The Jahn-Teller model as a treatment of molecular anharmonicity

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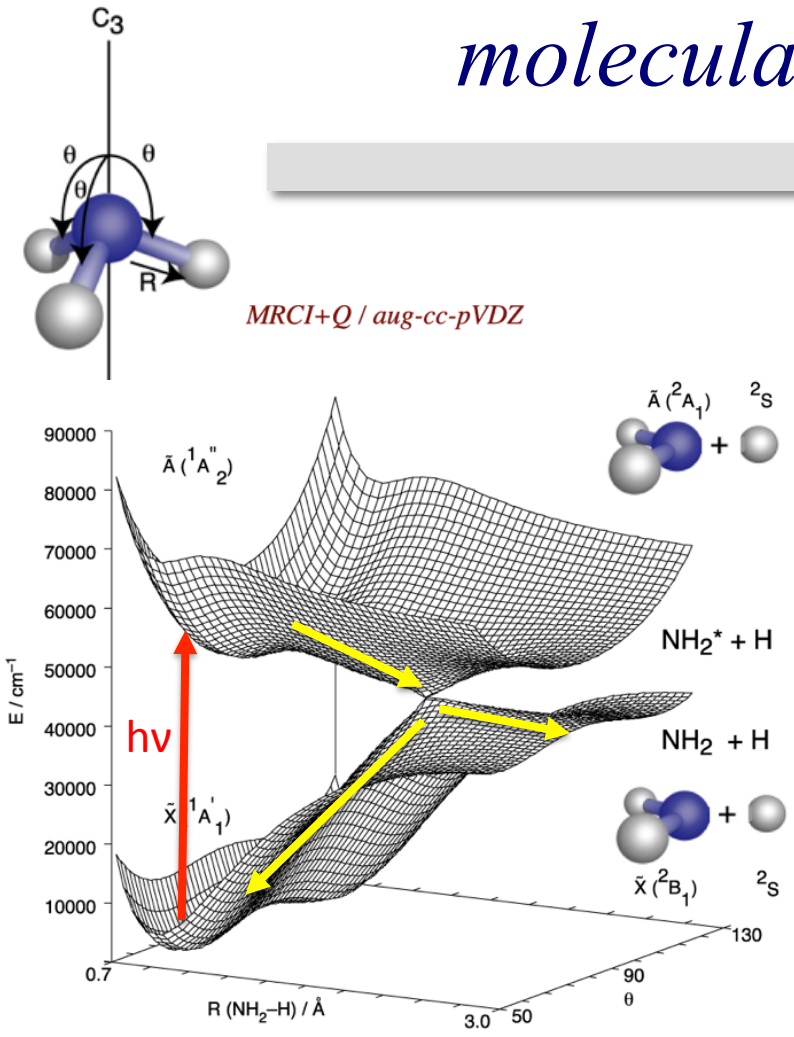
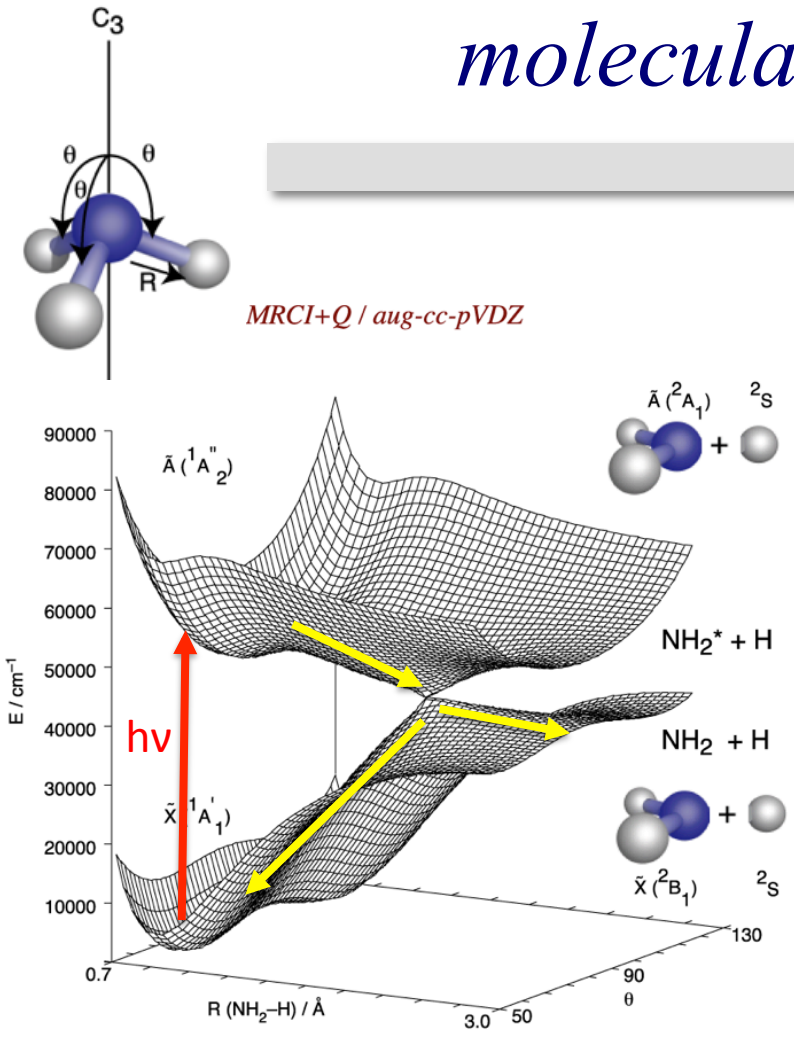
Large-amplitude motion as a driver of molecular anharmonicity



- Molecular interactions – and hence vibrational force constants – vary with nuclear geometry.

F.F. Crim, Spectroscopic probes and vibrational state control of chemical reaction dynamics in gases and liquids. Talk WA04, International Symposium on Molecular Spectroscopy, Columbus OH, 2006. http://molspect.chemistry.ohio-state.edu/symposium_61/symposium/Program/WA.html#WA04

Large-amplitude motion as a driver of molecular anharmonicity



- Molecular interactions – and hence vibrational force constants – vary with nuclear geometry.
- Consider the high-frequency vibrations as adiabatic functions of the large-amplitude coordinates.
- *Use the language of electronic spectroscopy to describe the dynamics on the vibrationally adiabatic surfaces.*
- Include all nonadiabatic couplings.

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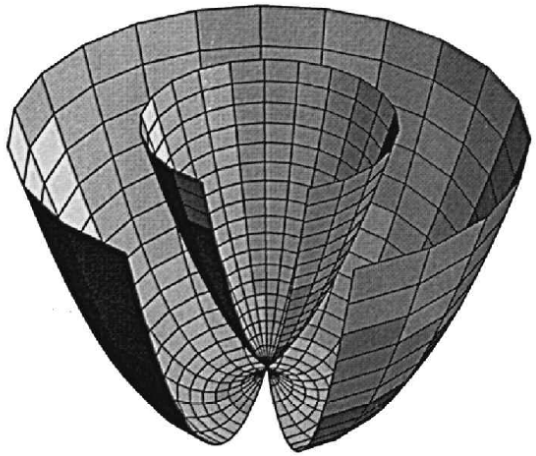
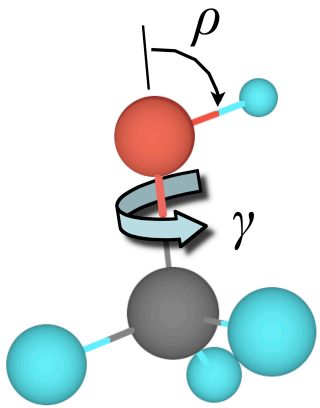
The Jahn-Teller Effect



T.A. Barckholtz and T.A. Miller,
Int. Rev, Phys. Chem. **17**, 435 (1998).

- Developed to treat relatively modest spontaneous distortion of symmetrical molecules relative to a symmetrical reference geometry.[1]
- Provides ***a general formalism*** for the interactions between (quasi)degenerate states, including the dependence on the nuclear coordinates.[2]

1. H. A. Jahn and E. Teller, Proc. R. Soc. A, 161, 220 (1937).
2. I. Bersuker, The Jahn-Teller Effect, Cambridge (2006).

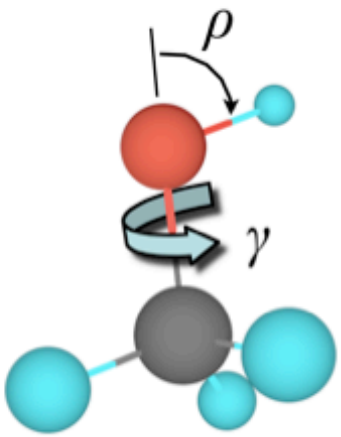


Methanol

The extended Jahn-Teller Effect: Going further from the symmetry point

- Combined 1st-order ($\rho e^{i\gamma}$) and 2nd-order ($\rho^2 e^{2i\gamma}$) Jahn-Teller couplings produce additional conical intersections.[1]
- Power-series expansion relative to the symmetry point yield extended Jahn-Teller models.[2]

1. J.W. Zwanziger and E.R. Grant, J. Chem. Phys. 87, 2954 (1987).
2. A. Viel and W. Eisfeld, J. Chem. Phys. 120, 4603 (2004); D. Opalka and W. Domcke, J. Chem. Phys. 132, 154108 (2010).



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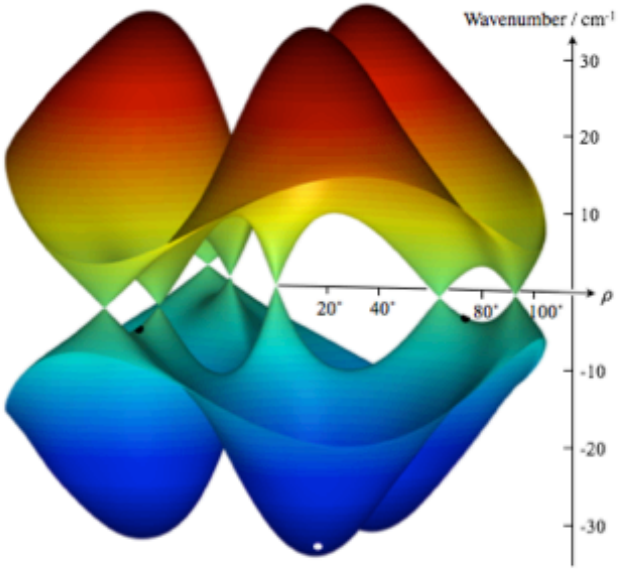
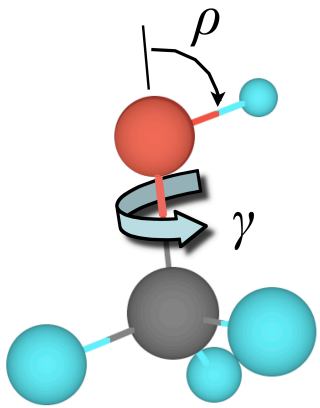


- Combined 1st-order ($\rho e^{i\gamma}$) and 2nd-order ($\rho^2 e^{2i\gamma}$) Jahn-Teller couplings produce additional conical intersections.[1]
- Power-series expansion relative to the symmetry point yield extended Jahn-Teller models.[2]
- The ***vibrational Jahn-Teller effect*** yields very large displacements.[3]
- *How should we handle very large displacements from the reference geometry?*

1. J.W. Zwanziger and E.R. Grant, J. Chem. Phys. 87, 2954 (1987).
2. A. Viel and W. Eisfeld, J. Chem. Phys. 120, 4603 (2004); D. Opalka and W. Domcke, J. Chem. Phys. 132, 154108 (2010).
3. B.P. Thappaliya, M.B. Dawadi, C. Ziegler, and D.S. Perry, Chem. Phys. 460, 31 (2015).



A Jahn-Teller expansion for large-amplitude motion

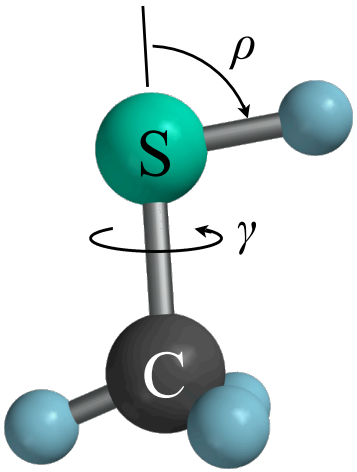
- FAST Hamiltonian: fast K.E. plus the whole potential energy: $H_f(\rho,\gamma) = T_f + V$
- SLOW Hamiltonian: slow K.E.

