LAM's LAMs

Two equivalent methyl internal rotations in 2,5-dimethylthiophene investigated by microwave spectroscopy

LAM Nguyen

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA)

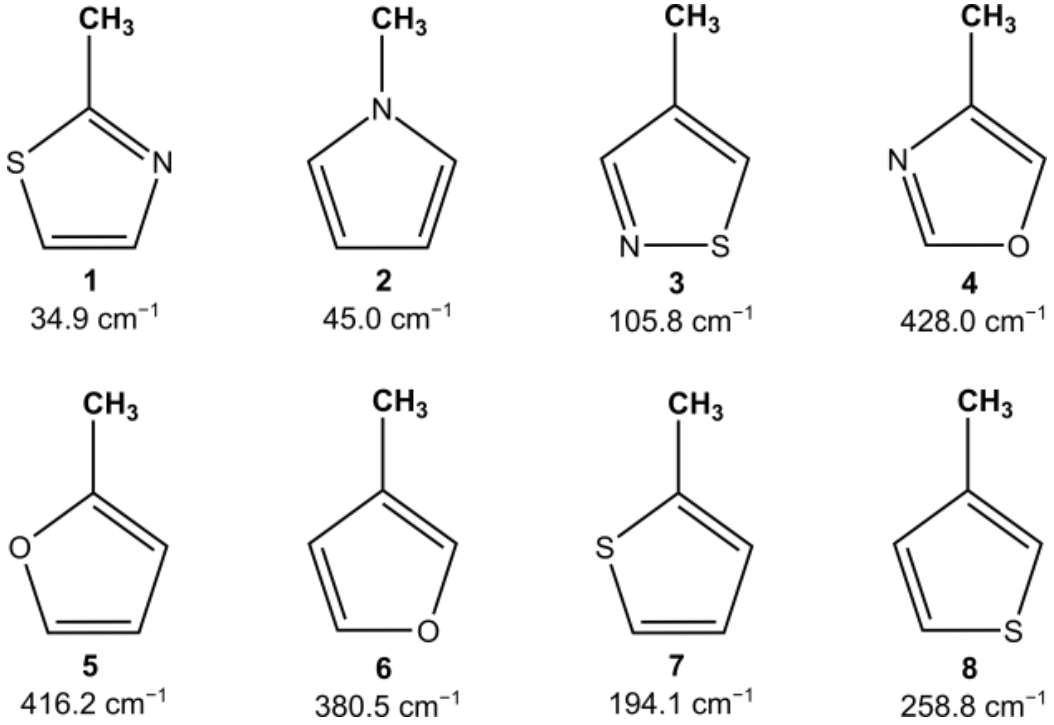
Université Paris-Est Créteil

VINH Van, WOLFGANG Stahl

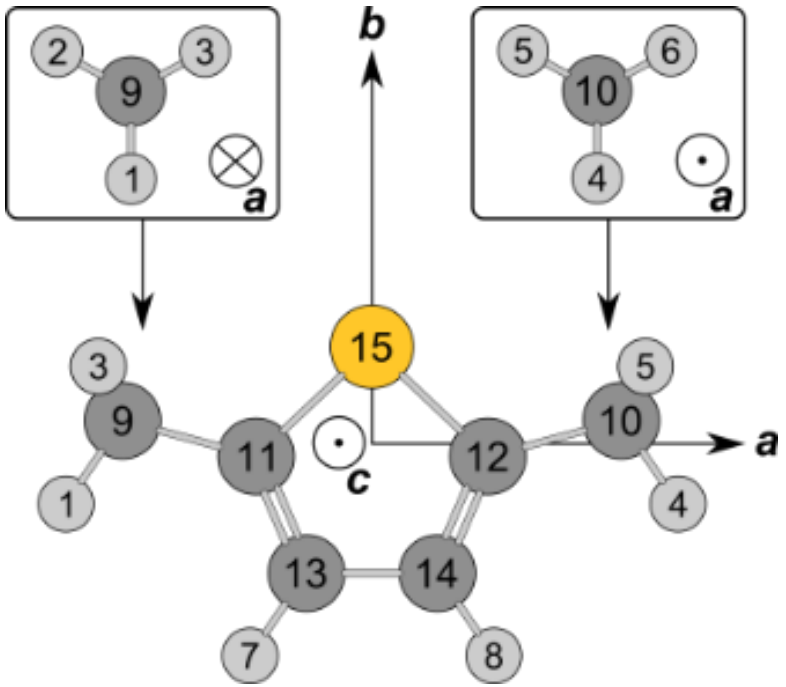
Institute of Physical Chemistry, RWTH Aachen University, Germany

Motivation

- Many monomethyl derivatives of unsaturated heterocyclic five-membered rings studied by microwave spectroscopy
- Barriers to internal rotation of the methyl group are unpredictable.
- Only one rule has been found out: Sulfur substitution decreases the barrier height.
- No dimethyl substituted version



