

Comparison of independently calculated
ab-initio normal-mode displacements for
the three C-H stretching vibrations of
methanol along the internal rotation path

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Did we really see no Berry phase change
in the normal mode displacements for
all three CH stretching vibrations?

Projected Frequency Calculations

Output = $\mathbf{v}(\gamma)$ and $\mathbf{d}_i(\gamma)$ functions

Internal rotation angle $\gamma = \text{LAM}$

(Large Amplitude Motion)

The Cartesian displacements $\mathbf{d}_i = \text{SAVs}$

(11 Small Amplitude Vibrations =

bond-length stretches and bond-angle bends)

Fix γ and calculate relaxed geometry and **SAVs**

there. Step γ to the next value and repeat.

γ used to be the torsion vibration, but it is now projected out and reclassified as a LAM.

The functions $v(\gamma)$ and $d_i(\gamma)$ take us mathematically into the land of Berry phase and conical intersections.

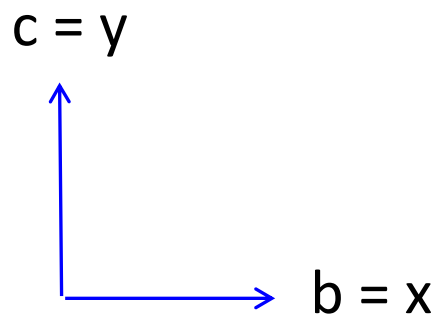
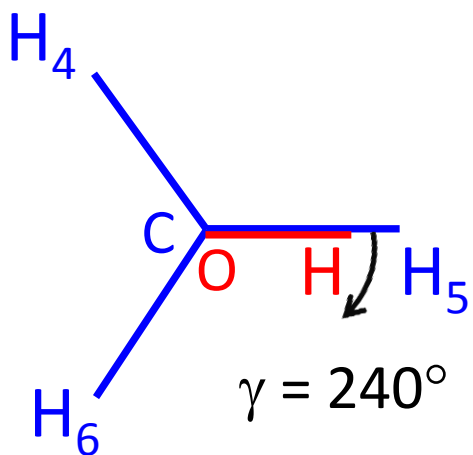
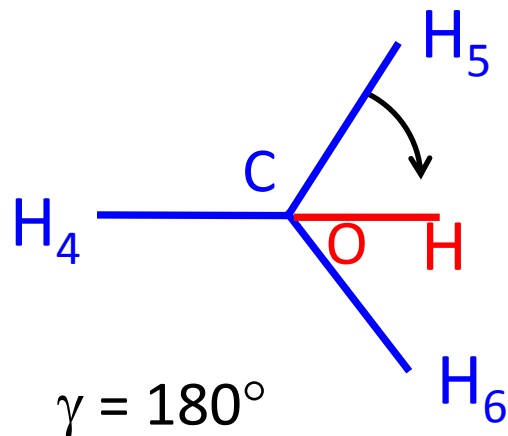
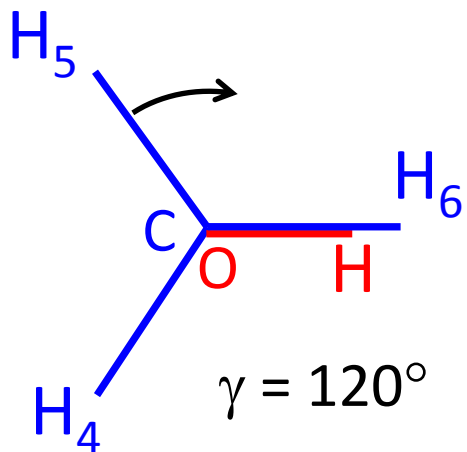
Conical intersections \neq topic of this talk.

But FC08: Conical Intersections between Vibrational Adiabatic Surfaces in Methanol
by M.B. Dawadi and D.S. Perry.

