FTIR Synchrotron Spectroscopy of the Lower Vibrational Modes of Methyl Mercaptan at the Canadian Light Source

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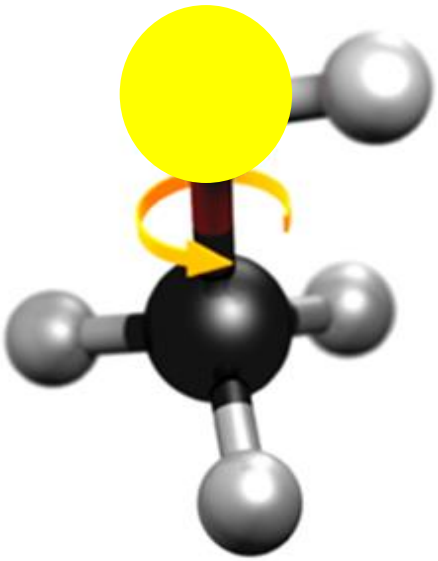
Vibrational Modes of $CH_3{}^{32}SH$

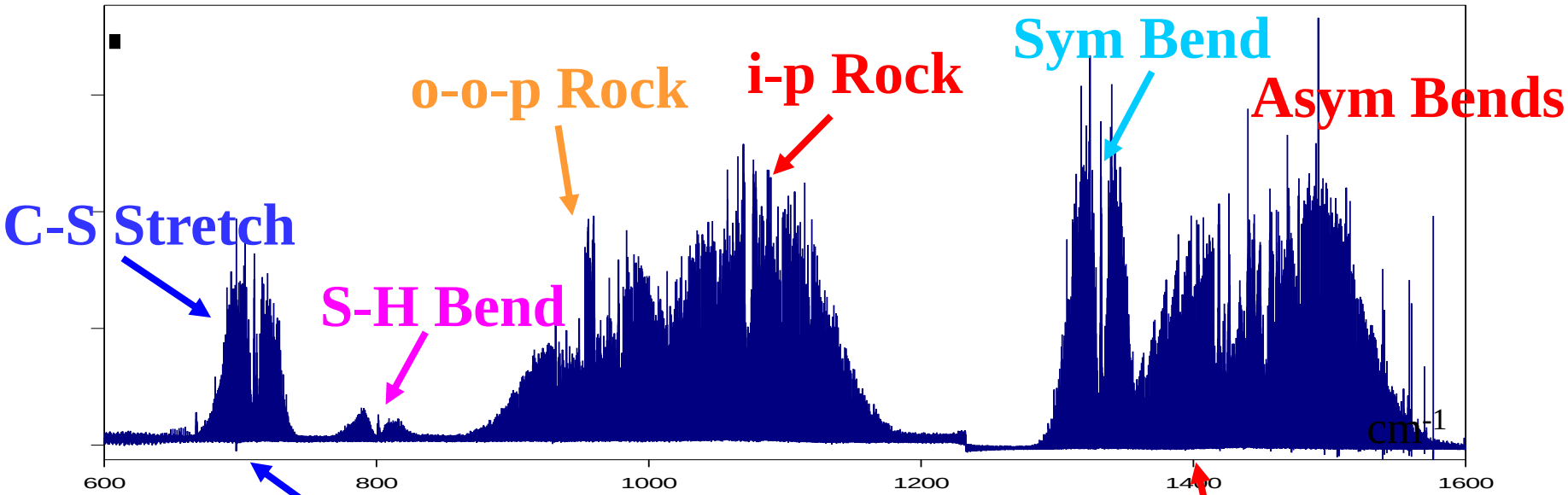
		Description	ν_{obs} / cm^{-1}
A'	ν_1	CH asym stretch	3015
	ν_2	CH sym stretch	2948
	ν_3	SH stretch	2605
	ν_4	CH_3 asym bend	1453
	ν_5	CH_3 sym bend	1332
	ν_6	CH_3 in-plane rock	1072
	ν_7	SH bend	802
	ν_8	CS stretch	710
A"	ν_9	CH asym stretch	3015
	ν_{10}	CH_3 o-o-p bend	1444
	ν_{11}	CH_3 o-o-p rock	956
	ν_{12}	CH_3 torsion	~200

