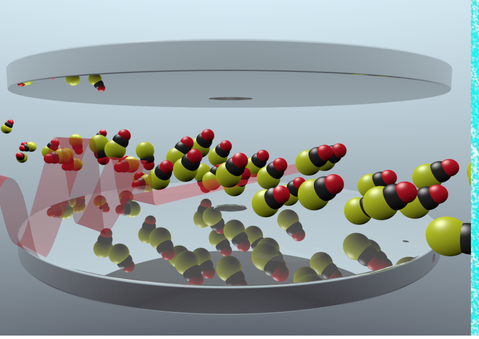
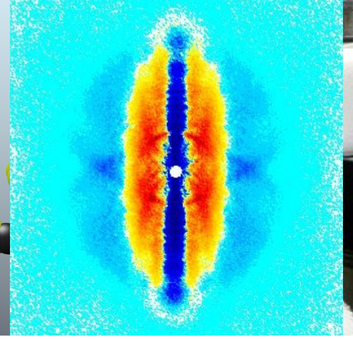
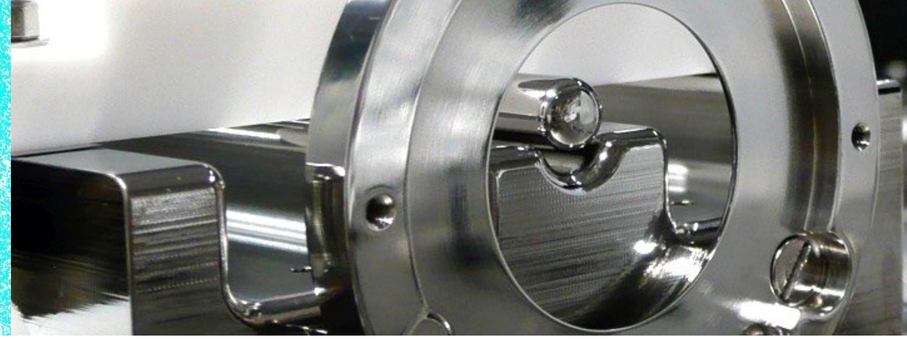
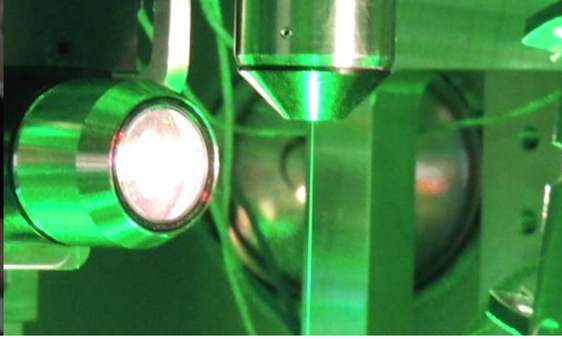

Predicting *para-ortho* conversion in ammonia

Guang Yang, Vinicius Silva de Oliveira, Christoph Heyl, Andrey Yachmenev, Ingmar Hartl, Jochen Küpper

Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg

Deutsches Elektronen-Synchrotron DESY

Department of Physics, Universität Hamburg

The Hamburg Center for Ultrafast Imaging, Universität Hamburg

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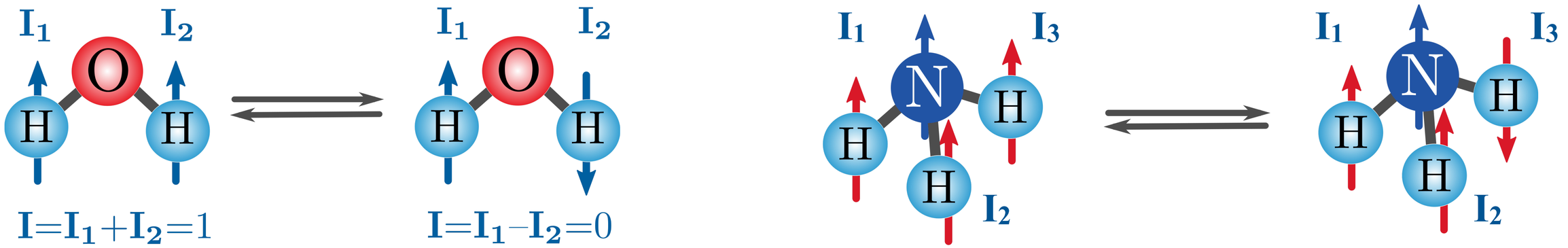
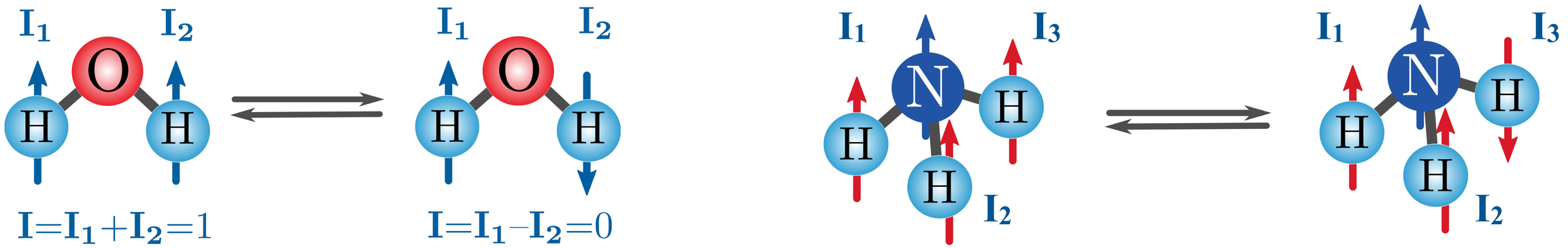
Nuclear-spin modifications of water and ammonia



***ortho*-H_2O** ***para*-H_2O** ***ortho*-NH_3** ***para*-NH_3**

Hama, Watanabe, *Chem. Rev.* **113**, 8783 (2013)
van Dishoeck, Herbst, Neufeld, *Chem. Rev.* **113**, 9043 (2013)

Nuclear-spin modifications of water and ammonia



***ortho*-H_2O** ***para*-H_2O** ***ortho*-NH_3** ***para*-NH_3**

Hama, Watanabe, *Chem. Rev.* **113**, 8783 (2013)
van Dishoeck, Herbst, Neufeld, *Chem. Rev.* **113**, 9043 (2013)

Microwave transitions between *para* and *ortho* states

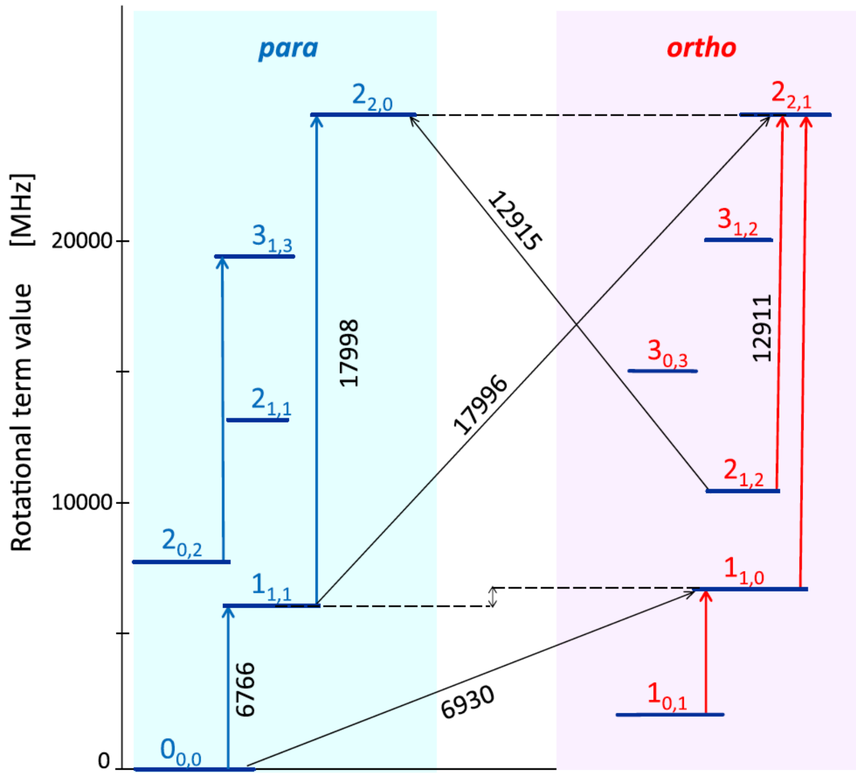
PRL **119,** 173401 (2017) PHYSICAL REVIEW LETTERS week ending 27 OCTOBER 2017

Detection of Microwave Transitions between Ortho and Para States in a Free Isolated Molecule