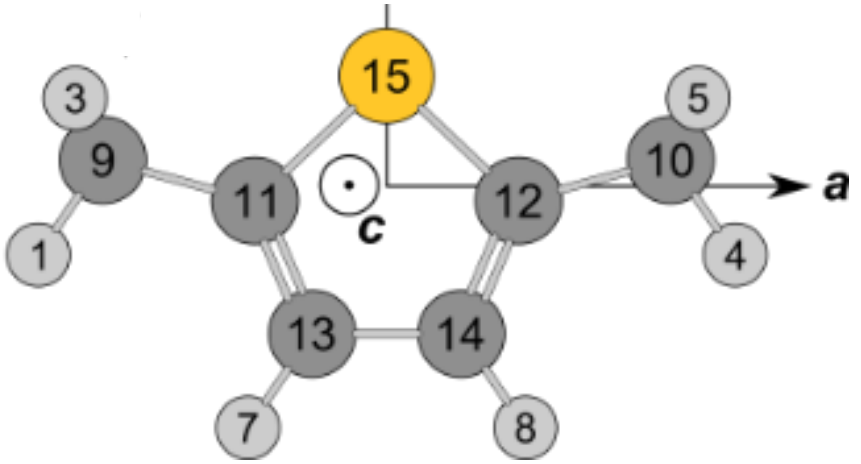
2,5-Dimethylthiophene



- Heterocyclic five-membered ring
- Unsaturate
- Dimethyl substituted
- C_{2v} symmetry

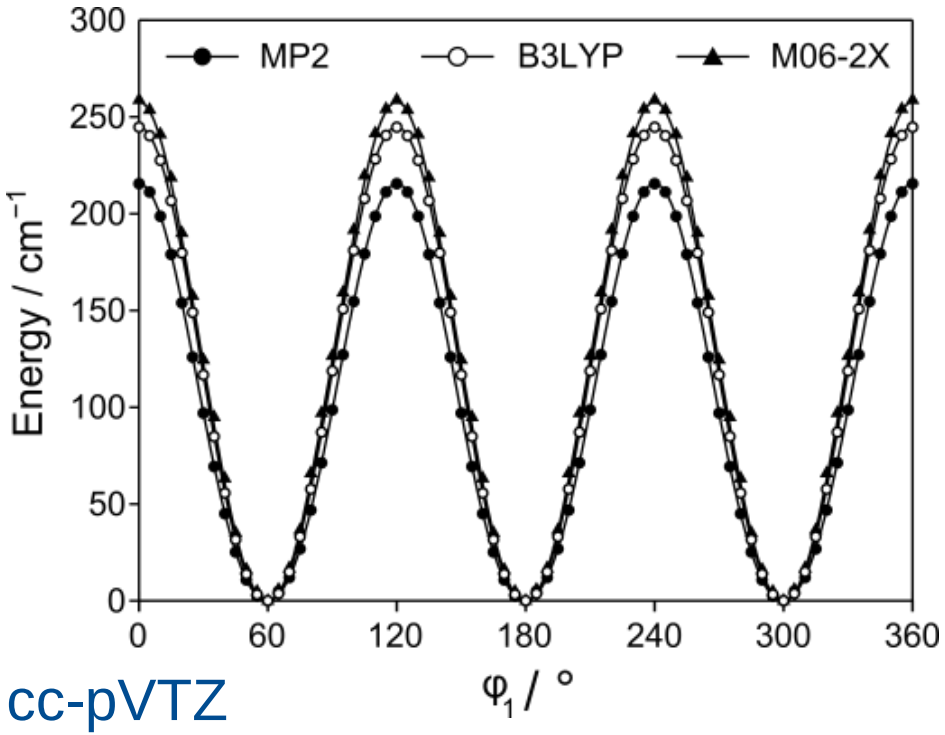
Conformational analysis

- Two conjugated double bonds force the thiophene frame to planarity → only one conformer is possible.
- 1 imaginary vibrational mode (bending vibration of the ring) (well-known spurious result for MP2/6-311++G(d,p) calculations)
- Various methods/basis sets



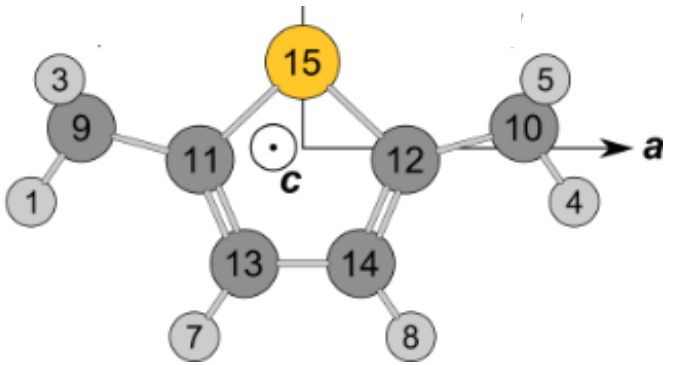
Predicted V_3 potentials

- Predicted barrier height: $\varphi_1 = \angle(S_{15},C_{12},C_{10},H_4)$, 1° step width
- Various methods/basis sets
- Negligible contributions of higher order terms



