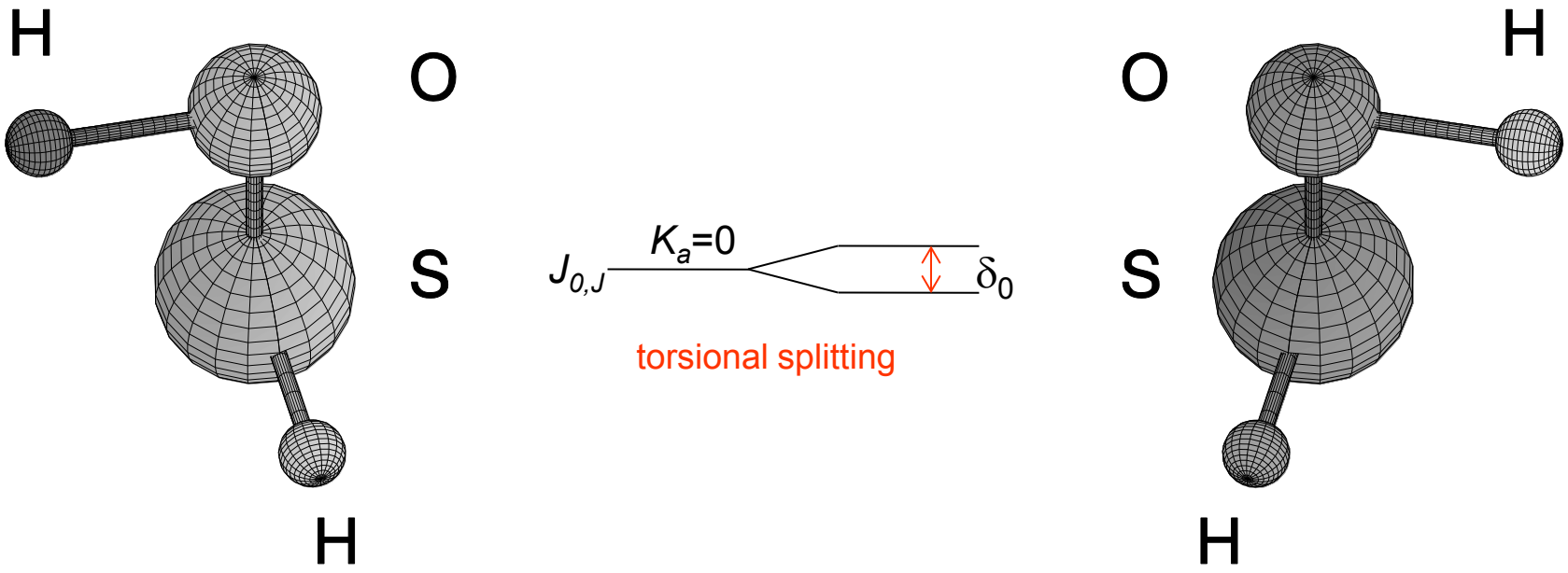
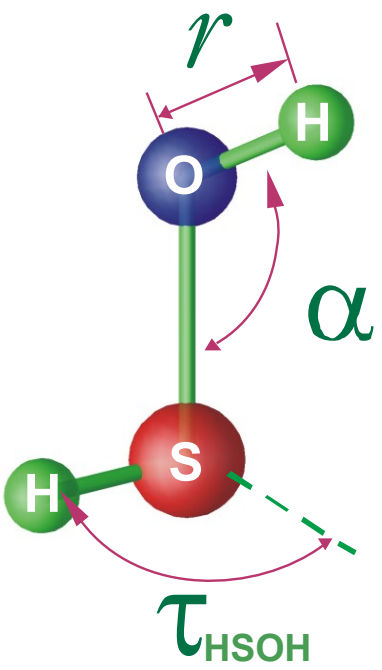
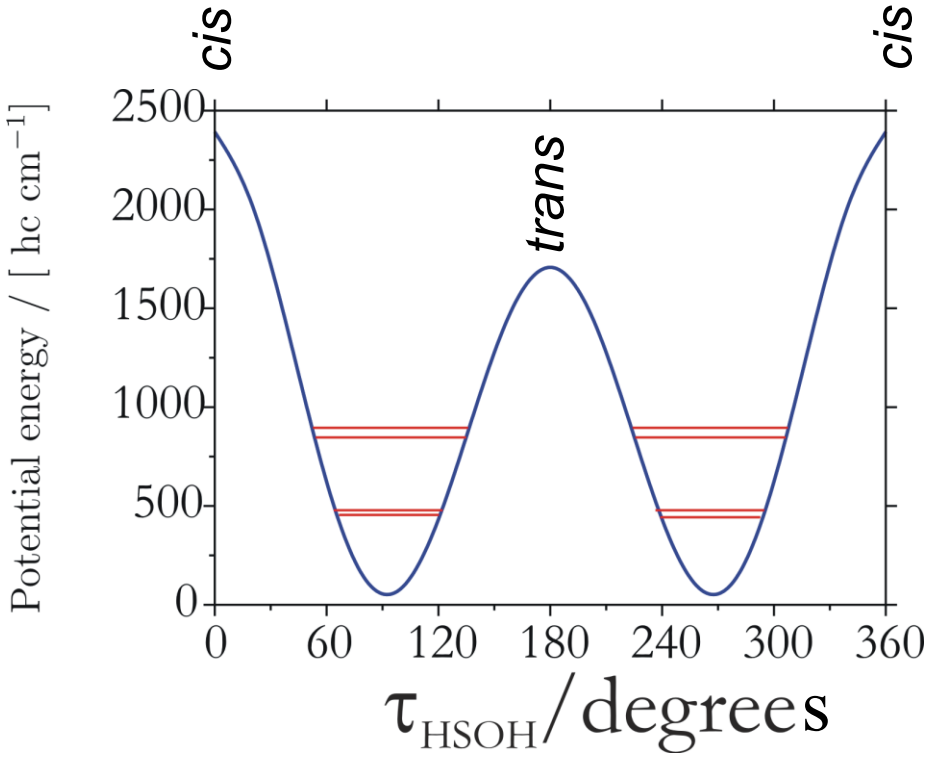
Torsional splittings and anomalous intensities in HSOH

- Two enantiomer minima
- Internal rotation about the SO bond, strongly coupled to the rotation about the *a* axis (associated with K_a)
- Torsional splittings



HSOH: Torsional potential





Torsional splittings show strong variation with K_a

HOOH, HSSH, HNCNH: Splittings "stagger" with K_a

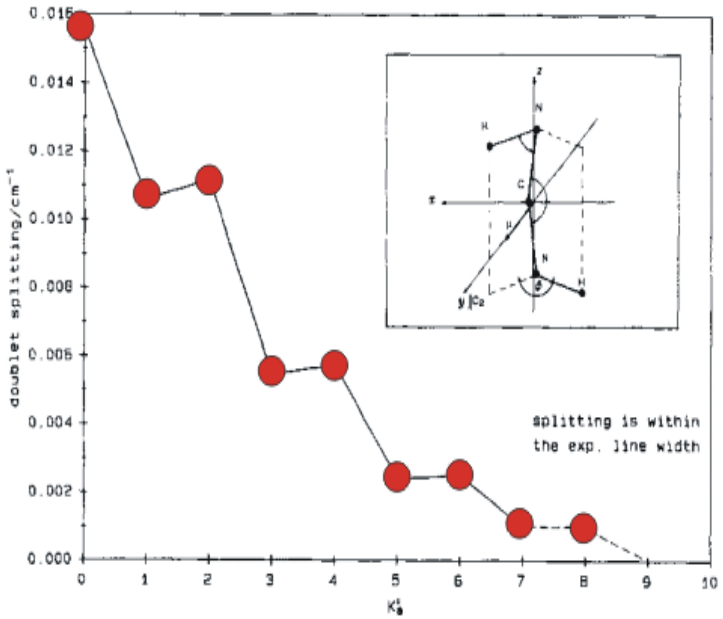


FIG. 13. Dependence of the torsional doublet splitting on K_a. The doublet splitting averaged over all J-values was obtained from the line positions of the $'Q_0$ branch for $K_a = 0$, the $'R_{K_a}$ branch for $K_a = 1$ to $K_a = 4$, the $'R_{K_a}$ and $'Q_{K_a}$ branches for $K_a = 5$ and 6, and from an analysis of the linewidth for $K_a = 7$. For $K_a = 8$ the splitting is identical to that for $K_a = 7$ within the experimental accuracy. For $K_a = 9$, no broadening of the $'R_{K_a}$ lines due to torsional doubling could be detected.

