Microwave Spectrum of 1-Adamantanol $C_{10}H_{15}$–OH

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ISMS, June 18–22, 2018

Outline

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- The large amplitude internal rotation

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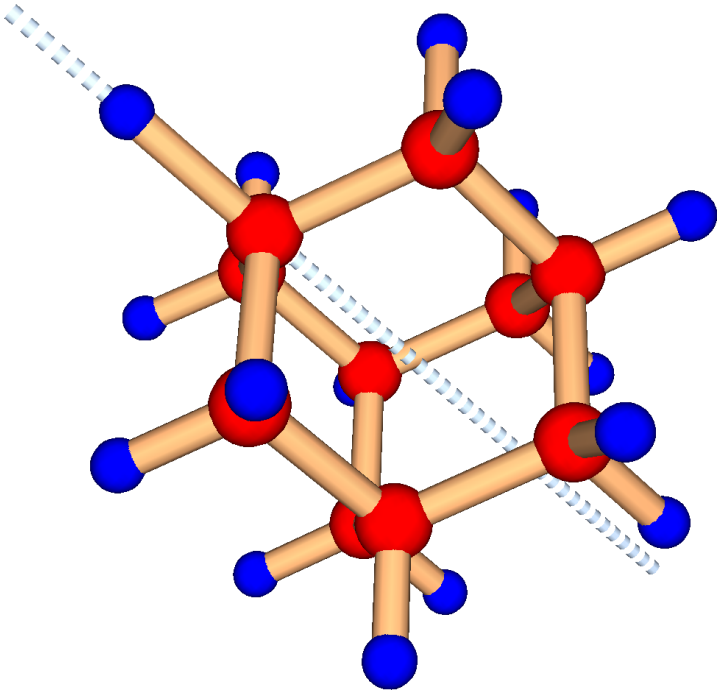
- Assignments
- Analysis results

Adamantanol

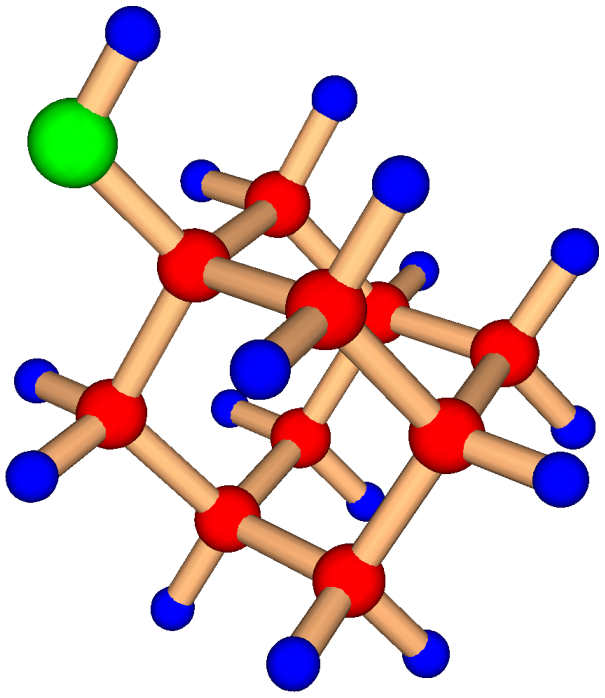
Adamantanol

In the C_{3v} adamantane molecule ($C_{10}H_{16}$), the apex hydrogen atom is replaced by a hydroxyl group



Adamantanol

1-adamantanol ($C_{10}H_{15}-OH$) has C_s symmetry



The large amplitude motion

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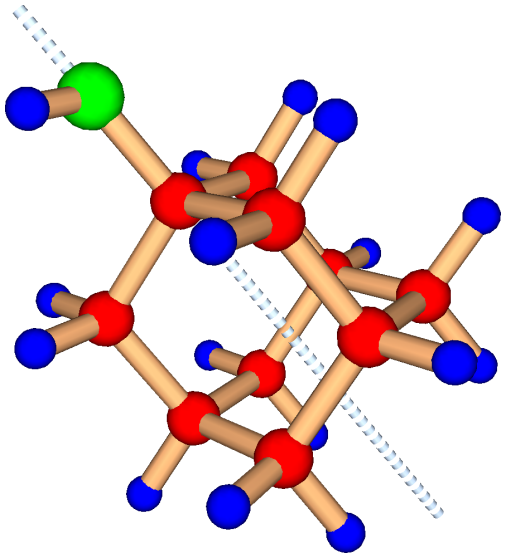
Adamantanol is a non-rigid molecule displaying internal rotation of its hydroxyl group



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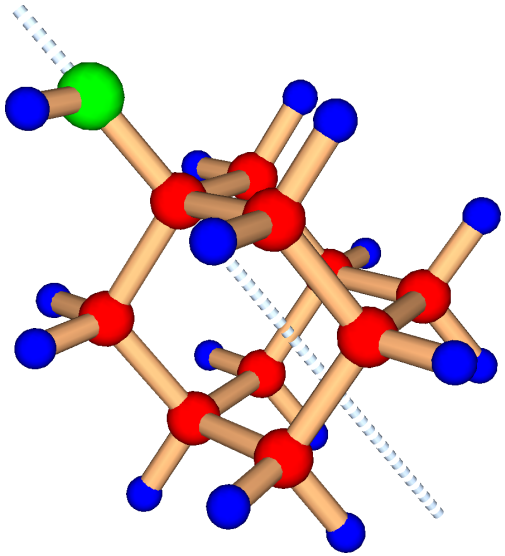

Like in CH_3OH or CH_3COH we have a C_s frame and a C_{3v} top

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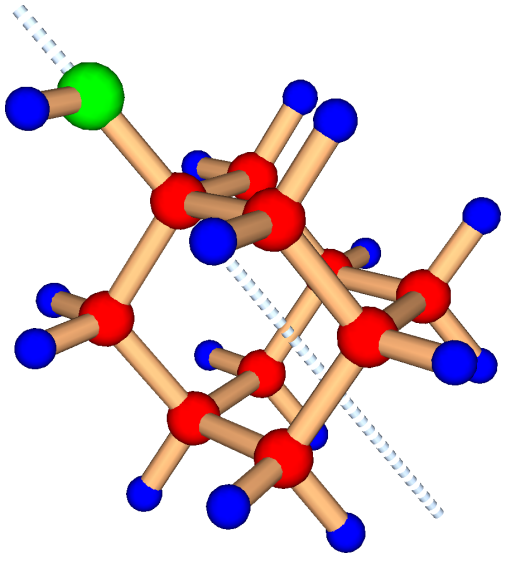

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Height of the potential barrier hindering the torsion is $V_3 \approx 400$ cm^{-1}

Previous spectroscopic investigations

[1] Craven, *Spectrochimica. Acta* **29A** (1973) 679

[2] Corbelli *et al.*, *J. Chem. Soc., Faraday Trans. 2* **83** (1987) 2225

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- Corbelli *et al.*[2] recorded a microwave spectrum in the 8–40 GHz frequency range
  - a-type R lines with unresolved K-structure
  - Q branch of b-type bands with unresolved J-structure
  - Analysis led to $V_3 = 410$ cm^{-1}