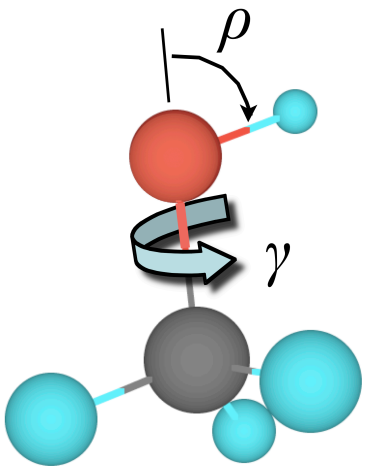
$$H_s = T_s = L^2/2\mu r^2$$

- Assume slow motion is approximately motion on a sphere: (ρ,γ)
- Expand the matrix elements of H_f in symmetry-adapted spherical harmonics:

$$H_f^{\Gamma}(\rho,\gamma) = \sum_{lm} c_{lm}\, Y_{lm}^{\Gamma}(\rho,\gamma)$$

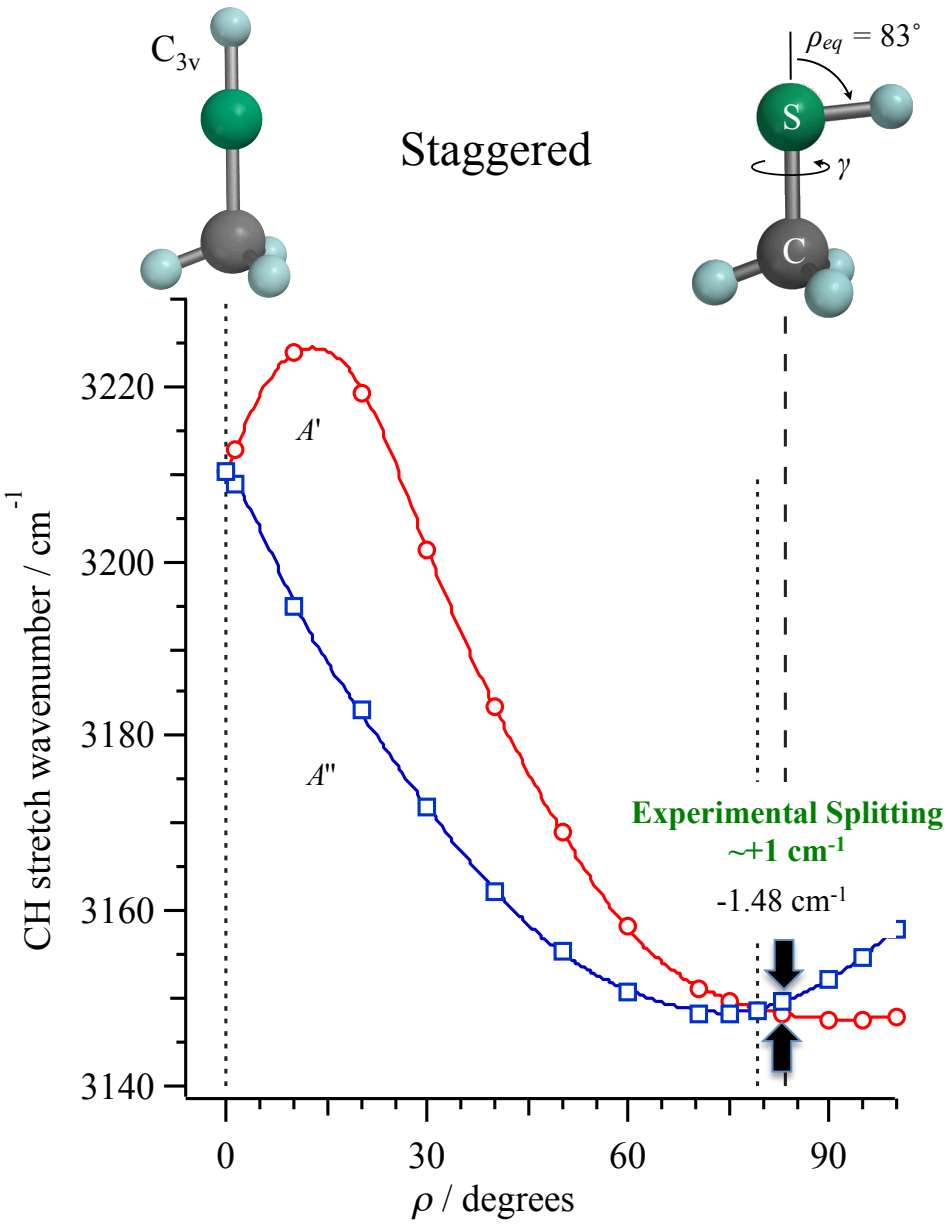
Application to E⊗e Systems: CH_3SH and CH_3OH





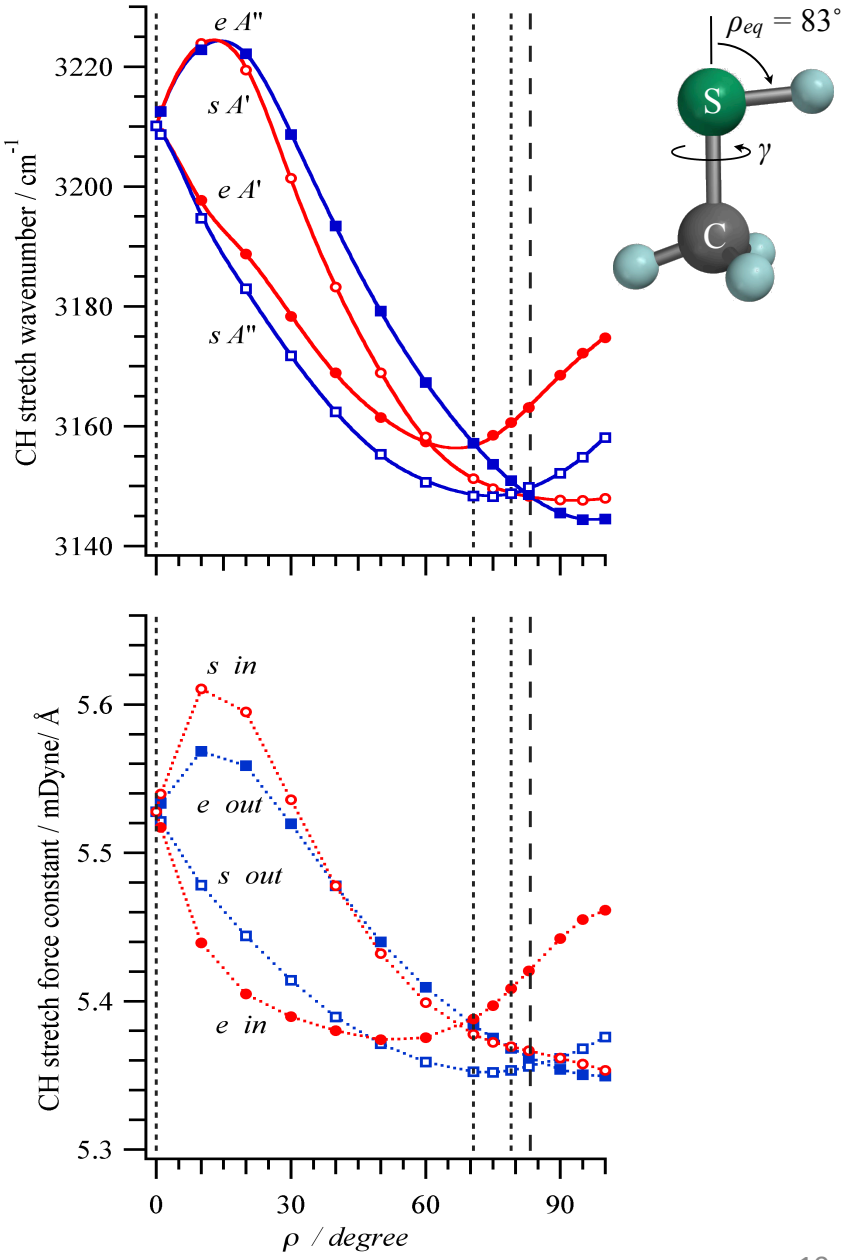
CH_3SH
Asymmetric CH stretch vibrations

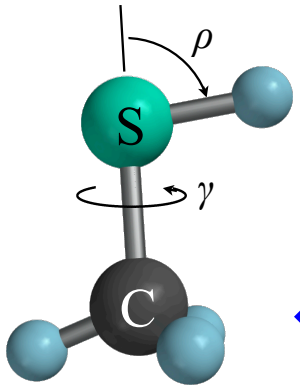
CCSD(T)/aug-cc-pVTZ
– nearly level-independent



Physical origin of the vibrational Jahn-Teller effect

➔ Variation of the harmonic CH bond force constants in the large-amplitude coordinate space





An E⊗e Jahn-Teller Model for Large-Amplitude Motion

- Use the Cartesian basis for the 2 asymmetric CH stretches

$$H_f = \begin{bmatrix} H_f^{a1} & 0 \\ 0 & H_f^{a1} \end{bmatrix} + \begin{bmatrix} H_{fxx}^{e} & H_{fxy}^{e} \\ H_{fxy}^{e} & -H_{fxx}^{e} \end{bmatrix}$$

- Expand coupling terms in the real spherical harmonics

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

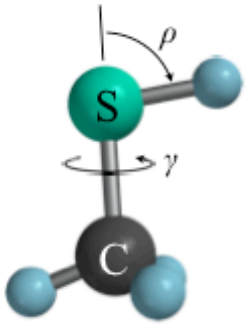
- Only symmetry-allowed terms appear ($l \geq |m|$):

A_1 terms H_f^{a1}: $m = 0, 3, 6, \ldots$

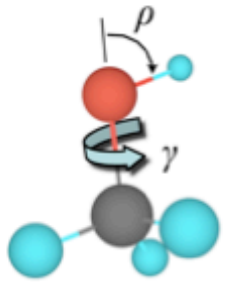
E terms H_{fxx}^{e}: $m = 1, 2, 4, 5, \ldots$ (cosine forms)

H_{fxy}^{e}: $m = -1, -2, -4, -5, \ldots$ (sine forms)

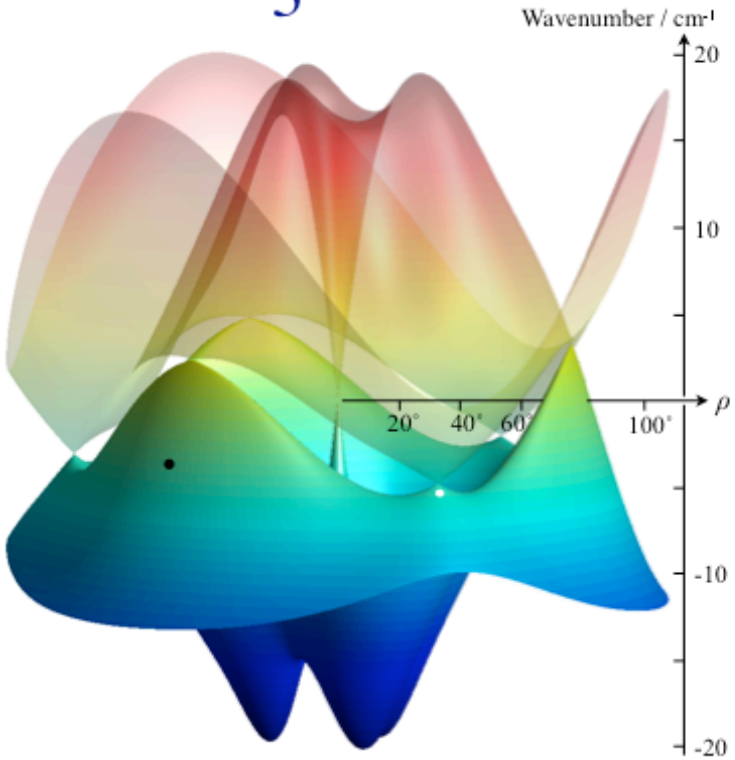
- The E terms are Jahn-Teller coupling of order $|m|$.