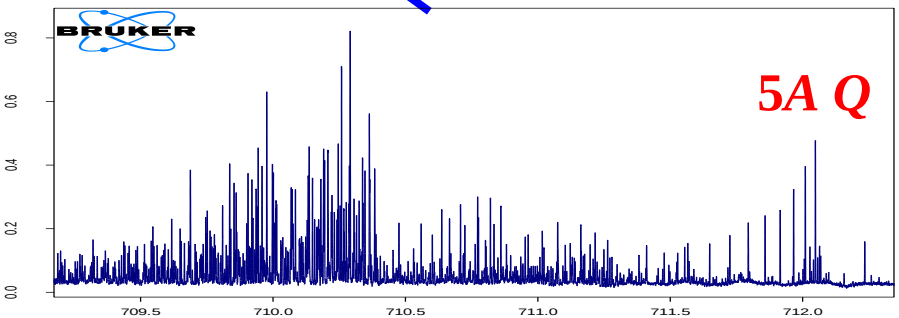


Vibrational Coupling to Torsional Ladder

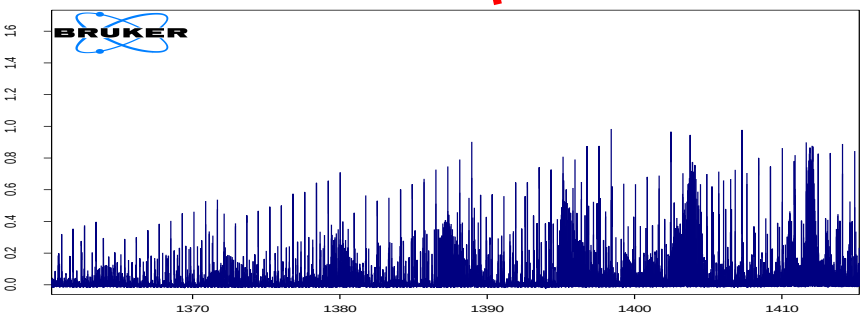
Wavenumbers from I. W. May and E. L. Page, Spectrochim. Acta. **24A** (1968) 1605-1615.