[1] Craven, *Spectrochimica. Acta* **29A** (1973) 679
[2] Corbelli *et al.*, *J. Chem. Soc., Faraday Trans. 2* **83** (1987) 2225

Important spectroscopic results

[1] Hougen *et al.*, *J. Molec. Spectrosc.* **163** (1994) 559

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The RAM[1] Hamiltonian can be used to describe the internal rotation:

$$H_{\mathrm{RAM}} = F(P_\alpha - \rho J_z)^2 + A{J_z}^2 + B{J_x}^2 + C{J_y}^2 + D_{xz}\{J_x, J_z\} + V(\alpha)$$

where:

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where:

Param.	Value/cm^{-1}	Param.	Value/cm^{-1}
A	20.058 974	D_{xz}	
B		F	20.114 247
C		ρ	

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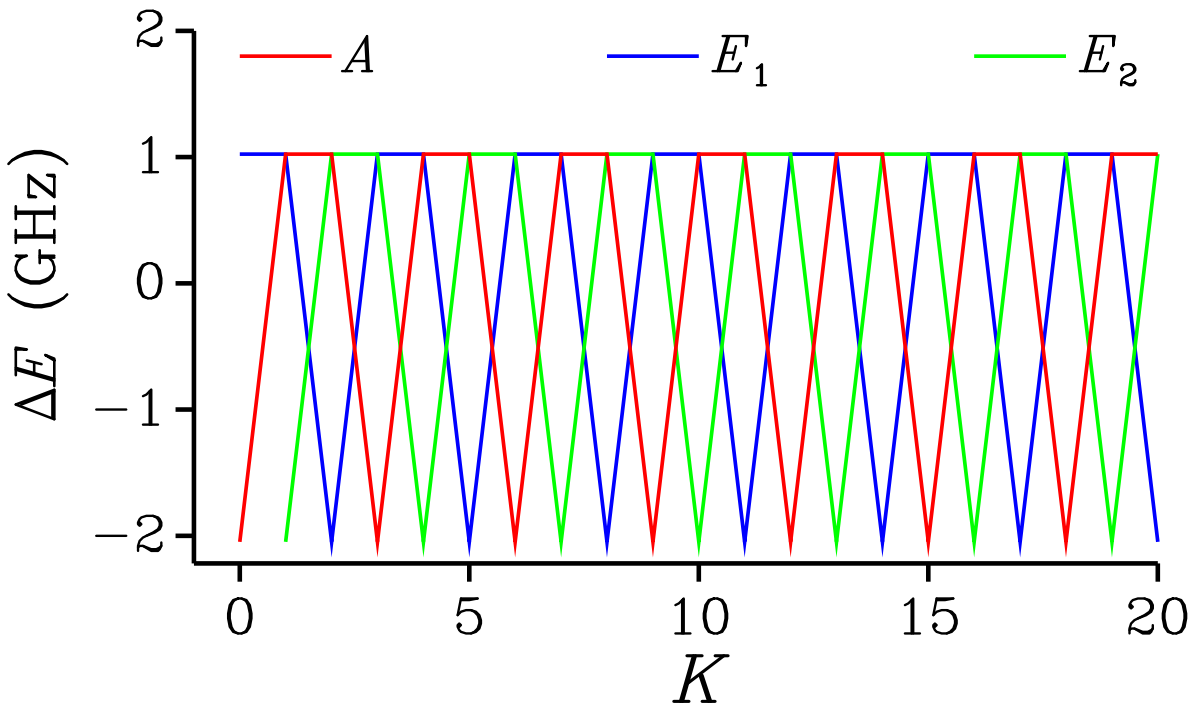
Torsional energy level diagram

[1] Lin & Swalen, *Rev. Mod. Phys.* **31** (1959) 841

Torsional energy level diagram

$\rho = 1$



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Torsional energy level diagram

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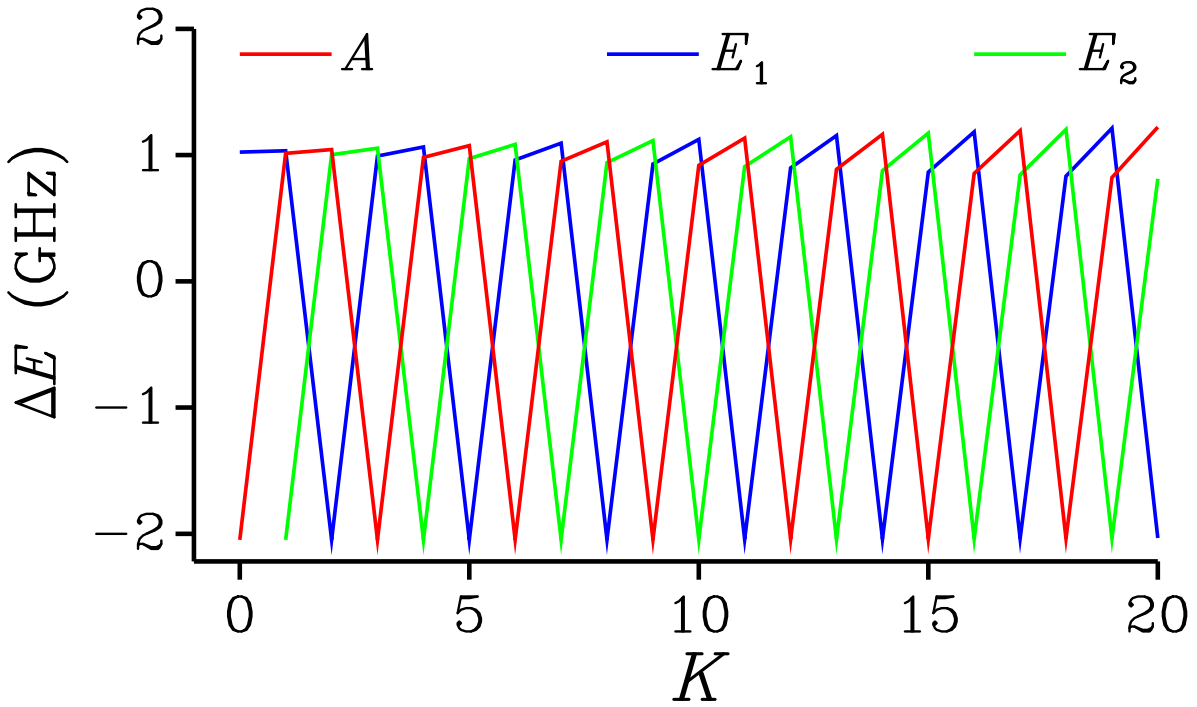