Example: HNCNH

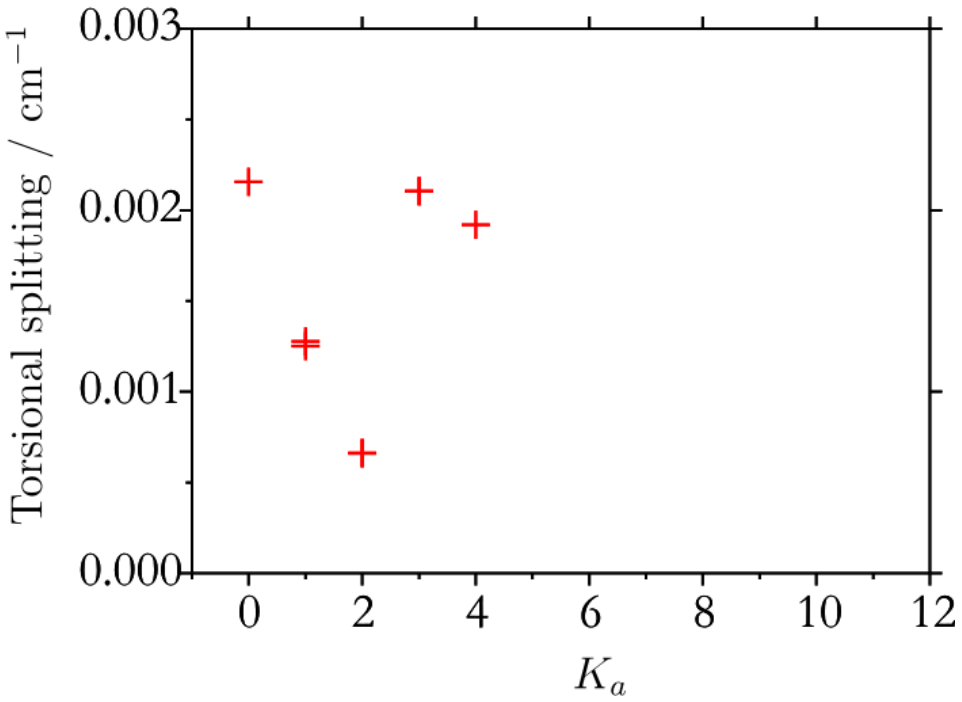
Experiment: M. Birk, M. Winnewisser, *J. Mol. Spectrosc*. **136**, 402 (1989)

Semi-empirical explanation by Hougen and co-workers for HOOH and HSSH:

J.T. Hougen, *Can. J. Phys*. **62,** 1392 (1984).

J.T. Hougen, B.M. DeKoven, *J. Mol. Spectrosc*. **98,** 375 (1983).

HSOH: No staggering, more complicated variation



Experiment

Cologne Terahertz spectrometer

First observation (for $K_a \leq 3$) in 2003

M. Behnke, J. Suhr, S. Thorwirth, F. Lewen, H. Lichau, J. Hahn, J. Gauss, K.M.T. Yamada, G. Winnewisser, *J. Mol. Spectrosc.* **221**, 121 (2003)
G. Winnewisser, F. Lewen, S. Thorwirth, M. Behnke, J. Hahn, J. Gauss, and E. Herbst, *Chem. Eur.* J **9**, 5501 (2003)
O. Baum, M. Koerber, O. Ricken, G. Winnewisser, S. N. Yurchenko, S. Schlemmer, K. M. T. Yamada, and T. F. Giesen, *J. Chem. Phys.* **129**, 224312 (2008).

Approach 0 (2004): Semi-empirical, following the ideas of Hougen:

J.T. Hougen, *Can. J. Phys*. **62,** 1392 (1984).
J.T. Hougen, B.M. DeKoven, *J. Mol. Spectrosc*. **98,** 375 (1983).

Ratio of I_a moments of inertia $I_{SH}/I_{total} \approx 1/3$.

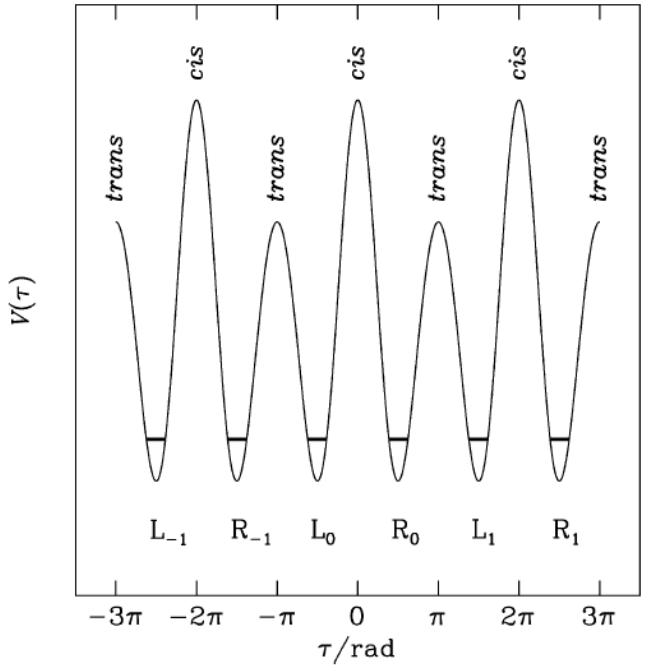
Pretend that $\tau_{HSOH} \in [-3\pi,3\pi]$

Molecule formally has $\boldsymbol{C}_{3v}$(M) symmetry

Do quantum mechanics under this assumption.

Subject results to „reality check“: A 2π rotation of the SH moiety relative to OH moiety must leave wavefunction unchanged.

K.M.T. Yamada, G. Winnewisser, and P. Jensen, *J. Mol. Struct.,* **695-696**, 323 (2004)



$\tau_{HSOH} \in [-3\pi, 3\pi]$

6×6 matrix:

$$\begin{pmatrix} Q & W_c & 0 & 0 & 0 & W_t \\ W_c & Q & W_t & 0 & 0 & 0 \\ 0 & W_t & Q & W_c & 0 & 0 \\ 0 & 0 & W_c & Q & W_t & 0 \\ 0 & 0 & 0 & W_t & Q & W_c \\ W_t & 0 & 0 & 0 & W_c & Q \end{pmatrix}$$

K.M.T. Yamada, G. Winnewisser, and P. Jensen, *J. Mol. Struct.*, **695-696**, 323 (2004)

Conclusion for HSOH (2009):

The torsional splittings of HSOH in the ground state for each K.

K	Δ_{tor}	Observed[a]/MHz	Calculated[b]/MHz
0	$2\lvert W_c + W_t \rvert$	64.5	63.9
1	$2\lvert W_c + W_t/2 - D_{ab} \rvert$	37.8	33.3
2	$2\sqrt{(W_c - W_t/2 + 2D_{ab})^2 + 3W_t^2/4}$	52.1	50.9
3	$2\lvert W_c + W_t - 9D_{12}^2/2(W_c + W_t) \rvert$	62.9	63.5
4	$2\sqrt{(W_c - W_t/2 - 4D_{ab})^2 + 3W_t^2/4}$	57.2	57.3
5	$2\sqrt{(W_c - W_t/2 + 5D_{ab})^2 + 3W_t^2/4}$	49.0	49.2
6	$2\lvert W_c + W_t - 36D_{12}^2/2(W_c + W_t) \rvert$		62.1
7	$2\sqrt{(W_c - W_t/2 - 7D_{ab})^2 + 3W_t^2/4}$		61.6
8	$2\sqrt{(W_c - W_t/2 + 8D_{ab})^2 + 3W_t^2/4}$		48.6
9	$2\lvert W_c + W_t - 81D_{12}^2/2(W_c + W_t) \rvert$		59.9
10	$2\sqrt{(W_c - W_t/2 - 10D_{ab})^2 + 3W_t^2/4}$		66.6

K. M. T. Yamada, Per Jensen, S. C. Ross, O. Baum, T. F. Giesen, and S. Schlemmer, *J. Mol. Structure* **927**, 96-100 (2009).

Approach 1 (2008): *Ab initio* potential energy surface + TROVE calculation of torsional splittings

Ab initio potential energy surface:

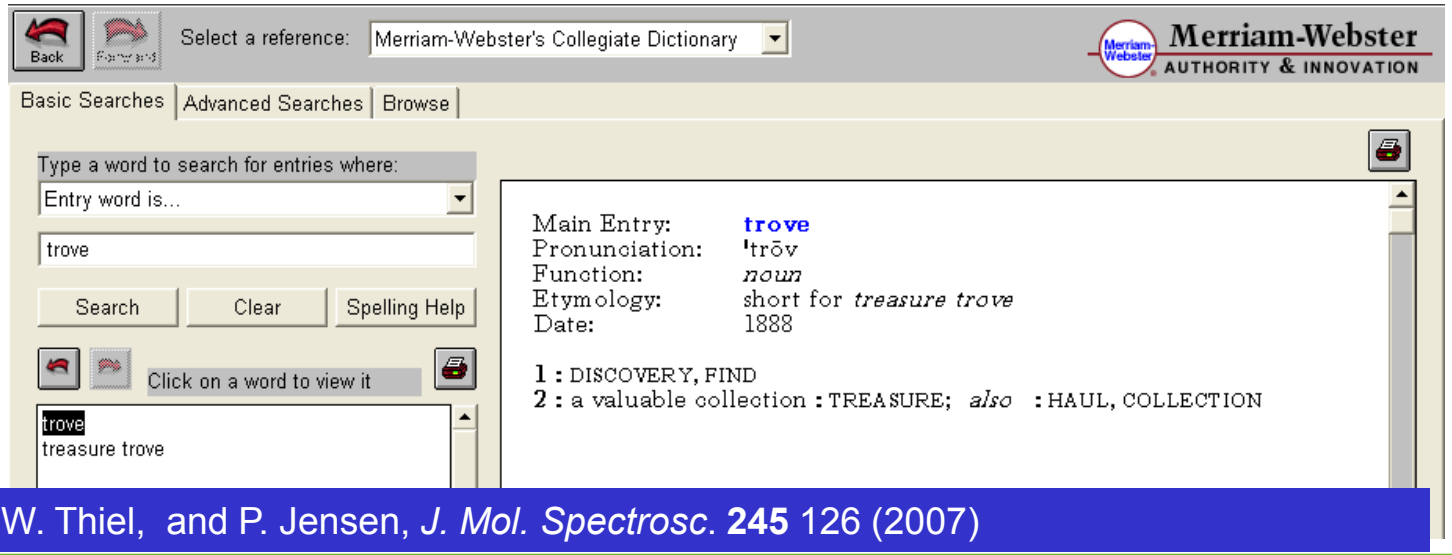
- CCSD(T) method
- 105000 data points with aug-cc-pVTZ basis set, energies up to 20000 cm^{-1} above equilibrium
- 10168 data points with aug-cc-PV(Q+*d*)Z basis set, energies up to 12000 cm^{-1} above equilibrium
- Simultaneous, weighted fitting to all data points, 762 parameters varied, standard error 2.8 cm^{-1}

R. I. Ovsyannikov, V.V. Melnikov, W. Thiel, Per Jensen, O. Baum, T. F. Giesen, and S. N. Yurchenko, *J. Chem. Phys.* **129**, 154314 (2008).
S. N. Yurchenko, A. Yachmenev, W. Thiel, O. Baum, T. F. Giesen, V. V. Melnikov, and Per Jensen: *J. Mol. Spectrosc.* **257**, 57 (2009).

