Magnetic Spin-Torsion Coupling in Methanol

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Overview

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1. Magnetic hyperfine couplings in a non-rigid molecule

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2. Spin-torsion effects in methanol

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2. Spin-torsion effects in methanol
3. Analysis

Magnetic hyperfine coupling in $^1\Sigma$ molecules

The spin-spin coupling[1]

$$E_{SS} = {\mu_N}^2 \sum_i g_i \sum_{j>i} g_j \frac{(\mathbf{I}_i \cdot \mathbf{I}_j) - 3(\mathbf{I}_i \cdot \mathbf{r}_{ij})(\mathbf{I}_j \cdot \mathbf{r}_{ij})/{r_{ij}}^2}{{r_{ij}}^3}$$

The spin-rotation coupling[1]

$$E_{SR} = -\frac{e\mu_N}{c} \sum_i g_i \mathbf{I}_i \cdot \sum_{j \neq i} Z_j \frac{\mathbf{r}_{ji} \times (\mathbf{v}_j - \gamma_i \mathbf{v}_i)}{{r_{ij}}^3}$$

[1] Gunther-Mohr, Townes, and van Vleck, *Phys. Rev.* **94** (1954) 1191

Magnetic hyperfine coupling in $^1\Sigma$ molecules

The two contributions to spin-rotation[1]

$$\mathbf{v}_i = \underbrace{\omega \times \mathbf{r}_i}_{\text{Rot.}} - \underbrace{\dot{\alpha}\lambda \times \sigma_i}_{\text{Torsion}} \quad \text{where} \quad \sigma_i \neq \mathbf{0} \quad \text{if} \quad i \in \text{top}$$

[1] Heuvel & Dymanus, *J. Mol. Spec.* **45** (1973) 282 & *J. Mol. Spec.* **47** (1973) 363

Magnetic hyperfine coupling in $^1\Sigma$ molecules

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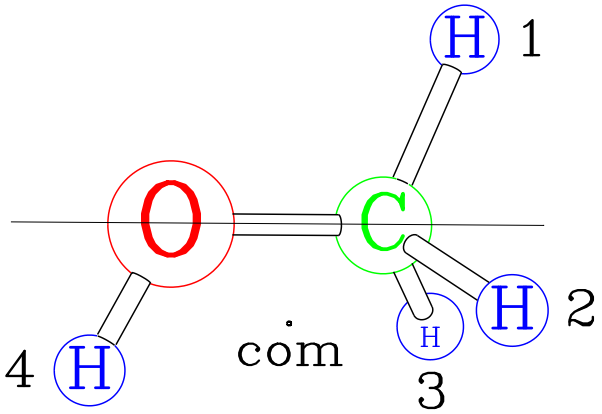
In methanol



$$\sigma_i = \begin{cases} \mathbf{r}_{\mathrm{CH}_i} & \text{for } i = 1 \text{ to } 3 \\ \mathbf{0} & \text{for } i = 4 \end{cases}$$

[1] Heuvel & Dymanus, *J. Mol. Spec.* **45** (1973) 282 & *J. Mol. Spec.* **47** (1973) 363

The 3 $\Delta J = 0$ magnetic coupling hyperfine operators

Spin-spin[1]
$$H_{ss} = \sum_{i<j}^{4} F(\mathbf{I}_i, \mathbf{I}_j, \mathbf{J}) S^{ij}(\alpha)$$

Spin-rotation[1]
$$H_{sr} = \sum_{i=1}^{4} (\mathbf{I}_i \cdot \mathbf{J}) E^{i}(\alpha)$$

Spin-torsion[2]
$$H_{st} = \sum_{i=1}^{4} (\mathbf{I}_i \cdot \mathbf{J}) G^{i}(\alpha)$$

[1] Thaddeus, Krisher, and Loubser, *J. Chem. Phys.* **40** (1964) 257

[2] Heuvel & Dymanus, *J. Mol. Spec.* **45** (1973) 282 & *J. Mol. Spec.* **47** (1973) 363

The 3 rovibrational coupling operators

Operator	Expression	Method
$S^{ij}(\alpha)$[1]	$\frac{2\sum_{\beta\gamma} R^{ij}_{\beta\gamma}(\alpha) J_\beta J_\gamma}{J(2J-1)(J+1)(2J+3)}$	Structure
$E^{i}(\alpha)$[1]	$\frac{\sum_{\beta\gamma} C^{i}_{\beta\gamma}(\alpha) J_\beta J_\gamma}{J(J+1)}$	*Ab initio*
$G^{i}(\alpha)$[2]	$\frac{\{\rho J_z + p_\alpha, \sum_\beta J_\beta d^i_\beta(\alpha)\}}{2J(J+1)}$	First order nuclear contribution only