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The new microwave data

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Spectrum type	Laboratory	Range (GHz)	Temperature
CP-FTMW	Hamburg	2–12	jet-cooled
		75–110	room
Cavity FTMW	Lille	2–16	jet-cooled
SMM	ISMO	75–110	room
		140–220	room

CP-FTMW spectrum in the 2–12 GHz region

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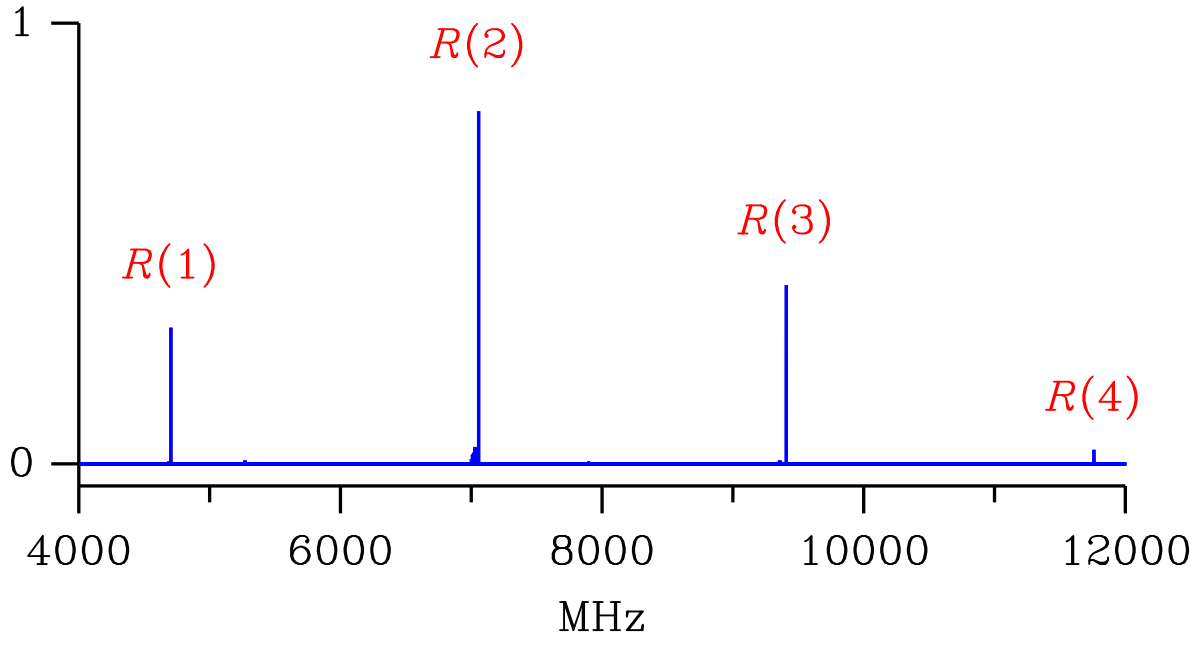

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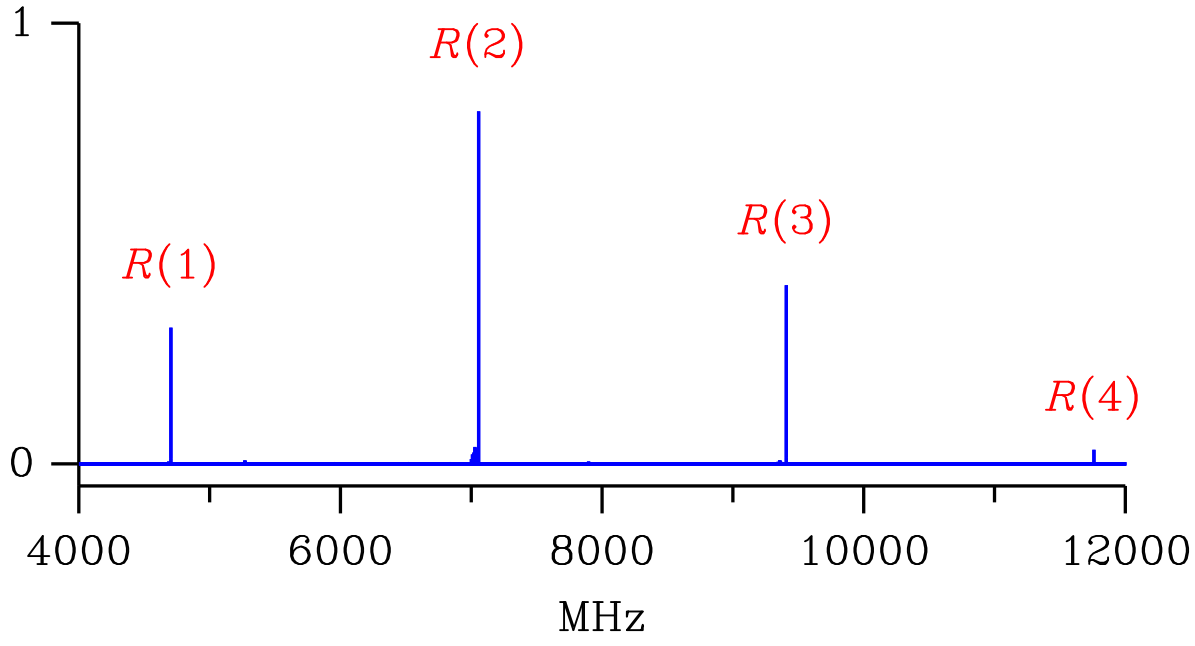

K-structure and asymmetry splitting unresolved

CP-FTMW spectrum in the 75–110 GHz region

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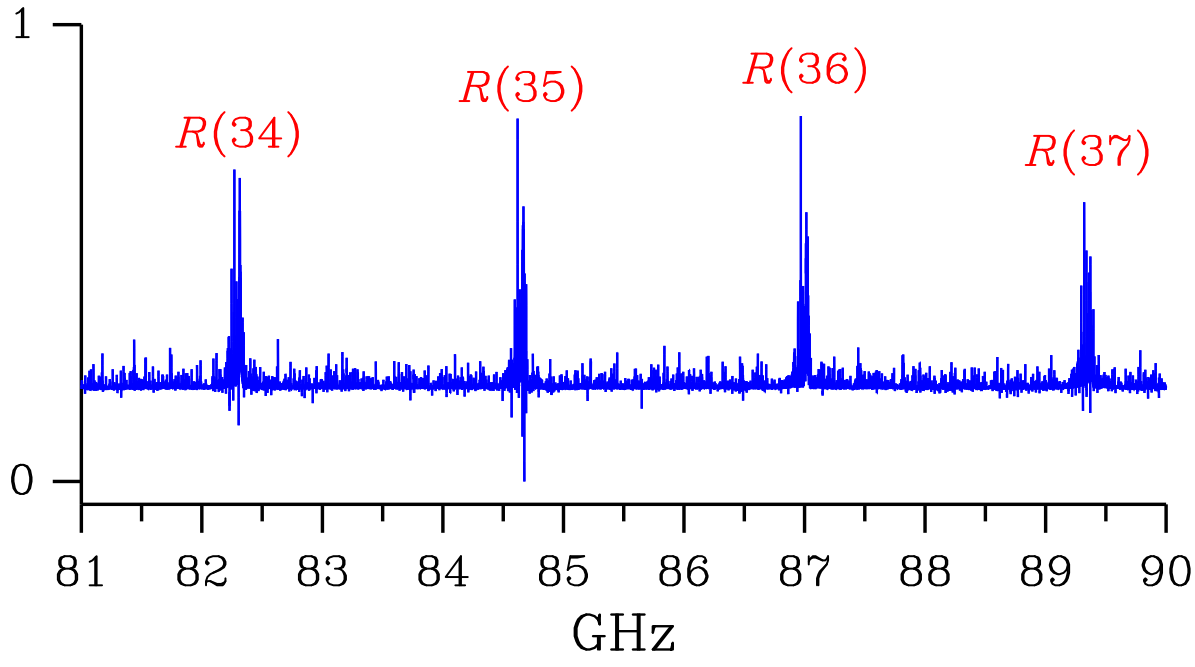