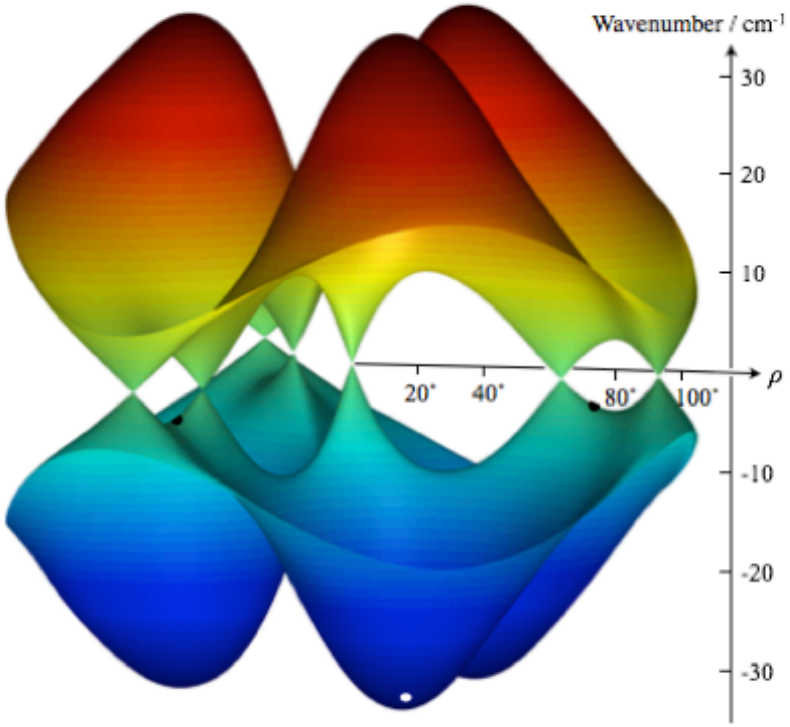
CH stretch adiabatic surfaces



CH_3SH

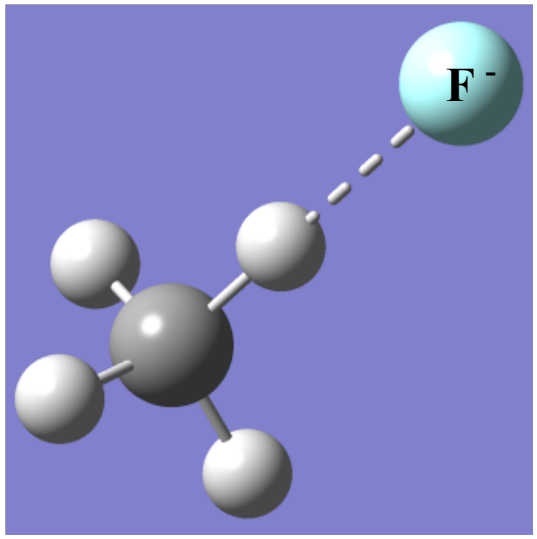


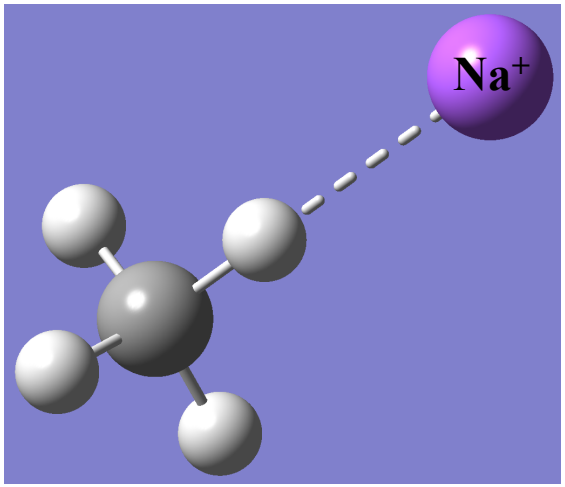
CH_3OH

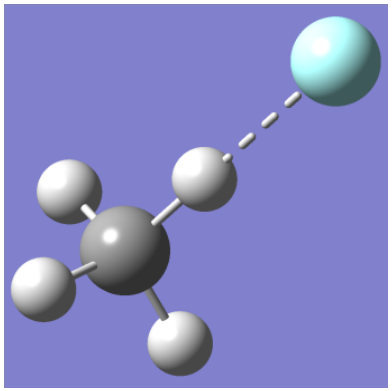


RMS of global fits: 0.2 cm^{-1}

Application to $T_2 \otimes e$ Systems: CH_4 - - F^- *and* CH_4 - - Na^+



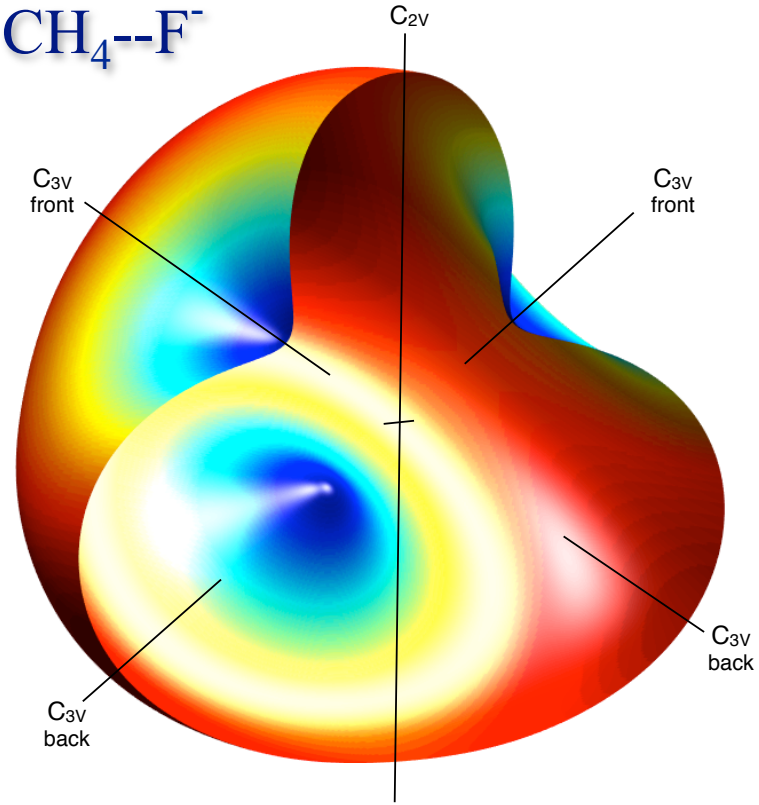




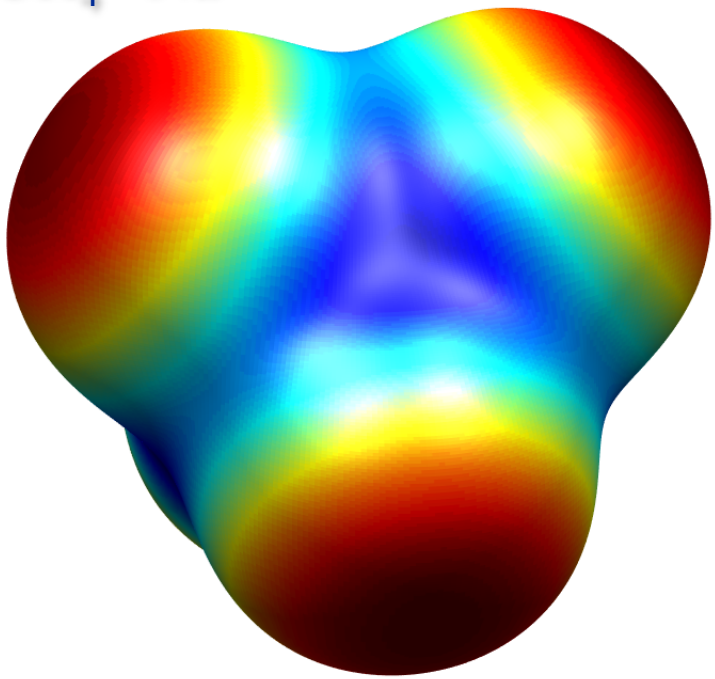
Electronic Potential Energy

MP2(full)/6-311++G(3df,2pd)

CH_4--F^-

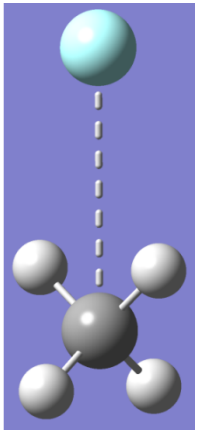


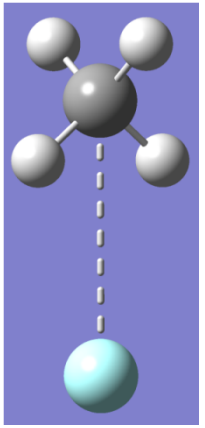
CH_4--Na^+

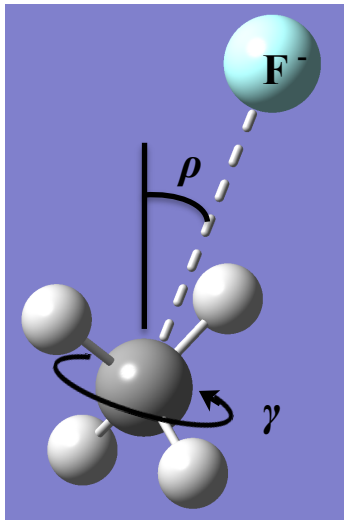


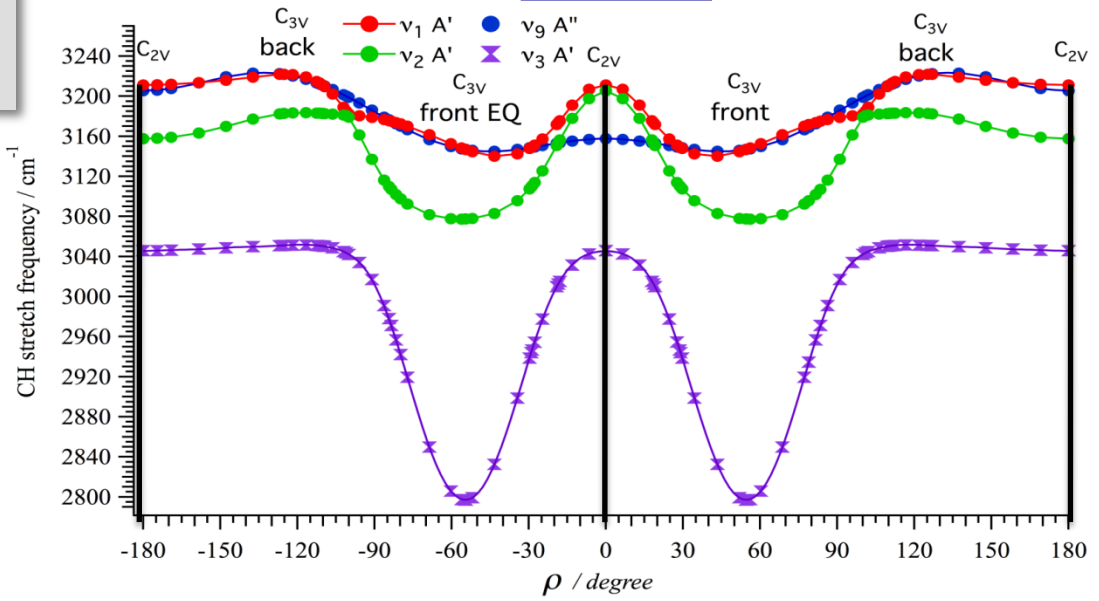
CH_4--F^-

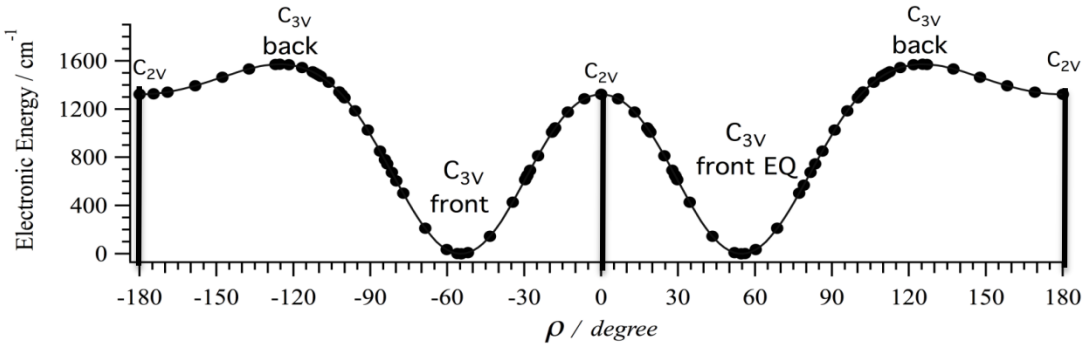
- Partially optimized points in a plane of symmetry along a circumference
- MP2(full)/6-311++G(3df,2pd)
- nearly level-independent











CH_4--F^-

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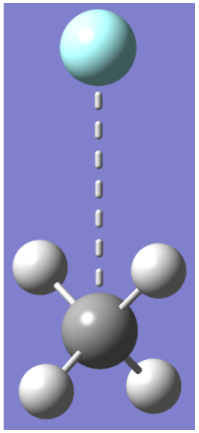
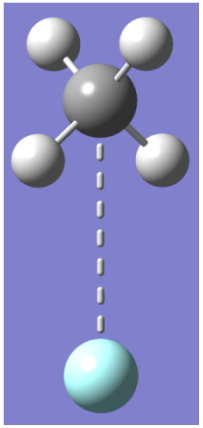
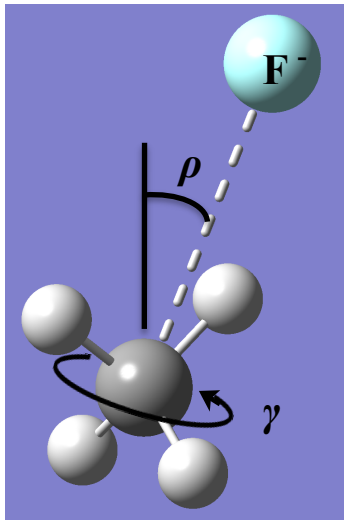
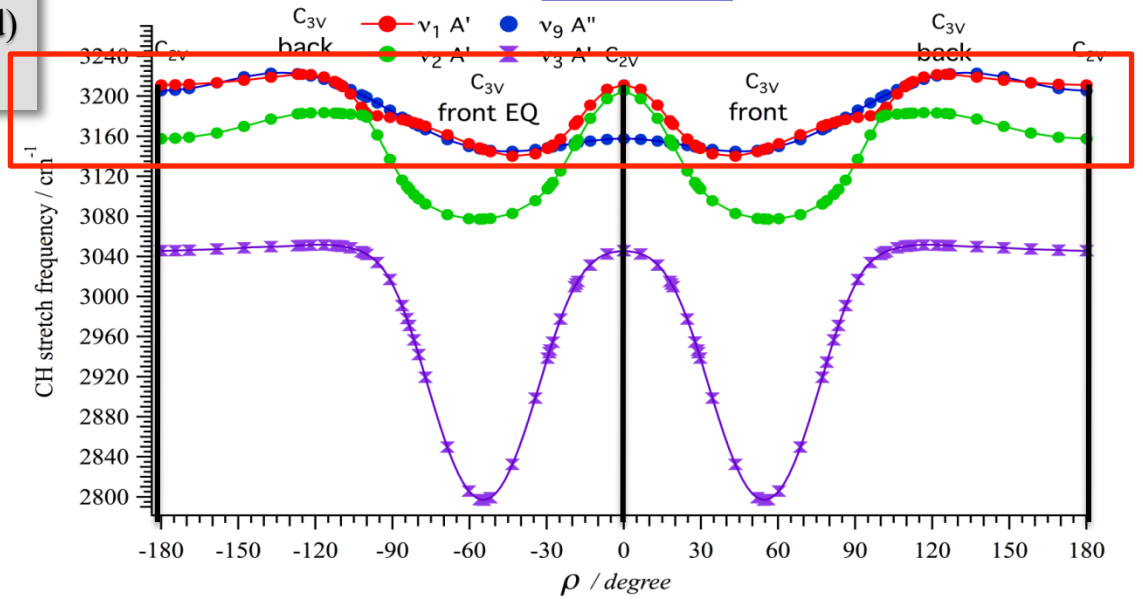
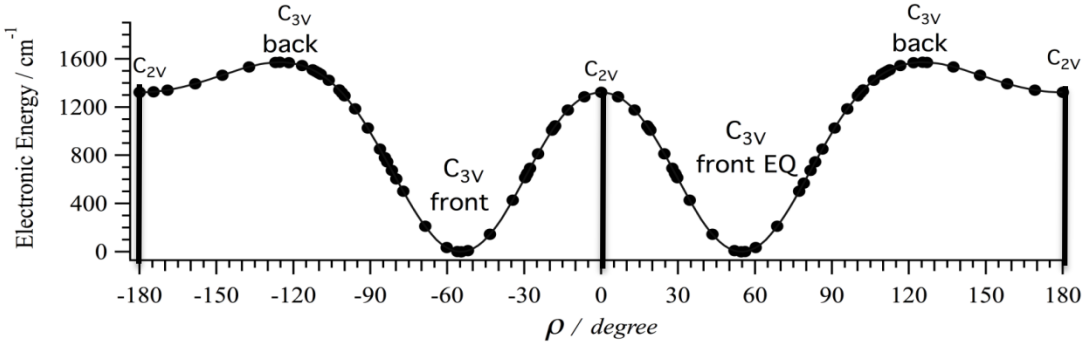
- nearly level-independent