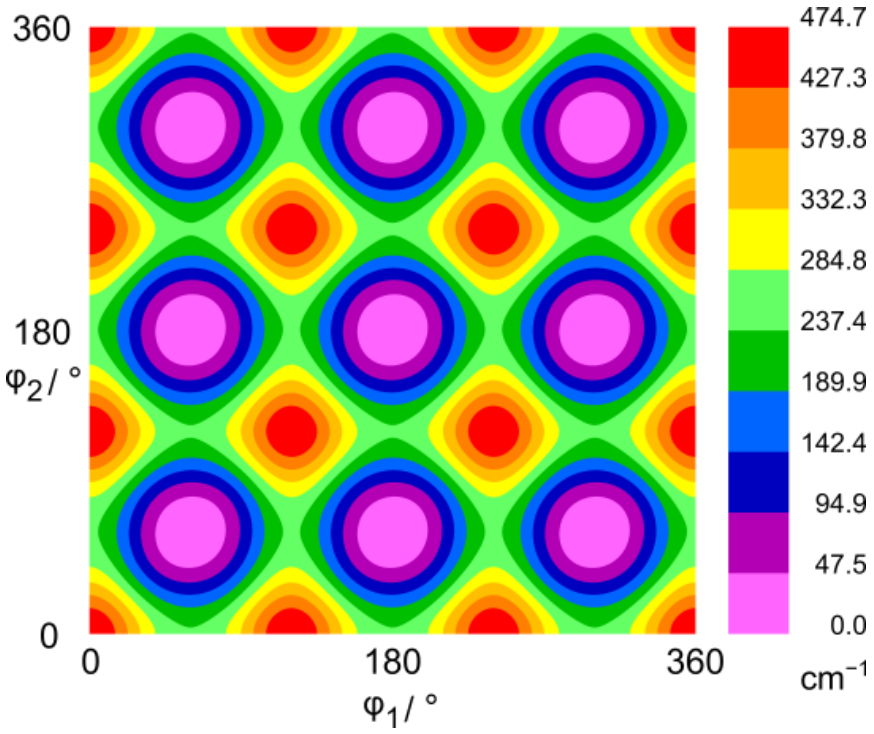
cc-pVTZ

- Geometry optimizations to a first order transition state of one methyl group using the Berny algorithm

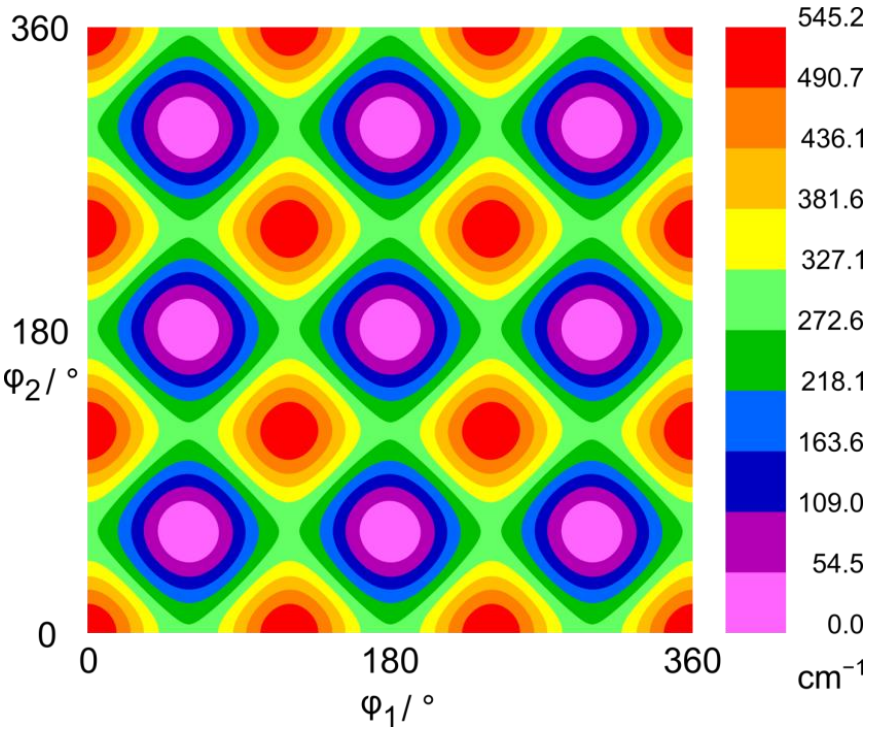


Potential energy surfaces

MP2



B3LYP



- φ_1 and φ_2 : rotations of the two methyl groups
- MP2 and B3LYP/6-311++G(d,p) levels of theory
- No significant coupling between the two tops