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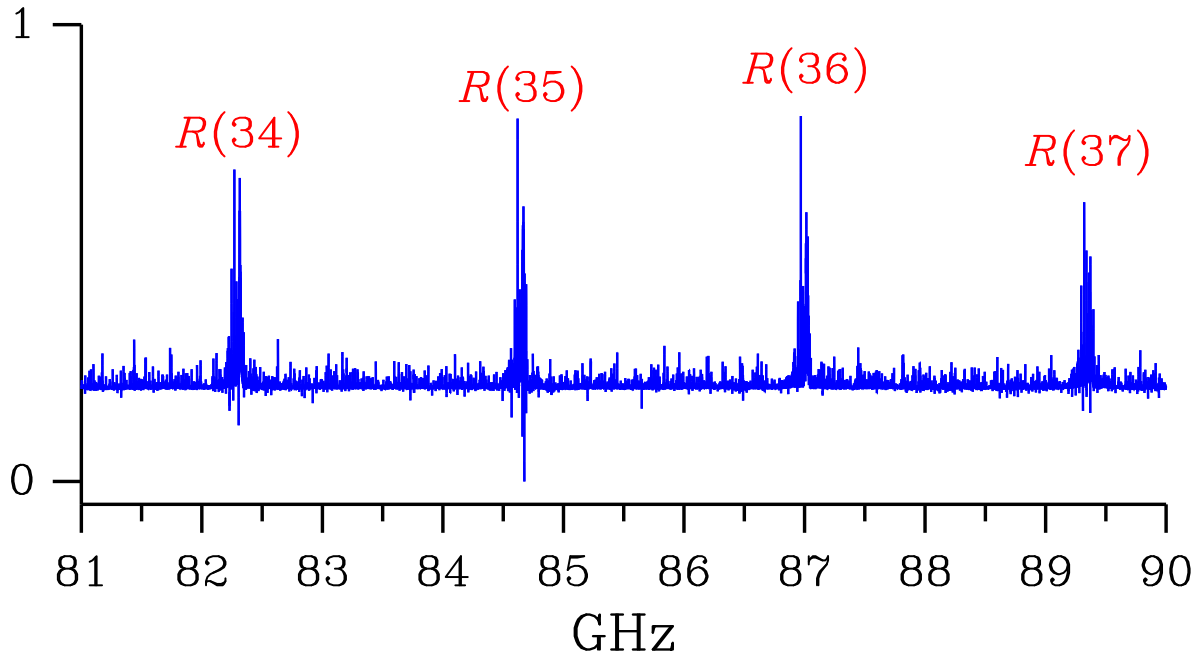

K-structure partially resolved but no asymmetry splitting

SMM spectrum in the 140–220 GHz region

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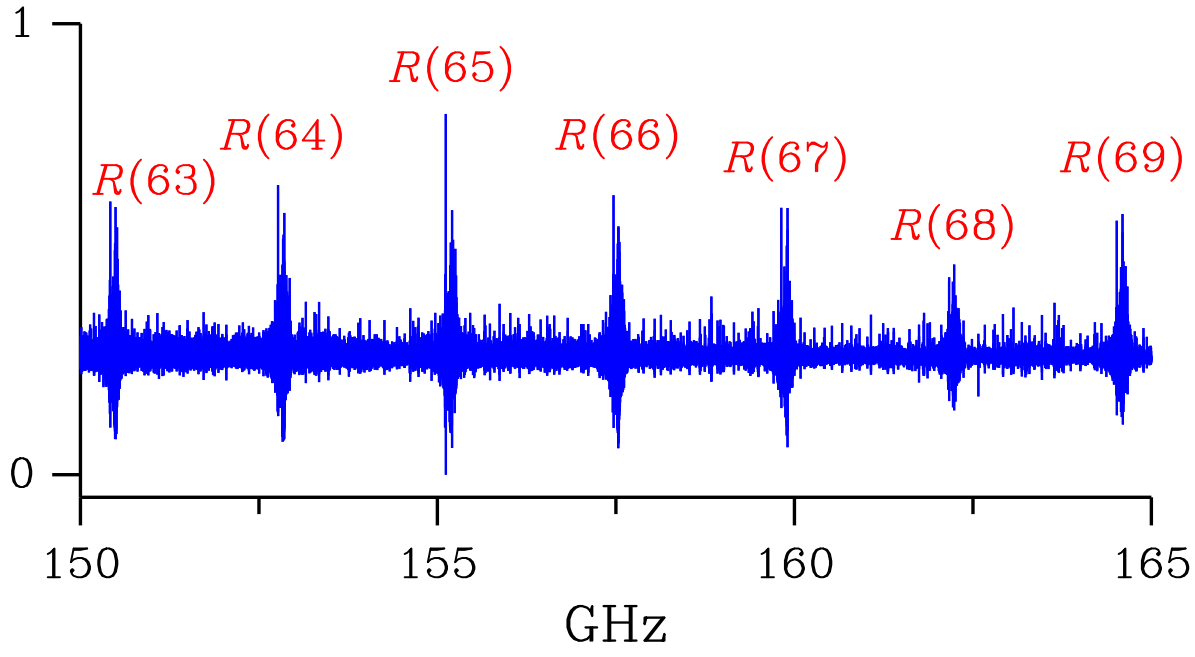