TROVE?

TROVE: Theoretical ROVibrational Energies:

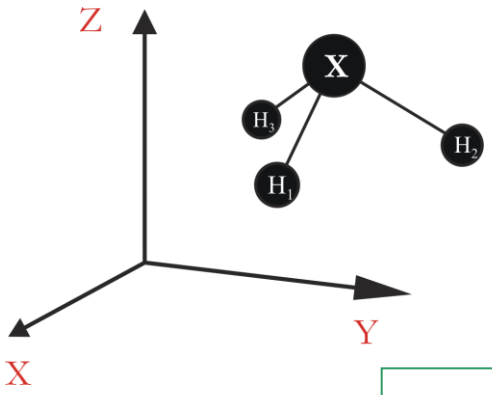
Variational calculations of rotation-vibration for a general polyatomic molecule in an isolated electronic state



S.N. Yurchenko, W. Thiel, and P. Jensen, *J. Mol. Spectrosc.* **245** 126 (2007)

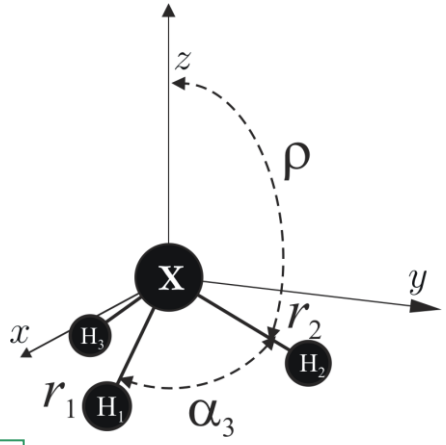
$$\left(\sum_{i=1}^{N} \frac{-\hbar^2}{2M_i}\nabla_i^2 + V\right)\Psi = E\Psi$$

Hamiltonian: Coordinate transformation



Laboratory fixed Cartesian coordinate system

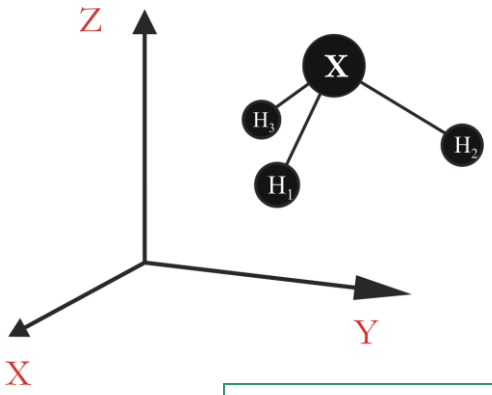
Body fixed internal coordinate system



$$\mathbf{R}_i = \mathbf{R}^{\mathrm{CM}} + S^{-1}(\theta,\phi,\chi)\left[\mathbf{R}_i^{\mathrm{MS}}(\mathbf{r})\right]$$

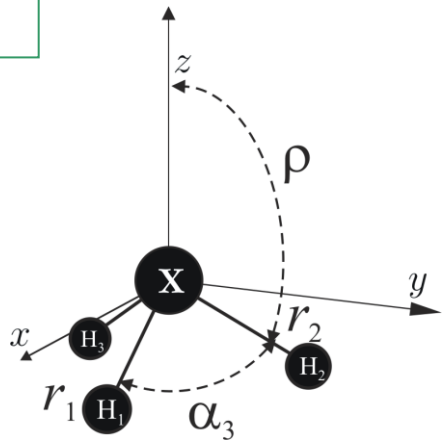
$$\left[\frac{1}{2}\sum_{\lambda=1}^{3N}\sum_{\mu=1}^{3N}\Pi_\lambda\, G_{\lambda,\mu}(\mathbf{r})\,\Pi_\mu + U(\mathbf{r}) + V(\mathbf{r})\right]\Psi = E\Psi$$

$$\left(\sum_{i=1}^{N}\frac{-\hbar^2}{2M_i}\nabla_i^2+V\right)\Psi=E\Psi$$



Laboratory fixed Cartesian coordinate system

Body fixed internal coordinate system



- The coordinate transformation is done by the program
- **„One transformation for all molecules“**

$$\left[\frac{1}{2}\sum_{\lambda=1}^{3N}\sum_{\mu=1}^{3N}\Pi_\lambda\, G_{\lambda,\mu}(\mathbf{r})\,\Pi_\mu+U(\mathbf{r})+V(\mathbf{r})\right]\Psi=E\Psi$$

Coordinate transformation: Definitions

$$\left[\frac{1}{2}\sum_{\lambda=1}^{3N}\sum_{\mu=1}^{3N}\Pi_\lambda\, G_{\lambda,\mu}(\mathbf{r})\,\Pi_\mu + U(\mathbf{r}) + V(\mathbf{r})\right]\Psi = E\Psi$$

Kinetic energy factor

$$G_{\lambda,\mu} = \sum_{\alpha=x,y,z}\sum_{i=1}\frac{s_{\lambda,i\alpha}s_{\mu,i\alpha}}{m_i}$$

Jacobian transformation matrix

$$\hat{P}_{iF} = \sum_{\lambda=1}^{3N} s_{\lambda,iF}\,\Pi_\lambda$$

$$\sum_{i=1}^{N}\sum_{F=X,Y,Z}\frac{\partial\xi_\lambda}{\partial R_{iF}}\frac{\partial R_{iF}}{\partial\xi_\mu} = \mathbf{s}_{\lambda,i}\cdot\mathbf{t}_{i,\mu} = \delta_{\lambda,\mu}$$

$$\mathbf{s}_{\lambda,i} = \left(\mathbf{t}_{i,\mu}\right)^{-1}$$

We solve these linear equations numerically by expanding as polynomials in the small amplitude coordinates.

G.O. Sørensen, *Topics in Current Chemistry* **82**, 99 (1979).

General strategy for calculating the eigenvalues and eigenfunctions of the resulting Hamiltonian

Variational calculation = Construction of Hamiltonian matrix in terms of suitable basis set, followed by numerical diagonalization of the matrix

A vibrational basis function is generated as a product of „one-dimensional“ (1D) vibrational basis functions, each one describing a single vibrational degree of freedom

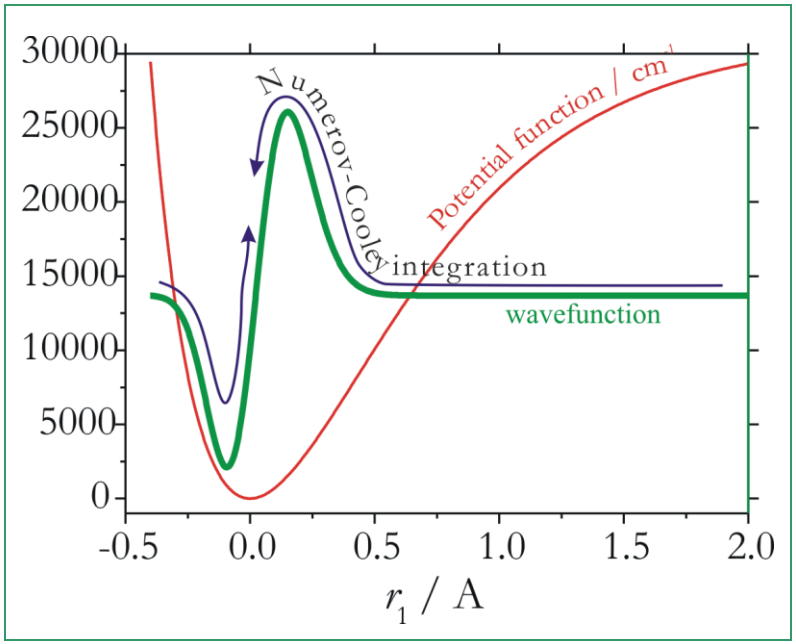
A rotation-vibration basis function is obtained by multiplying a vibrational basis function by a symmetric-top eigenfunction.

TROVE: S.N. Yurchenko, W. Thiel, and P. Jensen, *J. Mol. Spectrosc.* **245**, 126 (2007).

