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IMPROVED ANALYSIS OF THE ROTATION SPECTRUM OF META-CHLOROTOLUENE USING A FREE ROTOR BASIS AND NON-PERTURBATIVE HYPERFINE TREATMENT

MK11

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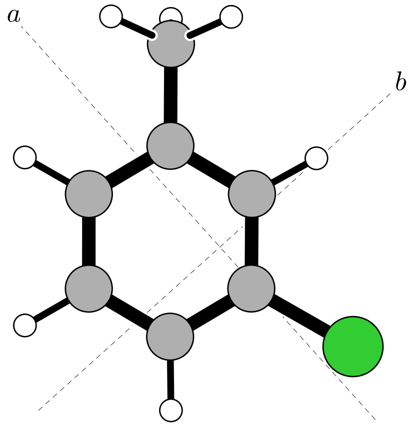
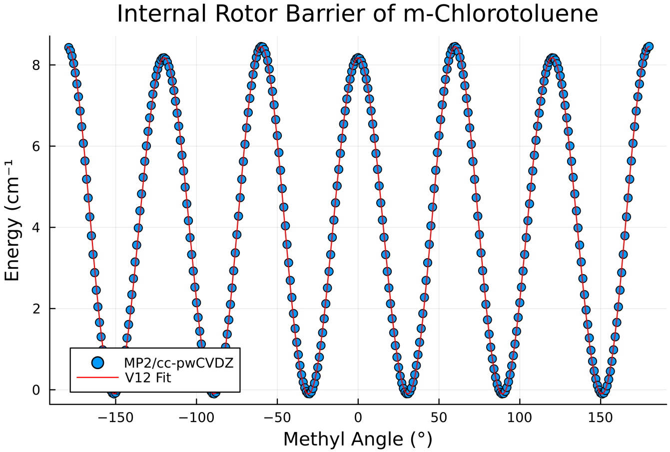
Meta-Chlorotoluene



Parameter	MP2/cc-pwCVDZ Value (MHz)
A	3308.3696
B	1181.5844
C	875.4647
χ_{zz}	−62.5295
χ_{xx}	27.782
χ_{yy}	34.746
χ_{xz}	−33.470



Expansion Term	MP2/cc-pwcVDZ (cm^{-1})
V_3	0.1207
V_6	8.4047
V_9	−0.3921
V_{12}	0.0465

Goal of the Code

Towards Free Rotor & Full Hyperfine Treatement

	Perturbative Spin Treatment	Complete Spin Treatment
Perturbative Torsions	(not useful)	SPFIT/SPCAT
Complete Torsions	XIAM, RAM36hf, BELGI-HYPERFINE	

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Single-diagonalization stage using free rotor & Hund's case (b) wavefunction for tidier derivatives & Wang transformations:

$$|\psi\rangle = |m\sigma\rangle |JSNK\rangle$$

User-definable higher order terms:

$$\hat{O}^{abcd}_{efgh} = \left(P^f_\alpha \cos g\alpha \sin h\alpha + \sin h\alpha \cos g\alpha P^f_\alpha \right) \otimes \left(N^a N^b_z (N^c_+ + N^c_-)(NS)^d S^e_z N_y^{1-\delta(h,0)} + N_y^{1-\delta(h,0)} S^e_z (NS)^d (N^c_+ + N^c_-) N^b_z N^a \right)$$

Allows for Watson A & S, Brown & Sears A, Nakagawa, and Xu!

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1. J and σ assigned automatically
2. m assigned by expectation value
3. Within each m, N is assigned by expectation value
4. Within each N & m pair, K is assigned energetically

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4. Within each N & m pair, K is assigned energetically

Generally gets close to RAM36 & XIAM assignments. Not perfectly consistent due to the off-diagonal in N matrix elements from spin

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Accelerated Levenberg-Marquardt:

$$(J^{\dagger}J - \lambda\,\mathrm{diag}(J^{\dagger}J))\,\delta = J^{\dagger}(y - f(x))$$

$$(J^{\dagger}J - \lambda\,\mathrm{diag}(J^{\dagger}J))\,\gamma = J^{\dagger}(y - f(x + \delta))$$

$$step = \delta + \gamma$$

If RMS would increase, step is recalculated with higher dampening parameter (λ).
Convergence checked against step size and RMS change.