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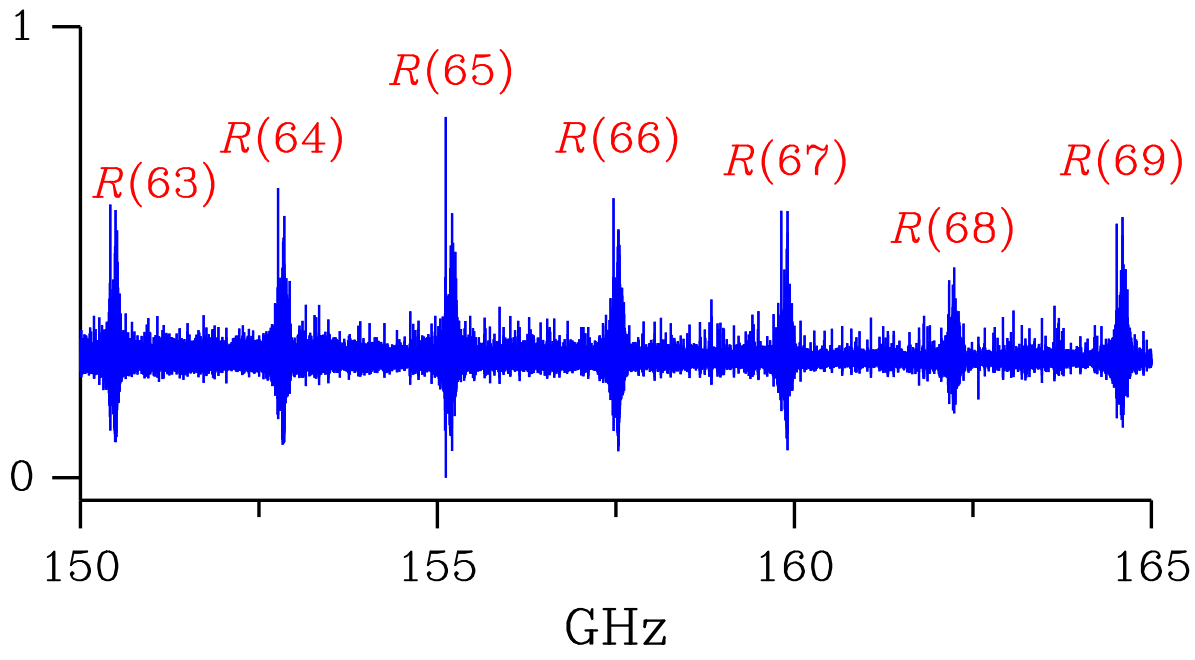

K-structure fully resolved but no asymmetry splitting

New assignment

[1] Lodyga, Kreglewski, Pracna, and Urban, Advanced graphical software for assignments of transitions in rovibrational spectra, *J. Molec. Spectrosc.* **243** (2007) 182

New assignment

a-type transitions were searched for in the SMM spectrum, recorded in the 75–110 GHz region, using the LWW software[1]

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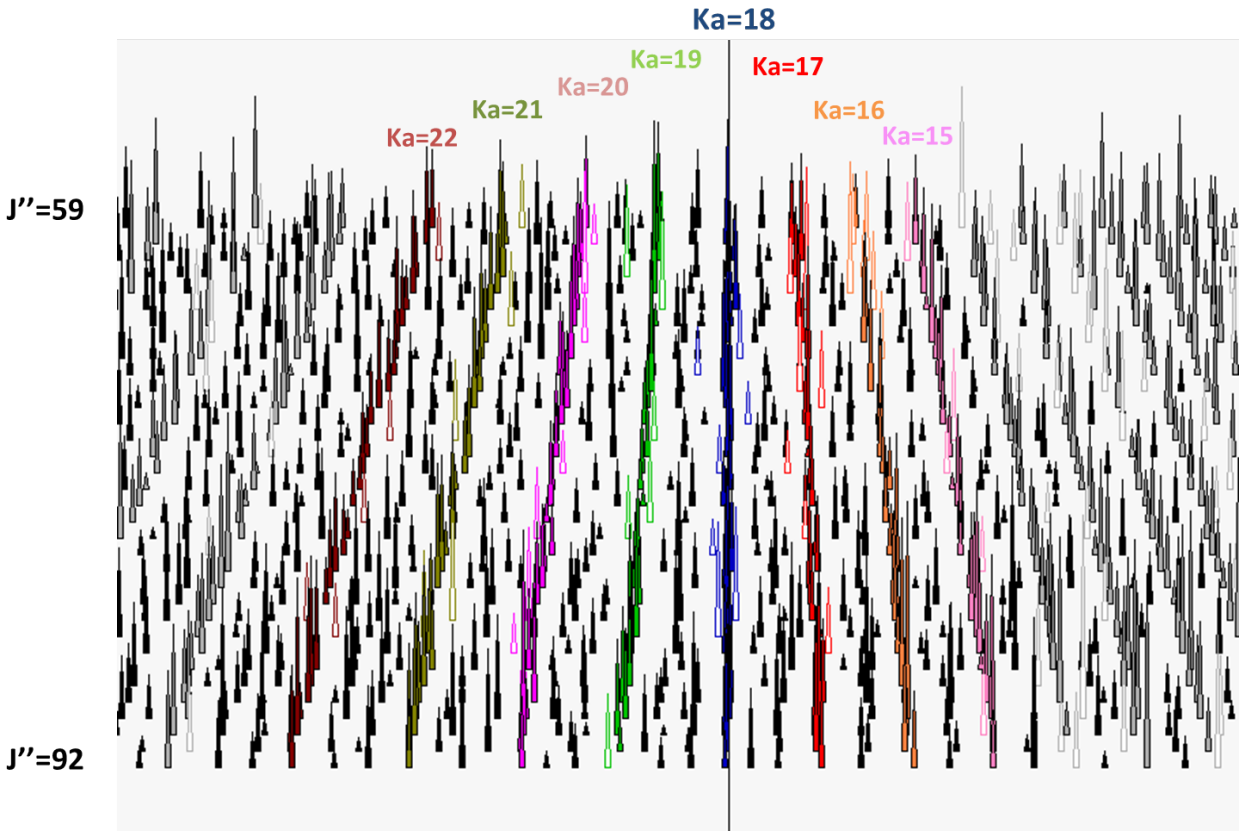