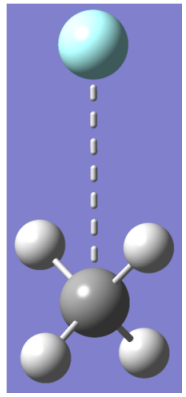


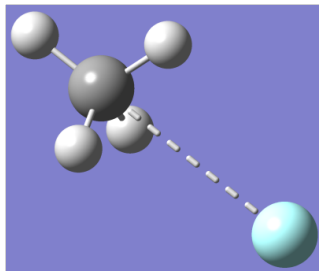


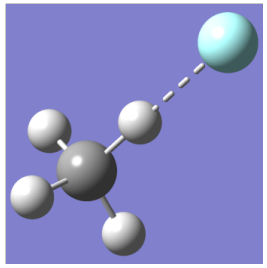


CH_4--F^-

- **MP2(full)/6-311++G(3df,2pd)**





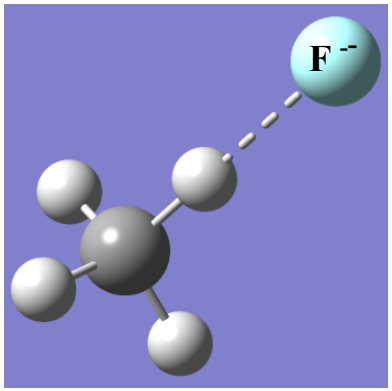


Tetrahedral symmetry

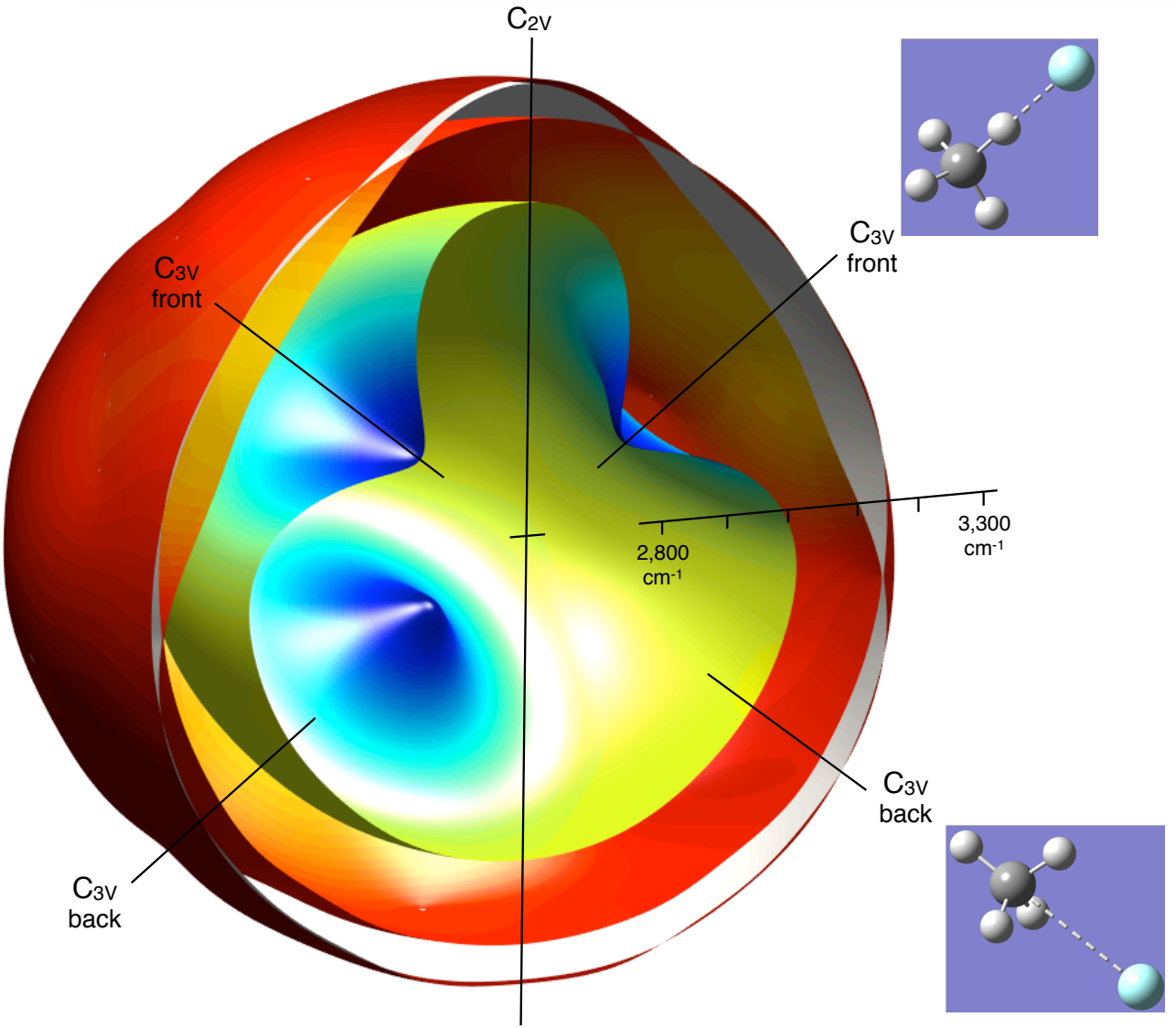
$T_2 \otimes e$ Jahn-Teller problem

$$H_f(\rho,\gamma) = \begin{bmatrix} H^{a_1} - \frac{1}{2} H^e_\vartheta + \frac{\sqrt{3}}{2} H^e_\varepsilon & H^{t_2}_z & H^{t_2}_y \\ H^{t_2}_z & H^{a_1} - \frac{1}{2} H^e_\vartheta - \frac{\sqrt{3}}{2} H^e_\varepsilon & H^{t_2}_x \\ H^{t_2}_y & H^{t_2}_x & H^{a_1} + H^e_\vartheta \end{bmatrix}$$

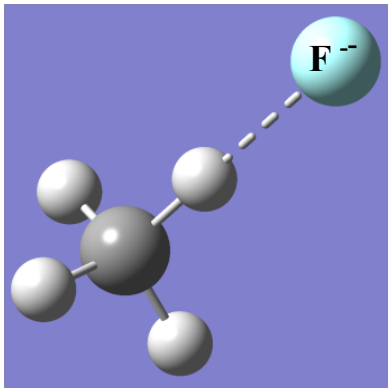
- a_1 terms: $H^{a_1}(\rho,\gamma) = \sum_i \alpha_i \, f_i^{a_1}(\rho,\gamma)$
- e terms: $H^e_j(\rho,\gamma) = \sum_i \varepsilon_i \, f^e_{i,j}(\rho,\gamma) \qquad j = \varepsilon, \vartheta$
- t_2 terms: $H^{t_2}_k(\rho,\gamma) = \sum_i \tau_i \, f^{t_2}_{i,k}(\rho,\gamma) \qquad k = x, y, z$
- Tetrahedral harmonics $f_i^\Gamma(\rho,\gamma)$ are linear combinations of spherical harmonics.
- The fit paramters are $\{\alpha_i, \varepsilon_i, \tau_i\}$.