Group theory

Symmetry labels

- Molecular symmetry group : G_{36}
- Different symmetry labels available (from different product decompositions of G_{36}) :
  - ➔ direct product $\boldsymbol{C_{3v}^{-}} \times \boldsymbol{C_{3v}^{+}}$ (Dreizler)
  - ➔ degeneracy letter A, E, G and a running index using permutation-inversion group (Bunker and Jensen)
- Our work: semi-direct product $(\boldsymbol{C_3^I} \times \boldsymbol{C_3^I}) \rtimes \boldsymbol{C_{2v}}$ (introduced bw Ezra and Altmann) using two intrinsic $\boldsymbol{C_3}$ groups of the internal rotors, which is an invariant subgroup of G_{36}, decomposes into four orbits under $\boldsymbol{C_{2v}}$

Group theory

Symmetry labels

- One representative of each orbit forms the first part of the symmetry label, e.g. (01).
- σ = 0, 1, 2 : A, E_a, E_b of the group C_3
- Each orbit ↔ little co-set (subgroups of C_{2v}) → second part of the symmetry labels

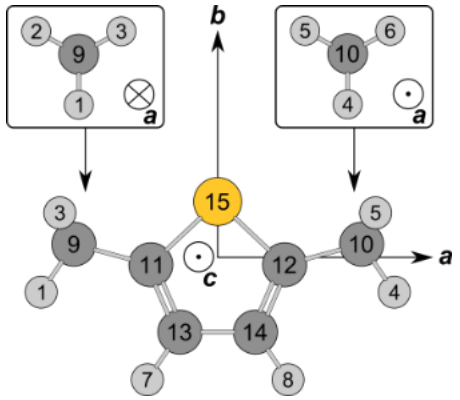
Orbit (σ_1, σ_2)	Little co-set
(00)	C_{2v}
(11), (22)	C_2
(12), (21)	C_s
(01), (10), (02), (20)	C_1

Character table of G_{36}

G_{36} [a]			E	a^{-1}	ab	ab^{-1}	P	bP	Q	aQ	R	
Equiv. rot. [b]			R^0	R^0	R^0	R^0	R_b^π	R_b^π	R_a^π	R_a^π	R_c^π	
S1 [c]	S2 [d]	S3 [e]	[f] 1	4	2	2	3	6	3	6	9	wt [g]
(00)·A_1	A_1	A_1A_1	1	1	1	1	1	1	1	1	1	36
(00)·B_1	A_2	A_2A_1	1	1	1	1	−1	−1	1	1	−1	28
(00)·A_2	A_3	A_1A_2	1	1	1	1	1	1	−1	−1	−1	36
(00)·B_2	A_4	A_2A_2	1	1	1	1	−1	−1	−1	−1	1	28
(12)·A'	E_1	E A_1	2	−1	2	−1	0	0	2	−1	0	16
(12)·A''	E_2	E A_2	2	−1	2	−1	0	0	−2	1	0	16
(11)·A	E_3	A_1E	2	−1	−1	2	2	−1	0	0	0	20
(11)·B	E_4	A_2E	2	−1	−1	2	−2	1	0	0	0	12
(01)·A	G	EE	4	1	−2	−2	0	0	0	0	0	64

[a] a = (1 2 3), b = (4 5 6), P = (1 4)(2 5)(3 6)(7 8)(9 10)(11 12)(13 14), Q = (1 4)(2 6)(3 5)(7 8)(9 10)(11 12)(13 14)*, R = (2 3)(5 6)*, for atom numbers see Fig. 2. [b] Equivalent rotations of the four-group. [c] Symmetry labels based on the semi-direct product $(C_3^{\mathrm{I}} \times C_3^{\mathrm{I}}) \rtimes C_{2v}$, see ref. 16. [d] Symmetry labels according to ref. 15. [e] Symmetry labels based on the direct product $C_{3v}^- \times C_{3v}^+$, see ref. 14. [f] Row between S3 and wt: number of elements in the respective class. [g] Spin statistical weight.

Direct product $C_{3v}^- \times C_{3v}^+$ (Dreizler)