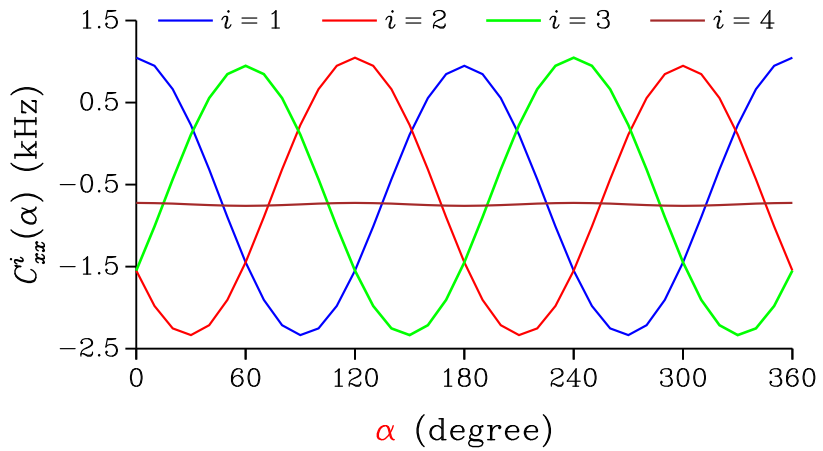
[1] Thaddeus, Krisher, and Loubser, *J. Chem. Phys.* **40** (1964) 257

[2] Heuvel & Dymanus, *J. Mol. Spec.* **45** (1973) 282 & *J. Mol. Spec.* **47** (1973) 363

Spin-rotation coupling tensor calculation

$$C^i_{\beta\gamma}(\alpha), \quad \text{with} \quad 1 \leq i \leq 4, \quad \beta, \gamma = x, y, z, \quad \text{and} \quad 0 \leq \alpha \leq 360^\circ$$

with ACES2[2] at the CCSD(T)[3] level with pVTZ[4] basis set.



[2] ACES2, Stanton, Gauss, *et al.*, 1992

[3] Raghavachari, Trucks, Pople, & Head-Goreon, *Chem. Phys. Lett.* **157** (1989) 479

[4] Dunning, *J. Chem. Phys.* **90** (1989) 1007

Symmetry considerations

Using the G_6 symmetry group[1]

$$H_{sr} = H_{sr}(A_1) \cdot O_{sr}(A_1) + H^h_{sr}(A_1) \cdot O^h_{sr}(A_1)$$
$$+ H_{sr}(E_a) \cdot O_{sr}(E_a) + H_{sr}(E_b) \cdot O_{sr}(E_b)$$

Hyperfine operators

$$H_{sr}(A_1) = (\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3) \cdot \mathbf{J}, \qquad H^h_{sr}(A_1) = \mathbf{I}_4 \cdot \mathbf{J}$$

$$H_{sr}(E_a) = \frac{1}{2}(2\mathbf{I}_1 - \mathbf{I}_2 - \mathbf{I}_3) \cdot \mathbf{J}, \quad H_{sr}(E_b) = \frac{\sqrt{3}}{2}(\mathbf{I}_2 - \mathbf{I}_3) \cdot \mathbf{J}$$

Rovibrational operators

$$O_{sr}(A_1) = \frac{1}{3}(E^1 + E^2 + E^3), \qquad O^h_{sr}(A_1) = E^4$$

$$O_{sr}(E_a) = \frac{1}{3}(2E^1 - E^2 - E^3), \quad O_{sr}(E_b) = \frac{1}{\sqrt{3}}(E^2 - E^3)$$

[1] Hougen, Kleiner, & Godefroid, *J. Mol. Spec.* **163** (1994) 559

Accounting for the torsion

For an n non-degenerate A_1 or A_2 level[1–3]

$$O_{sr}(A_1) \quad \text{and} \quad O^h_{sr}(A_1)$$

This leads to the hyperfine spin-rotation coupling Hamiltonian

$$H_{\text{Hfs}} = C_S^{sr} H_{sr}(A_1) + C_S^{sr,h} H^h_{sr}(A_1)$$

where

$$C_S^{sr} = \langle n|O_{sr}(A_1)|n\rangle \quad \text{and} \quad C_S^{sr,h} = \langle n|O^h_{sr}(A_1)|n\rangle$$

[1] Wolf, Williams, & Weatherly, *J. Chem. Phys.* **47** (1967) 5101
[2] Coudert & López, *J. Mol. Spec.* **239** (2006) 135
[3] Tudorie, Coudert, Huet, Jegouso, & Sedes, *J. Chem. Phys.* **134** (2011) 074314

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$$H \quad _1)$$

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Similar results for the spin-torsion and spin-spin couplings.

Doubly degenerate E-type levels should be treated in the same way.

[1] Wolf, Williams, & Weatherly, *J. Chem. Phys.* **47** (1967) 5101
[2] Coudert & López, *J. Mol. Spec.* **239** (2006) 135
[3] Tudorie, Coudert, Huet, Jegouso, & Sedes, *J. Chem. Phys.* **134** (2011) 074314

Summary

Level Symmetry	Spin-rotation	Spin-torsion	Spin-spin	N
	Coupling constants			
A_1/A_2	C_S^{sr} & $C_S^{sr,h}$	C_S^{st} & $C_S^{st,h}$	C_S^{ss} & $C_S^{ss,h}$	6
E	Same + C_A^{sr}	Same + C_A^{st}	Same + C_A^{ss} & $C_A^{ss,h}$	10
	Hyperfine coupling operators			
A_1/A_2	$H_{sr}(A_1)$ & $H_{sr}^h(A_1)$		$H_{ss}(A_1)$ & $H_{ss}^h(A_1)$	4
E	Same + $H_{sr}(E_a)$ & $H_{sr}(E_b)$		Same + $H_{ss}(E_a)$, $H_{ss}^h(E_a)$, $H_{ss}(E_b)$, & $H_{ss}^h(E_b)$	10