FTIR Spectrum of the Lower Bands of CH_3SH



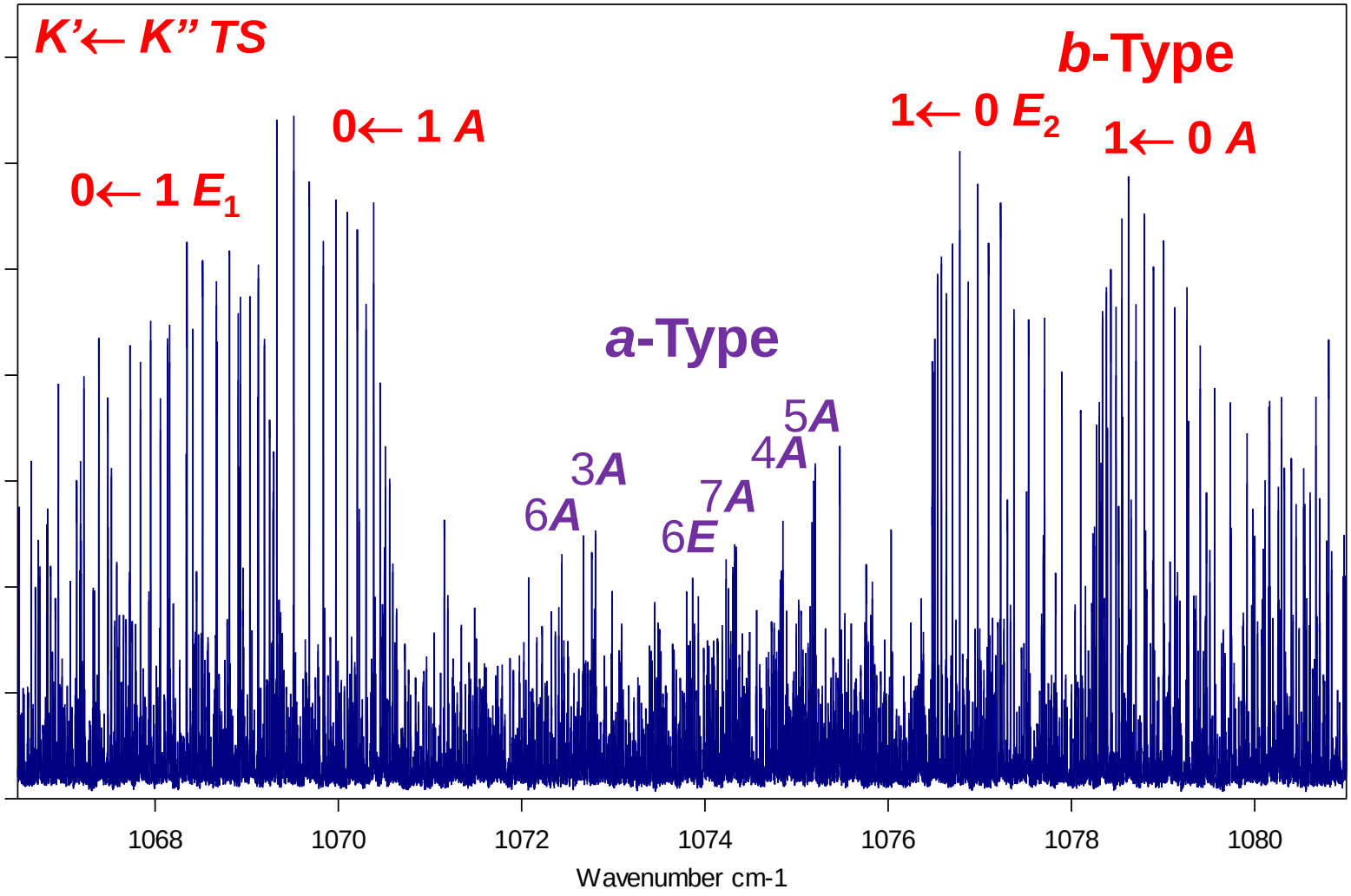


C-S Stretch

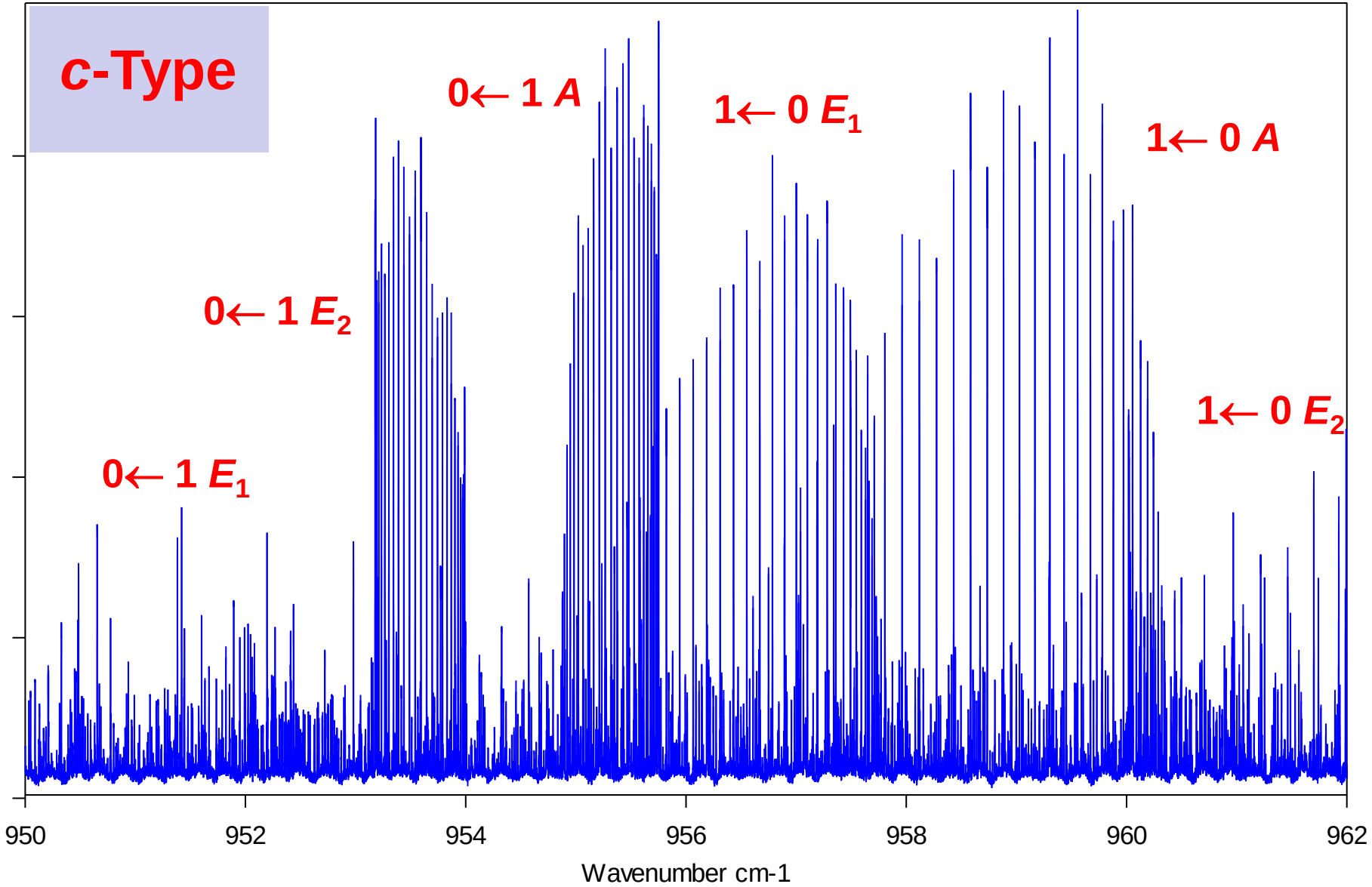


CH_3 Asymmetric Bends

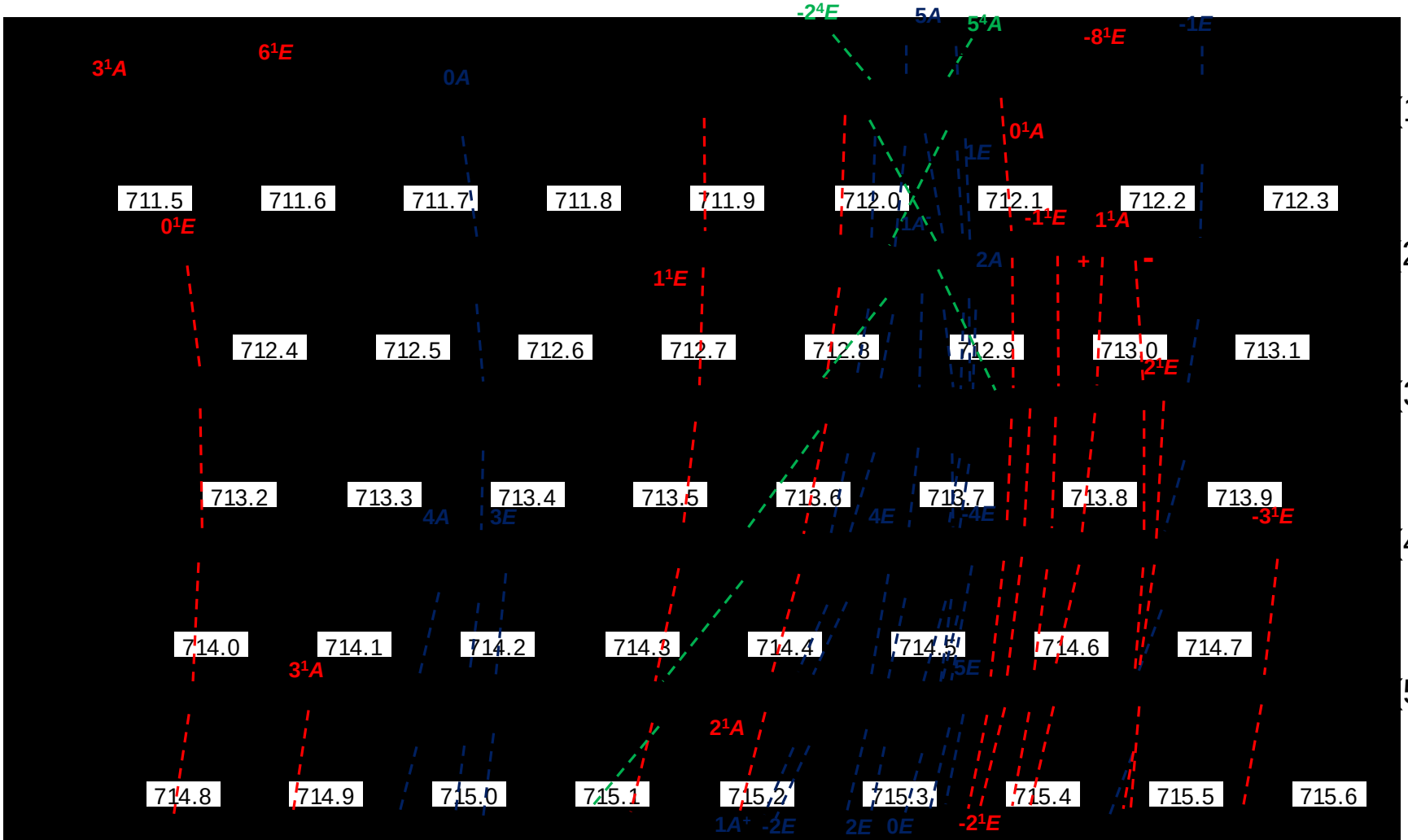