Hideto Kanamori,[1,*] Zeinab. T. Dehghani,[1] Asao Mizoguchi,[1] and Yasuki Endo[2]
[1]*Department of Physics, Tokyo Institute of Technology, Tokyo 152-8551, Japan*
[2]*Department of Applied Chemistry, National Chiao, Tung University, Hsinchu 30010, Taiwan*
(Received 9 August 2017; published 25 October 2017)

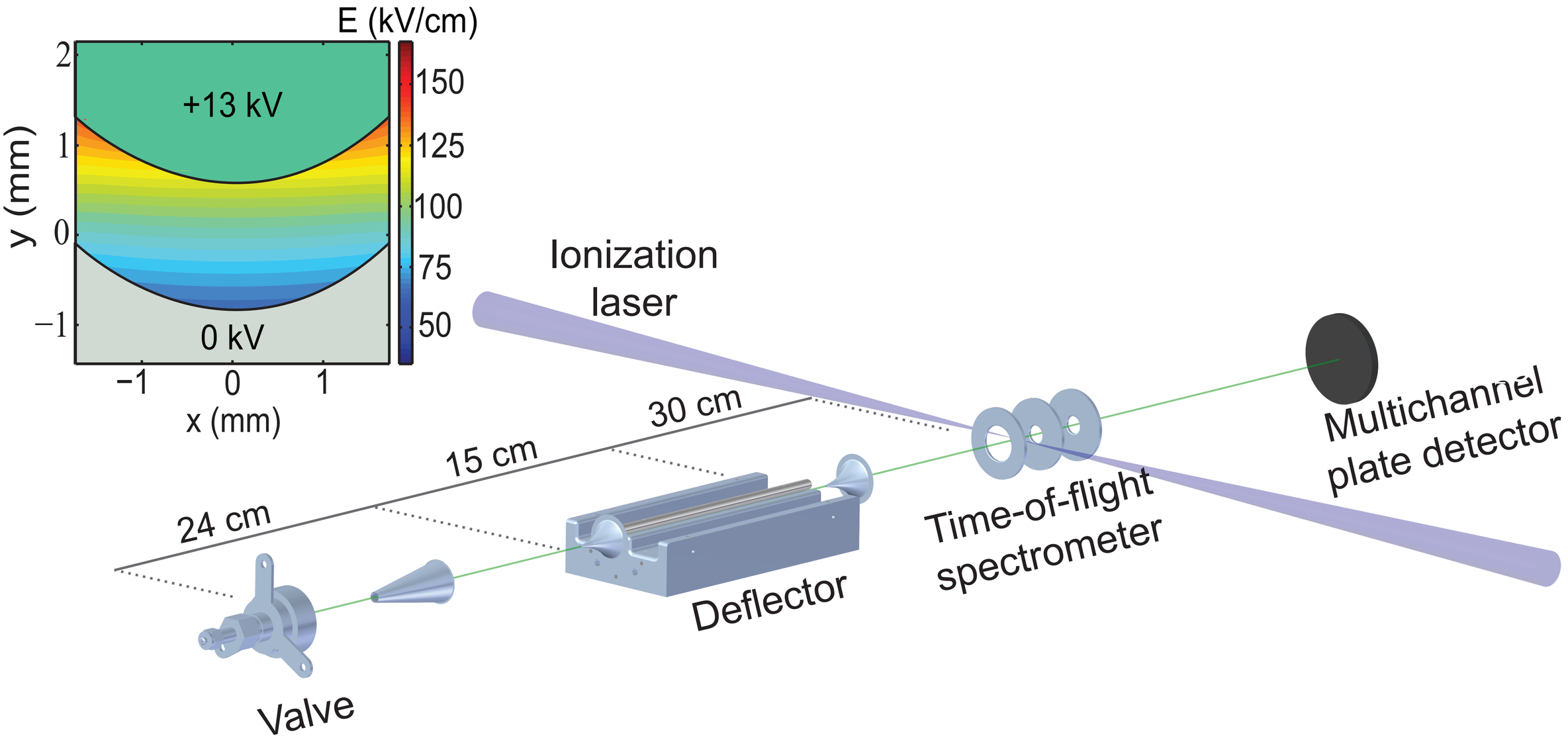
Microwave transitions between the ortho and para states of the S_2Cl_2 molecule in a free isolated condition are observed for the first time. In the theoretical treatment, we derive eigenfunctions of an effective Hamiltonian including the ortho-para interaction to calculate the intensities and frequencies of forbidden ortho-para transitions in the cm-wave region and pick up some promising candidates for the spectroscopic detection. In the experiment, transitions of the S_2Cl_2 molecule under a supersonic jet condition are observed with a Fourier transform microwave spectrometer. Seven hyperfine resolved rotational transitions including the lowest rotational level are detected as the ortho-para transitions at the predicted frequencies within the experimental errors. The observed intensities are about 10^{-3} times the allowed transitions, which are consistent with the predictions based on the intensity-borrowing model. This result suggests that the ortho-para conversion of this molecule occurs in a few thousand years through spontaneous emission even in a circumstance where molecular collisions occur rarely like in interstellar space.