Fit to $T_2 \otimes e$ Jahn-Teller Hamiltonian



RMS=0.52 cm^{-1}



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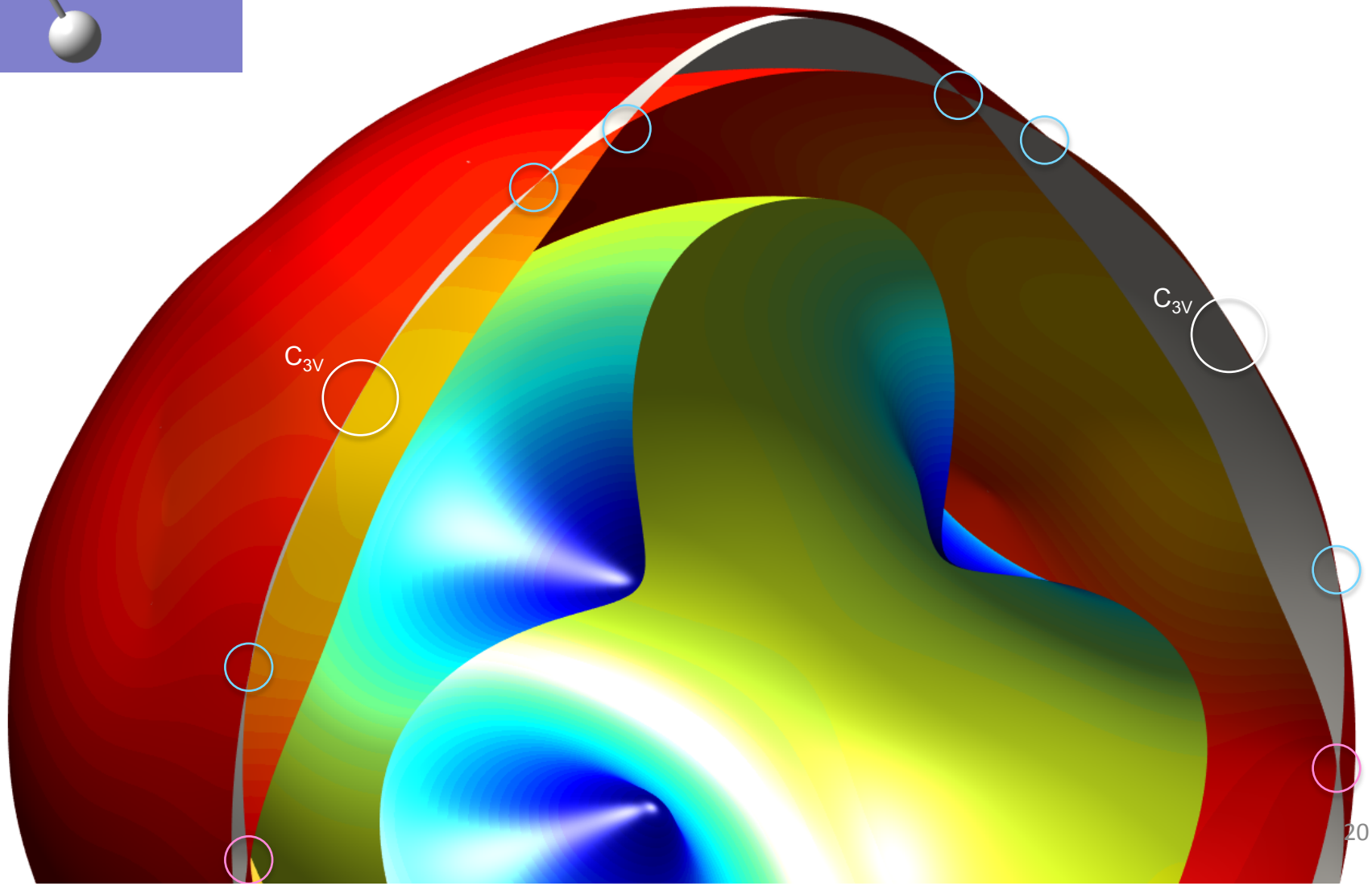
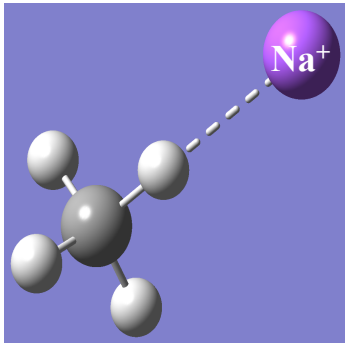
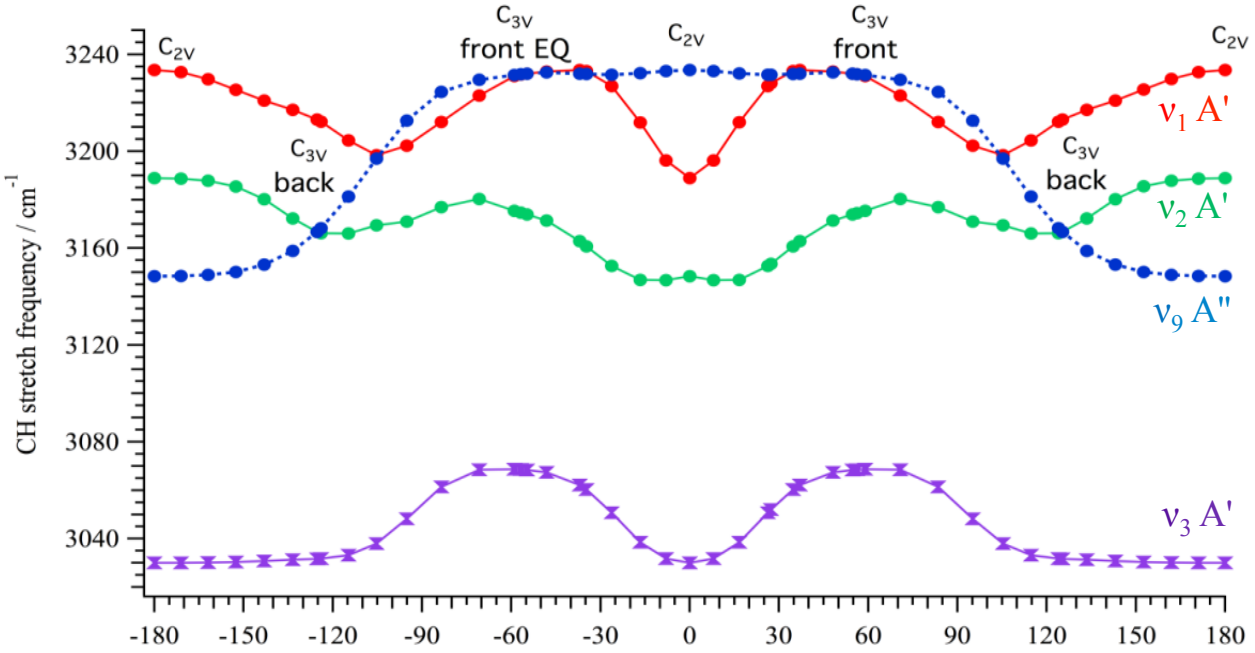
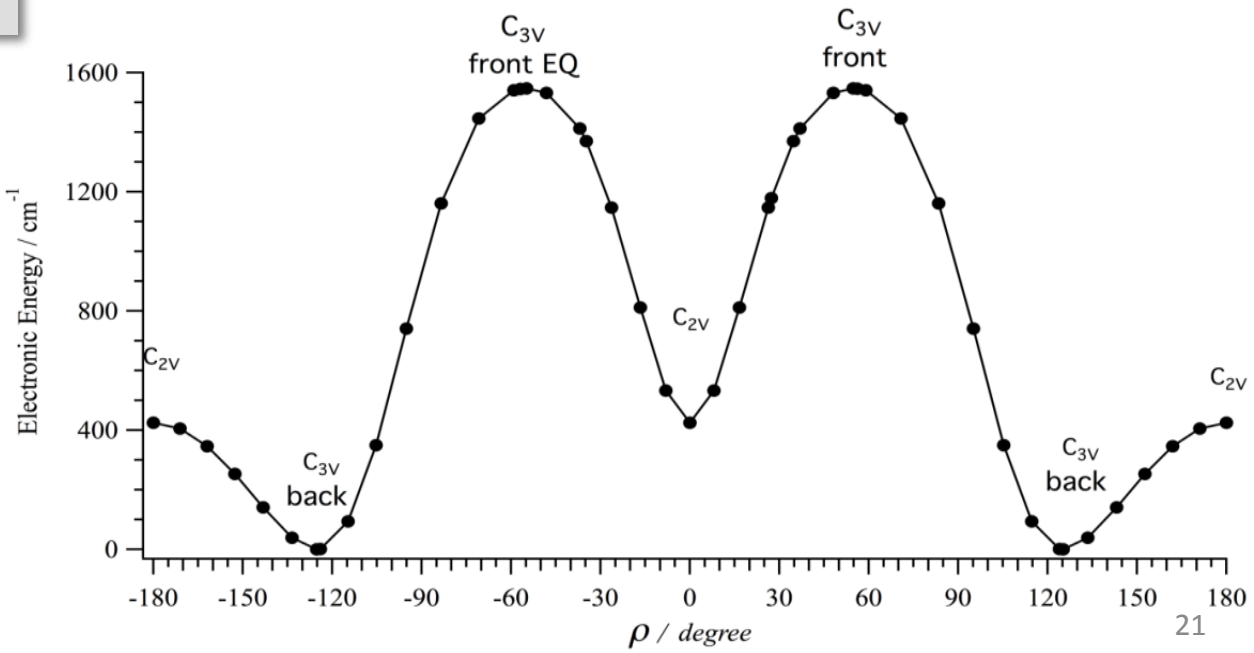


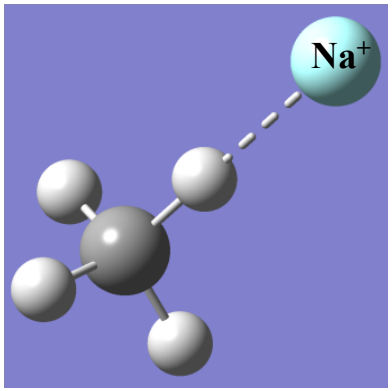


CH_4--Na^+

MP2(full)/6-311++G(3df,2pd)