CH_3SH In-Plane Methyl-Rocking Band Origin



CH_3SH Out-of-Plane Methyl-Rocking Band Origin



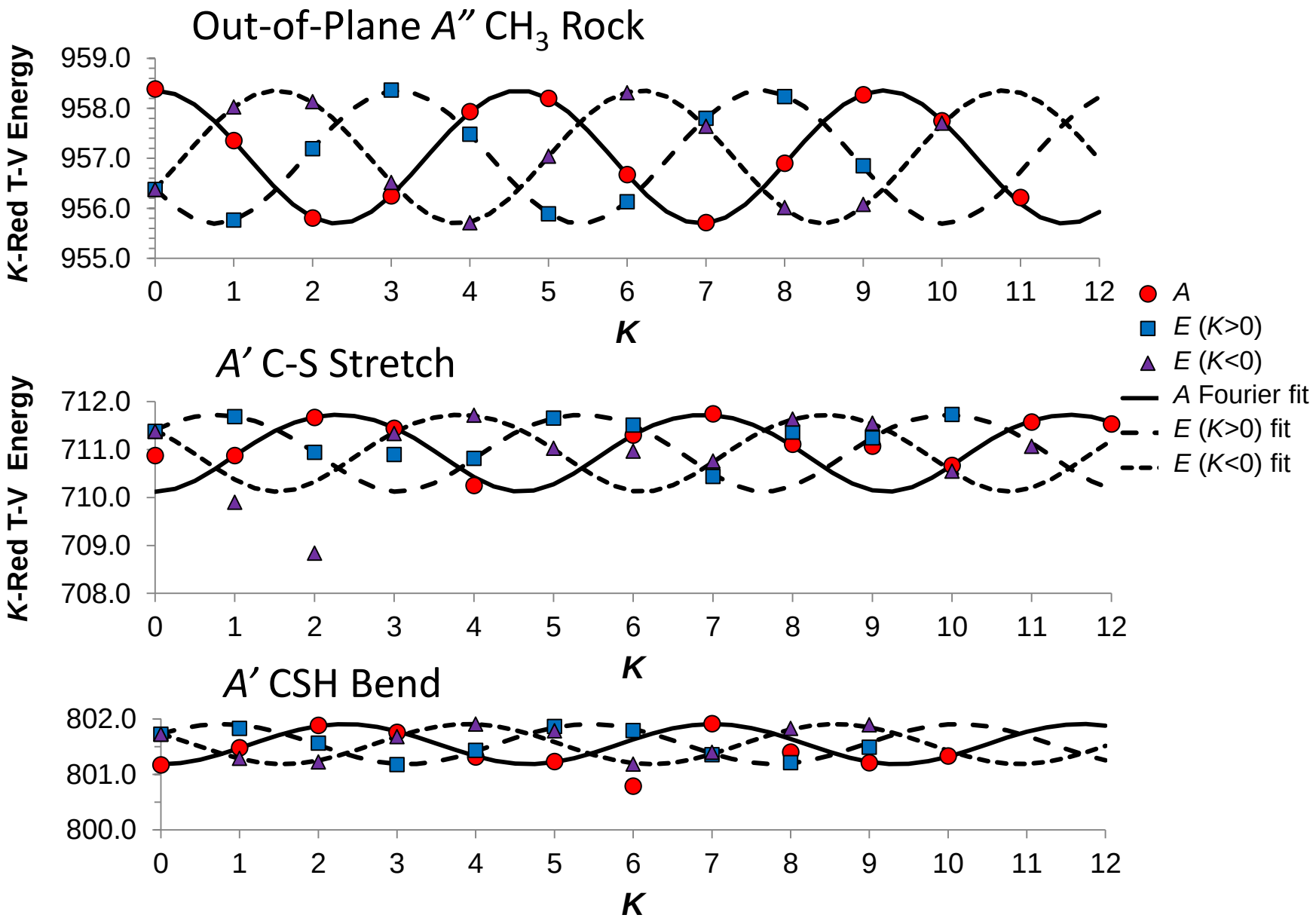
Loomis-Wood Plot for the C-S Stretch Band of CH_3SH