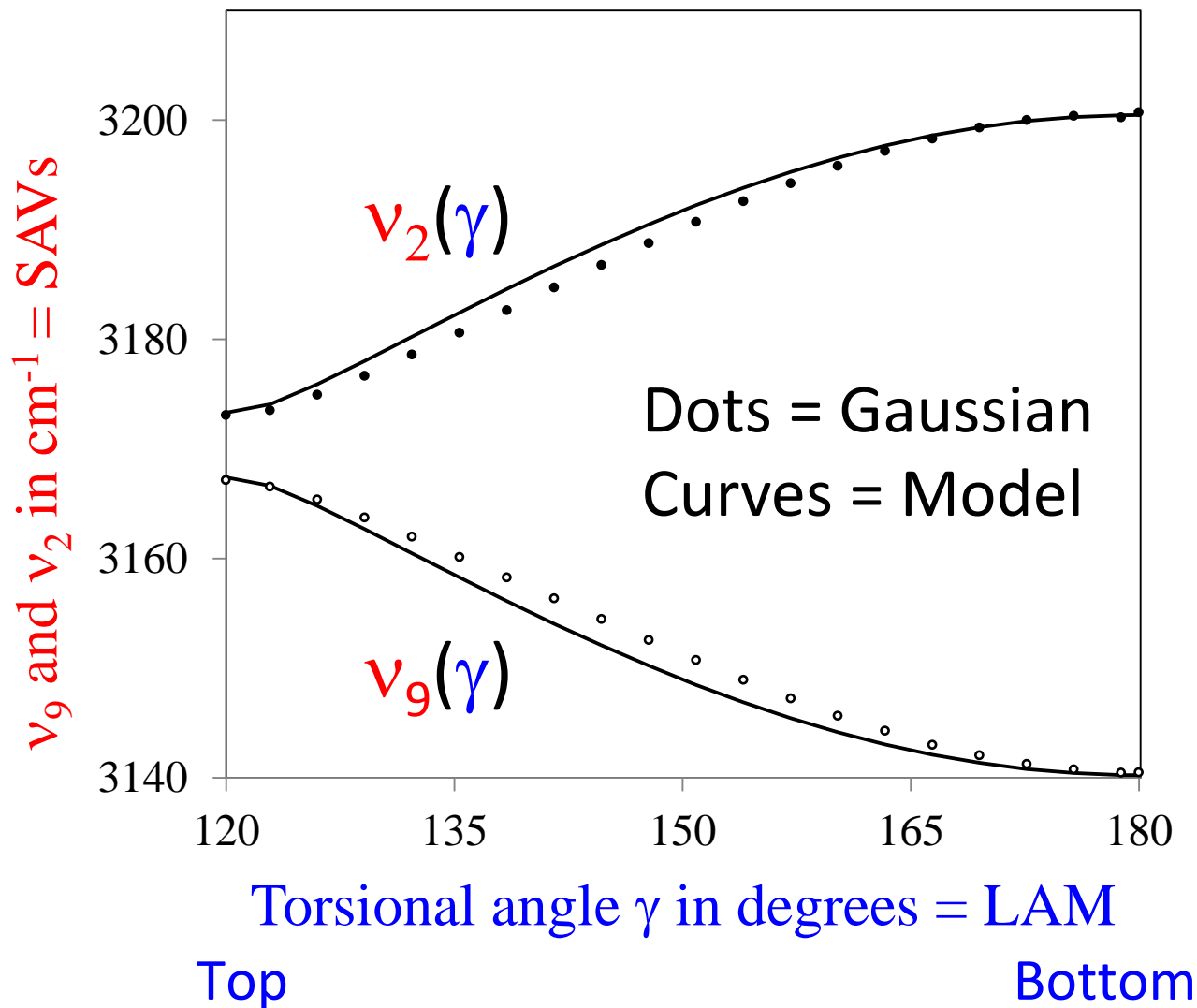
Conical intersections also arise in the vibronic Jahn-Teller effect, which has an enormous literature (from the past 50 years) and its own international meeting.

Back to projected frequency calculations

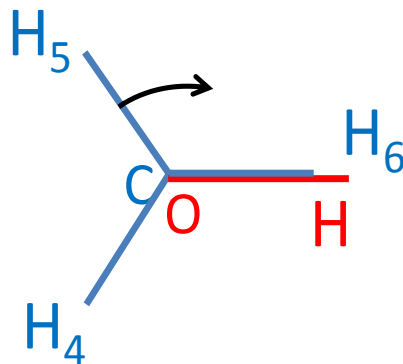
Atom Labels



Methanol Results: example of $\nu(\gamma)$ curves for two C-H stretching normal modes