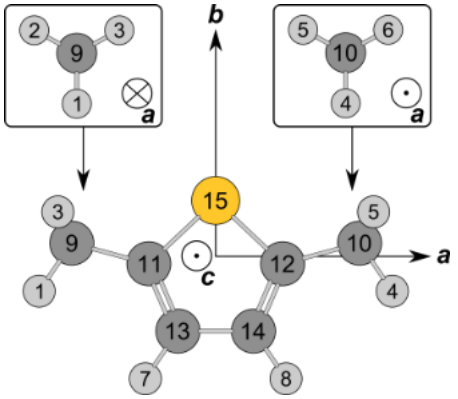


Character table of G_{36}

G_{36}[a]			E	a^{-1}	ab	ab^{-1}	P	bP	Q	aQ	R	
Equiv. rot.[b]			R^0	R^0	R^0	R^0	R_b^π	R_b^π	R_a^π	R_a^π	R_c^π	
S1[c]	S2[d]	S3[e]	[f] 1	4	2	2	3	6	3	6	9	wt[g]
(00)·A_1	A_1	A_1A_1	1	1	1	1	1	1	1	1	1	36
(00)·B_1	A_2	A_2A_1	1	1	1	1	−1	−1	1	1	−1	28
(00)·A_2	A_3	A_1A_2	1	1	1	1	1	1	−1	−1	−1	36
(00)·B_2	A_4	A_2A_2	1	1	1	1	−1	−1	−1	−1	1	28
(12)·A'	E_1	E A_1	2	−1	2	−1	0	0	2	−1	0	16
(12)·A''	E_2	E A_2	2	−1	2	−1	0	0	−2	1	0	16
(11)·A	E_3	A_1E	2	−1	−1	2	2	−1	0	0	0	20
(11)·B	E_4	A_2E	2	−1	−1	2	−2	1	0	0	0	12
(01)·A	G	EE	4	1	−2	−2	0	0	0	0	0	64

[a] a = (1 2 3), b = (4 5 6), P = (1 4)(2 5)(3 6)(7 8)(9 10)(11 12)(13 14), Q = (1 4)(2 6)(3 5)(7 8)(9 10)(11 12)(13 14)*, R = (2 3)(5 6)*, for atom numbers see Fig. 2. [b] Equivalent rotations of the four-group. [c] Symmetry labels based on the semi-direct product $(C_3^{\mathrm{I}} \times C_3^{\mathrm{I}}) \rtimes C_{2v}$, see ref. 16. [d] Symmetry labels according to ref. 15. [e] Symmetry labels based on the direct product $C_{3v}^- \times C_{3v}^+$, see ref. 14. [f] Row between S3 and wt: number of elements in the respective class. [g] Spin statistical weight.

permutation-inversion group (Bunker and Jensen), A, E, G and a running index

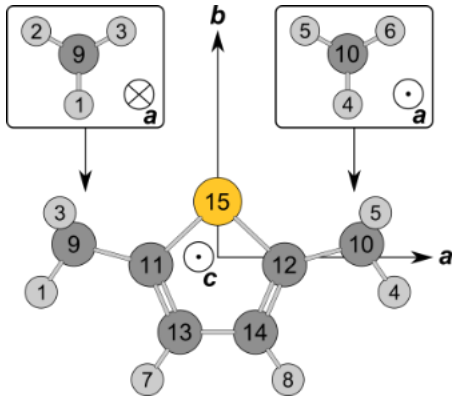


Character table of G_{36}

G_{36}[a]			E	a^{-1}	ab	ab^{-1}	P	bP	Q	aQ	R	
Equiv. rot.[b]			R^0	R^0	R^0	R^0	R_b^π	R_b^π	R_a^π	R_a^π	R_c^π	
S1[c]	S2[d]	S3[e]	[f] 1	4	2	2	3	6	3	6	9	wt[g]
$(00)\cdot A_1$	A_1	A_1A_1	1	1	1	1	1	1	1	1	1	36
$(00)\cdot B_1$	A_2	A_2A_1	1	1	1	1	−1	−1	1	1	−1	28
$(00)\cdot A_2$	A_3	A_1A_2	1	1	1	1	1	1	−1	−1	−1	36
$(00)\cdot B_2$	A_4	A_2A_2	1	1	1	1	−1	−1	−1	−1	1	28
$(12)\cdot A'$	E_1	E A_1	2	−1	2	−1	0	0	2	−1	0	16
$(12)\cdot A''$	E_2	E A_2	2	−1	2	−1	0	0	−2	1	0	16
$(11)\cdot A$	E_3	A_1E	2	−1	−1	2	2	−1	0	0	0	20
$(11)\cdot B$	E_4	A_2E	2	−1	−1	2	−2	1	0	0	0	12
$(01)\cdot A$	G	EE	4	1	−2	−2	0	0	0	0	0	64

[a] a = (1 2 3), b = (4 5 6), P = (1 4)(2 5)(3 6)(7 8)(9 10)(11 12)(13 14), Q = (1 4)(2 6)(3 5)(7 8)(9 10)(11 12)(13 14)*, R = (2 3)(5 6)*, for atom numbers see Fig. 2. [b] Equivalent rotations of the four-group. [c] Symmetry labels based on the semi-direct product $(C_3^I \times C_3^I) \rtimes C_{2v}$, see ref. 16. [d] Symmetry labels according to ref. 15. [e] Symmetry labels based on the direct product $C_{3v}^- \times C_{3v}^+$, see ref. 14. [f] Row between S3 and wt: number of elements in the respective class. [g] Spin statistical weight.