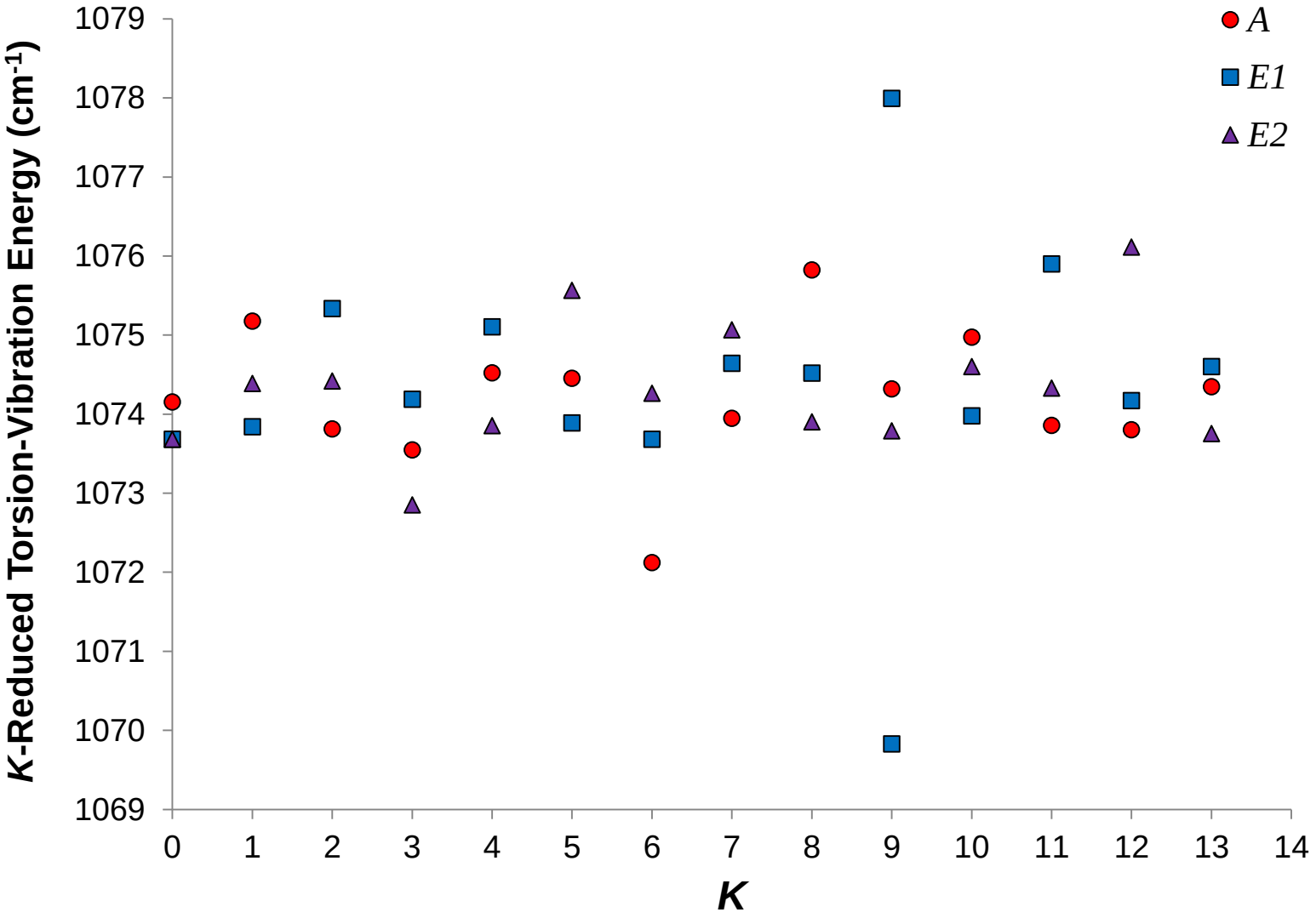
in Blue indicate $\nu_t = 0$ sub-branches; in Red are $\nu_t = 1$; in Green are perturbation-induced $\nu_t = 4 \leftarrow 0$ sub-branches appearing via intensity borrowing

Sub-branch labeling is $K^{\nu t}TS$.