Hyperfine coupling constants numerical evaluation

Symmetry adapted operators for spin-torsion

$$O_{st}(\Gamma) = \frac{\{\rho J_z + p_\alpha, \sum_\beta J_\beta S_\beta^\Gamma(\alpha)\}}{2J(J+1)}$$

with

$$S_\beta^{A_1}(\alpha) = \begin{cases} s_\beta^0 + s_\beta^3 \cos 3\alpha & \text{for } \beta = x, z \\ s_\beta^3 \sin 3\alpha & \text{for } \beta = y \end{cases}$$

Hyperfine coupling constants numerical evaluation

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$O_{st}(A_1)$		$O_{st}(E_a)$		$O_{st}^h(A_1)$	
s_x^0	7.74826	s_x^1	−12.01180	$s_x^{0,h}$	53.46121
s_x^3	−0.14834	s_x^2	0.69876	$s_x^{3,h}$	−0.43484
s_y^3	−0.06417	s_y^1	−8.61518	$s_y^{3,h}$	−0.22573
		s_y^2	0.15320		
s_z^0	−27.51335	s_z^1	2.09658	$s_z^{0,h}$	59.98014
s_z^3	0.08271	s_z^2	−0.51433	$s_z^{3,h}$	0.18517

Hyperfine coupling constants numerical evaluation

Symmetry adapted operators for spin-torsion

$$O_{st}(\Gamma) = \frac{\{\rho J_z + p_\alpha, \sum_\beta J_\beta S^\Gamma_\beta(\alpha)\}}{2J(J+1)}$$

with

$$S^{A_1}_\beta(\alpha) = \begin{cases} s^0_\beta + s^3_\beta \cos 3\alpha & \text{for } \beta = x, z \\ s^3_\beta \sin 3\alpha & \text{for } \beta = y \end{cases}$$

$O_{st}(A_1)$		$O_{st}(E_2)$		$O^h_{st}(A_1)$	
s^0_x	7.748	s_x	12.61186	s_x	53.46121
s^3_x	−0.14834	s^2_x	0.69876	$s^{3,h}_x$	−0.43484
s^3_y	−0.06417	s^1_y	−8.61518	$s^{3,h}_y$	−0.22573
		s^2_y	0.15320		
s^0_z	−27.51335	s^1_z	2.09658	$s^{0,h}_z$	59.98014
s^3_z	0.08271	s^2_z	−0.51433	$s^{3,h}_z$	0.18517

92 constants arise

Hyperfine coupling constants values

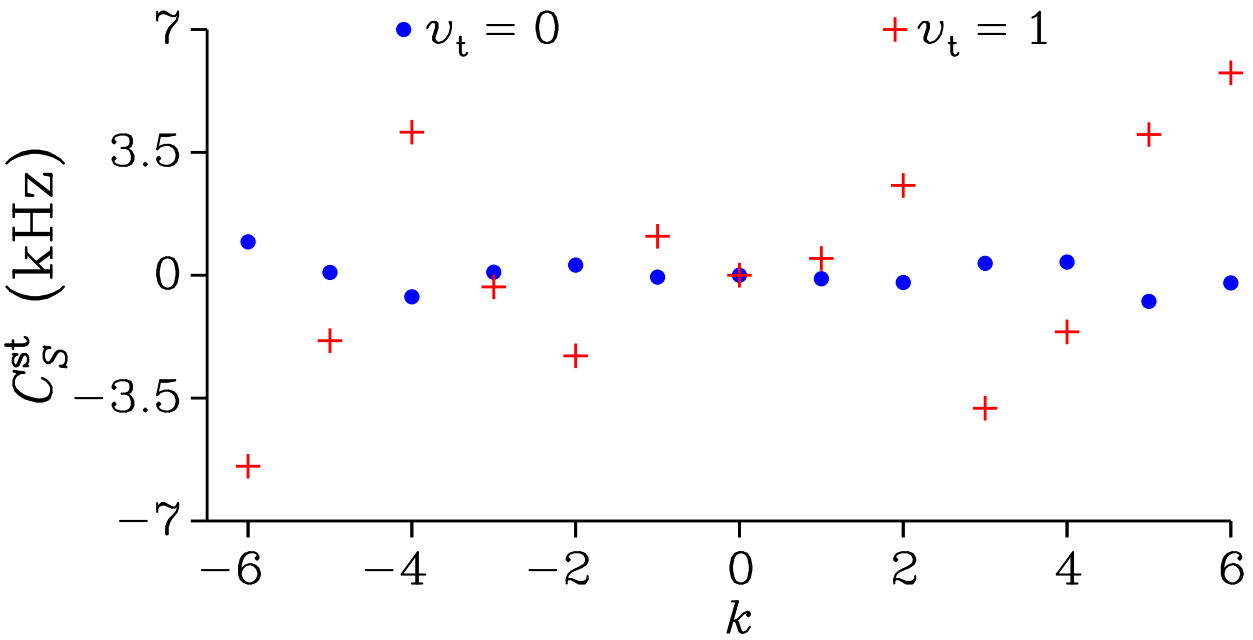
Rotation-torsion energies and eigenvectors obtained from a fit of the high-resolution data[1]