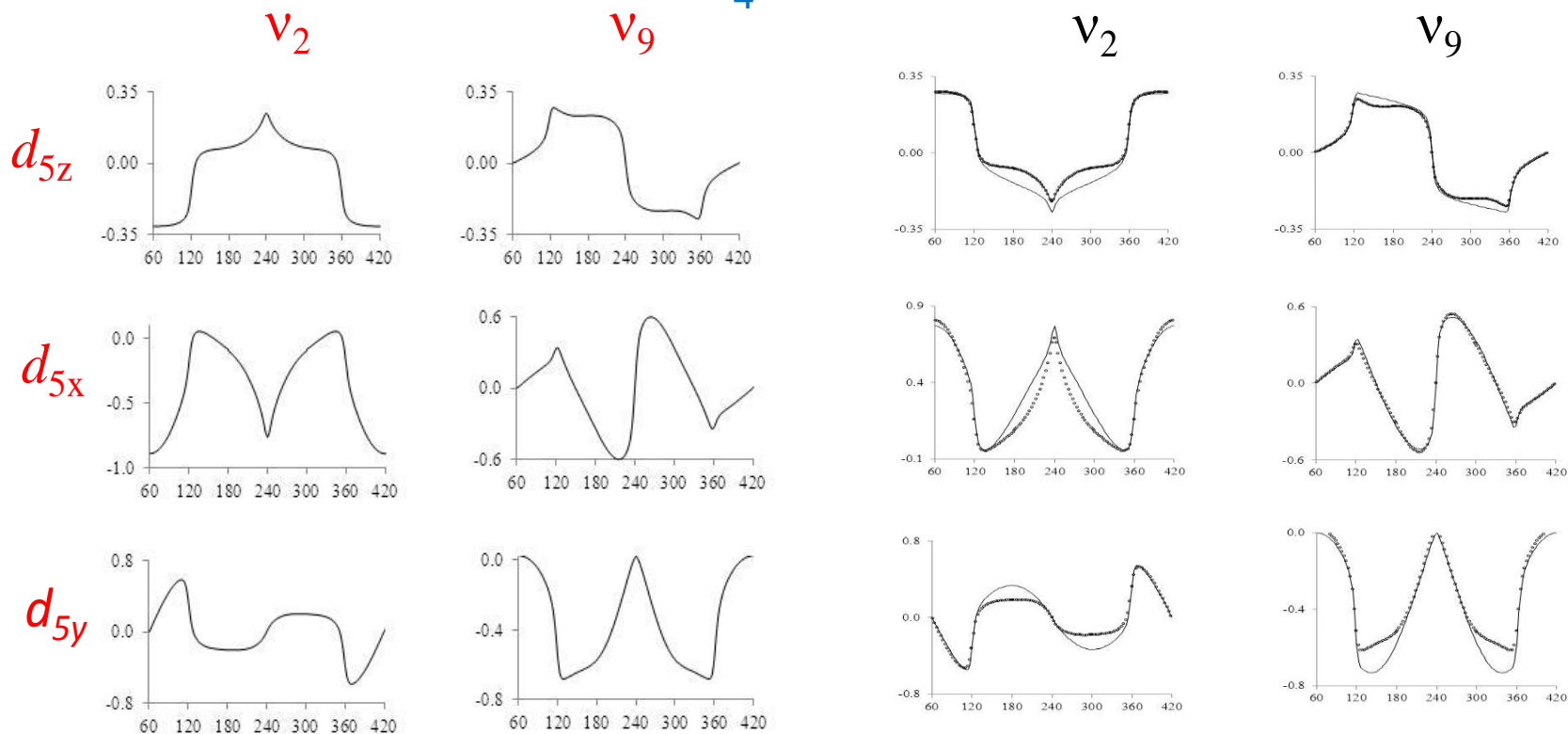


Cartesian coordinates $d(\gamma)$ for atom H_5 for v_2 and v_9



Ab Initio

Model



Model – solid line
Ab Initio - dots

What is geometric or Berry phase?

It is a property of $\psi_{\text{fast}}(\mathbf{q};\mathbf{Q})$ in systems divided into **fast** (\mathbf{q}) and **slow** (\mathbf{Q}) motions such that

$$\psi_{\text{fast}}(\mathbf{q};\mathbf{Q}) \rightarrow \pm \psi_{\text{fast}}(\mathbf{q};\mathbf{Q} \text{ goes around a loop})$$

when the **slow** coordinate(s) \mathbf{Q} are taken once around a closed loop (**once around a circle**).

The concept first arose when treating the **Jahn-Teller effect** in doubly degenerate electronic states and doubly degenerate vibrational states.