K-Reduced Torsion-Vibration Energies



K-Reduced Torsion-Vibration Energies for the *A′* In-Plane CH_3 Rock



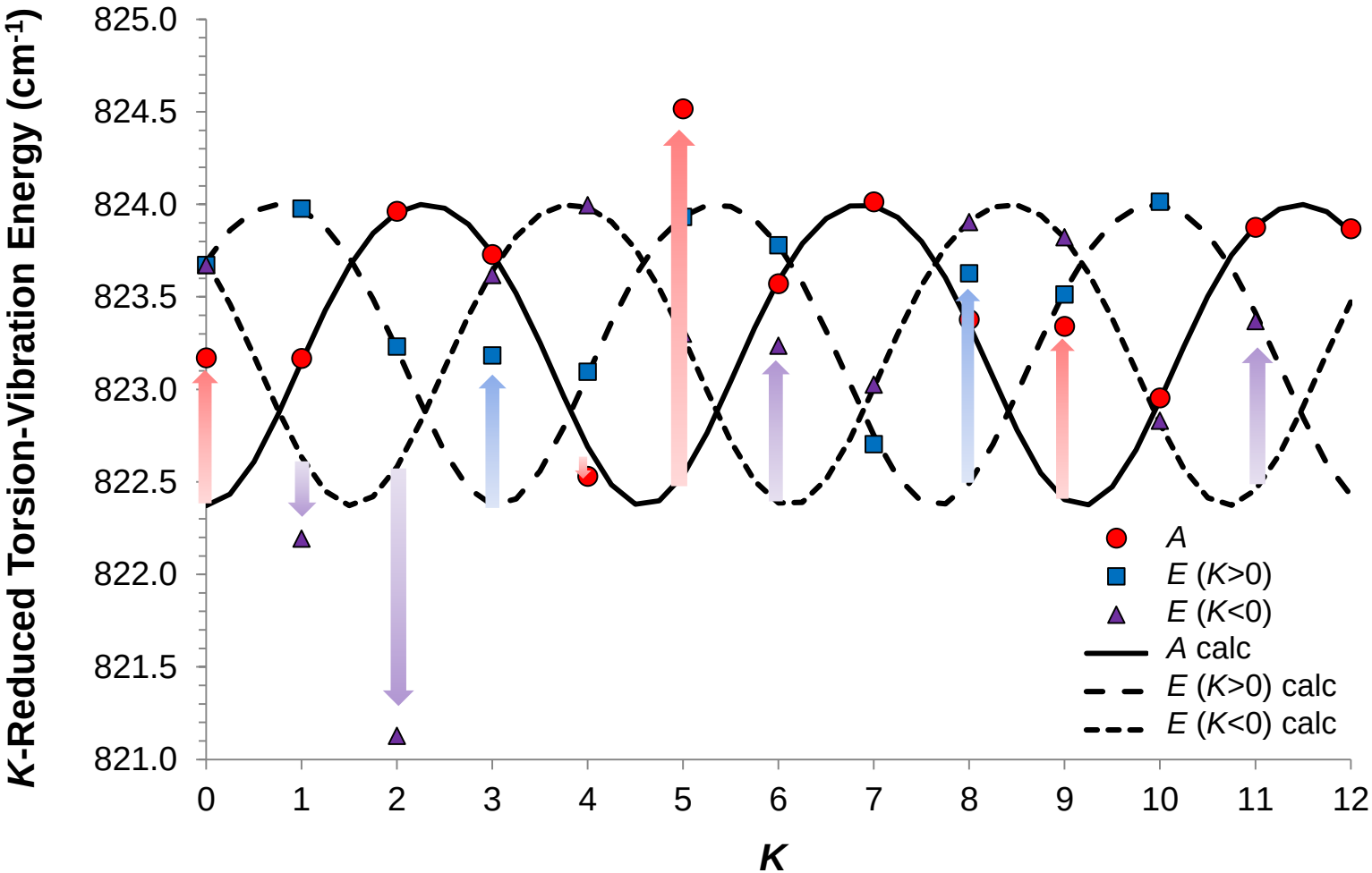
Fourier Fits to the Torsion-Vibration $v_t = 0$ Substate Origins

$$E_0(K,\sigma) = E_0 - a_1\cos[(\rho K + \sigma)2\pi/3] + a_2\cos[(\rho K + \sigma)4\pi/3] + (A - B)K^2 - D_K K^4$$