Level	C_S^{sr}	$C_S^{sr,h}$	C_S^{ss}	$C_S^{ss,h}$	C_S^{st}	$C_S^{st,h}$
$1_{01}\ A_2$	−0.71	−1.80	−4.22	2.17	0.0	0.0
$1_{11}\ A_2$	−6.68	−7.94	2.11	−1.04	3.31	−7.22
$1_{10}\ A_1$	−6.64	−6.95	2.11	−1.13	3.31	−7.22
$2_{02}\ A_1$	−0.71	−1.80	−1.01	0.52	0.0	0.0
$2_{12}\ A_1$	−2.71	−4.18	−0.50	0.27	1.11	−2.40
$2_{11}\ A_2$	−2.68	−3.19	−0.50	0.25	1.10	−2.40
$3_{03}\ A_2$	−0.71	−1.81	−0.47	0.24	0.0	0.0
$3_{13}\ A_2$	−1.72	−3.24	−0.35	0.19	0.55	−1.20
$3_{12}\ A_1$	−1.69	−2.25	−0.35	0.18	0.55	−1.20

[1] Xu, Fisher, Lees, Shi, Hougen, Pearson, Drouin, Blake, & Braakman, *J. Mol. Spec.* **251** (2008) 305

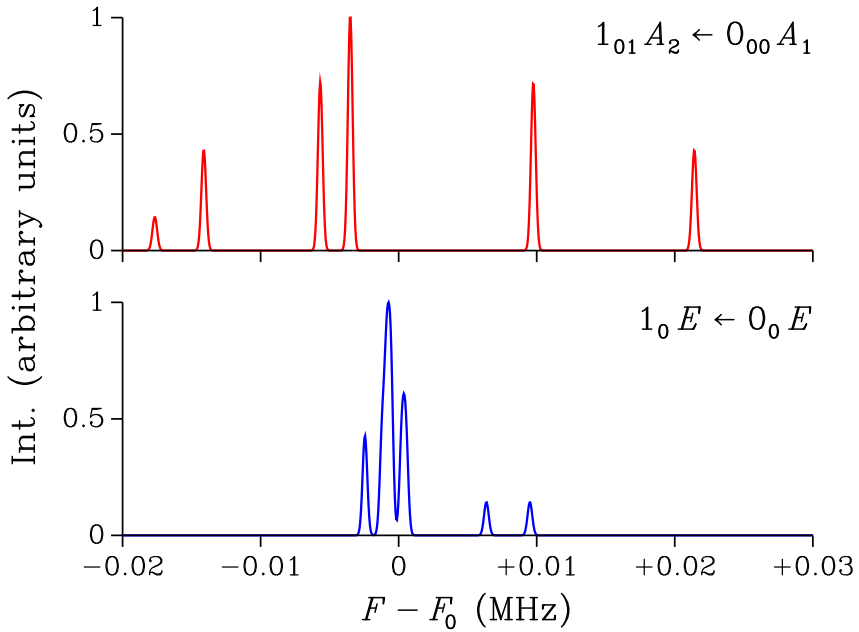
Hyperfine coupling constants values-*Continued*

C_S^{st} for a J_k E-type levels with $J = 6$ and $-6 \leq k \leq 6$.



Hyperfine coupling constants values-*Continued*

Calculated hyperfine pattern for the $1_{01}\,A_2 \leftarrow 0_{00}\,A_1$ transition at 48 372 MHz and the $1_0\,E \leftarrow 0_0\,E$ transition at 48 376 MHz[1]

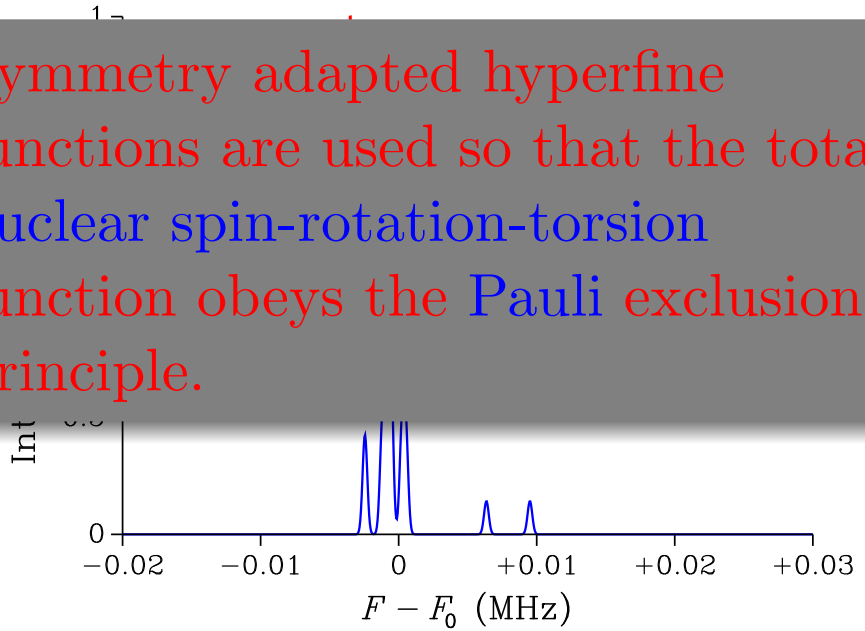


[1] Tudorie, Coudert, Huet, Jegouso, & Sedes, *J. Chem. Phys.* **134** (2011) 074314

Hyperfine coupling constants values-*Continued*

Calculated hyperfine pattern for the $1_{01}\ A_2 \leftarrow 0_{00}\ A_1$ transition at 48 372 MHz and the $1_0\ E \leftarrow 0_0\ E$ transition at 48 376 MHz[1]

Symmetry adapted hyperfine functions are used so that the total nuclear spin-rotation-torsion function obeys the Pauli exclusion principle.