Torsional Test Case

2-butynoic acid

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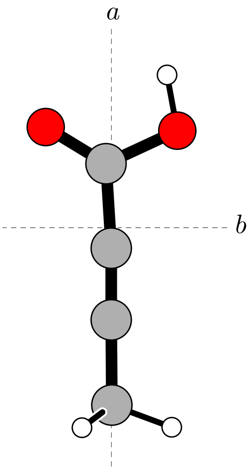
Parameter (units)	Operator	westerfit	RAM36
A (MHz)	$\mathcal{N}_z^2$	11269.9001(11)	11269.90006(66)
B (MHz)	$\mathcal{N}_x^2$	1752.18588(15)	1752.18588(15)
C (MHz)	$\mathcal{N}_y^2$	1529.58083(15)	1529.58083(15)
D_{ab} (MHz)	$\{\mathcal{N}_z, \mathcal{N}_x\}$	−16.185(24)	−16.1845(48)
F (cm^{-1})	$\mathcal{P}_\alpha^2$	5.66(*fixed*)	5.66(*fixed*)
ρ	$\mathcal{P}_\alpha \mathcal{N}_z$	0.071528698(37)	0.071528698(37)
V_3 (cm^{-1})	$\frac{1}{2}(1 - \cos 3\alpha)$	1.00899(41)	1.00900(42)
$-D_N$ (kHz)	$\mathcal{N}^4$	−0.0440(17)	−0.0440(17)
$-D_{NK}$ (kHz)	$\mathcal{N}^2 \mathcal{N}_z^2$	−11.3517(96)	−11.351(11)
$-D_K$ (kHz)	$\mathcal{N}_z^4$	−2.65(21)	−2.65(21)
d_1 (kHz)	$\{\mathcal{N}^2, \mathcal{N}_+^2 + \mathcal{N}_-^2\}$	−0.0240(13)	−0.01200(65)
d_2 (kHz)	$\mathcal{N}_+^4 + \mathcal{N}_-^4$	−0.0308(38)	−0.0154(19)
F_N (kHz)	$\mathcal{P}_\alpha \mathcal{N}^2$	−37.253(95)	−37.255(96)
ρ_{bc} (kHz)	$\{\mathcal{N}_z, \mathcal{N}_+^2 + \mathcal{N}_-^2\}\mathcal{P}_\alpha$	−0.7500(62)	−0.748(63)
ρ_N (kHz)	$\mathcal{P}_\alpha \mathcal{N}_z \mathcal{N}^2$	35.205(35)	35.204(36)
ρ_K (kHz)	$\mathcal{P}_\alpha \mathcal{N}_z^3$	15.04(74)	15.05(74)
Number of lines		89	89
rms (kHz)		2.5	2.6



Hyperfine Test Case

A states of m-chloro-35-toluene

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Parameter (units)	westerfit	SPFIT
A (MHz)	3373.3279(23)	3373.33216(42)
B (MHz)	1195.33178(25	1195.337969(43)
C (MHz)	882.49857(25)	882.5014296(262)
χ_{zz} (MHz)	−59.897(58)	−59.8964(23)
χ_{xz} (MHz)	32.28(89)	33.0452(287)
$\chi_{xx} - \chi_{yy}$	−5.958(78)	−5.9533(31)
Number of lines	240	
rms (kHz)	24.8	