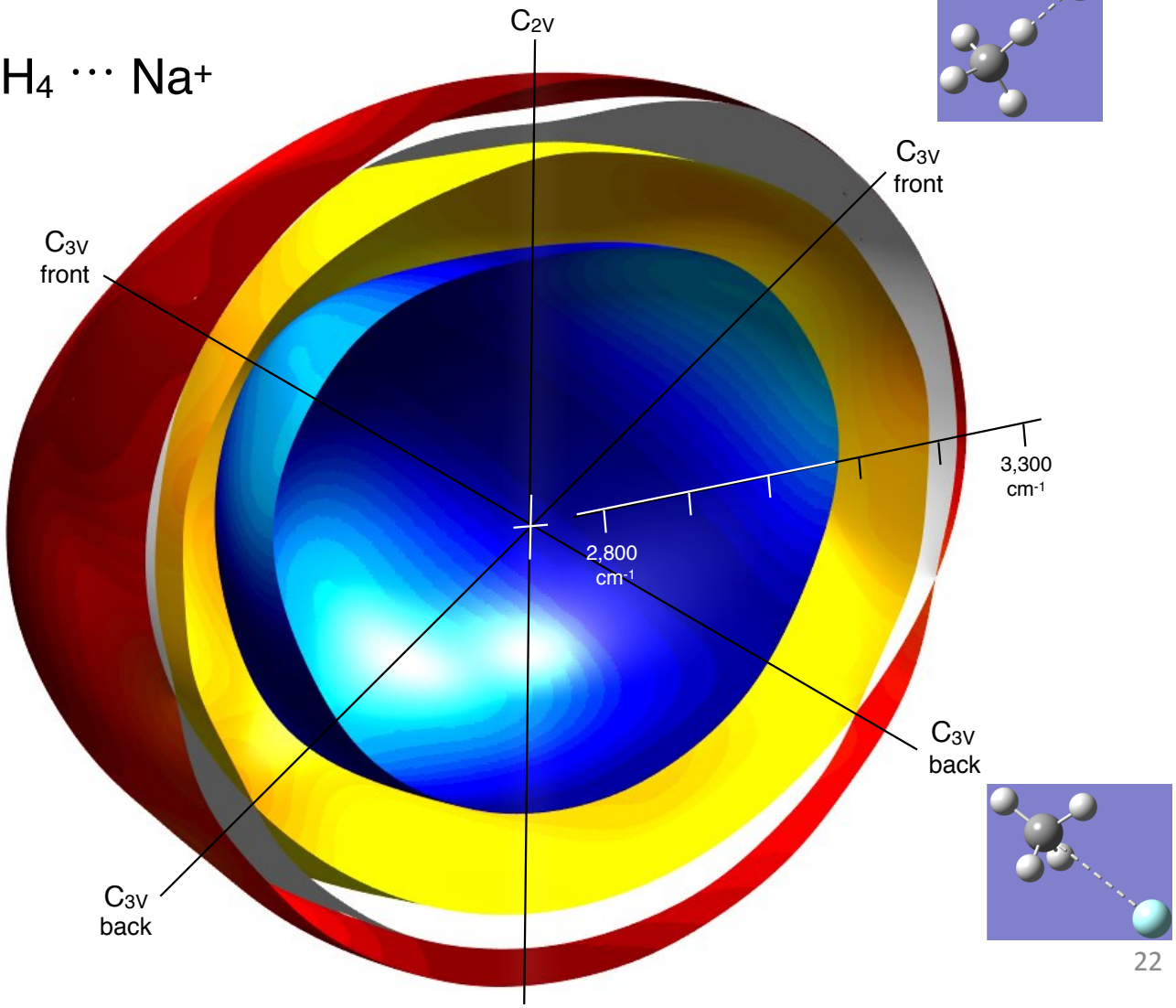




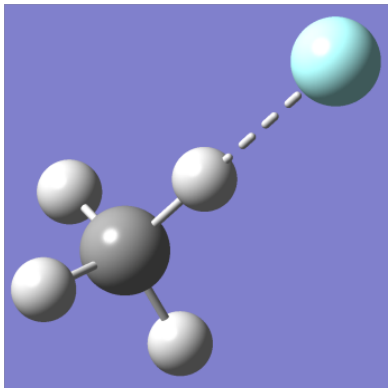


Fit to $T_2 \otimes e$ Jahn-Teller Hamiltonian

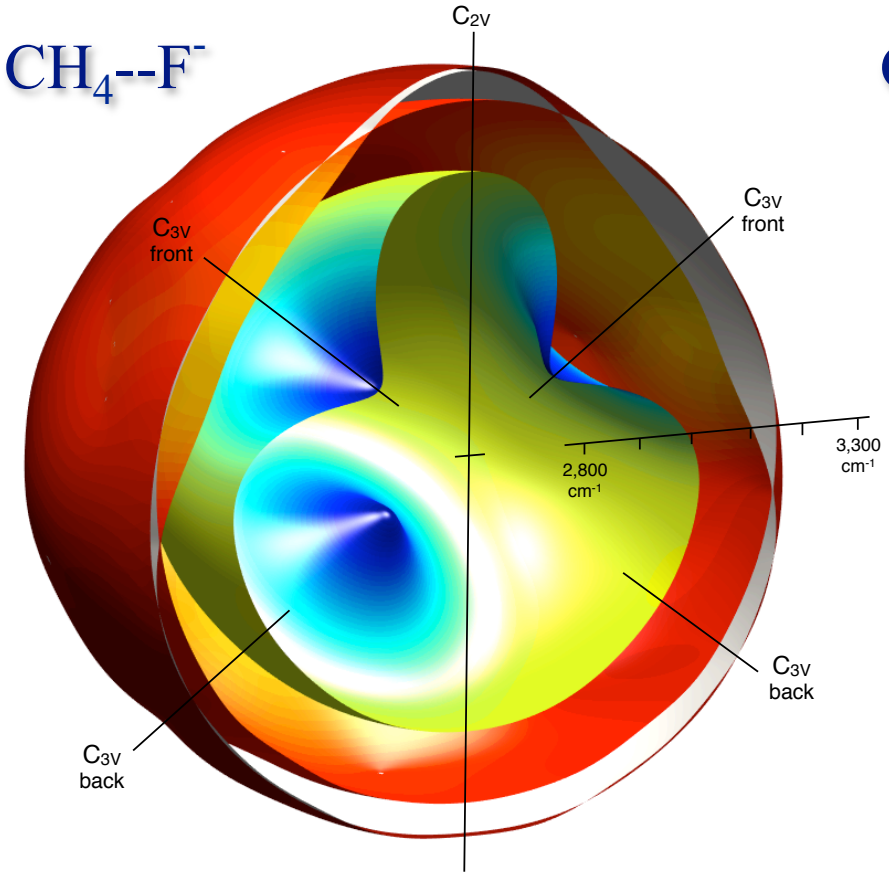
$CH_4 \cdots Na^+$

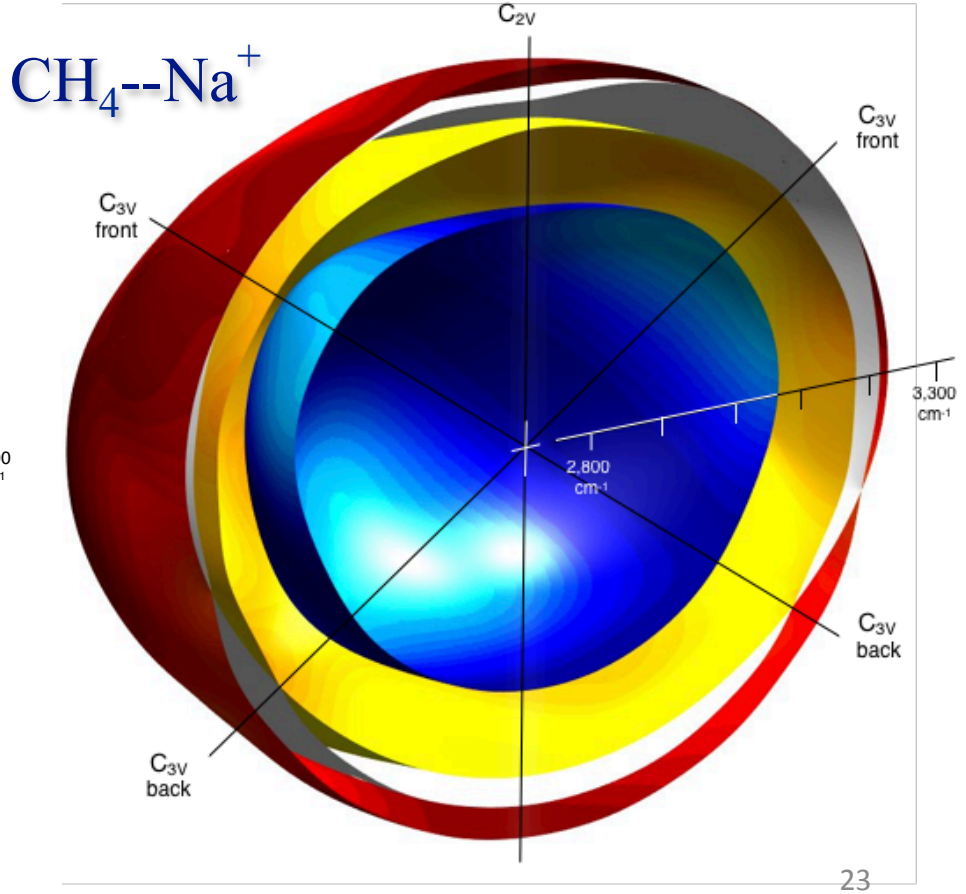


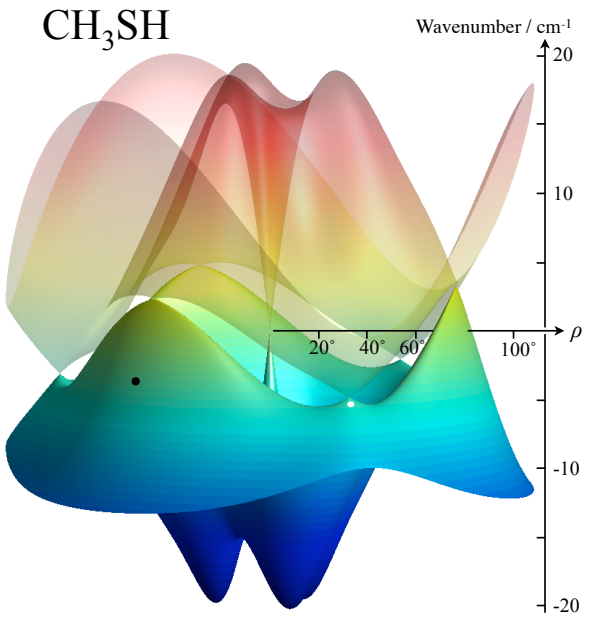
RMS=0.37 cm^{-1}

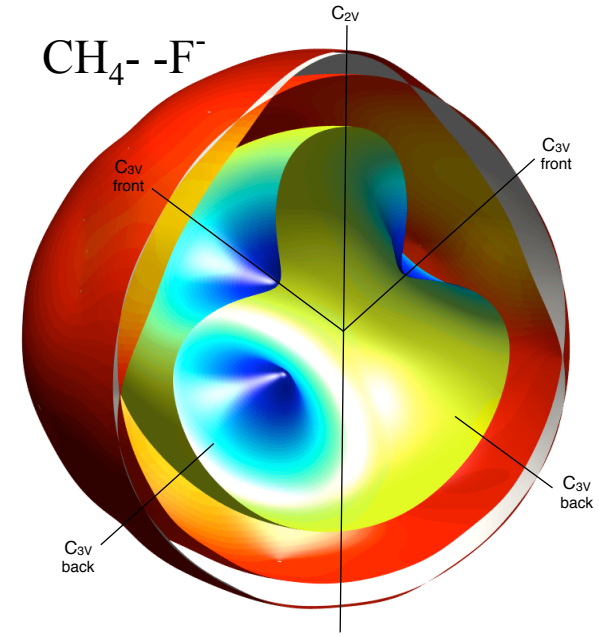


Comparison of F^- and Na^+ complexes





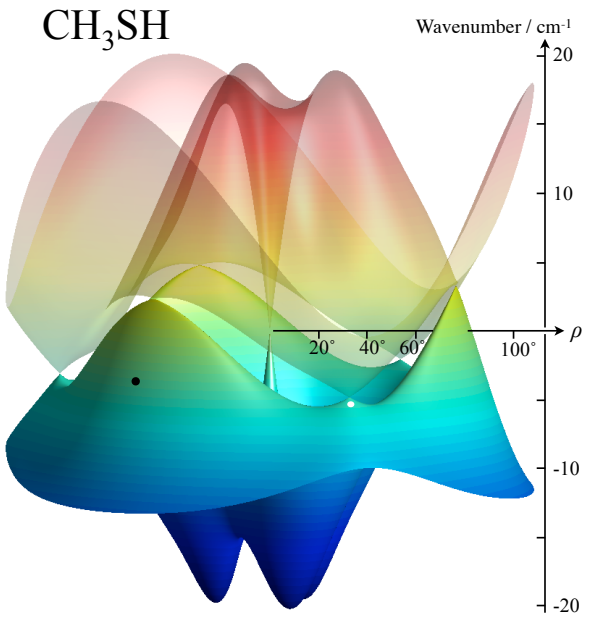


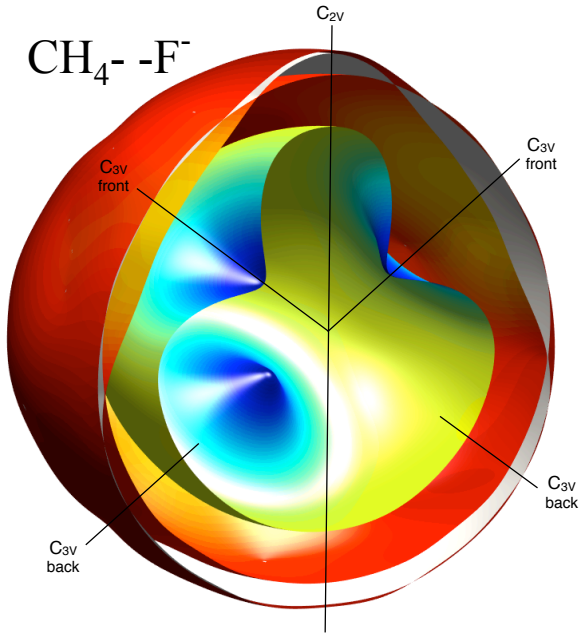


Summary

The Jahn-Teller Hamiltonian can treat the anharmonicity resulting from large-amplitude motion:

- Spherical harmonics treat the whole range of motion even-handedly.
- A general approach to interacting (quasi-) degenerate states.
- Multiple vibrational conical intersections.
- Apply the language of electronic spectroscopy to vibrational problems.





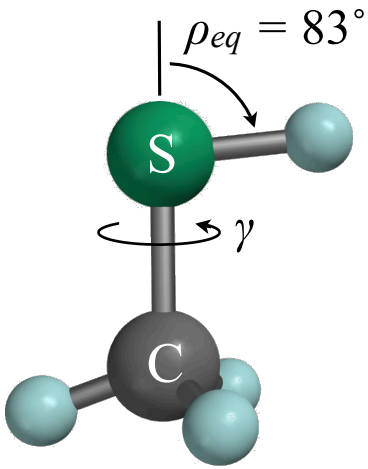
More Considerations

Advantages:

- For the coupled dynamics in the large-amplitude space, use a spherical harmonic basis:
  - K.E. operator is diagonal.
  - P.E. matrix elements from simple formulae.
- Reduced-dimensional treatment allows insight into dynamics.
- Essential features are independent of the *ab initio* level.

What's left out:

- Explicit mixing of A_1 and T_2 vibrations in CH_4.
- Coupling to other low-frequency degrees of freedom.



CH stretch vibrations in CH_3SH

- Asymmetric CH stretches are quasi-degenerate.

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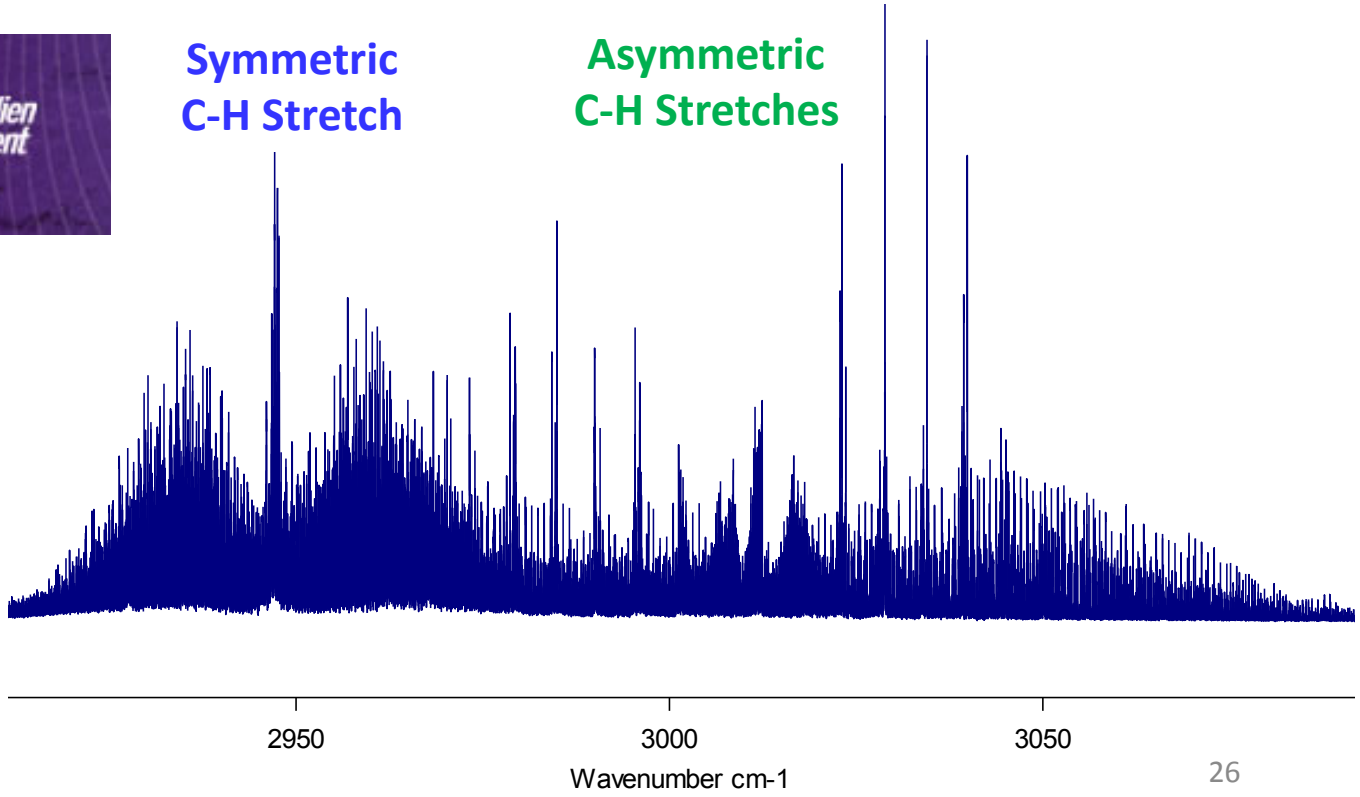
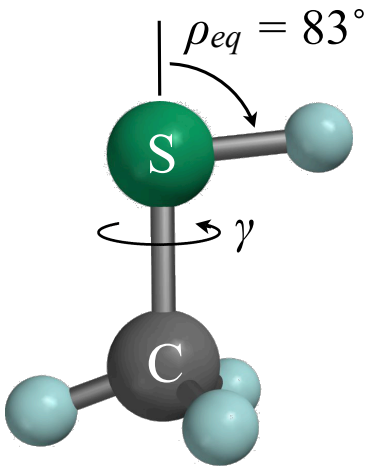
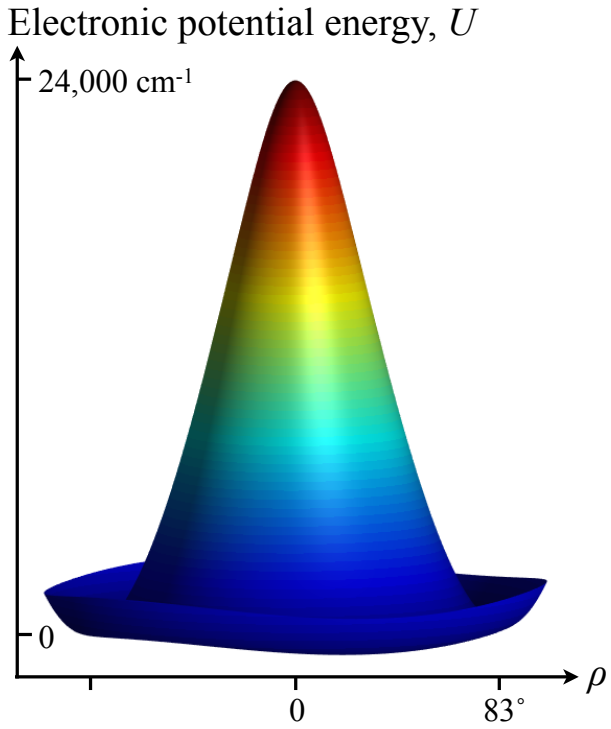