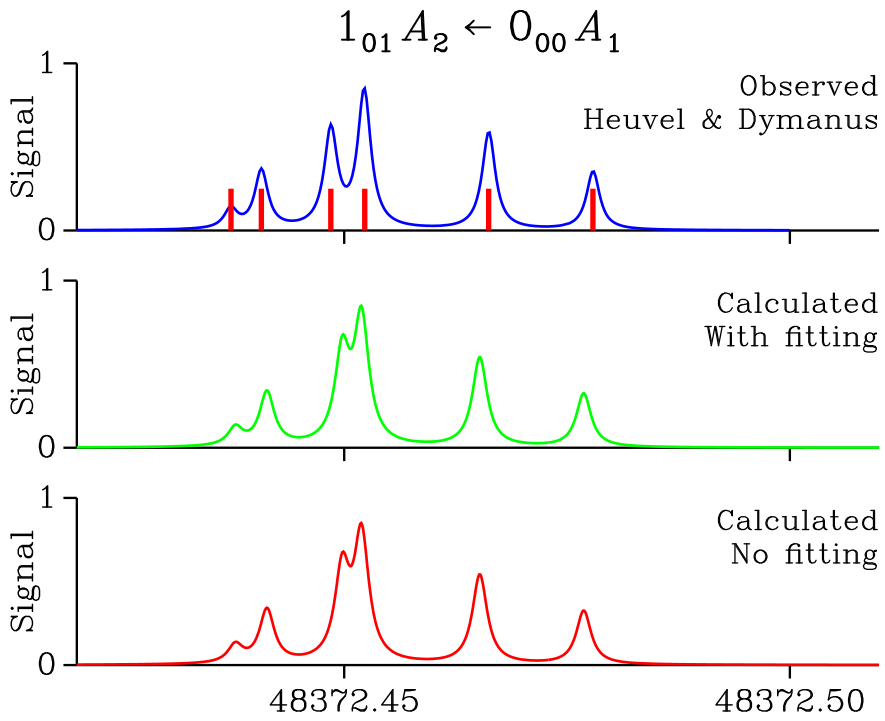
[1] Tudorie, Coudert, Huet, Jegouso, & Sedes, *J. Chem. Phys.* **134** (2011) 074314

Analysis: experimental data set

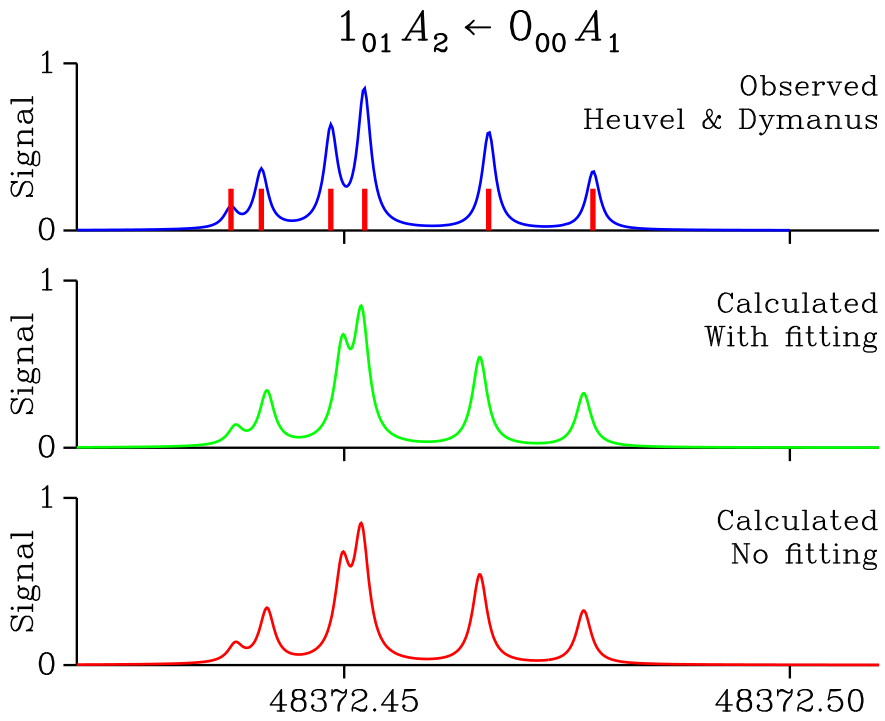
Transition	F	Spectrometer	Hyp
$2_{11}\ A_2 \leftarrow 2_{12}\ A_1$	2502.8	Ref. 1 & Lille	S
$3_{12}\ A_1 \leftarrow 3_{13}\ A_2$	5005.3	Ref. 1 & Lille	D
$5_{15}\ A_2 \leftarrow 6_{06}\ A_1$	6668.5	Hannover & Lille	D
$9_{-1}\ E \leftarrow 8_{-2}\ E$	9936.2	Hannover & Lille	
$4_{32}\ A_1 \leftarrow 5_{23}\ A_2$	9978.7	Lille	
$2_{0}\ E \leftarrow 3_{-1}\ E$	12178.6	Hannover & Lille	D
$6_{15}\ A_2 \leftarrow 6_{16}\ A_1$	17513.3	Ref. 1	D
$2_{1}\ E \leftarrow 3_{0}\ E$	19967.4	Hannover	S
$3_{2}\ E \leftarrow 3_{1}\ E$	24928.7	Hannover	D
$4_{2}\ E \leftarrow 4_{1}\ E$	24933.5	Hannover	D
$2_{2}\ E \leftarrow 2_{1}\ E$	24934.4	Hannover	S
$5_{2}\ E \leftarrow 5_{1}\ E$	24959.1	Hannover	D
$6_{2}\ E \leftarrow 6_{1}\ E$	25018.1	Hannover	D
$1_{01}\ A_2 \leftarrow 0_{00}\ A_1$	48372.4	Ref. 1	M