Semi-direct product $(\boldsymbol{C_3^I \times C_3^I}) \rtimes \boldsymbol{C_{2v}}$ (Similar to Erham)

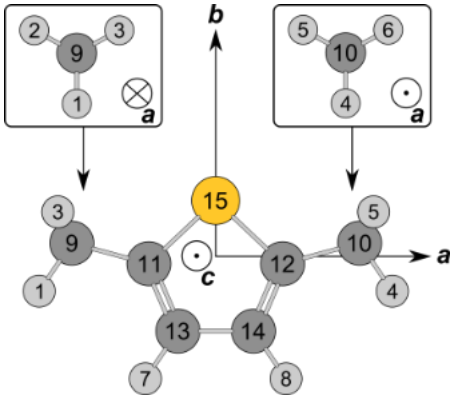


Character table of G_{36}

G_{36}[a]			E	a^{-1}	ab	ab^{-1}	P	bP	Q	aQ	R	
Equiv. rot.[b]			R^0	R^0	R^0	R^0	R_b^π	R_b^π	R_a^π	R_a^π	R_c^π	
S1[c]	S2[d]	S3[e]	[f] 1	4	2	2	3	6	3	6	9	wt[g]
$(00)\cdot A_1$	A_1	A_1A_1	1	1	1	1	1	1	1	1	1	36
$(00)\cdot B_1$	A_2	A_2A_1	1	1	1	1	−1	−1	1	1	−1	28
$(00)\cdot A_2$	A_3	A_1A_2	1	1	1	1	1	1	−1	−1	−1	36
$(00)\cdot B_2$	A_4	A_2A_2	1	1	1	1	−1	−1	−1	−1	1	28
$(12)\cdot A'$	E_1	E A_1	2	−1	2	−1	0	0	2	−1	0	16
$(12)\cdot A''$	E_2	E A_2	2	−1	2	−1	0	0	−2	1	0	16
$(11)\cdot A$	E_3	A_1E	2	−1	−1	2	2	−1	0	0	0	20
$(11)\cdot B$	E_4	A_2E	2	−1	−1	2	−2	1	0	0	0	12
$(01)\cdot A$	G	EE	4	1	−2	−2	0	0	0	0	0	64

[a] $a = (1\ 2\ 3)$, $b = (4\ 5\ 6)$, $P = (1\ 4)(2\ 5)(3\ 6)(7\ 8)(9\ 10)(11\ 12)(13\ 14)$, $Q = (1\ 4)(2\ 6)(3\ 5)(7\ 8)(9\ 10)(11\ 12)(13\ 14)^*$, $R = (2\ 3)(5\ 6)^*$, for atom numbers see Fig. 2. [b] Equivalent rotations of the four-group. [c] Symmetry labels based on the semi-direct product $(C_3^{\mathrm{I}} \times C_3^{\mathrm{I}}) \rtimes C_{2v}$, see ref. 16. [d] Symmetry labels according to ref. 15. [e] Symmetry labels based on the direct product $C_{3v}^- \times C_{3v}^+$, see ref. 14. [f] Row between S3 and wt: number of elements in the respective class. [g] Spin statistical weight.

Spin statistical weight calculated from 256 nuclear spin functions arising from 8 protons



Group theory

Selection rules

- Dipole moment vector $\Gamma_\mu = (\mathbf{00}) \cdot \mathbf{A_2}$
- Selection rules: $\mathbf{\Gamma_i} \times \mathbf{\Gamma}_\mu \times \mathbf{\Gamma_j} \supset (\mathbf{00}).\mathbf{A_1}$
- If K_a and K_c are known, the torsional state can be labeled conveniently by the first part (σ_1,σ_2) of the full symmetry label.

ee ↔ oo transitions	wt	eo ↔ oe transitions	wt
$(00)\cdot A_1 \leftrightarrow (00)\cdot A_2$	36	$(00)\cdot B_1 \leftrightarrow (00)\cdot B_2$	28
$(12)\cdot A' \leftrightarrow (12)\cdot A''$	16	$(12)\cdot A' \leftrightarrow (12)\cdot A''$	16
$(11)\cdot A \leftrightarrow (11)\cdot A$	20	$(11)\cdot B \leftrightarrow (11)\cdot B$	12
$(01)\cdot A \leftrightarrow (01)\cdot A$	64	$(01)\cdot A \leftrightarrow (01)\cdot A$	64

Microwave spectrum

- Molecular beam FT microwave spectroscopy
- 2 – 26.5 GHz Cavity (Aachen) and 26.5 – 40 GHz Cavity (Paris)

High resolution

- Line widths in the range 10 – 25 kHz → measurement accuracy better than 2 kHz
- Doppler effect; carrier gas: helium