1D vibrational basis functions

- Harmonic oscillator functions
- Morse oscillator functions
- Numerical function generated by Numerov-Cooley integration

$$H^{\mathrm{1D}}_{\mathrm{str.}}\ \psi^{\mathrm{1D}}_{i_s} = E^{\mathrm{str.}}_{i_s}\ \psi^{\mathrm{1D}}_{i_s}$$



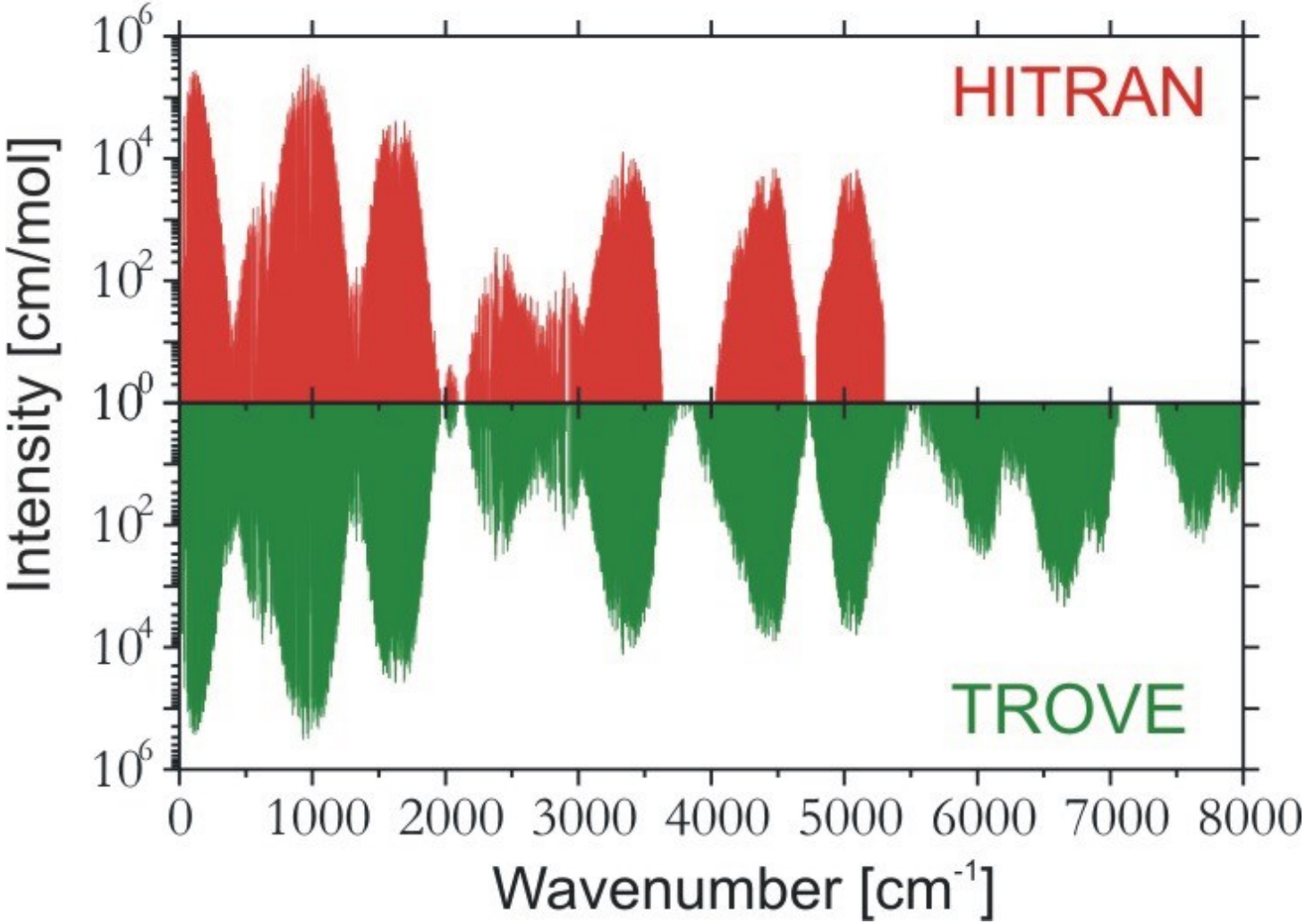
Rotation-vibration basis functions

- Vibrational basis function $\phi_{vib} = |n_1\rangle |n_2\rangle |n_3\rangle |n_4\rangle \ldots$
- Rotation-vibration basis function $\phi_{rot\text{-}vib} = \phi_{vib} \times |J,k,m\rangle$
- Construction of matrix
- (Symmetrization)
- Numerical diagonalization of matrix
- (Calculation of intensities from rotation-vibration eigenfunctions)

TROVE: S.N. Yurchenko, W. Thiel, and P. Jensen, *J. Mol. Spectrosc.* **245**, 126 (2007).

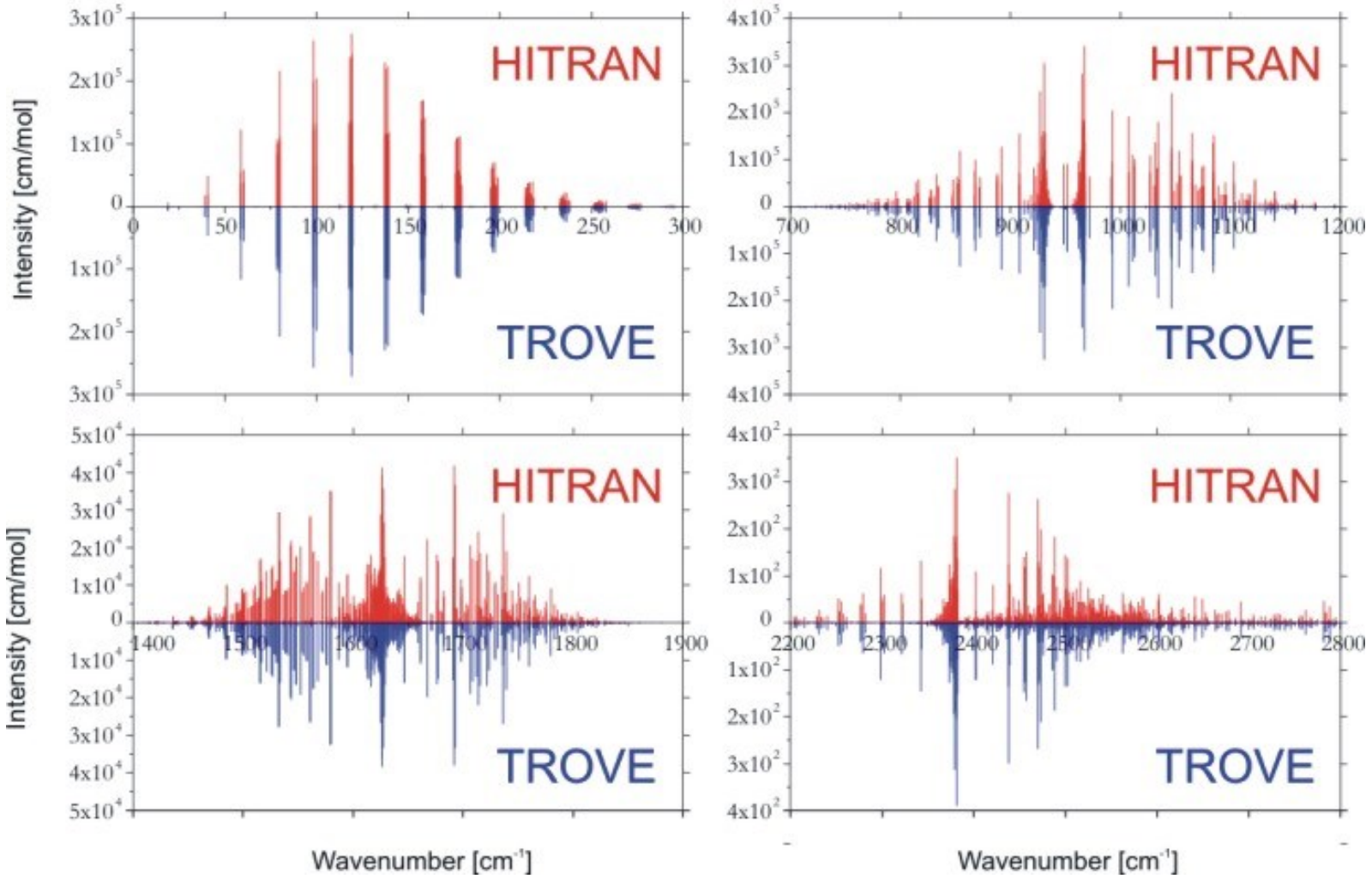
Start of parenthetic remark about NH_3 spectrum simulations

Parenthetic remark: NH_3 spectrum simulations (T=300K)



S. N. Yurchenko, R. J. Barber, A. Yachmenev, W. Thiel, Per Jensen, and J. Tennyson, *J. Phys. Chem. A* **113**, 11845-11855 (2009).

NH_3: Absorption intensities at T=300K, 3.25 million transitions



S. N. Yurchenko, R. J. Barber, A. Yachmenev, W. Thiel, Per Jensen, and J. Tennyson, *J. Phys. Chem. A* **113**, 11845-11855 (2009).