[1] Heuvel & Dymanus, *J. Mol. Spec.* **45** (1973) 282

Analysis results: observed & calculated hfs. patterns



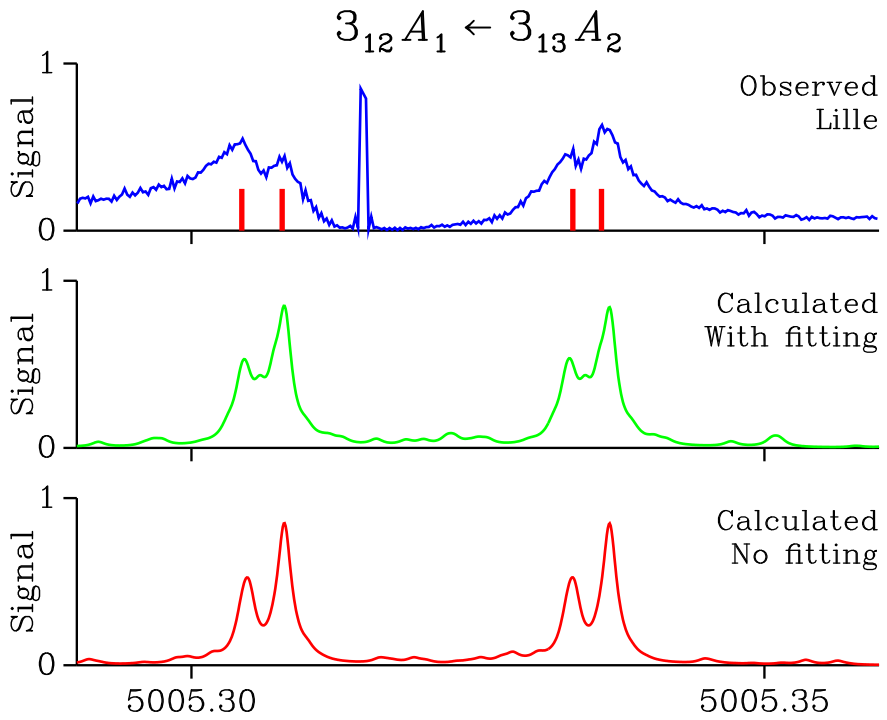
Analysis results: observed & calculated hfs. patterns



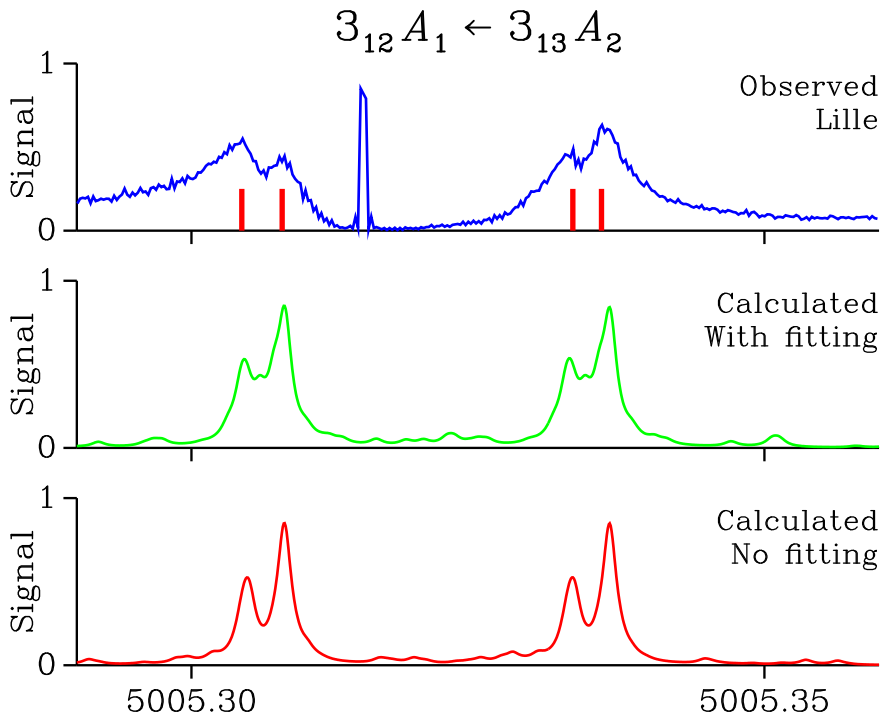
Dominated by spin-spin coupling

$$C_S^{sr} = -0.71 \quad C_S^{sr,h} = -1.80 \quad C_S^{ss} = -4.22 \quad C_S^{ss,h} = -2.17$$