Parameter	Ground	C-S Stretch	CSH Bend	CH_3 Rock A"	CH_3 Rock A'
E_0	0.6737	710.9807	801.5503	957.0436	1074.0
a_1	**0.65287**	**0.80125**	**0.36219**	**–1.33263**	**?**
a_2	0.00167	-0.0583	-0.004023	-0.0188	
A-B	3.004472	3.004592	3.020647	3.000452	3.045
D_K	2.03E-05	1.44E-05	1.549E-05	2.702E-05	
ρ	0.651753	0.653632	0.641697	0.648306	
S.D.		0.0241	0.0311	0.0310	
# Origins		35	30	32	
# Fitted		25	27	32	
ν_{vib}	0	710.3070	800.8766	956.3699	1073.3
"V_3" [1-D]	**443.93**	**419.95**	**515.45**	**363.82**	

Fermi Perturbations to the C-S Stretch $v_t = 0$ Levels

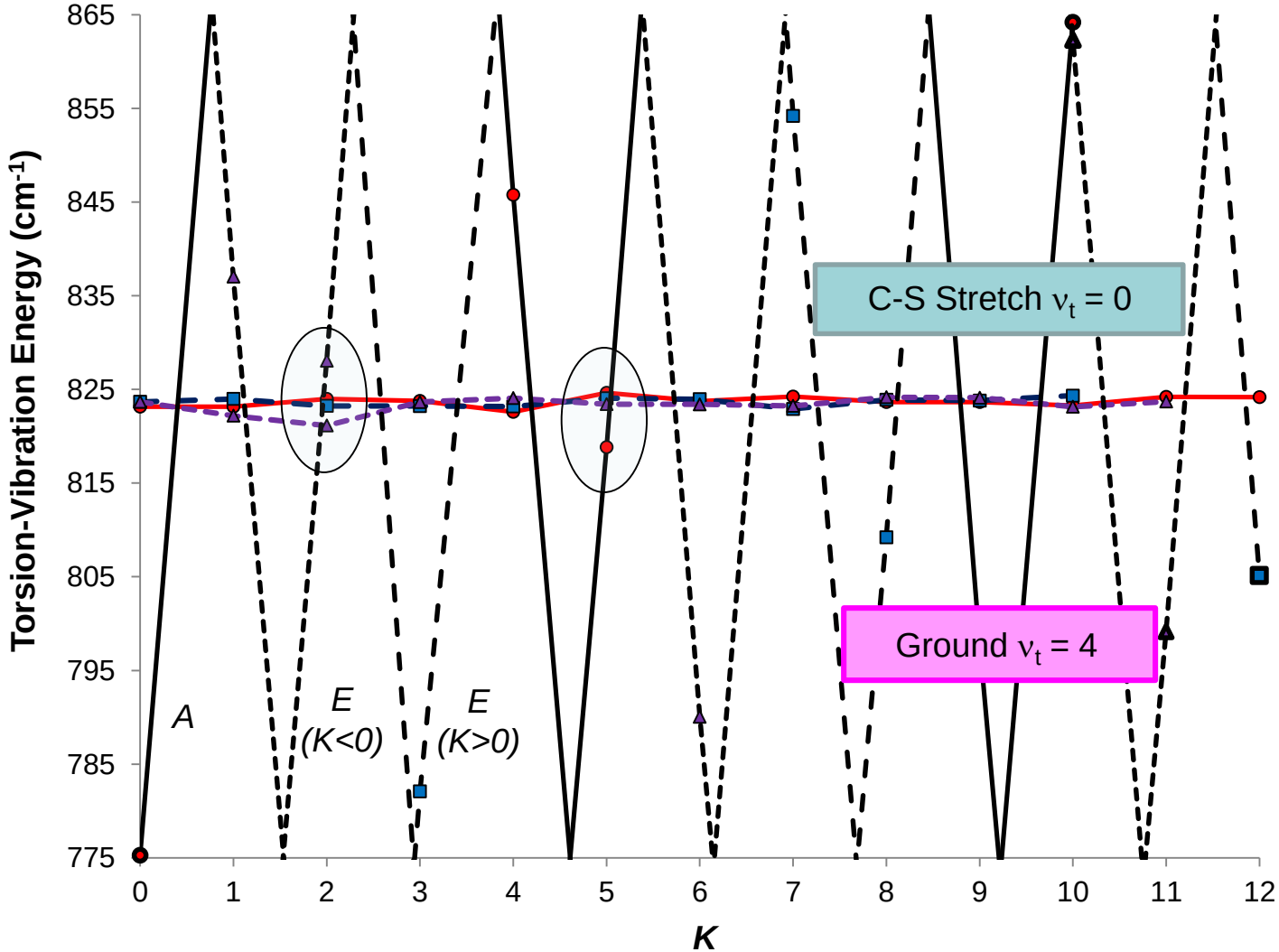
The curves are calculated Fourier-series fits to the *K*-reduced substate origins. Those origins with large deviations highlighted by arrows are perturbed by anharmonic Fermi resonances with $v_t = 4$ excited torsional levels of the ground state, and were excluded from the fit.