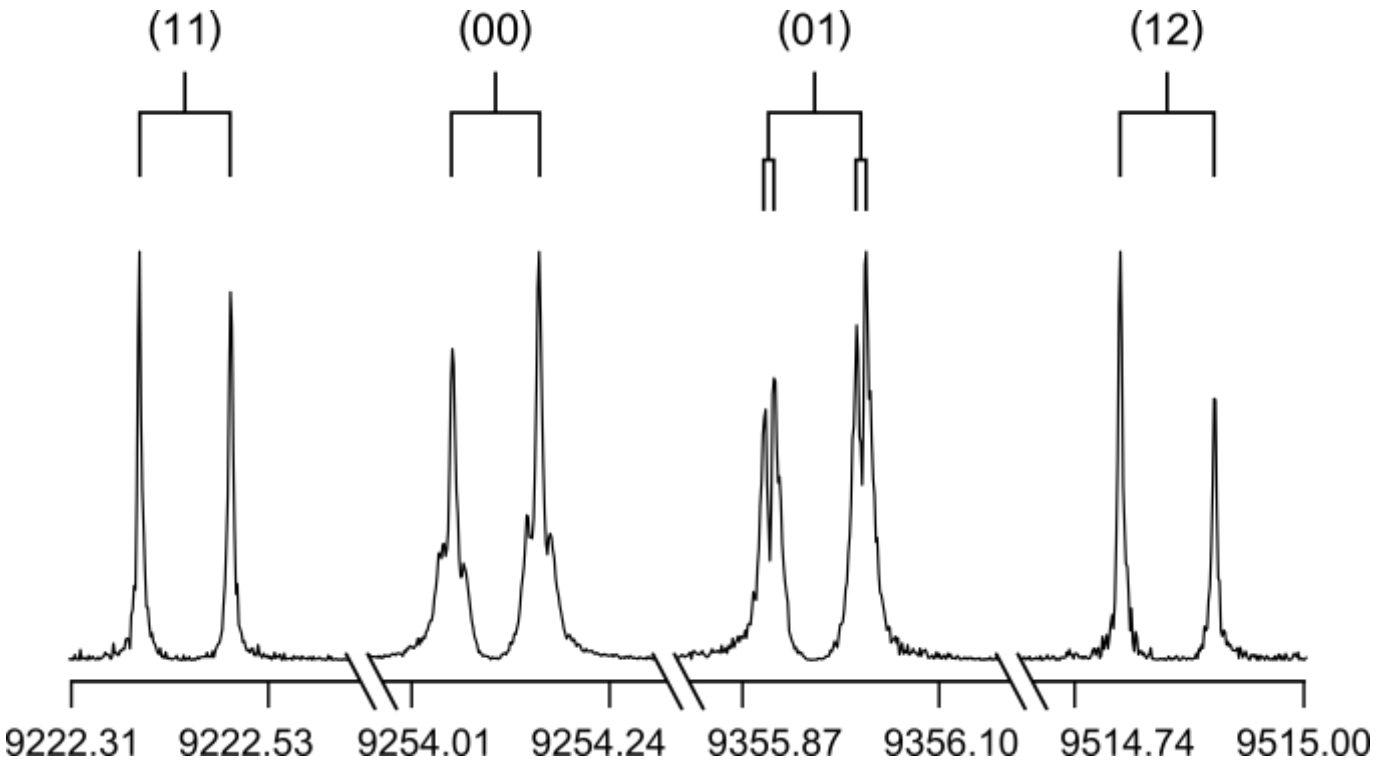
Broadband scan

- Series of automatically recorded spectra in the high resolution mode
- 250 kHz step width, 50 decays per step
- Frequency range : 8.5 – 12.0 GHz

Microwave spectrum

- A typical high resolution spectrum
- Only *b*-type transitions
- $J \leq 7$ and $K_a \leq 5$

$3_{21} \leftarrow 3_{12}$



Molecular parameters

Par.[a]	Unit	Fit I	Fit II	Calc.[b]
A	GHz	4.97224360(42)	4.96500697(89)	4.9414
B	GHz	1.74696506(27)	1.74694756(13)	1.7426
C	GHz	1.31337981(20)	1.313336623(81)	1.3094
Δ_J	kHz	0.0684(28)	0.0672(11)	0.0630
Δ_{JK}	kHz	0.2071(93)	0.1579(37)	0.171
Δ_K	kHz	3.2158(98)	0.9161(43)	0.803
δ_J	kHz	0.0196(14)	0.01839(51)	0.0171
δ_K	kHz	0.136(23)	0.1031(89)	0.0390
V_3	cm^{-1}		247.95594(30)	241.2
I_α	$uÅ^2$		3.16442(39)	
$\angle(i,a)$	°		14.5931(78)[c]	14.90
$\angle(i,b)$	°		75.4069(78)	75.10
$\angle(i,c)$	°		90.00(fixed)	89.96
F_{12}	GHz		−7.320(12)	
D_{pi2J}	kHz		−2.78(25)	
D_{pi2K}	kHz		−98.9(42)	
D_{pi2-}	kHz		1.97(19)	
σ^d	kHz	2.6	1.9	
N^e		41	157	