Analysis results: observed & calculated hfs. patterns



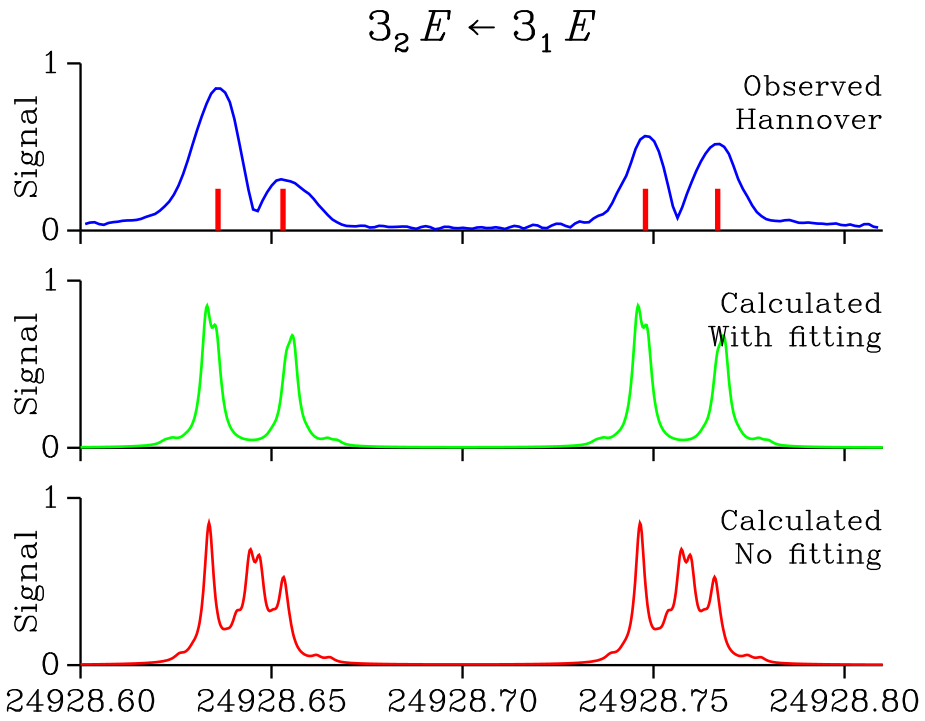
Analysis results: observed & calculated hfs. patterns



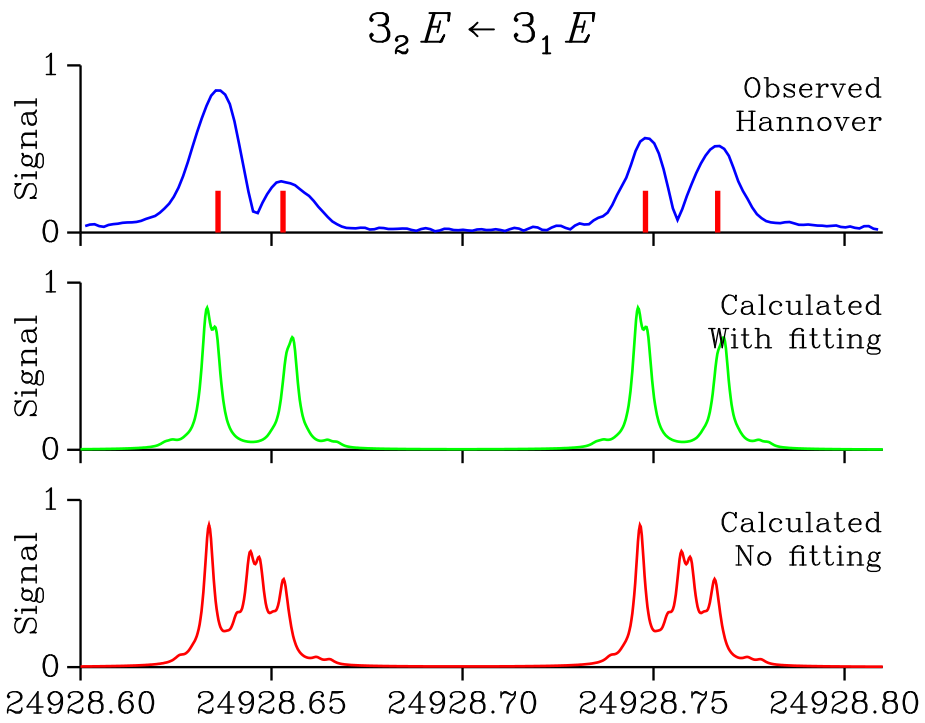
Dominated by spin-rotation from the hydroxyl group

$$C_S^{sr'} = -1.69 \quad C_S^{sr,h'} = -2.25 \quad C_S^{ss'} = -0.35 \quad C_S^{ss,h'} = -0.18$$
$$C_S^{sr''} = -1.72 \quad C_S^{sr,h''} = -3.24 \quad C_S^{ss''} = -0.35 \quad C_S^{ss,h''} = -0.19$$