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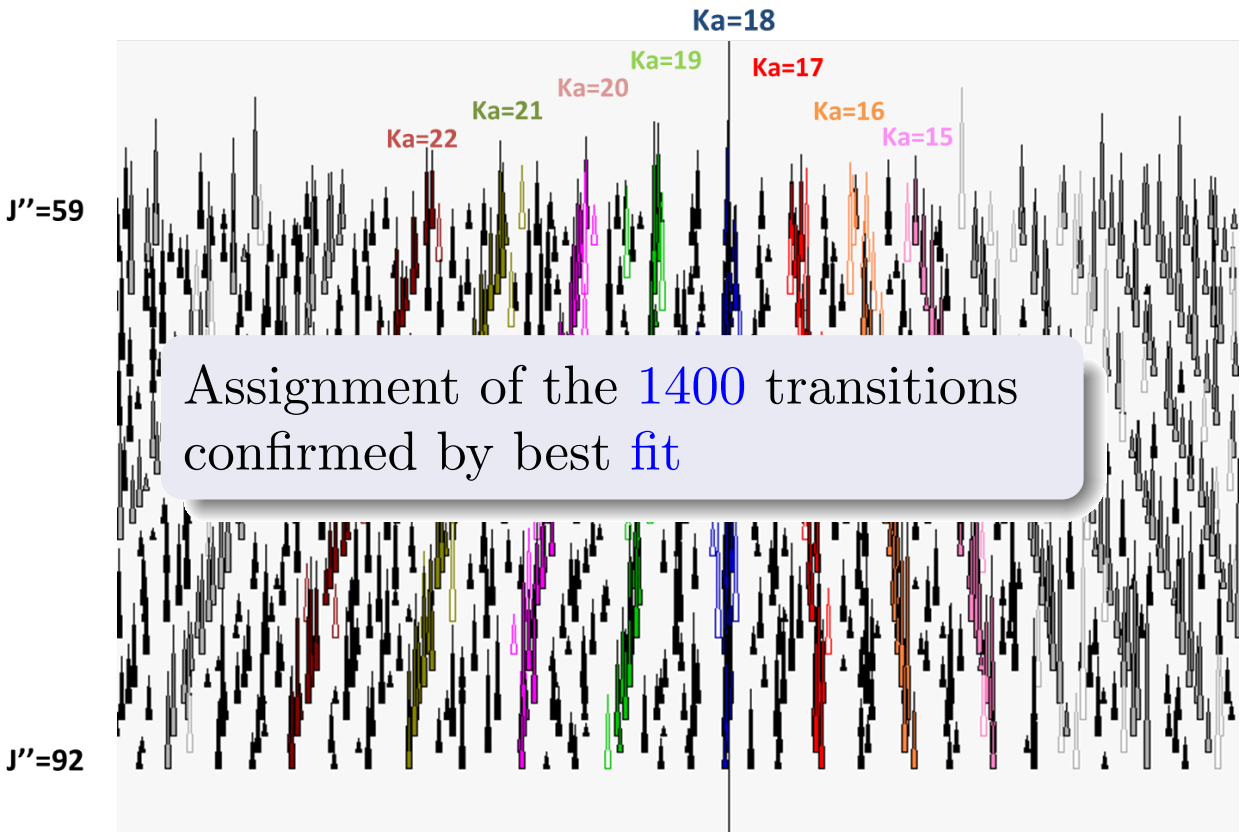

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Preliminary analysis

[1] Corbelli *et al.*, *J. Chem. Soc., Faraday Trans. 2* **83** (1987) 2225
[2] Hougen, *J. Molec. Spectrosc.* **114** (1985) 395
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  - Accounts for the rotational dependence of the torsional splitting

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Obs. vs. Calc. spectra in the 27 to 38 GHz region

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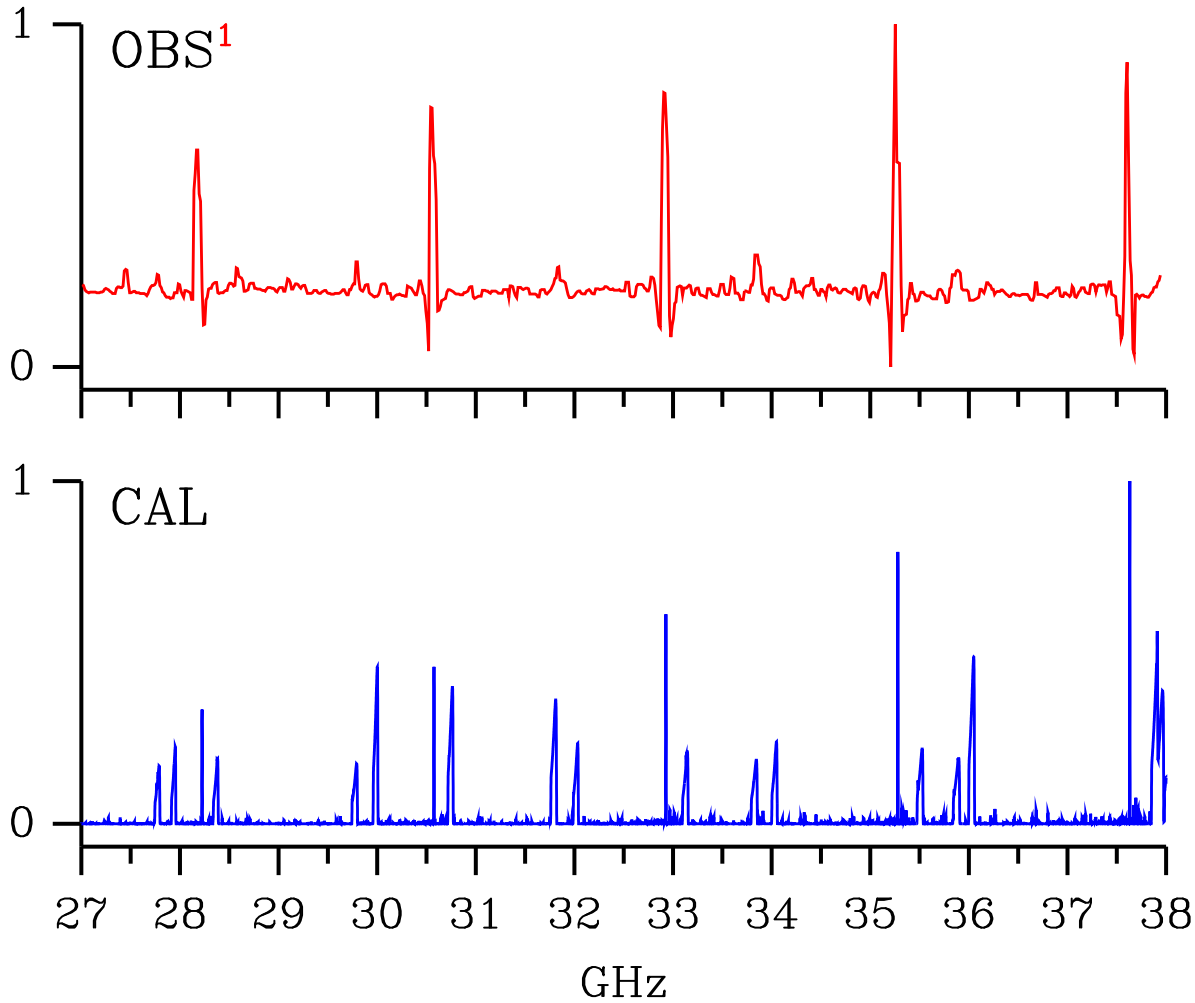
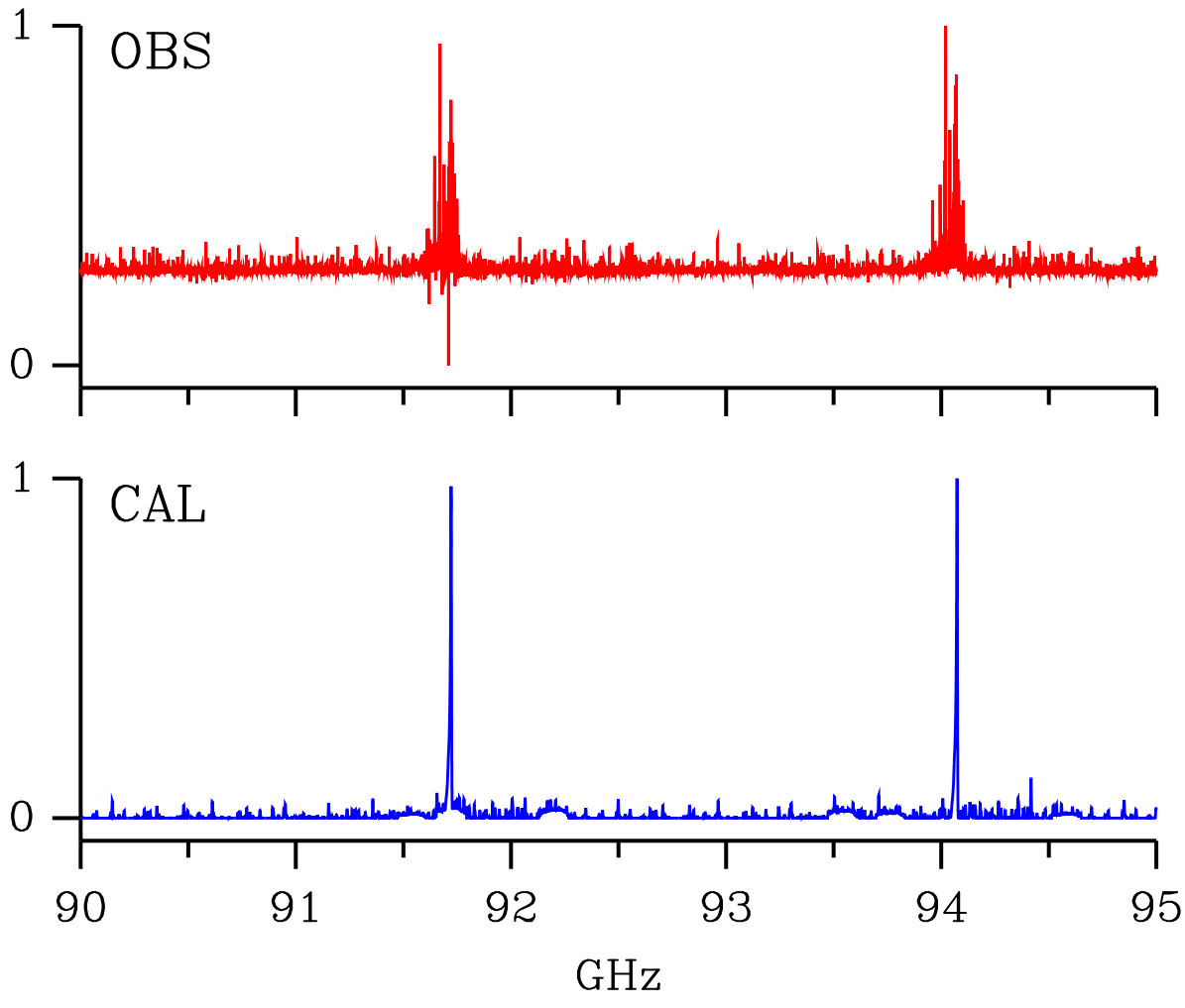
Obs. vs. Calc. spectra in the 27 to 38 GHz region



