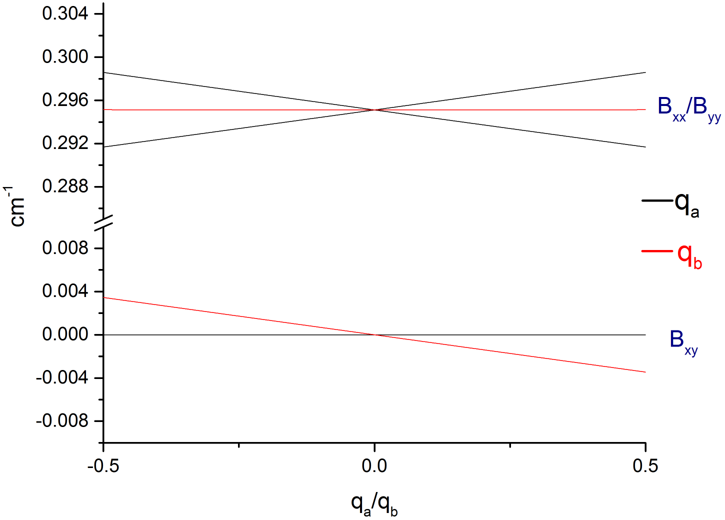
- Derivatives taken by uniform grid central finite differentiation in Cartesian coordinates

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

Vibrational Mode Frequency	$\frac{\partial B_{xx}}{\partial q_a}$ in cm^{-1}
846.7	-0.00726066
1072.7	0.006906353
1421	0.00175759
3165.9	0.000909696

Cartesian coordinates provided courtesy of Dr. John Stanton

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

$$\gamma = 1$$

T. Codd et al., *SOCJT 2 User Manual*, 2014

Results from Cyclopentadienyl Vibrationless State

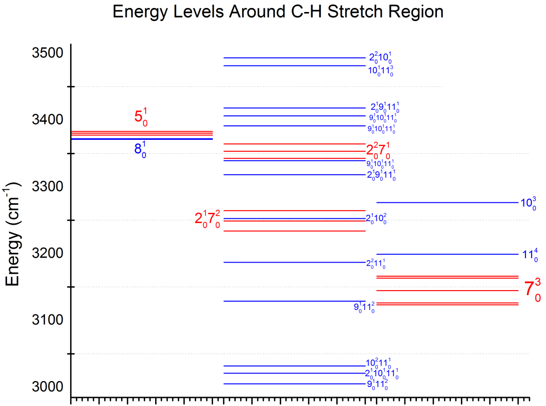
Vibrational Frequency	$< q >$	$\frac{\partial B_{xx}}{\partial q_a}$ in cm^{-1}
853.9	1.332448803	-0.00726066
1133.9	-1.943826112	0.006906353
1512.2	-2.604903871	0.00175759
3371.8	0.029440343	0.000909696
Calculated h_1	-0.00691 cm^{-1}	
Magnitude Experimental h_1	0.00706[a] cm^{-1}	

---

[a] Lian Yu et al. *Chem. Phys. Letters* **162**, 431, (1989)

Extension to Vibrationally Excited States

- SOCJT 2 produces eigenvalues and eigenvectors for all vibrational states
- Predicting h_1 requires a calculation of $< q >$



Energy Levels Around C-H Stretch Region

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

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