Why was the lack of a Berry phase change in these figures interesting? Interesting = code word for:
(i) difficult for others to believe, and therefore
(ii) worrisome for Li-Hong Xu, Ron Lees, and me.

Methanol has inverted A-above-E torsional splittings in two of its three C-H stretching fundamental states, discovered by D. Perry et al., but of interest to others.

It was sometimes assumed that this inversion happens because of a Berry phase change in the $\mathbf{d}_i(\gamma)$ vectors. If this assumption is correct, then Li-Hong, Ron and I have somehow made a terrible mistake in our projected frequency calculations.

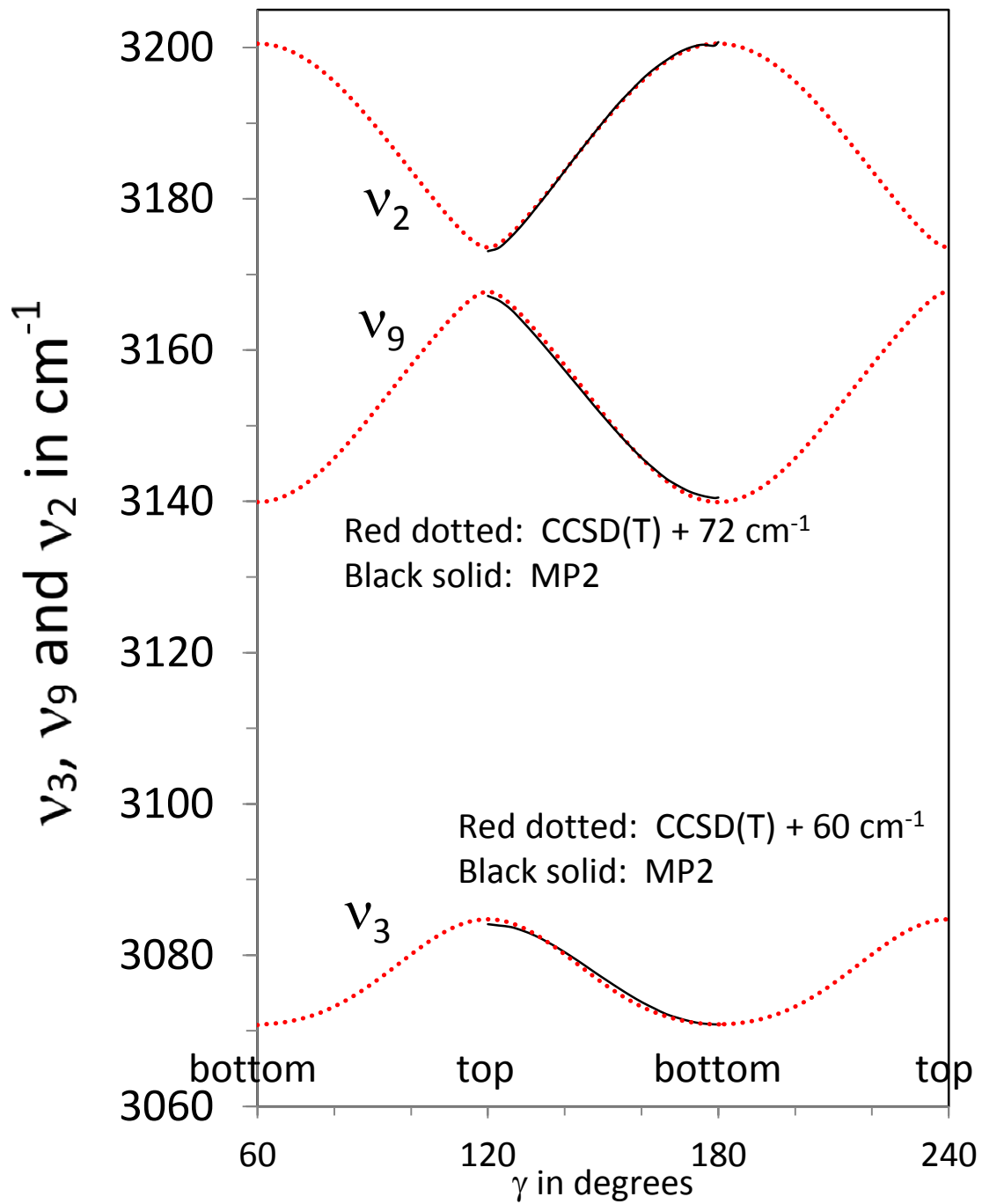
Some controversy in the lit. Is there a +1 or a -1 Berry phase change in the $d_i(\gamma+2\pi)$'s? We found +1 = no change.