Nair, K. R., et al. 2019, Journal of Molecular Spectroscopy, 361, 1

Hyperfine + Spin-Rotation Test Case

Iodo-perfluoropropane

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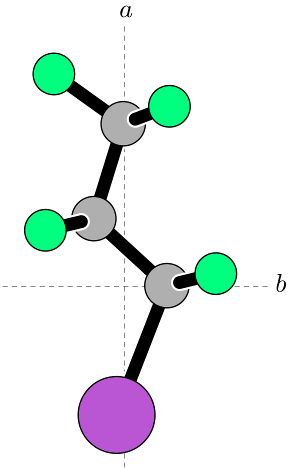
Parameter (units)	westerfit	SPFIT
A (MHz)	1572.12814(11)	1572.127966(99)
B (MHz)	398.458628(35)	398.458568(34)
C (MHz)	382.831179(35)	382.831125(34)
χ_{zz} (MHz)	−1798.4057(57)	−1798.4013(48)
$\chi_{xx} - \chi_{yy}$ (MHz)	−366.213(26)	−366.224(13)
$\lvert\chi_{xy}\rvert$ (MHz)	991.7039(43)	991.7058(35)
C_{aa} (kHz)	1.98(15)	2.19(16)
C_{bb} (kHz)	0.90(15)	0.91(11)
C_{cc} (kHz)	1.36(15)	1.30(10)
$-D_N$ (kHz)	−0.008408(38)	−0.008305(39)
$-D_{NK}$ (kHz)	−0.01023(11)	−0.00986(12)
$-D_K$ (kHz)	−0.0516(12)	−0.05172(94)
d_1 (kHz)	−0.008290(25)	−0.000394(11)
d_2 (kHz)	0.0000887(52)	0.0000377(25)
Number of lines	776	776
rms (kHz)	5.0	5.14



Moderate Barrier Torsion + Hyperfine Test Case

2-fluoro-4-chlorotoluene

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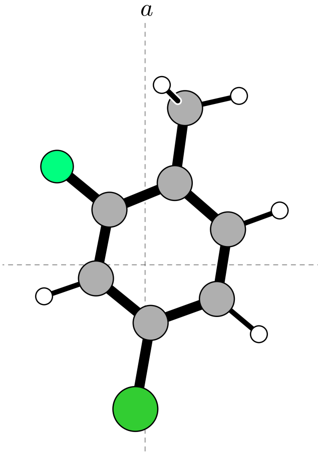
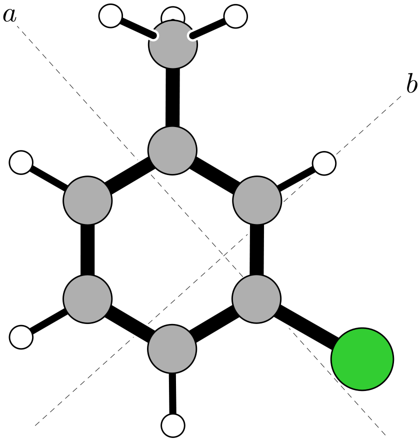
Parameter (units)	westerfit	RAM36hf
A (MHz)	3029.76(37)	3036.35(23)
B (MHz)	865.54(13)	859.11(23)
C (MHz)	672.37(13)	672.4555(45)
D_{ab} (MHz)	−119.0(17)	−125.9(14)
χ_{zz} (MHz)	−69.19(11)	−69.443(72)
$\chi_{xx} - \chi_{yy}$ (MHz)	2.375(67)	2.329(51)
F (cm^{-1})	5.392521(*fixed*)	5.392521(*fixed*)
ρ	0.017976(35)	0.018022728(84)
V_3 (cm^{-1})	222.55(14)	227.22(12)
$-D_N$ (kHz)	−0.00803(33)	−0.00809(22)
Number of lines	310	312
rms (kHz)	11.3	7.5



Meta-Chlorotoluene

Despair!