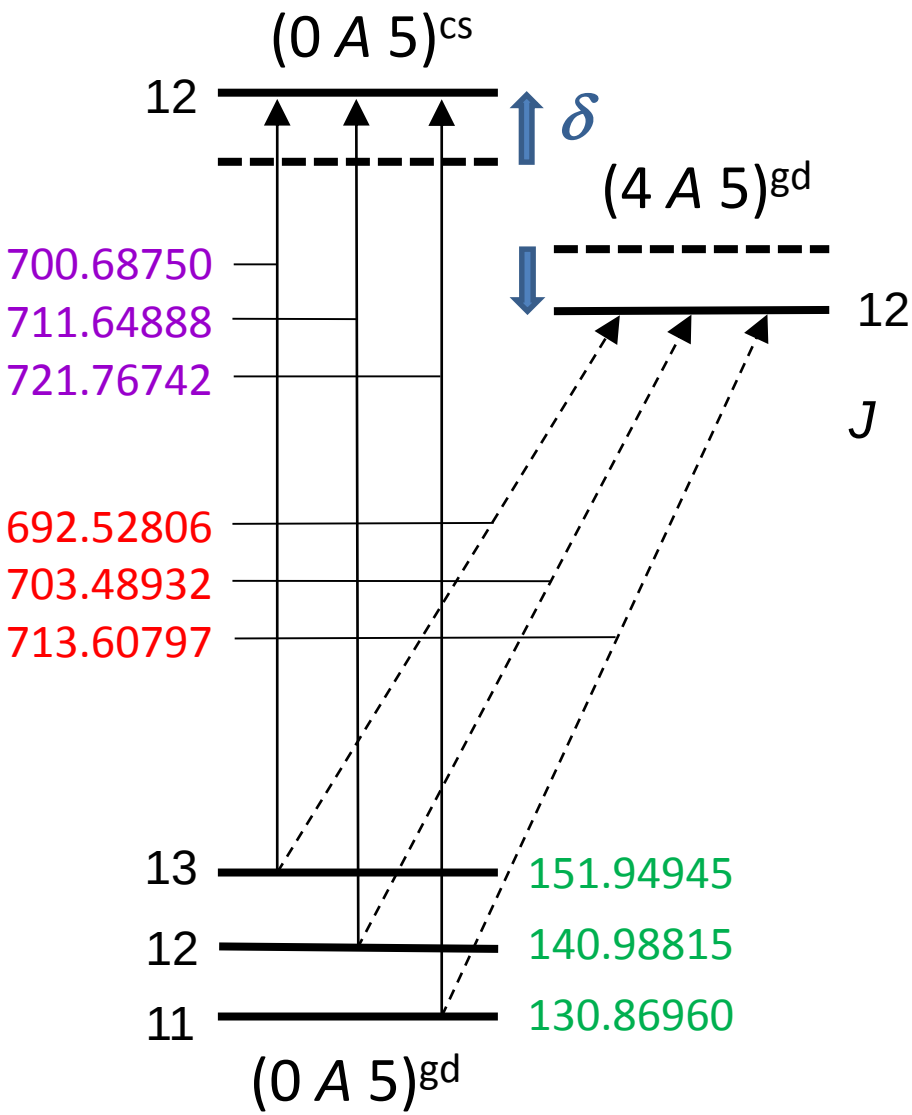
Energies are referenced to the bottom of the torsional barrier, 112.17587 cm^{-1} below the 0_0 *A* $\nu_t = 0$ level.

Fermi Resonances between v_t = 0 C-S Stretch and v_t = 4 Ground Levels

Where the v_t = 4 curves pass through the C-S stretch v_t = 0 state, anharmonic resonances can occur between close levels of the same torsional symmetry.



Fermi-Induced Forbidden Sub-band for the 5*A* Resonance



Fermi Interaction at J = 12

$\delta(5A, 12) = 1.97$

$\Delta E(12) = 8.20$

$\Delta E_o(12) = 4.26$

Interaction Parameter W

$\Delta E = \sqrt{(\Delta E_o^2 + W^2)}$

$W = 0.5 * \sqrt{(\Delta E^2 - \Delta E_o^2)}$

$\boldsymbol{W = 3.50\ \mathrm{cm}^{-1}}$

$|b/a|^2 = (\Delta E - \Delta E_o)/(\Delta E + \Delta E_o)$

$= \mathbf{0.32}$

Summary

- The four lowest vibrational bands in the FTIR synchrotron spectrum of $CH_3{}^{32}SH$ have been analyzed at high resolution, and term values and substate origins have been determined.
- Both the C-S stretch and CSH bend show the normal torsional energy pattern while the out-of-plane CH_3 rock is inverted, and all have been fitted to a Fourier model to characterize the torsional structure. The in-plane rock does not display the expected oscillatory behaviour and does not conform to the traditional Hamiltonian model.
- Substantial variation in the Fourier amplitudes suggests significant differences in torsional barrier height among the modes.
- A complex network of interactions among the vibrational modes and high-v_t torsional ground-state levels leads to numerous perturbations in the spectrum, with interaction constants of up to several cm^{-1} plus forbidden sub-bands.

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