Absorption intensities at *T*=1500K, 1.1 billion transitions, list is essentially finished, collaboration Yurchenko/Tennyson

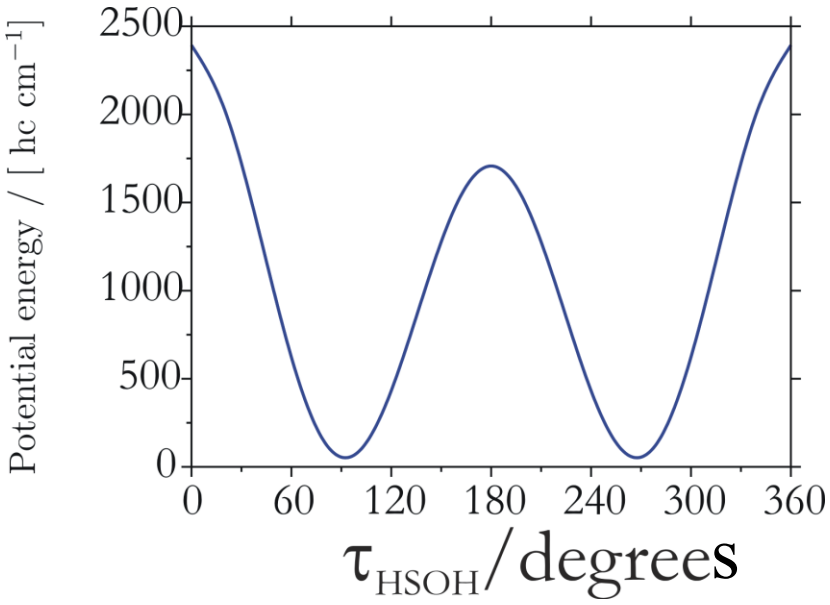
End of parenthetic remark about NH_3 spectrum simulations

Back to HSOH

HSOH: *Ab initio*

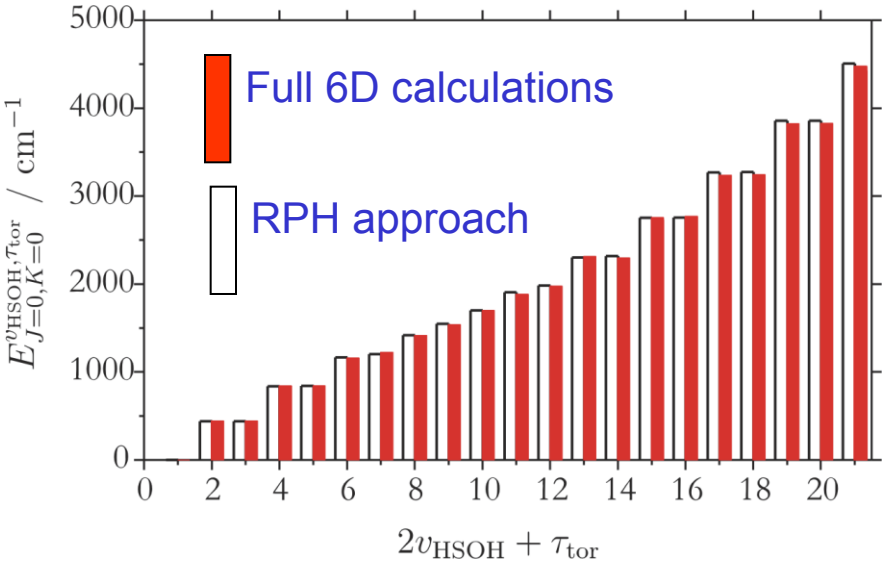
~12000 points

CCSD(T)/aug-cc-pV(Q+d)Z



TROVE

$J = 0 \ldots 40$, $v_{\mathrm{HSOH}} \leq 42$

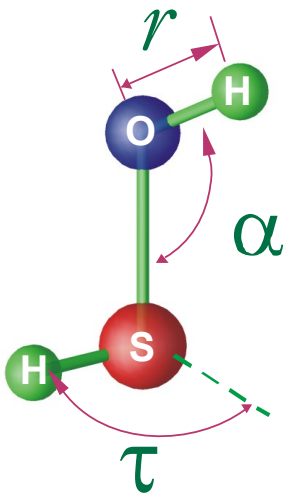


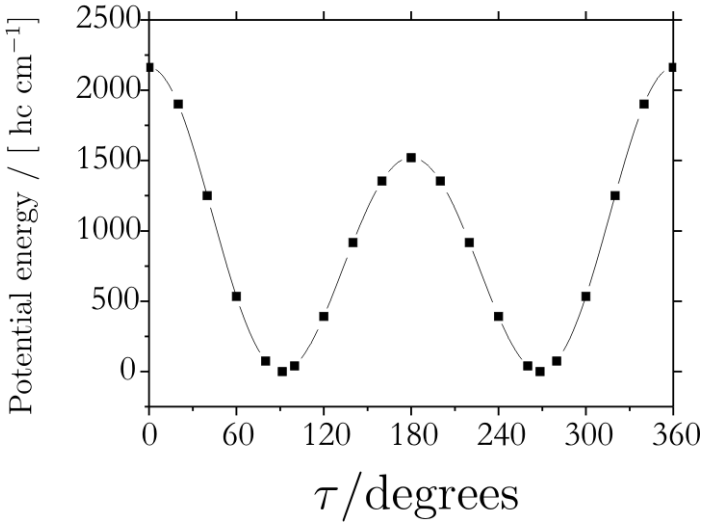
RPH approach: expansion around MEP

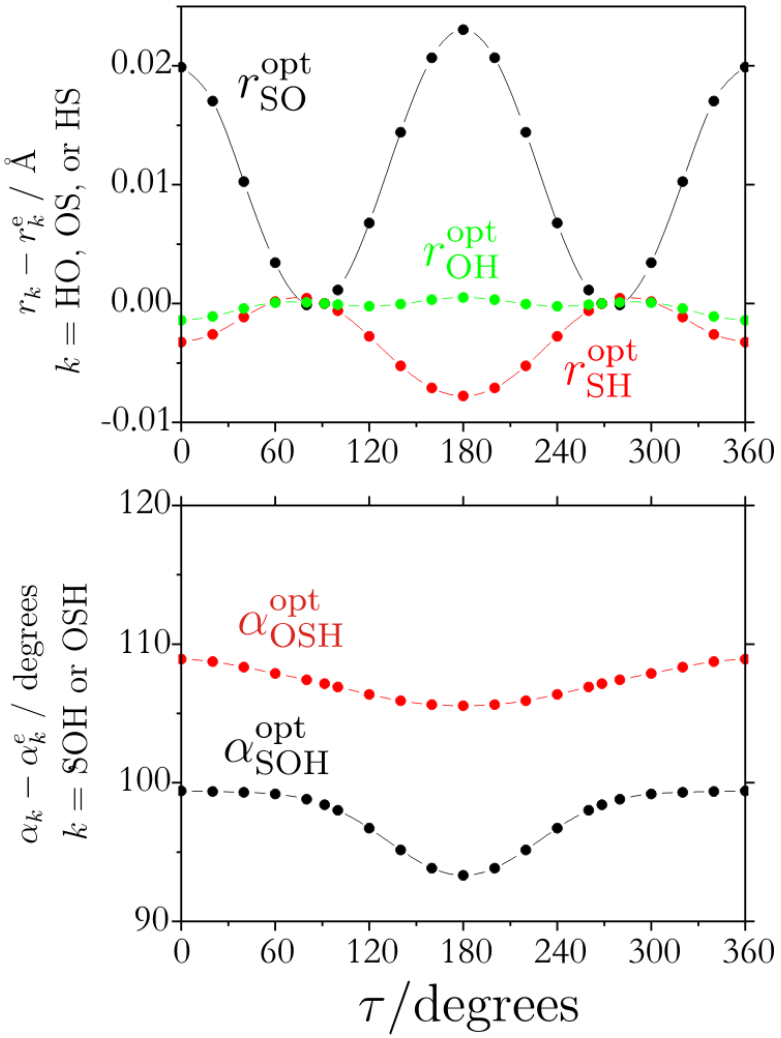
$$\Psi_{J,\Gamma,i} = |0\rangle\,|0\rangle\,|0\rangle\,|0\rangle\,|0\rangle \sum_{v_{\mathrm{HSOH}},\tau_{\mathrm{tor}},K,\tau_{\mathrm{rot}}} C^{K,\tau_{\mathrm{rot}},v_{\mathrm{HSOH}},\tau_{\mathrm{tor}}}_{J,\Gamma,i}\,|v_{\mathrm{HSOH}},\tau_{\mathrm{tor}}\rangle\,|J,K,\tau_{\mathrm{rot}}\rangle$$

S. N. Yurchenko, A. Yachmenev, W. Thiel, O. Baum, T. F. Giesen, V. V. Melnikov, and Per Jensen: *J. Mol. Spectrosc.* **257**, 57 (2009).

HSOH: Minimum energy path







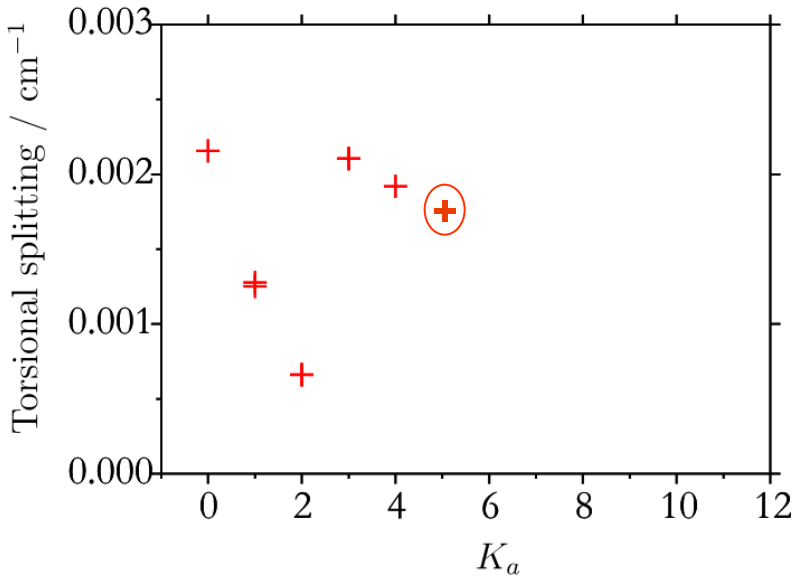
R. I. Ovsyannikov, V.V. Melnikov, W. Thiel, Per Jensen, O. Baum, T. F. Giesen, and S. N. Yurchenko, *J. Chem. Phys.* **129**, 154314 (2008).
O. Baum, M. Koerber, O. Ricken, G. Winnewisser, S. N. Yurchenko, S. Schlemmer, K. M. T. Yamada, and T. F. Giesen, *J. Chem. Phys.* **129**, 224312 (2008).