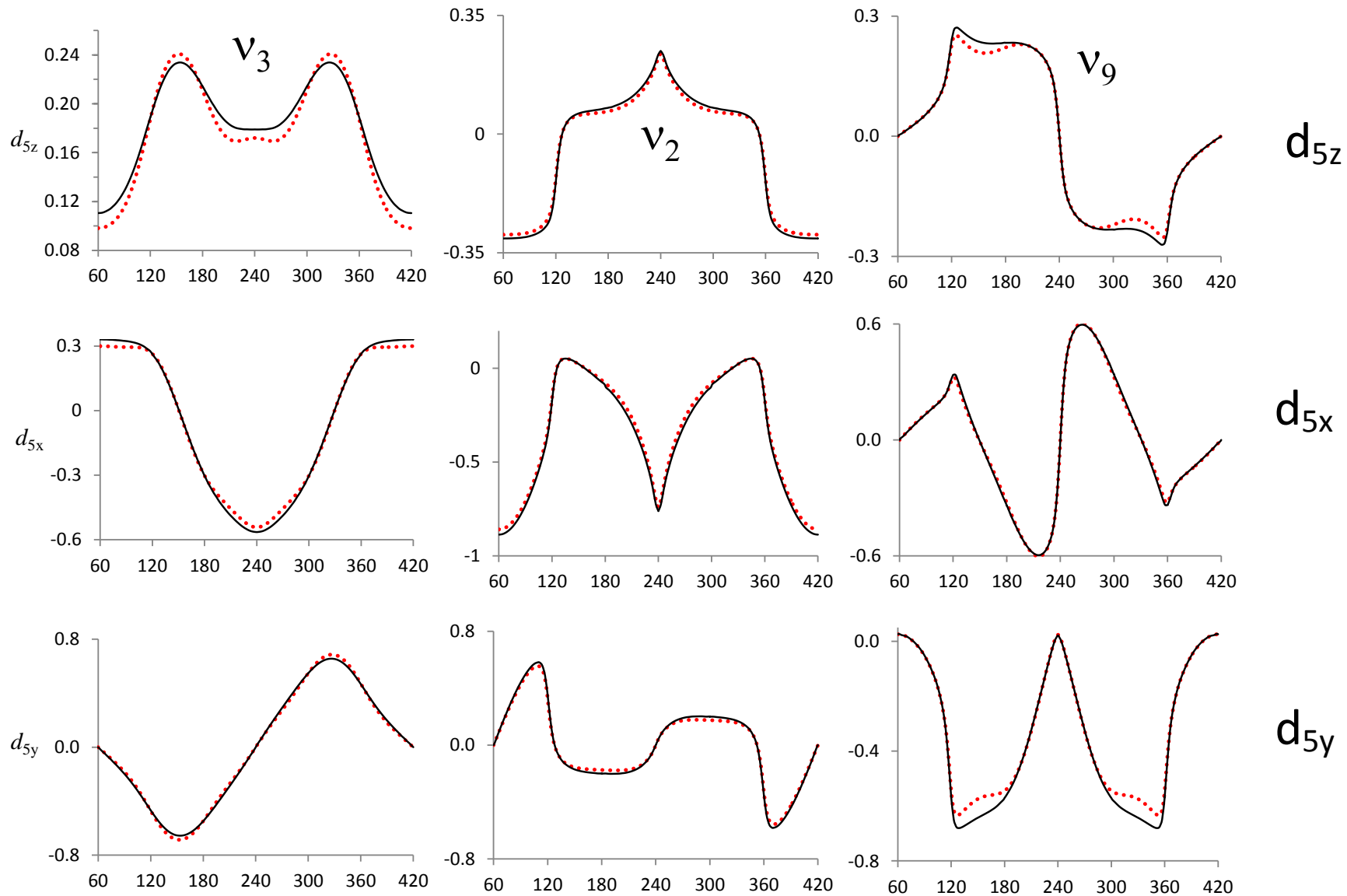
But two papers reported a Berry phase of -1:

1. D.S. Perry, J. Mol. Spectrosc. 257 (2009) 1-10. But there is no real disagreement with Perry, because one term was deliberately neglected in his model calculations. OSU 2013 Talk + Q&A.