CH stretch vibrations in CH_3SH

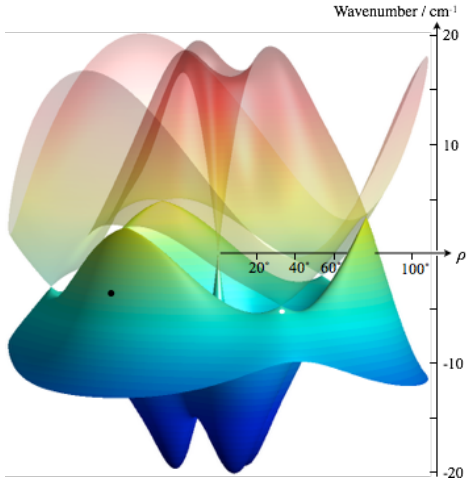
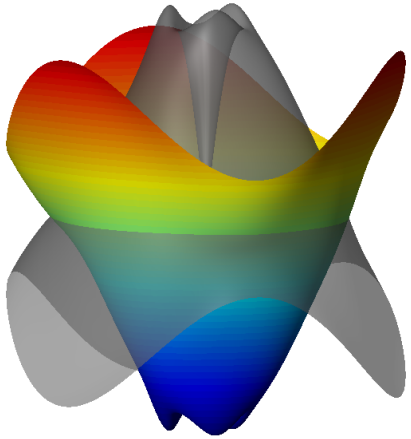
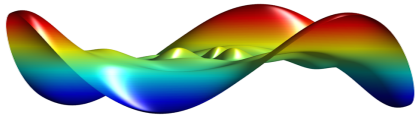
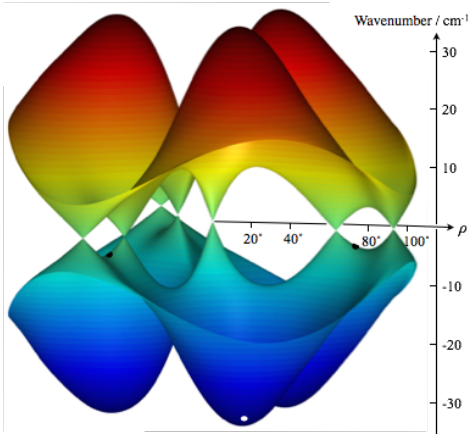
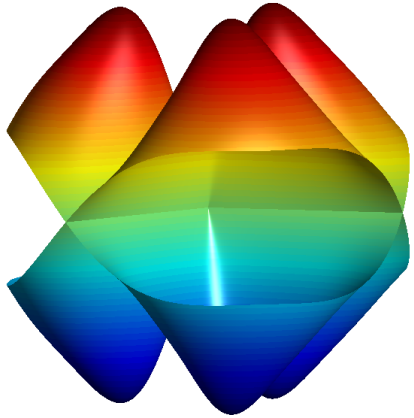
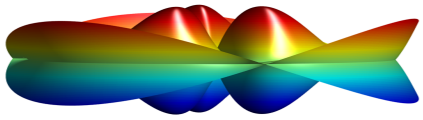


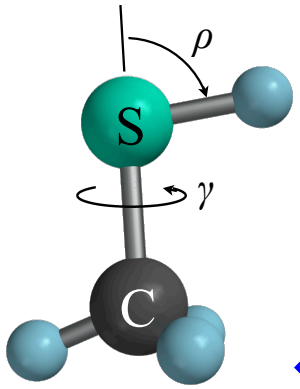
- Asymmetric CH stretches are quasi-degenerate.
- Degeneracy is required at C_{3v} ($\rho = 0$), not at $\rho_{eq} = 83^\circ$.
- In CH_3OH the two asymmetric CH stretches are ν_2 and ν_9.
  - 42 cm^{-1} apart
  - Split by Jahn-Teller coupling

➔ *Extend the Jahn-Teller model to very large ρ.*

CH_3SH *and* CH_3OH *Diabatization*

3 diabatization schemes correspond to Xu, Hougen, Lees' **3** limiting cases. J. Mol. Spectrosc. 293-294, 38 (2013).

	Adiabatic	Diabatic	Coupling
CH_3SH		Jahn-Teller 1st-order 	
CH_3OH		1st- and 2nd-orders equal 	



An E⊗e Jahn-Teller Model for Large-Amplitude Motion

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

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

with $U^{m\gamma}(\rho) = \sum_{l=m,m+1,\ldots} b_{lm}^{a1} \frac{Y_{lm}(\rho,\gamma)}{\cos m\gamma}$ Electronic potential

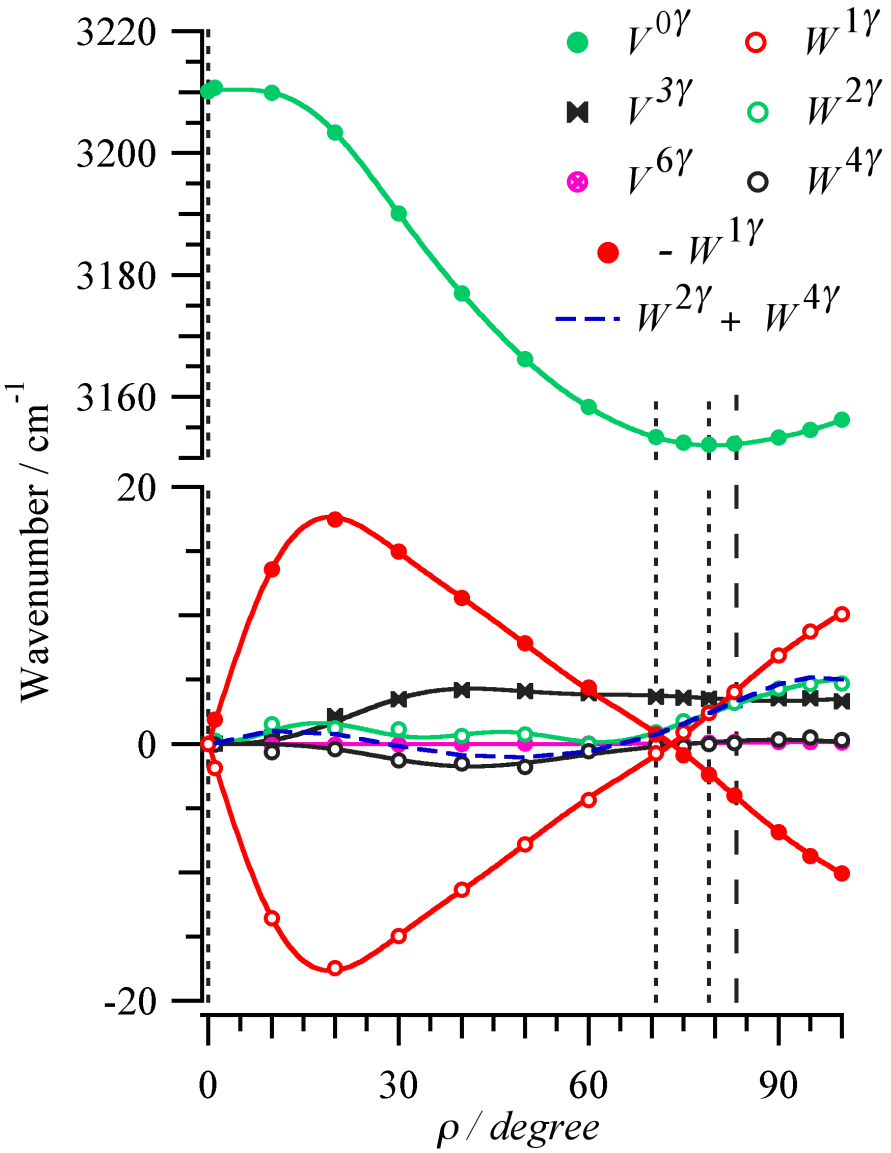
$V^{m\gamma}(\rho) = \sum_{l=m,m+1,\ldots} c_{lm}^{a1} \frac{Y_{lm}(\rho,\gamma)}{\cos m\gamma}$ Diagonal vibrational energies

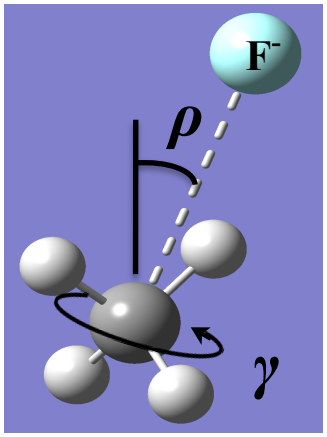
$W^{m\gamma}(\rho) = \sum_{l=m,m+1,\ldots} c_{lm}^{e} \frac{Y_{lm}(\rho,\gamma)}{\cos m\gamma}$ Jahn-Teller coupling terms of order $m = 1, 2, 4$.

Fit to the Jahn-Teller Hamiltonian

CCSD(T)/aug-cc-pVTZ

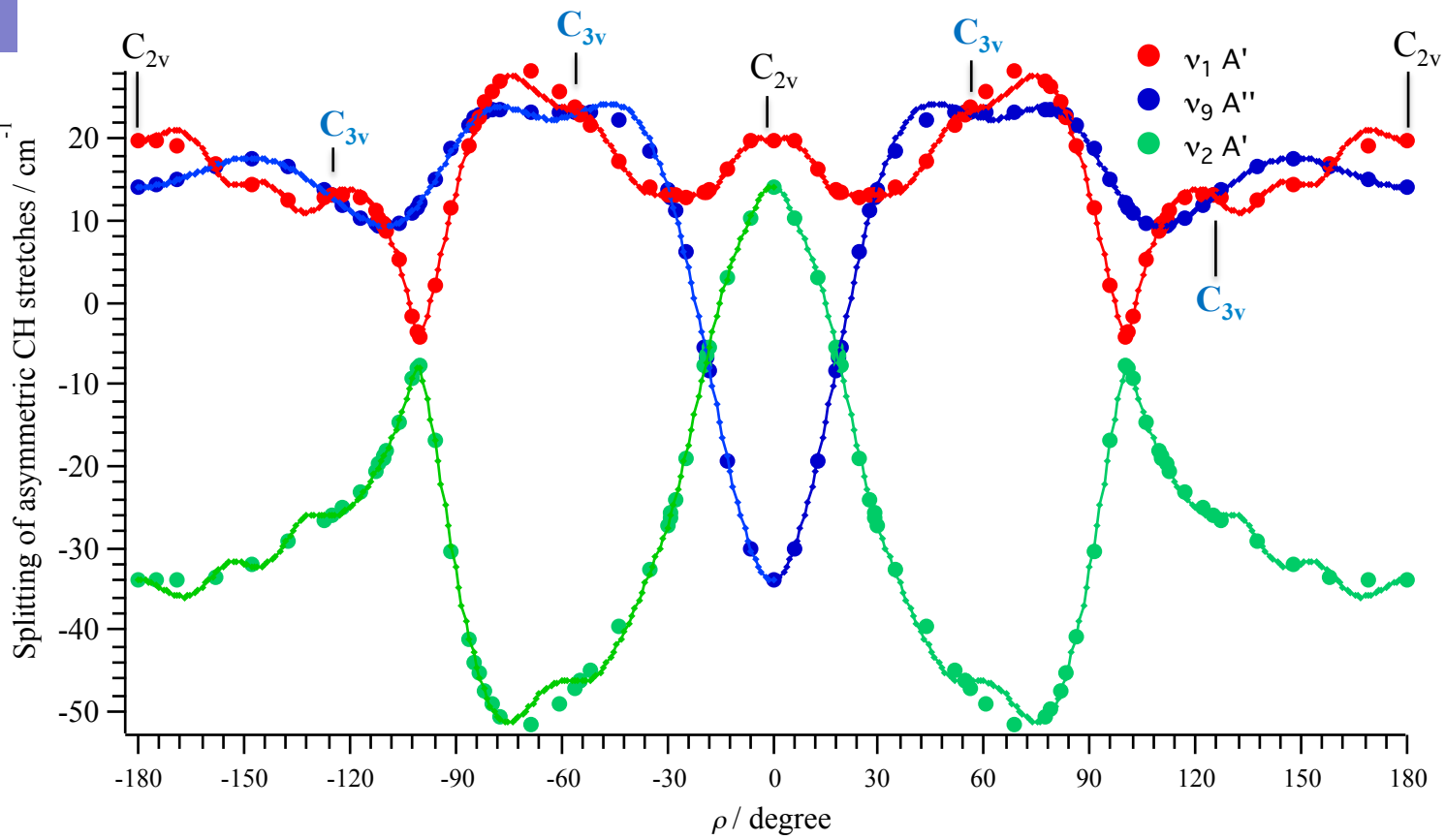
- Conical intersections occur where even and odd coupling orders cancel.
- Global RMS of fit = 0.2 cm^{-1}