HSOH rotation-torsion levels: experiment *vs* TROVE

				Term values (cm^{-1})			Splitting (cm^{-1})		
J	K_a	K_c	Γ	obs	calc	exp-calc	calc	exp	exp-calc
4	0	4	A'	10.04696	10.05037	-0.00341			
4	0	4	A"	10.04911	10.05252	-0.00341	0.00215	0.00215	0.00000
4	1	3	A"	16.35885	16.36110	-0.00225			
4	1	3	A'	16.36011	16.36236	-0.00225	0.00126	0.00126	0.00000
4	1	4	A'	16.21151	16.21314	-0.00164			
4	1	4	A"	16.21277	16.21440	-0.00163	0.00126	0.00127	0.00000
4	2	2	A"	34.99521	34.99509	0.00011			
4	2	2	A'	34.99698	34.99694	0.00004	0.00184	0.00177	-0.00007
4	2	3	A'	34.99506	34.99495	0.00011			
4	2	3	A"	34.99683	34.99679	0.00004	0.00184	0.00177	-0.00007
4	3	1	A'	66.17016	66.17467	-0.00452			
4	3	1	A"	66.17226	66.17681	-0.00455	0.00213	0.00210	-0.00004
4	3	2	A"	66.17016	66.17467	-0.00452			
4	3	2	A'	66.17226	66.17681	-0.00455	0.00214	0.00210	-0.00004
4	4	0	A'	109.79888	109.82657	-0.02770			
4	4	0	A"	109.80079	109.82854	-0.02774	0.00196	0.00192	-0.00004
4	4	1	A"	109.79888	109.82657	-0.02770			
4	4	1	A'	109.80079	109.82854	-0.02774	0.00196	0.00192	-0.00004

Basis set: $\nu_{HSOH} \leq 42$

HSOH torsional splittings

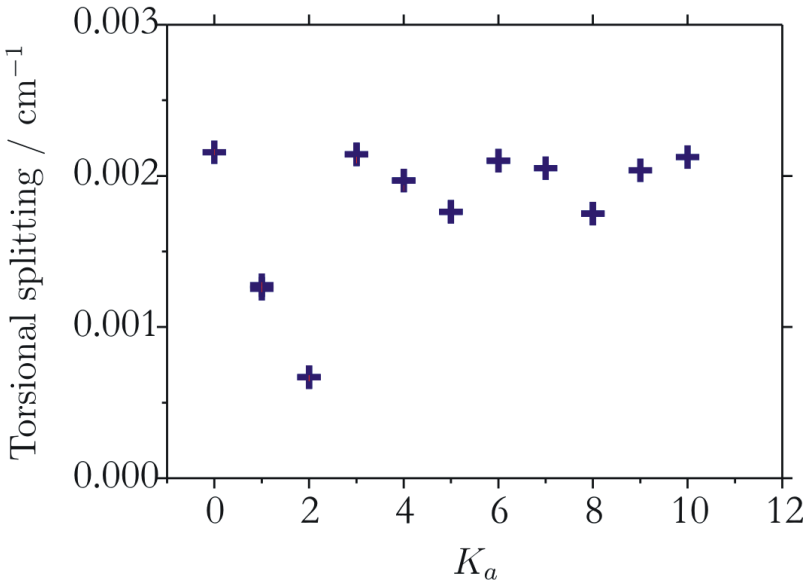


Experiment

Cologne Terahertz spectrometer

Theory

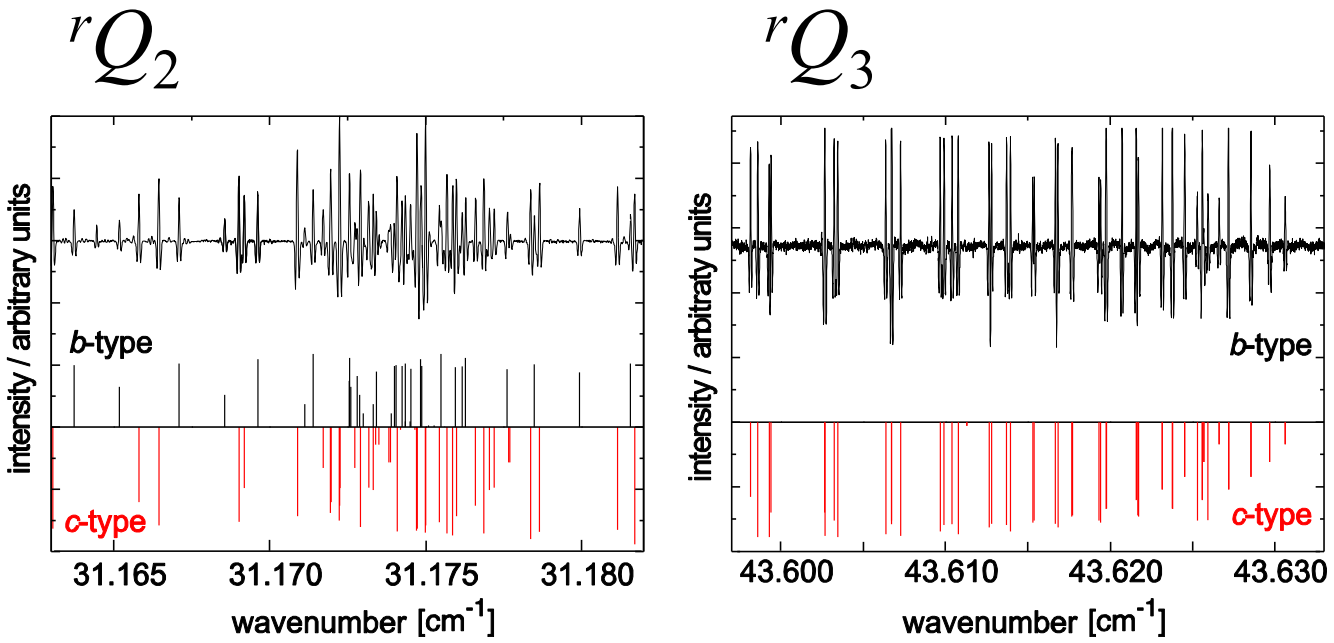
TROVE calculations



R. I. Ovsyannikov, V.V. Melnikov, W. Thiel, Per Jensen, O. Baum, T. F. Giesen, and S. N. Yurchenko, *J. Chem. Phys.* **129**, 154314 (2008).
O. Baum, M. Koerber, O. Ricken, G. Winnewisser *et al.*, *J. Chem. Phys.* **129**, 224312 (2008).

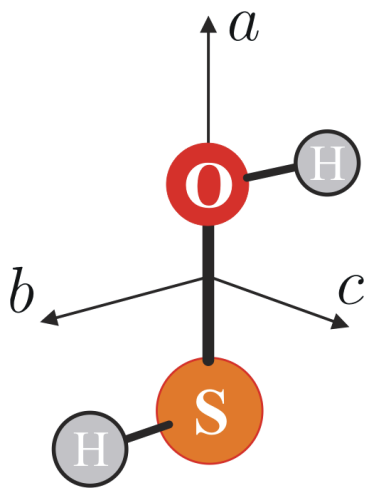
HSOH "intensity anomaly" in the rotational spectrum

Experiment:



No *b*-type transitions for $^rQ_3$.
Why?

O. Baum, M. Koerber, O. Ricken, G. Winnewisser, S. N. Yurchenko, S. Schlemmer, K. M. T. Yamada, and T. F. Giesen, *J. Chem. Phys.*, **129**, 224312 (2008).