2. B. Fehrens, D. Luckhaus, M. Quack, M. Willeke, T.R. Rizzo, J. Chem. Phys. 119 (2003) 5534-5544. Not enough info in paper to know what is going on here. We need to contact the authors.

Confirmation of our results came from re-examining high-level CCSD(T) calculations from 7 years ago [J.M. Bowman, X. Huang, N.C. Handy, S. Carter, J. Phys. Chem. A 111 (2007) 7317-7321]. $d_i(\gamma)$ curves obtained from their old files show no Berry phase change, and \therefore agree with our lower-level 6-311+G(3df,2p) MP2 results = Take-home message of this talk.





Torsional Angle in Degrees for a Complete Internal Rotation: $60^\circ \leq \gamma \leq 420$

Solid black = MP2, Dotted red = CCSD(T)

Unexpected additional confirmation came from the anonymous referee's comments on the joint paper being presented in this talk:

“I enjoyed reading this paper. I didn't believe the results at first. In fact I was sure they were wrong, so I carried out a parallel calculation using a different set of electronic structure calculations. My results agree with the authors in all ways. This work should be published.”

Conclusions:

Three separate calculations give no Berry phase change in $d_i(\gamma)$ plots for the C-H stretches in CH₃OH.

Inverted A/E splittings in the CH stretching fundamentals of methanol are not as closely related to a Berry phase change in the $d_i(\gamma)$ plots as was initially thought.

Li-Hong, Ron, and I should now go back to our original goal of trying to get J , K , and ν assignment help (= magnitudes and signs of perturbation coefficients) from the theoretical $\nu(\gamma)$ and $d_i(\gamma)$ curves given by a projected frequency calculation.

From L-H, Ö, P, and S (1958): **Two electronic energy surfaces** plotted above the **2-D vibrational plane** (Use polar coordinates $r \equiv Q$ and ϕ in the plane)

For CH_3OH : **two CH vibrational surfaces** (ν_2, ν_9) above the **2-Dimensional C-O-H bending plane** ($Q_{\text{bend}}, \gamma_{\text{tors}}$).