[1] Corbelli *et al.*, *J. Chem. Soc., Faraday Trans. 2* **83** (1987) 2225

Obs. vs. Calc. spectra in the 90 to 95 GHz region

Obs. vs. Calc. spectra in the 90 to 95 GHz region



Obs. vs. Calc. spectra near 140 GHz

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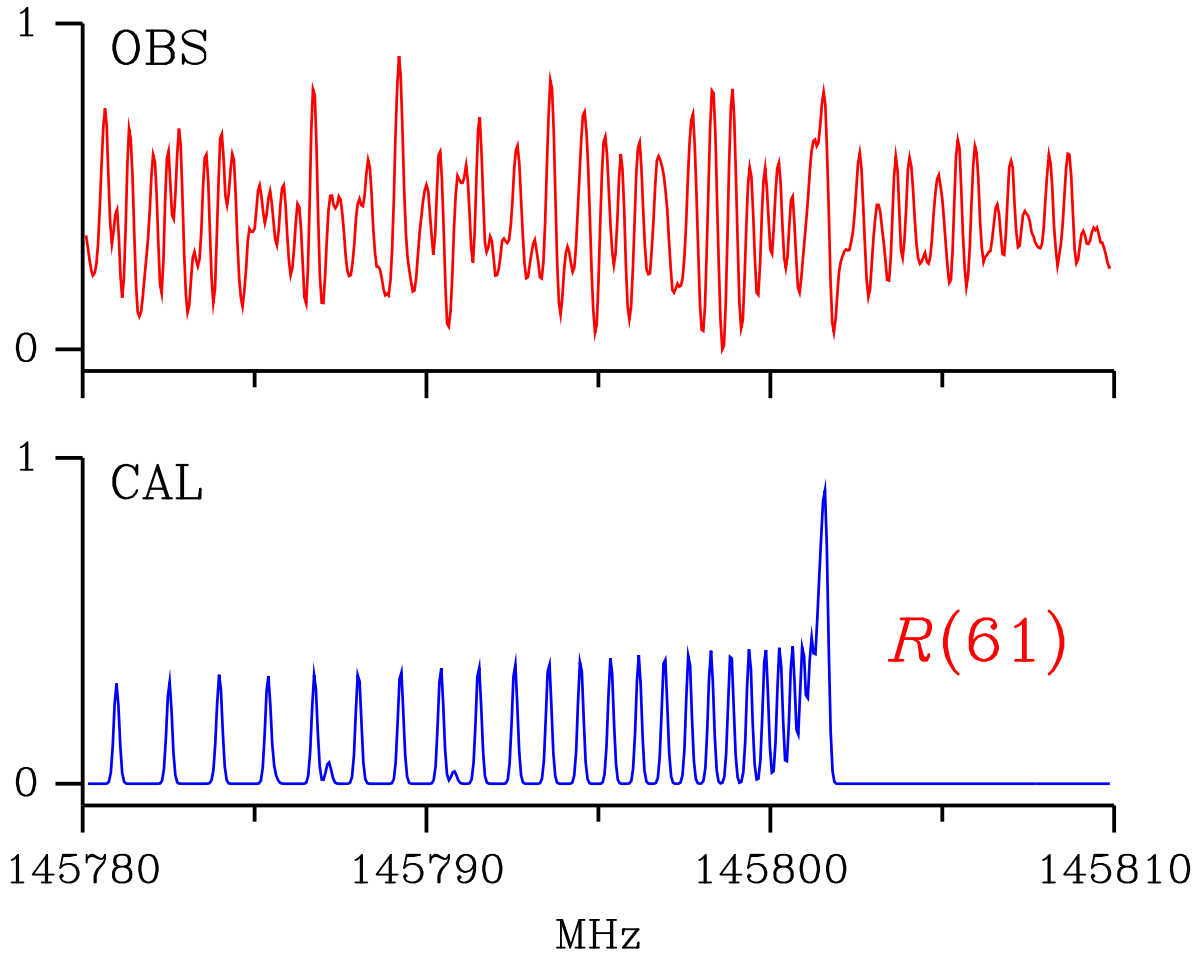