Parameter (units)	westerfit
A (MHz)	3131.34(32)
B (MHz)	1393.7592(24)
C (MHz)	882.5027(24)
D_{ab} (MHz)	−626.7339(48)
χ_{zz} (MHz)	−33.2(24)
χ_{xz} (MHz)	51.68(33)
$\chi_{xx} - \chi_{yy}$ (MHz)	−32.69(25)
F (cm^{-1})	5.26805(*fixed*)
ρ	0.01663(13)
V_3 (cm^{-1})	0.5(28)
V_6 (cm^{-1})	14(19)
$-D_N$ (kHz)	−0.0209(22)
$-D_{NK}$ (kHz)	0.1500(59)
$-D_K$ (kHz)	−0.8000(21)
Number of lines	336
rms (kHz)	17.7



	MP2/cc-pwCVDZ		MP2/6-311G(2p,3d)	
V_3 (cm^{-1})	0.1207	0.9310(59)	2.452	0.8840(79)
V_6 (cm^{-1})	15.87(8)	8.4047	(unresolved)	-10.991
rms (kHz)	29.6	29.6	66.4	29.5

Nair, K. R., et al. 2019, Journal of Molecular Spectroscopy, 361, 1

Meta-Chlorotoluene

Unresolved Frustrations of V_3 & V_6

	MP2/cc-pwCVDZ		MP2/6-311G(2p,3d)	
V_3 (cm^{-1})	0.1207	0.9310(59)	2.452	0.8840(79)
V_6 (cm^{-1})	15.87(8)	8.4047	(unresolved)	-10.991
rms (kHz)	29.6	29.6	66.4	29.5

- Seems $V_3 < 1$ cm^{-1}
- Seems $V_6 > 5$ cm^{-1}

Nair, K. R., et al. 2019, Journal of Molecular Spectroscopy, 361, 1

What Went Wrong

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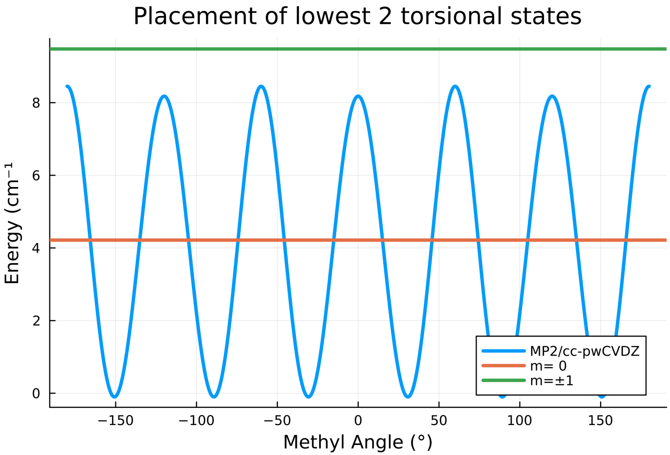

- Hard to fit V_3 & V_6 with only one v_t state
- Even low ro-tor states above barrier
- Not enough torsional information

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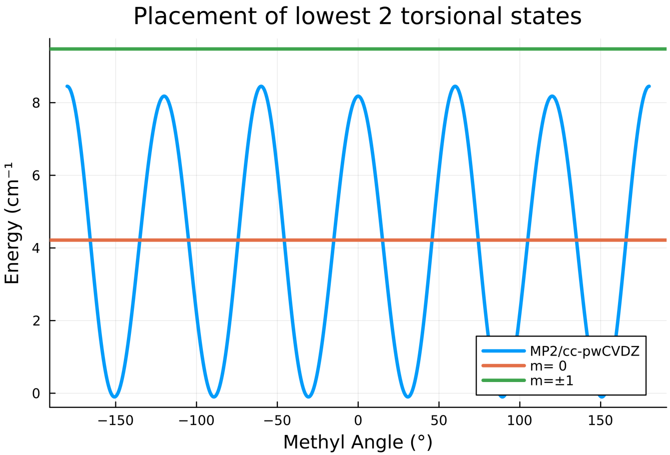

- Hard to fit V_3 & V_6 with only one v_t state
- Even low ro-tor states above barrier
- Not enough torsional information
- Anyone up for taking warmer spectra for me?

westerfit is now public!

Please use my code

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- Single stage Rho Axis Method!
- Full spin treatment!
- User-definable Operators!
- Modified Levenberg–Marquardt fitting!
- More legible documentation than SPFIT!

https://github.com/wes648/westerfit