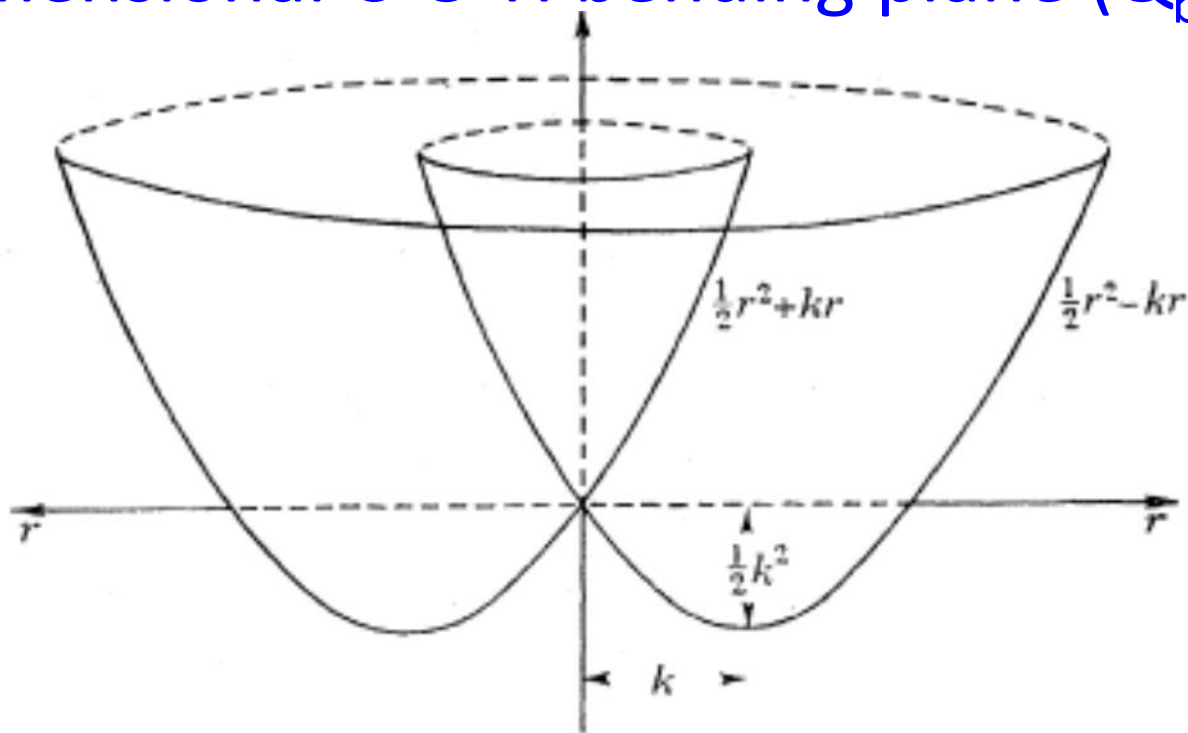


FIGURE 3. Diagram indicating Jahn-Teller splitting of nuclear potential function into two branches, $\frac{1}{2}r^2 \pm kr$.

Three-parameter **Stretch-Torsion** Hamiltonian

$$H = (1/2m_H)(P_x^2 + P_y^2) + (1/2)k_E(S_x^2 + S_y^2) \quad (\text{H.O.})$$

$$+ (1/4)k_1[e^{+i\gamma}(S_x - iS_y)^2 + e^{-i\gamma}(S_x + iS_y)^2] \quad (\text{J-T})$$

$$+ (1/4)k_2[e^{-2i\gamma}(S_x - iS_y)^2 + e^{+2i\gamma}(S_x + iS_y)^2] \quad (\text{R-T})$$

= **Doubly degenerate** Harmonic oscillator

+ **Jahn-Teller-like** **torsion-vibration** term

+ **Renner-Teller-like** **torsion-vibration** term

From this model it is possible to show that:

$$\text{If } |k_1| > |k_2|, \text{ then } \mathbf{d}_i(\gamma+2\pi) = -\mathbf{d}_i(\gamma)$$

$$\text{If } |k_1| < |k_2|, \text{ then } \mathbf{d}_i(\gamma+2\pi) = +\mathbf{d}_i(\gamma)$$

But Cartesian displacement vector plots of $\mathbf{d}_i(\gamma)$ from proj-freq-calc will give one of these results directly.

Where are we going with this methanol work?

In principle, we want to see if Gaussian calculations can help Ron Lees sort out the many perturbations and other strange interactions that complicate assignment and analysis of the SAV infrared (vibration-torsion-rotation) spectrum of methanol.

But we are a long way away from that goal now. Present stage = trying to understand what quantum chemistry vibrational results “really mean,” so we can apply them to vibration-rotation interactions.

Group theory uses **3 groups**

C_s = point group of CH_3OH at equilibrium

G_6 = permutation-inversion group of CH_3OH

C_{3v} = G_6 = point group of CH_3F (CH_3-O-H)

Symmetry of vibrational coordinates **S** and **Q**

ν_3	ν_2	ν_9	
A'	<u>A'</u>	<u>A''</u>	S and Q in C_s point group
A_1	E		S in G_6 PI group, like
(A	E)		S and Q in C_{3v} point group of CH_3F
A_1	A_1	A_2	S and Q in G_6 PI group

Now get the eigenvectors of H_{JT} in the basis set $\Lambda = |\pm 1\rangle$ for energies $E_{\pm}(Q) = E_e + (\frac{1}{2})kQ^2 \pm k_{JT}Q$

	$ \Lambda = -1\rangle$	$ \Lambda = +1\rangle$
$\langle \Lambda = -1 $	$E_e + (\frac{1}{2})kQ^2$	$k_{JT}Qe^{-i\phi}$
$\langle \Lambda = +1 $	$k_{JT}Qe^{+i\phi}$	$E_e + (\frac{1}{2})kQ^2$

$$\begin{bmatrix} +1 \\ +e^{+i\phi} \end{bmatrix}$$

E_+

$$\begin{bmatrix} +1 \\ -e^{+i\phi} \end{bmatrix}$$

E_-

$$\begin{bmatrix} +e^{-i\phi/2} \\ +e^{+i\phi/2} \end{bmatrix}$$

E_+

$$\begin{bmatrix} +e^{-i\phi/2} \\ -e^{+i\phi/2} \end{bmatrix}$$

E_-

Complex

$$\psi(\phi+2\pi) = +\psi(\phi)$$

Real

$$\psi(\phi+2\pi) = -\psi(\phi)$$