Analysis results: observed & calculated hfs. patterns

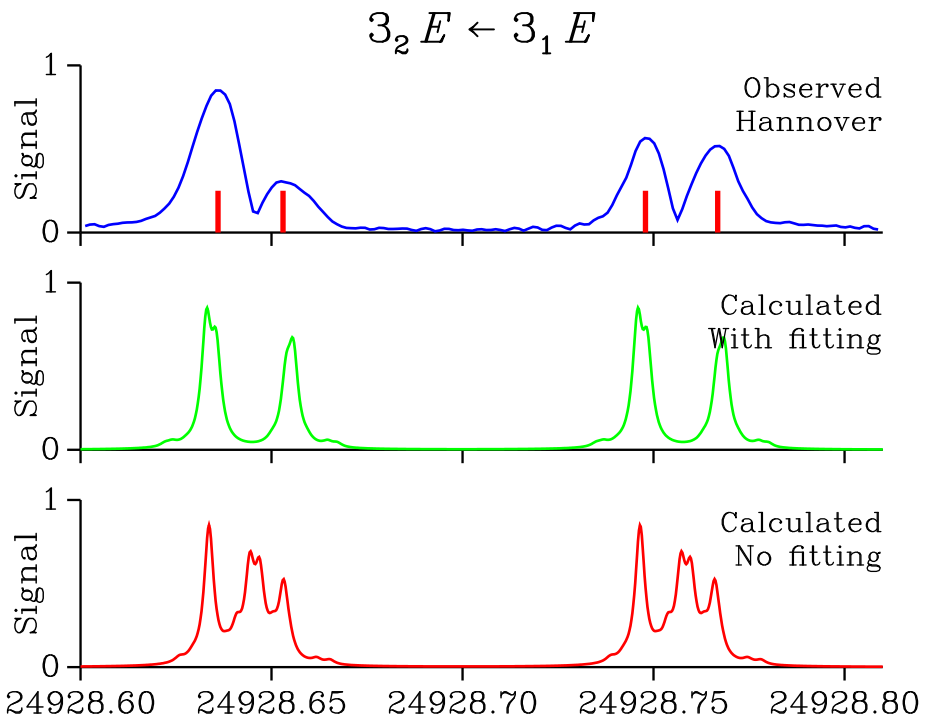


Analysis results: observed & calculated hfs. patterns



Predicted spin-rotation splitting from the methyl group was too large

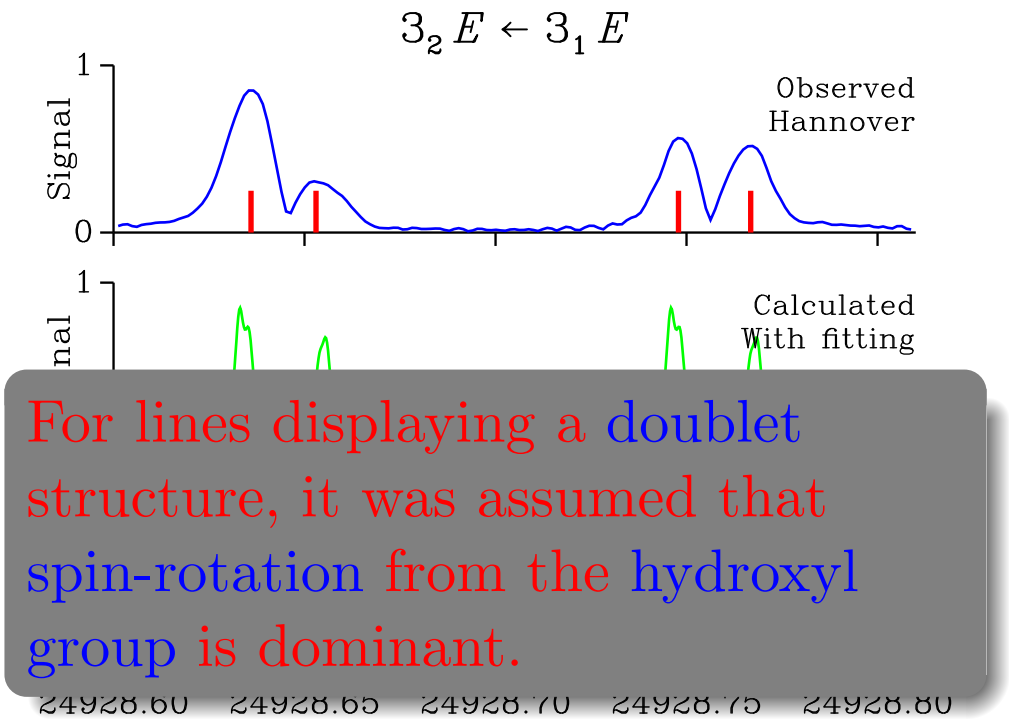
Analysis results: observed & calculated hfs. patterns



Predicted spin-rotation splitting from the methyl group was too large

Also dominated by spin-rotation from the hydroxyl group

Analysis results: observed & calculated hfs. patterns



For lines displaying a doublet structure, it was assumed that spin-rotation from the hydroxyl group is dominant.

Predicted spin-rotation splitting from the methyl group was too large

Also dominated by spin-rotation from the hydroxyl group

Analysis results: parameters (kHz)

Parameter	No fitting	Fit I	Fit II
c_{zz}^{0}	-12.626	$-2.094(974)$	$-1.766(910)$
$c_{zz}^{0,h}$	-12.877	$-25.802(1060)$	$-28.535(1055)$
$s_{zz}^{0,h}$	59.980	0.0[1]	69.290(12625)
12 center frequencies			
STD (unitless)		1.2	1.1

[1] Constrained value.

Thank you
for your attention