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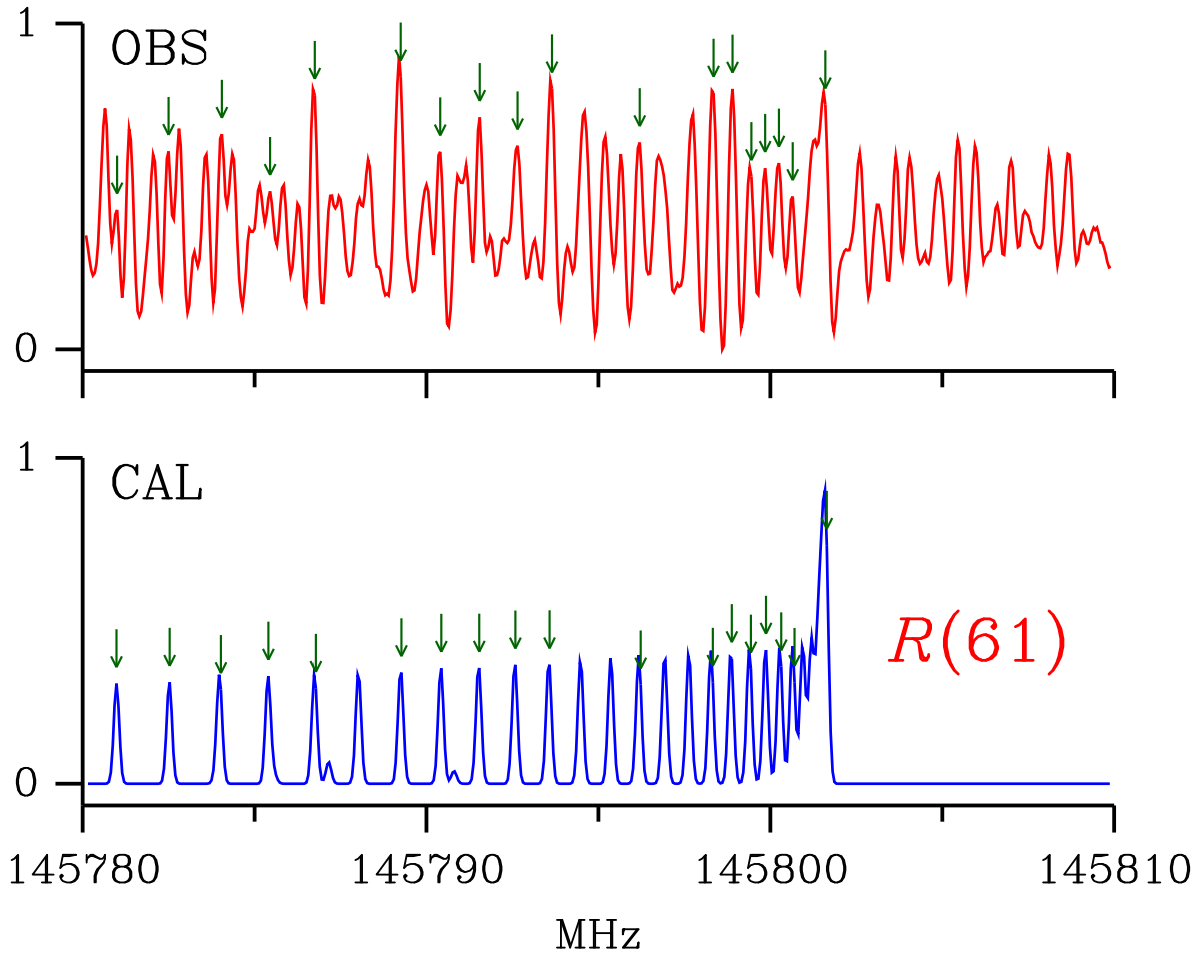

Obs. – Calc. table for *b*-type bands

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K'	Γ'	K''	Γ''	F[1]	O − C
5	A	4	A	8458	−0.11
6	E_2	5	E_1	10350	1.00
8	A	7	A	14152	−0.02
9	E_2	8	E_1	16067	0.61
10	E_1	9	E_1	17991	0.24
11	A	10	A	19926	−0.13
12	E_2	11	E_1	21873	−0.46
13	E_1	12	E_1	23833	−0.64
14	A	13	A	25807	−0.49
15	E_2	14	E_1	27796	0.21
16	E_2	15	E_1	29798	−1.23
17	A	16	A	31818	−0.41
18	E_2	17	E_1	33854	0.12
19	E_2	18	E_1	35906	−0.09
20	A	19	A	37975	−0.42
21	E_2	20	E_1	40062	−0.16

F and O − C in MHz

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F and O − C in MHz

A, tunneling splitting, and rotational dependence from this data set only

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Parameter values

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Parameter values

Param.	Value/cm^{-1}	Param.	Value/cm^{-1}
h_1	$-0.034\ 144(490)$	Ω_z	$124.024(20)^\circ$
A	$0.074\ 740(38)$	H_{JKK}	$-0.223\ 2(19) \times 10^{-12}$
$B = C$	$0.039\ 227\ 50(42)$	H_{JJK}	$0.507\ 6(21) \times 10^{-13}$
D_{KJ}	$0.784\ 80(35) \times 10^{-8}$	H_{JJJ}	$0.236(23) \times 10^{-15}$
D_{JJ}	$0.831\ 37(37) \times 10^{-9}$		

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h_1	$-0.034\ 144(490)$	Ω_z	$124.024(20)^\circ$
A	$0.074\ 740(38)$	H_{JKK}	$-0.223\ 2(19) \times 10^{-12}$
$B = C$	$0.039\ 227\ 50(42)$	H_{JJK}	$0.507\ 6(21) \times 10^{-13}$
D_{KJ}	$0.784\ 80(35) \times 10^{-8}$	H_{JJJ}	$0.236(23) \times 10^{-15}$
D_{JJ}	$0.831\ 37(37) \times 10^{-9}$		

1470 data. Unitless standard deviation is 0.9

[1] Hougen, *J. Molec. Spectrosc.* **114** (1985) 395
[2] Coudert & Hougen, *J. Molec. Spectrosc.* **130** (1988) 13

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Ω_z is expected to be $\rho \times 120^\circ = 119.668^\circ < 120^\circ$

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2. assign b-type transitions in the new spectra

Thank You

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Many thanks to PALM
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