Microwave and millimeter-wave rotational spectroscopy of 3-methylcatechol

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The 3-methylcatechol molecule (3MC)

- 3MC is present in the atmosphere during biomass burning events.
- 3MC has three large amplitude motions: the two torsions τ_1, τ_2 of the hydroxyl groups and the internal rotation τ_3 of the methyl group.

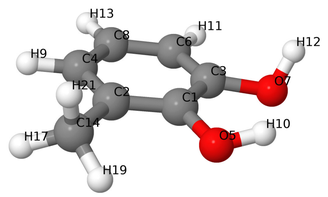

Figure 1: The 3MC molecule with $\tau_1 = D(\mathrm{H10-O5-C1-C3}) = 20°$, $\tau_2 = D(\mathrm{H12-O7-C3-C6}) = 70°$ and $\tau_3 = 30°$.

- 3MC has been recently studied by Hazrah *et al.* [1]
- The electronic energy $V(\tau_1, \tau_2, \tau_3)$ is 2π-periodic in τ_1, τ_2 and $\frac{2\pi}{3}$-periodic in τ_3

FTMW spectroscopy

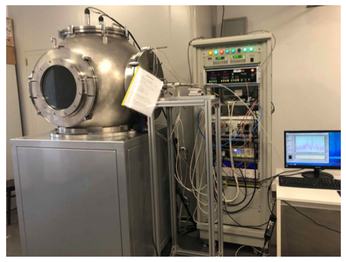

Figure 3: Spectrometer at the CQU.

- Coaxially oriented beam-resonator arrangement (COBRA) pulsed jet Fourier-transform microwave (PJ-FTMW) spectrometer (covering 2-20 GHz) at Chongqing university.
- Due to the instrumental Doppler effect, each rotational transition appears as a doublet.
- Additionally, the rotational transitions displayed a doublet due to the methyl internal rotation.

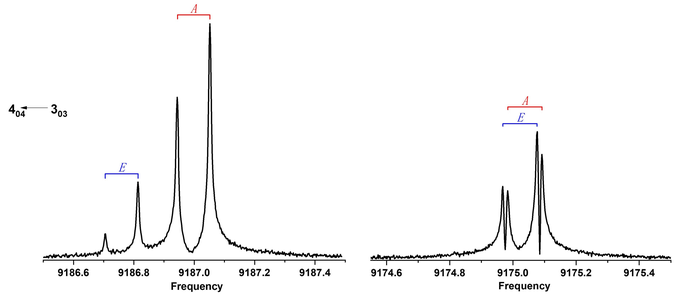

Figure 4: Recorded $4_{04} \leftarrow 3_{03}$ rotational transition of rotamer 1 and 2 exhibiting splittings (A/E) arising from the methyl internal rotation. Each component line exhibits the instrumental Doppler doubling.

References

[1] A. S. Hazrah, M. H. Al-Jabiri, and W. Jäger. Structure and conformations of 3-methylcatechol: A rotational spectroscopic and theoretical study. *J. Mol. Spectrosc.*, 390:111715, 2022.

Three-dimensional potential energy surface

The three-dimensional potential energy surface $V(\tau_1, \tau_2, \tau_3)$ with the B3LYP-D3(BJ) functional and the aug-cc-pVDZ atomic orbital basis set has only three minima.

Rotamer 1 $\Delta E_{\mathrm{ZPE}}(0°, 0°, 0°) = 0$ | Rotamer 2 $\Delta E_{\mathrm{ZPE}}(180°, 180°, 0°) = 92.8\ \mathrm{cm}^{-1}$ | Rotamer 3 $\Delta E_{\mathrm{ZPE}}(180°, 0°, 0°) = 1429.7\ \mathrm{cm}^{-1}$

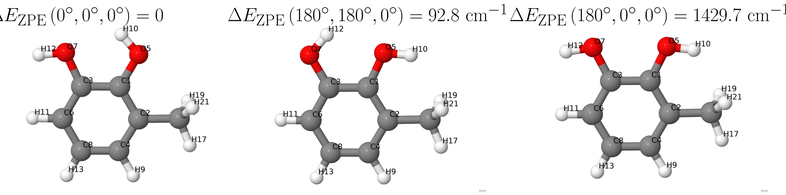

Figure 2: The three stable rotamers of 3MC and their relative energies with the B3LYP-D3(BJ) functional (including zero-point energy) and the aug-cc-pVTZ atomic orbital basis set.