XIAM

Molecular parameters

Par.[a]	Unit	Fit I	Fit II	Calc.[b]
A	GHz	4.97224360(42)	4.96500697(89)	4.9414
B	GHz	1.74696506(27)	1.74694756(13)	1.7426
C	GHz	1.31337981(20)	1.313336623(81)	1.3094
Δ_J	kHz	0.0684(28)	0.0672(11)	0.0630
Δ_{JK}	kHz	0.2071(93)	0.1579(37)	0.171
Δ_K	kHz	3.2158(98)	0.9161(43)	0.803
δ_J	kHz	0.0196(14)	0.01839(51)	0.0171
δ_K	kHz	0.136(23)	0.1031(89)	0.0390
V_3	cm^{-1}		247.95594(30)	241.2
I_α	$uÅ^2$		3.16442(39)	
$\angle(i,a)$	°		14.5931(78)[c]	14.90
$\angle(i,b)$	°		75.4069(78)	75.10
$\angle(i,c)$	°		90.00(fixed)	89.96
F_{12}	GHz		−7.320(12)	
D_{pi2J}	kHz		−2.78(25)	
D_{pi2K}	kHz		−98.9(42)	
D_{pi2-}	kHz		1.97(19)	
σ^d	kHz	2.6	1.9	
N^e		41	157	

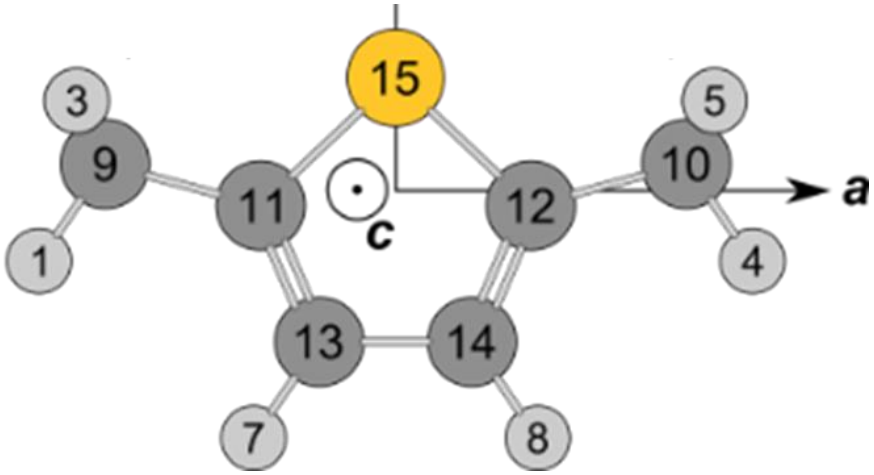
XIAM

Molecular parameters

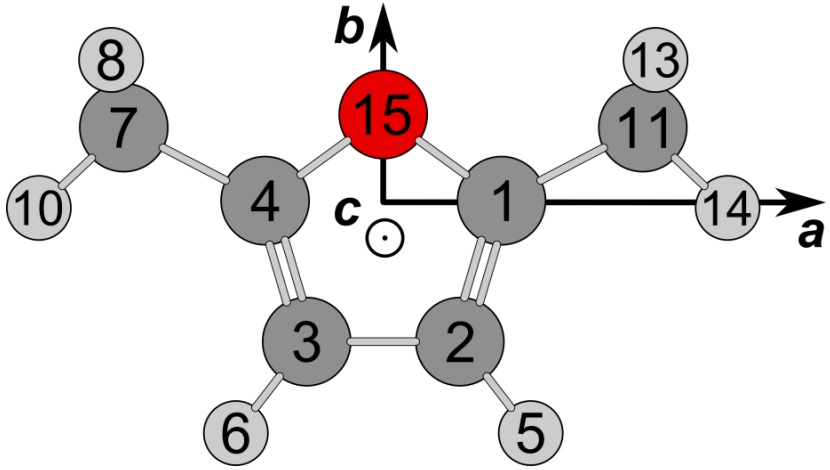
Par.[a]	Unit	Fit I	Fit II	Calc.[b]
A	GHz	4.97224360(42)	4.96500697(89)	4.9414
B	GHz	1.74696506(27)	1.74694756(13)	1.7426
C	GHz	1.31337981(20)	1.313336623(81)	1.3094
Δ_J	kHz	0.0684(28)	0.0672(11)	0.0630
Δ_{JK}	kHz	0.2071(93)	0.1579(37)	0.171
Δ_K	kHz	3.2158(98)	0.9161(43)	0.803
δ_J	kHz	0.0196(14)	0.01839(51)	0.0171
δ_K	kHz	0.136(23)	0.1031(89)	0.0390
V_3	cm^{-1}		247.95594(30)	241.2
I_α	$uÅ^2$		3.16442(39)	
$\angle(i,a)$	°		14.5931(78)[c]	14.90
$\angle(i,b)$	°		75.4069(78)	75.10
$\angle(i,c)$	°		90.00(fixed)	89.96
F_{12}	GHz		−7.320(12)	
D_{pi2J}	kHz		−2.78(25)	
D_{pi2K}	kHz		−98.9(42)	
D_{pi2-}	kHz		1.97(19)	
σ^d	kHz	2.6	1.9	
N^e		41	157	

XIAM

2,5-Dimethylthiophene vs. 2,5-Dimethylfurane



247.95594(30) cm^{-1}



440.7543(19) cm^{-1}

- XIAM works well in both cases, but we only have $J \leq 7$ and $K_a \leq 5$
- Erham or PAM-C2v-2tops are much more suited for higher J and K_a transitions as well as torsional excited states.