DOI: 10.1103/PhysRevLett.119.173401



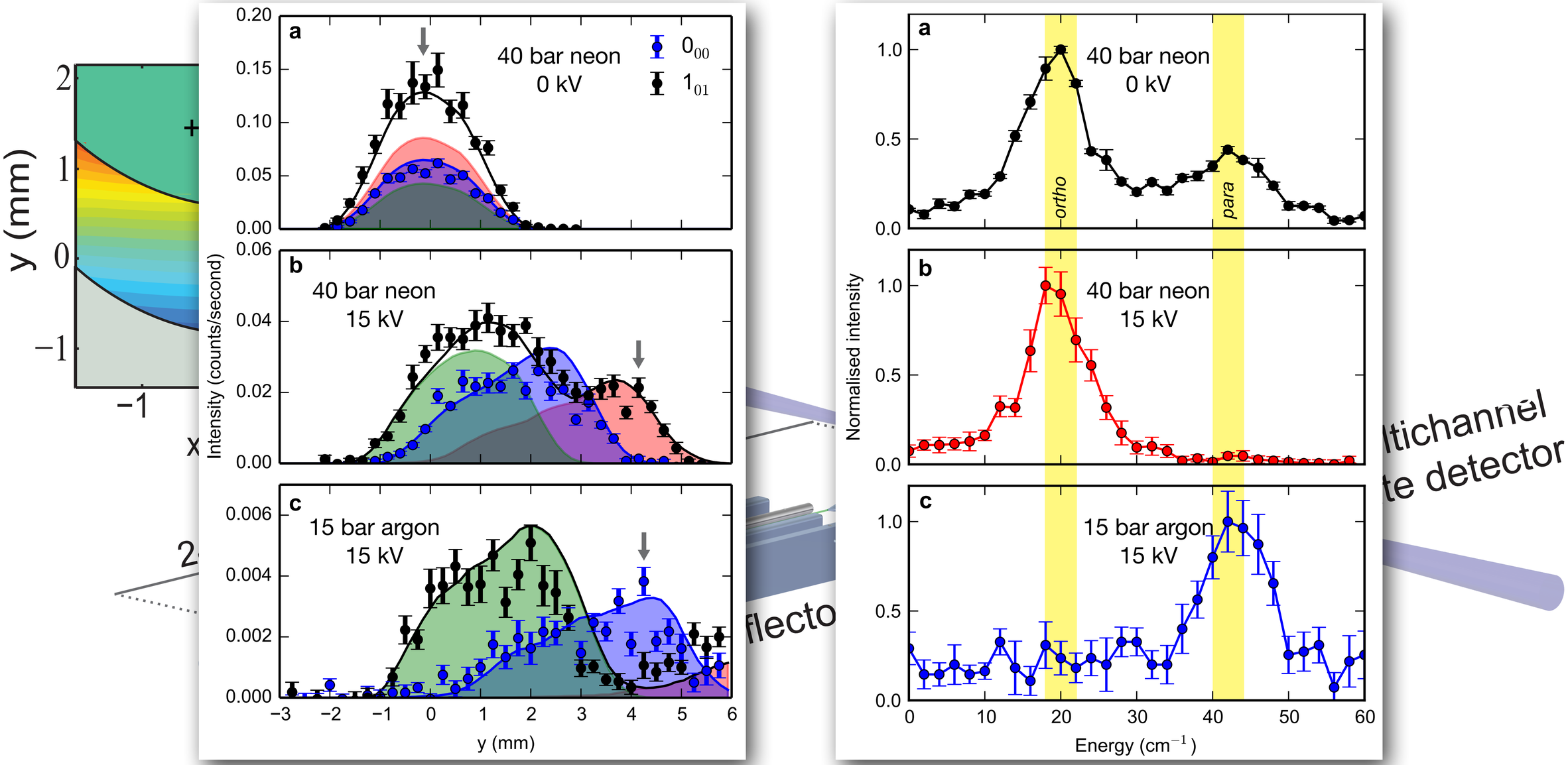
Kanamori, Dehghani, Mizoguchi, Endo, *Phys. Rev. Lett.* **119**, 173401 (2017)