$\bar{\mu}_a$, $\bar{\mu}_b$, $\bar{\mu}_c$ are dipole moment components along the principal axes

$\bar{\mu}_a$ is small for HSOH

When rotation and vibration are separable, there are *b*-type and *c*-type transitions with the intensity ratio

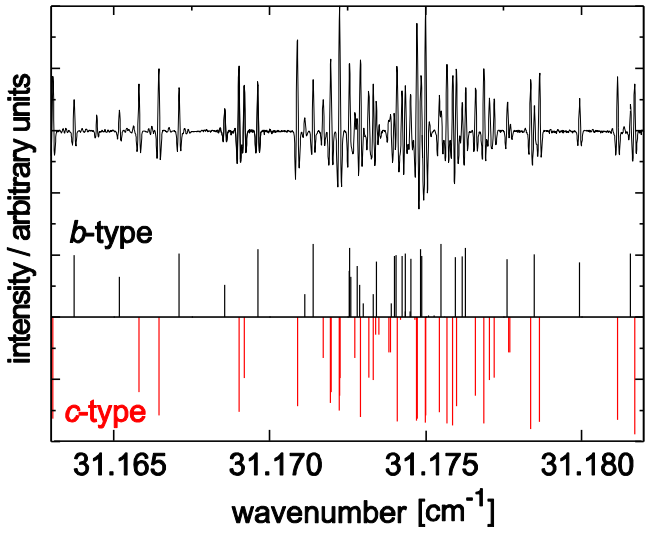
$$\frac{I_b}{I_c} \approx \frac{\bar{\mu}_b^2}{\bar{\mu}_c^2} \approx 0.28$$

From theoretical dipole moment

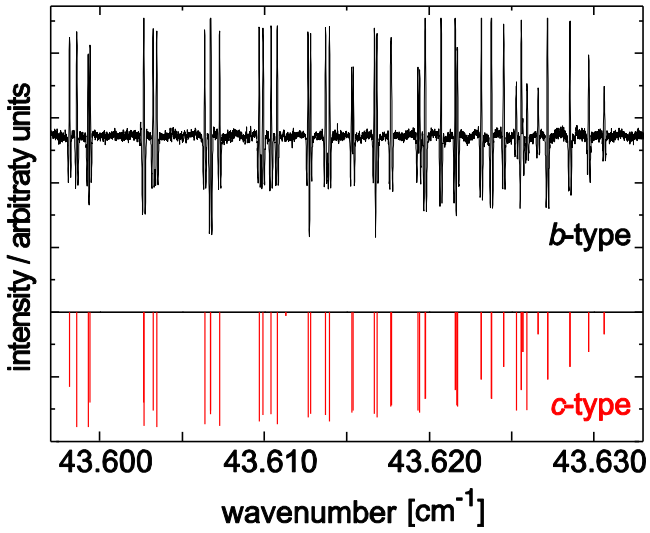
b/*c* intensity ratio is 0.22 for $^{r}Q_0$ and 0.23 for $^{r}Q_1$.

However, for higher *K*:

$^{r}Q_2$



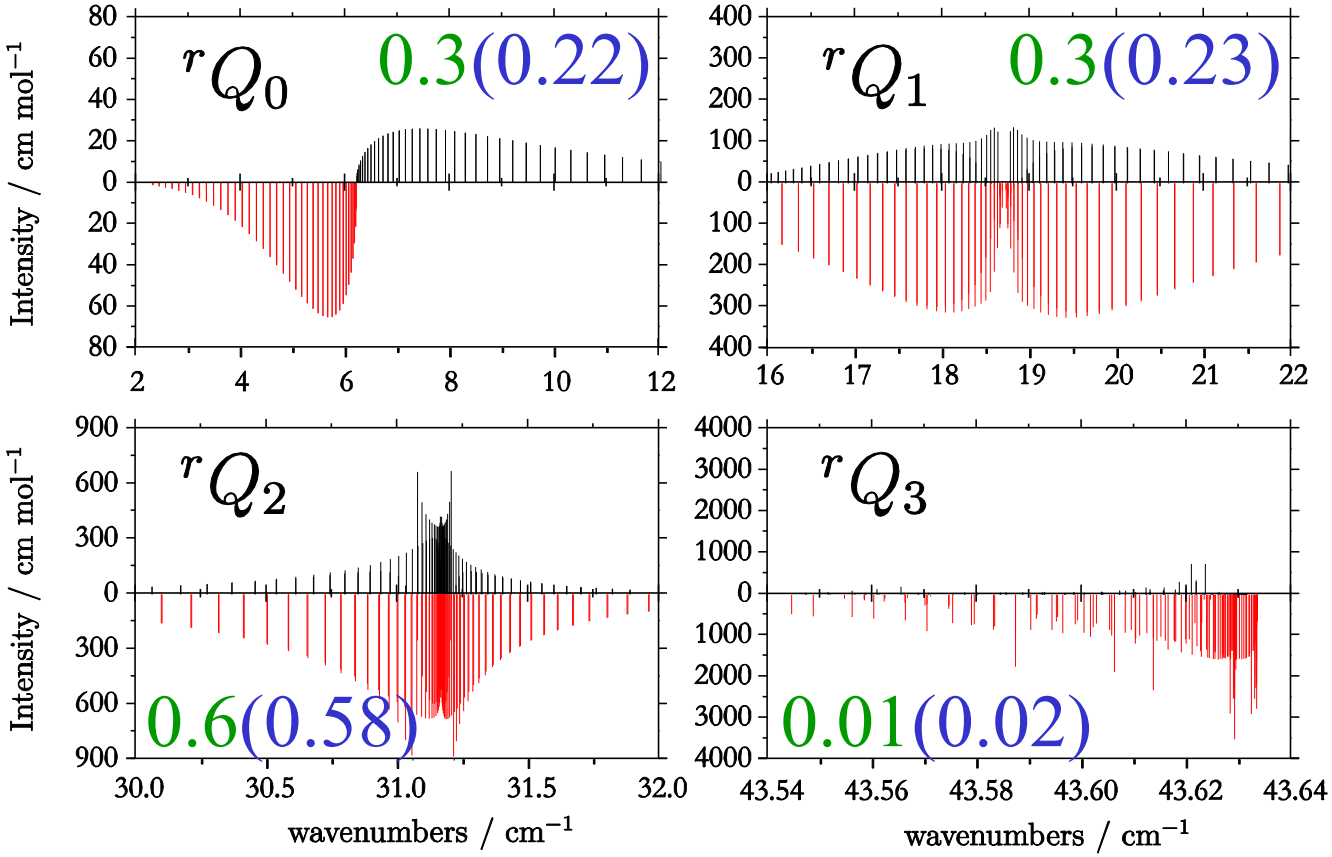
$^{r}Q_3$



$$\frac{I_b}{I_c} \approx 0.58 \qquad \frac{I_b}{I_c} \approx 0.02$$

O. Baum, M. Koerber, O. Ricken, G. Winnewisser, S. N. Yurchenko, S. Schlemmer, K. M. T. Yamada, and T. F. Giesen, *J. Chem. Phys.*, **129**, 224312 (2008).

TROVE theoretical simulations:



A. Yachmenev, S. N. Yurchenko, Per Jensen, O. Baum, T. F. Giesen, and W. Thiel, *Phys. Chem. Chem. Phys.* **12**, 8387 - 8397 (2010).

Explanation: Torsion-rotation interaction

For a given K_a-value there are four torsion-rotation states [two K_c-values $\times$ ($\pm$ torsional parity)]

$$
\begin{aligned}
\Psi^{A'(1)}_{J,K_a,i} &\approx \quad c_{J,K_a}|J,K_a,0\rangle\phi^{(\mathrm{vib})}_{K_a,0} + s_{J,K_a}|J,K_a,1\rangle\phi^{(\mathrm{vib})}_{K_a,1},\\
\Psi^{A'(2)}_{J,K_a,i} &\approx -s_{J,K_a}|J,K_a,0\rangle\phi^{(\mathrm{vib})}_{K_a,0} + c_{J,K_a}|J,K_a,1\rangle\phi^{(\mathrm{vib})}_{K_a,1},\\
\Psi^{A''(1)}_{J,K_a,i} &\approx \quad c_{J,K_a}|J,K_a,0\rangle\phi^{(\mathrm{vib})}_{K_a,1} + s_{J,K_a}|J,K_a,1\rangle\phi^{(\mathrm{vib})}_{K_a,0},\\
\Psi^{A''(2)}_{J,K_a,i} &\approx -s_{J,K_a}|J,K_a,0\rangle\phi^{(\mathrm{vib})}_{K_a,1} + c_{J,K_a}|J,K_a,1\rangle\phi^{(\mathrm{vib})}_{K_a,0},
\end{aligned}
$$

where $c_{J,K_a} = \cos(\theta_{J,K_a})$ and $s_{J,K_a} = \sin(\theta_{J,K_a})$ with the mixing angle $\theta_{J,K_a} \in [0, \pi/4]$ so that $c_{J,K_a} \geq s_{J,K_a}$.