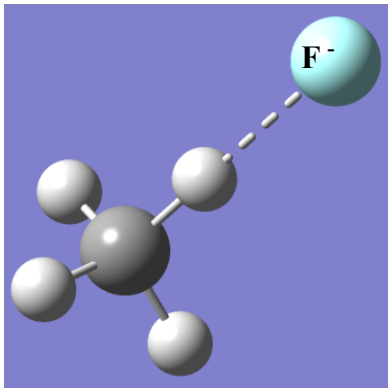


Fit to $T_2 \otimes e$ Jahn-Teller Hamiltonian

- Relative energies of T_2 vibrations
- e and t_2 coupling terms

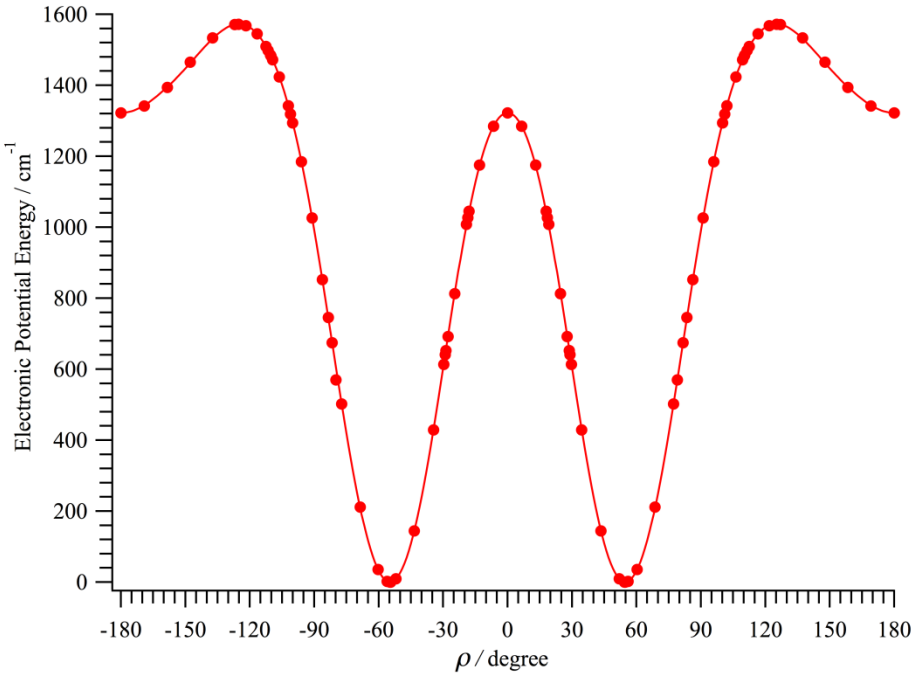


RMS=0.52 cm^{-1}

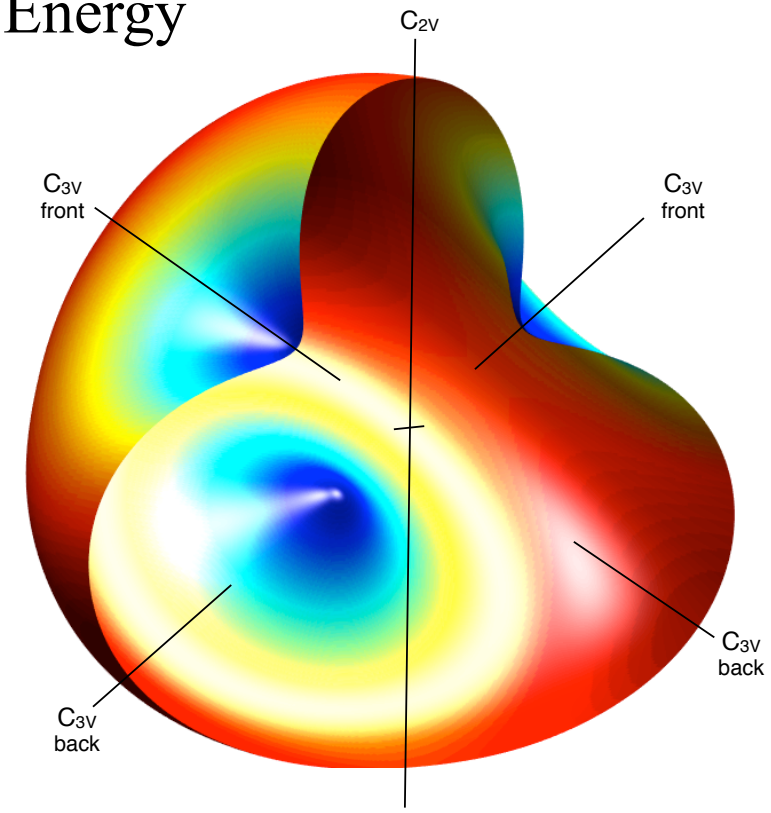


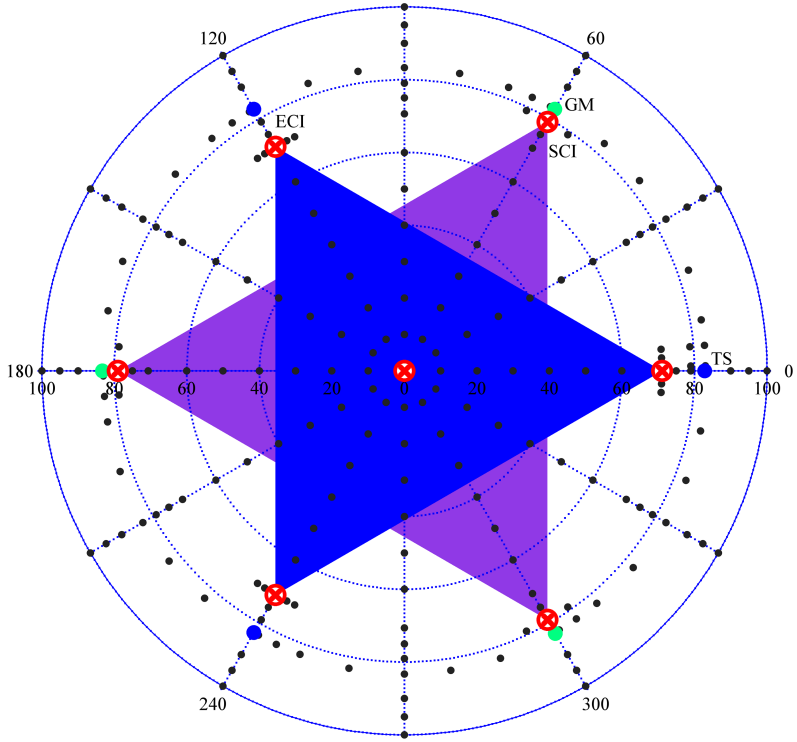
Fit to $T_2 \otimes e$ Jahn-Teller Hamiltonian

Electronic Potential Energy



RMS=0.73 cm^{-1}




120
60
ECI
GM
SCI
180
0
TS
100
80
60
40
20
0
20
40
60
80
100
240
300

CH_3SH

Fourier term [r]	Parameter [s]	Value	Fourier term [r]	Parameter [c]	Value
$U^{0\gamma}$	$a_0^{(0)}$	3.30095E4 (4.E1)	$V^{0\gamma}$	$b_1^{(0)}$	1.12453E4 (5.E-1)
	$a_1^{(0)}$	-1.50622E4 (5.E1)		$b_1^{(0)}$	-2.42011E1 (6.E-1)
	$a_2^{(0)}$	3.0758E4 (4.E1)		$b_2^{(0)}$	7.0836E1 (3.E-1)
	$a_3^{(0)}$	-2.04977E3 (2.E1)		$b_4^{(0)}$	1.05213E1 (1.E-1)
	$a_4^{(0)}$	3.42375E3 (1.E1)		$b_8^{(0)}$	-5.95254E-1 (9.E-2)
	$a_6^{(0)}$	8.42112E2 (1.E0)		$b_{10}^{(0)}$	-1.19588E0 (9.E-2)
	$a_8^{(0)}$	2.79798E2 (3.E-1)		$b_{12}^{(0)}$	-5.04997E-1 (9.E-2)
	$a_{10}^{(0)}$	1.05715E2 (2.E-1)		$b_{14}^{(0)}$	2.28496E-1 (8.E-2)
	$a_{12}^{(0)}$	4.05045E1 (2.E-1)	$V^{3\gamma}$	$b_3^{(3)}$	7.88918E0 (2.E-1)
	$a_{14}^{(0)}$	1.63229E1 (1.E-1)		$b_4^{(3)}$	1.16344E-1 (2.E-1)
	$a_{16}^{(0)}$	7.09012E0 (1.E-1)		$b_5^{(3)}$	3.78829E0 (2.E-1)
	$a_{18}^{(0)}$	2.04663E0 (9.E-2)		$b_7^{(3)}$	1.73914E0 (1.E-1)
$U^{3\gamma}$	$a_3^{(3)}$	5.98817E2 (2.E0)		$b_9^{(3)}$	6.10201E-1 (9.E-2)
	$a_4^{(3)}$	-1.95957E2 (3.E0)		$b_{11}^{(3)}$	1.29995E-1 (2.E-2)
	$a_5^{(3)}$	2.90249E2 (2.E0)	$V^{6\gamma}$	$b_6^{(6)}$	6.69021E-2 (3.E-2)
	$a_7^{(3)}$	3.02098E1 (2.E0)		$b_7^{(6)}$	2.3168E-2 (2.E-2)
	$a_8^{(3)}$	1.36379E1 (2.E0)	$W^{1\gamma}$	$c_1^{(1)}$	9.24198E0 (2.E-1)
	$a_9^{(3)}$	1.76821E1 (8.E-1)		$c_2^{(1)}$	-1.97897E1 (3.E-1)
	$a_{11}^{(3)}$	2.53787E0 (7.E-2)		$c_3^{(1)}$	-2.87824E0 (6.E-2)
	$a_{13}^{(3)}$	3.6708E0 (1.E-1)		$c_5^{(1)}$	-6.37778E0 (9.E-2)
	$a_{15}^{(3)}$	4.89657E-1 (4.E-2)		$c_7^{(1)}$	-2.91523E0 (8.E-2)
	$a_{17}^{(3)}$	6.46955E-1 (1.E-1)		$c_9^{(1)}$	-1.14541E0 (7.E-2)
$U^{6\gamma}$	$a_6^{(6)}$	-1.19922E-1 (3.E-2)		$c_{11}^{(1)}$	-2.17707 E-1 (2.E-2)
	$a_8^{(6)}$	-5.66397E-1 (3.E-2)	$W^{4\gamma}$	$c_5^{(4)}$	-6.54657E-1 (1.E-1)
$W^{2\gamma}$	$c_2^{(2)}$	3.97752E0 (1.E-1)		$c_6^{(4)}$	-7.48121E-1 (2.E-1)
	$c_4^{(2)}$	-4.14124E0 (2.E-1)		$c_{10}^{(4)}$	2.40606E-1 (9.E-2)
	$c_5^{(2)}$	2.58245E0 (1.E-1)	Calculation method		CCSD(T)
	$c_{10}^{(2)}$	6.90844E-1 (9.E-2)	Basis set		aug-cc-pVTZ
	$c_{12}^{(2)}$	2.68789E-1 (8.E-2)	RMS (vibrational part) [t]		0.20
			RMS (overall) [t]		0.26
				N_{data} [u]	114

CH_4- -F^-

	A1 terms			Elec-tronic	Sym CH	avg T2
	f_a					
	l	*c/s*	*|m|*	*ai*	*ai*	*ai*
a1	0		0	3672	10630	11240
a2	3	s	2	-1390	-205.9	-86.61
a3	4	c	0, 4	495.9	106	21.74
a4	6	c	0, 4	-64.11	-52.44	9.447
a5	7	s	2, 6	26.12	19.79	-10.59
a6	8	c	0, 4, 8	-6.558	-1.341	8.133
a7	9	s	2, 6	7.13	0.829	-2.608
a8	10	c	0, 4, 8	-8.239	-5.461	1.998
a9	11	s	2, 6, 10	1.148	1.421	-1.143
a10	12	c	0, 4, 8, 12	-1.257	-0.8662	-3.688

E terms

	f_e		*f_f*			*ei*
	l	*c/s*	*|m|*	*c/s*	*|m|*	
e1 =	2	c	2	-	0	**-14.59**
e2 =	4	c	2	c	0, 4	**11.77**
e3 =	5	s	4	s	2	**20.82**
e4 =	6	c	2, 6	c	0, 4	**30.93**
e5 =	7	s	4	s	2, 6	**9.676**
e6 =	8	c	2, 6	c	4, 8	**2.366**
e7 =	9	s	4, 8	s	2, 6	**6.581**
e8 =	10	c	2, 6, 10	c	4, 8	**-7.449**
e9 =	11	s	4, 8	s	2, 6, 10	**-1.246**

T2 terms

	f_x, f_y		*f_z*		*ti*
	l	*c/s*	*|m|*	*c/s*	*|m|*	
tz1 =	1	c, s	1	-	0	**8.99**
tz2 =	2	s, c	1	s	2	**-40.15**
tz3 =	3	c, s	1, 3	-	0	**-14.1**
tz4 =	4	s, c	1, 3	s	2	**0.5376**
tz5 =	5	c, s	1, 3, 5	-	0	**8.929**
tz6 =	5	c, s	1, 3, 5	c	4	**7.849**
tz7 =	6	s, c	1, 3, 5	s	2	**-2.196**
tz8 =	6	s, c	1, 3, 5	s	6	**4.099**
tz9 =	7	c, s	1, 3, 5, 7	-	0	**-4.442**
tz10 =	7	c, s	1, 3, 5, 7	c	4	**8.133**
tz11 =	8	s, c	1, 3, 5, 7	s	2	**0.583**
tz12 =	8	s, c	1, 3, 5, 7	s	6	**-3.101**
tz13 =	9	c, s	1, 3, 5, 7, 9	-	0	**-3.367**
tz15 =	9	c, s	1, 3, 5, 7, 9	c	8	**-9.713**
tz14 =	10	s, c	1, 3, 5, 7, 9	s	2	**-2.899**