Room temperature mm-wave spectroscopy

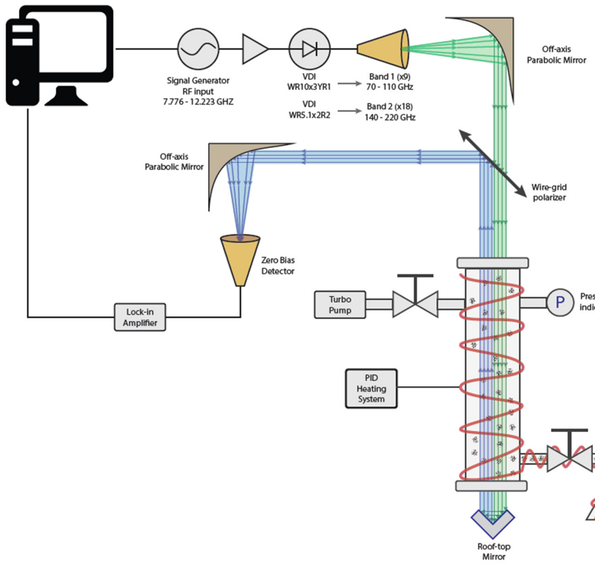

Figure 5: Mm-wave spectrometer at LPCA.

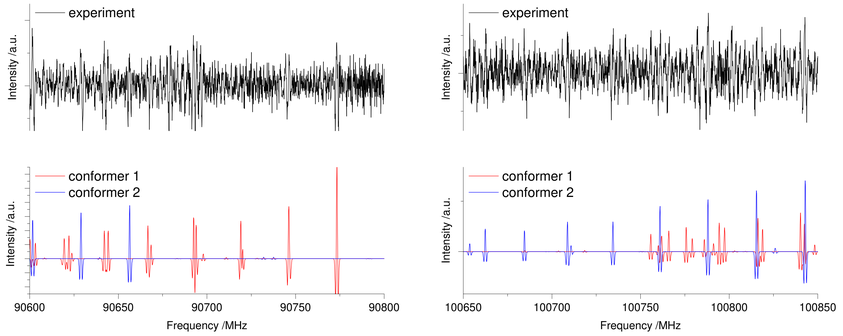

Figure 6: Experimental and simulated mm-wave spectra of 3MC.

One-dimensional scan of the torsional potential

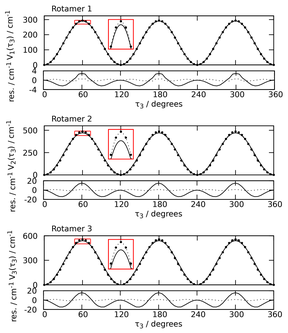

Figure 7: One-dimensional torsional potential as a function of the torsional coordinate τ_3 (B3LYP-D3(BJ), aug-cc-pVTZ atomic orbital basis set).

Table 1: V_3 and V_6 parameters of the fits of the one-dimensional scan of the torsional potential from quantum chemical calculations.

Conformer	B3LYP-D3(BJ)		MP2	
	V_3/cm^{-1}	$(V_3, V_6)/\mathrm{cm}^{-1}$	V_3/cm^{-1}	$(V_3, V_6)/\mathrm{cm}^{-1}$
1	290.6	(293.0, −3.6)	308.7	(313.8, −7.7)
2	471.1	(485.0, −20.8)	545.4	(563.5, −27.2)
3	538.9	(553.6, −22.0)	WIP	WIP

Experimental spectroscopic parameters

Table 2: The experimental spectroscopic parameters of 3MC obtained with XIAM. Standard errors are indicated in units of the least significant digits of the value of the constant.

	Rotamer 1	
	MW	global
A/MHz	2308.70897(27)	2308.70885(22)
B/MHz	1806.48978(29)	1806.48963(22)
C/MHz	1020.11684(15)	1020.116685(85)
Δ_J/kHz	0.0567(34)	0.0531(12)
δ_j/kHz	-0.0293(19)	-0.02758(97)
δ_k/kHz		-0.00699(39)
V_3/cm^{-1}	301.763(27)	301.764(26)
D_{pi2J}/kHz	-12.1(20)	-12.2(19)
D_{pi2-}/kHz	-31.6(23)	-31.7(22)
δ/rad	0.47880(70)	0.47878(68)
$N_t/N_{line}{}^a$	178/178	MW:178/178 mm-wave: 159/69
RMS/kHz	4.4	132
J_{max}	5	38
$K_{a,max}$	4	12
$\lvert\mu_a\rvert$, $\lvert\mu_b\rvert$, $\lvert\mu_c\rvert$ /D		strong, weak, none
	Rotamer 2	
	MW	global
A/MHz	2306.98276(41)	2306.98278(23)
B/MHz	1803.02104(36)	1803.02140(14)
C/MHz	1018.80940(20)	1018.809197(55)
Δ_J/kHz	0.0503(47)	0.05486(62)
δ_j/kHz	-0.0212(29)	-0.02901(49)
δ_k/kHz		-0.00771(21)
V_3/cm^{-1}	537.7(15)	538.5(10)
D_{pi2J}/kHz		
D_{pi2-}/kHz		
δ/rad	0.492(17)	0.486(11)
N_t/N_{line}	66/66	MW:66/66 mm-wave: 512/126
RMS/kHz	2.9	147
J_{max}	6	51
$K_{a,max}$	3	13
$\lvert\mu_a\rvert$, $\lvert\mu_b\rvert$, $\lvert\mu_c\rvert$ /D		strong, weak, none

[a]Number of transitions/lines in the fit.