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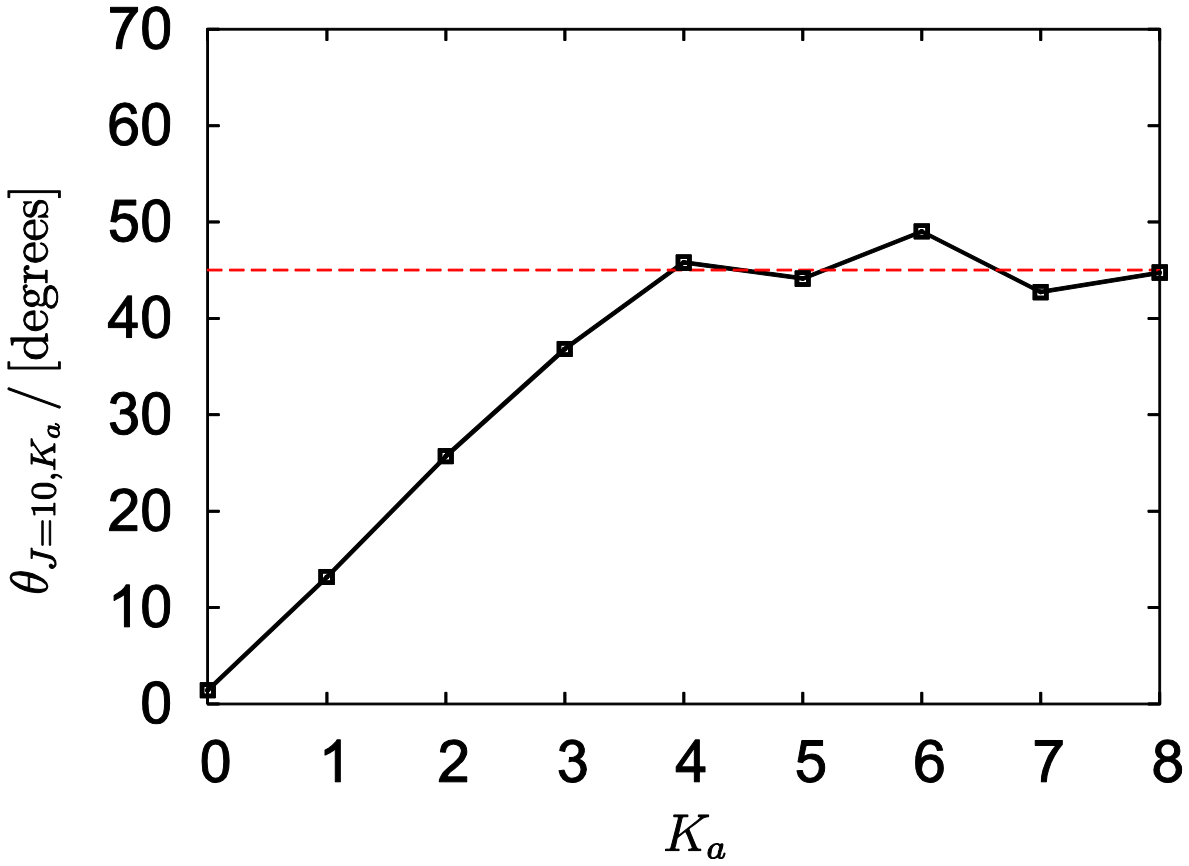
„Interaction angle“ $\theta_{J,Ka}$

$\theta_{J,Ka} \approx 0°$ for low K_a – no interaction.
$\theta_{J,Ka} \approx 45°$ for high K_a – 50-50 mixing.



Approximate line strengths

$$
\begin{aligned}
S_{A'(1)\leftrightarrow A''(1)} &= S_{A'(2)\leftrightarrow A''(2)} = g_{\mathrm{ns}}\, A(J, K_a) \\
&\times \Big[\cos^2\left(\theta_{J,K_a+1} - \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_b | \phi^{(\mathrm{vib})}_{K_a+1,0} \right\rangle^2 \\
&\qquad + \sin^2\left(\theta_{J,K_a+1} + \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_c | \phi^{(\mathrm{vib})}_{K_a+1,1} \right\rangle^2 \Big]
\end{aligned}
$$

$$
\begin{aligned}
S_{A'(1)\leftrightarrow A''(2)} &= S_{A'(2)\leftrightarrow A''(1)} = g_{\mathrm{ns}}\, A(J, K_a) \\
&\times \Big[\cos^2\left(\theta_{J,K_a+1} + \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_c | \phi^{(\mathrm{vib})}_{K_a+1,1} \right\rangle^2 \\
&\qquad + \sin^2\left(\theta_{J,K_a+1} - \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_b | \phi^{(\mathrm{vib})}_{K_a+1,0} \right\rangle^2 \Big]
\end{aligned}
$$

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Approximate line strengths

$\theta_{J,Ka} \approx \theta_{J,Ka+1} \approx 0°$, low K_a

$$S_{A'(1)\leftrightarrow A''(1)} = S_{A'(2)\leftrightarrow A''(2)} = g_{\mathrm{ns}}\, A(J, K_a)$$
$$\times \Big[\cos^2\left(\theta_{J,K_a+1} - \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_b | \phi^{(\mathrm{vib})}_{K_a+1,0} \right\rangle^2$$
$$+ \sin^2\left(\theta_{J,K_a+1} + \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_c | \phi^{(\mathrm{vib})}_{K_a+1,1} \right\rangle^2 \Big]$$

b-type

1

0

$$S_{A'(1)\leftrightarrow A''(2)} = S_{A'(2)\leftrightarrow A''(1)} = g_{\mathrm{ns}}\, A(J, K_a)$$
$$\times \Big[\cos^2\left(\theta_{J,K_a+1} + \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_c | \phi^{(\mathrm{vib})}_{K_a+1,1} \right\rangle^2$$
$$+ \sin^2\left(\theta_{J,K_a+1} - \theta_{J,K_a}\right) \left\langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_b | \phi^{(\mathrm{vib})}_{K_a+1,0} \right\rangle^2 \Big]$$

c-type

1

0

Approximate line strengths

$\theta_{J,Ka} \approx \theta_{J,Ka+1} \approx 45°$, high K_a

$$S_{A'(1)\leftrightarrow A''(1)} = S_{A'(2)\leftrightarrow A''(2)} = g_{\mathrm{ns}}\, A(J, K_a)$$
$$\times \Big[\cos^2\left(\theta_{J,K_a+1} - \theta_{J,K_a}\right) \langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_b | \phi^{(\mathrm{vib})}_{K_a+1,0} \rangle^2$$
$$+ \sin^2\left(\theta_{J,K_a+1} + \theta_{J,K_a}\right) \langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_c | \phi^{(\mathrm{vib})}_{K_a+1,1} \rangle^2 \Big]$$

„Hybrid“

1

1

$$S_{A'(1)\leftrightarrow A''(2)} = S_{A'(2)\leftrightarrow A''(1)} = g_{\mathrm{ns}}\, A(J, K_a)$$
$$\times \Big[\cos^2\left(\theta_{J,K_a+1} + \theta_{J,K_a}\right) \langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_c | \phi^{(\mathrm{vib})}_{K_a+1,1} \rangle^2$$
$$+ \sin^2\left(\theta_{J,K_a+1} - \theta_{J,K_a}\right) \langle \phi^{(\mathrm{vib})}_{K_a,0} | \bar{\mu}_b | \phi^{(\mathrm{vib})}_{K_a+1,0} \rangle^2 \Big]$$

Missing

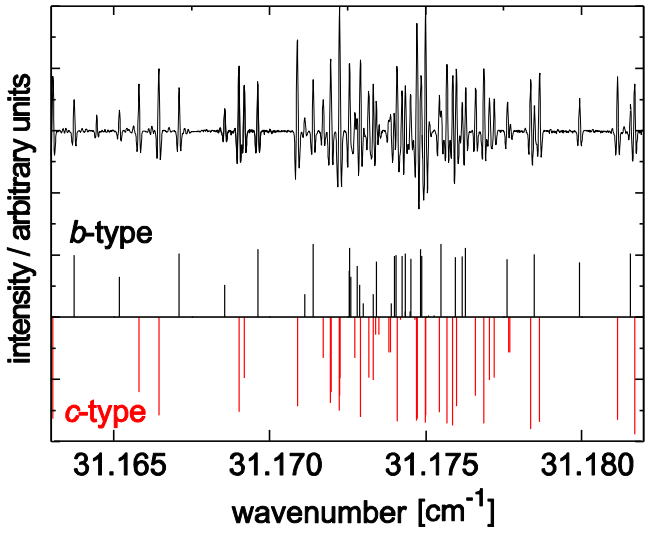
0

0

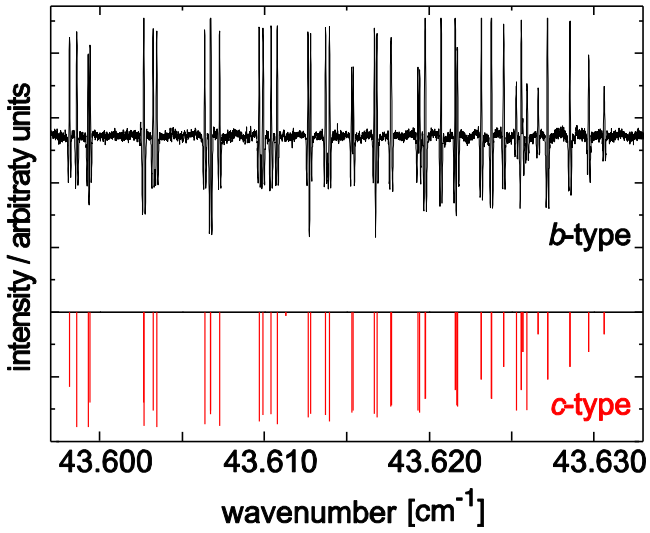
b/*c* intensity ratio is 0.22 for $^{r}Q_0$ and 0.23 for $^{r}Q_1$.

However, for higher *K*:

$^{r}Q_2$



$^{r}Q_3$



$$\frac{I_b}{I_c} \approx 0.58 \qquad \frac{I_b}{I_c} \approx 0.02$$

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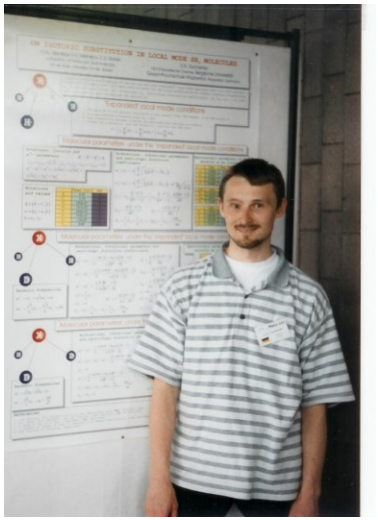
Thanks & Acknowledgments



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