Spatial separation of *para* and *ortho* water



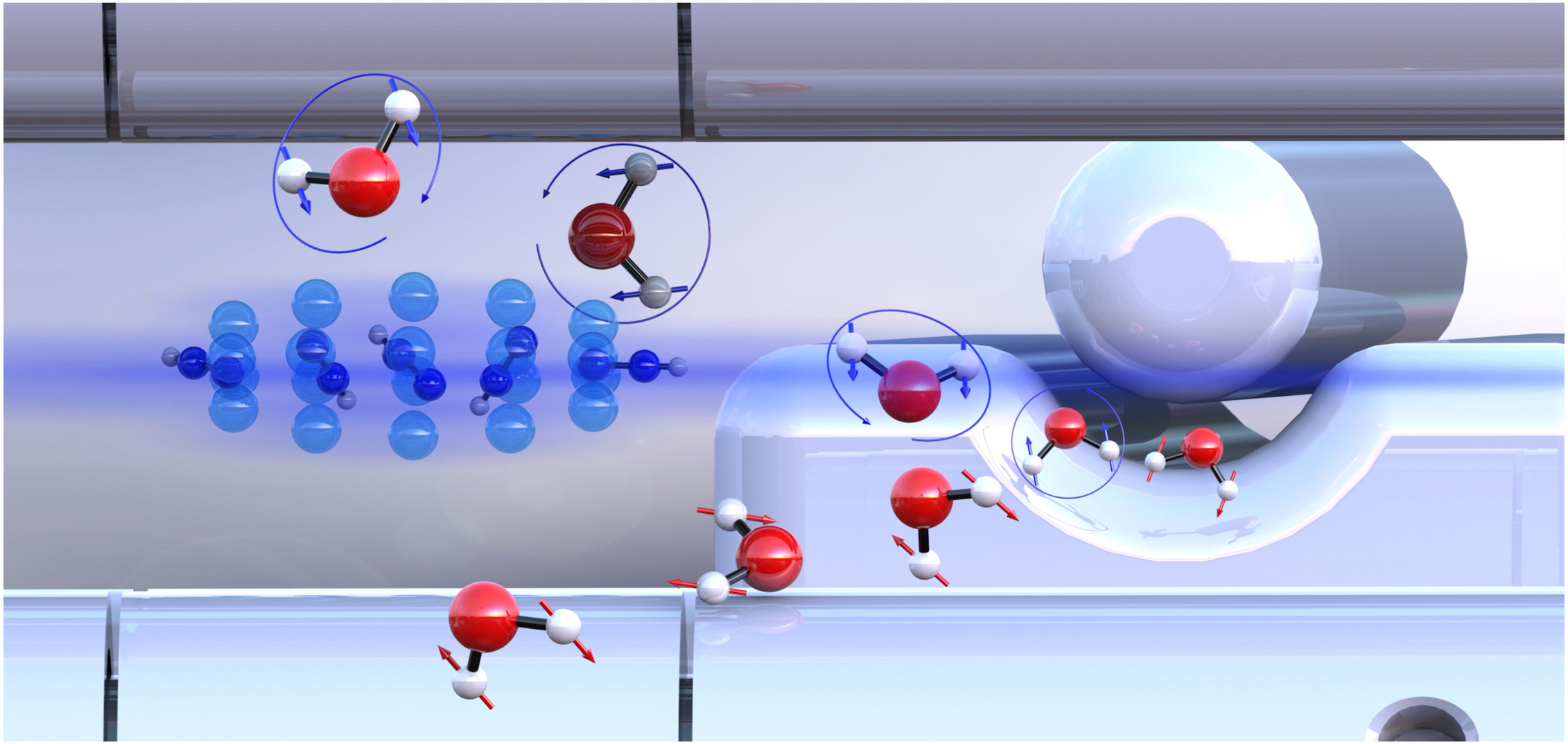
Horke, Chang, Długołęcki, Küpper, *Angew. Chem. Int. Ed.* **53**, 11965 (2014, VIP)

Spatial separation of *para* and *ortho* water



Horke, Chang, Długołęcki, Küpper, *Angew. Chem. Int. Ed.* **53**, 11965 (2014, VIP)

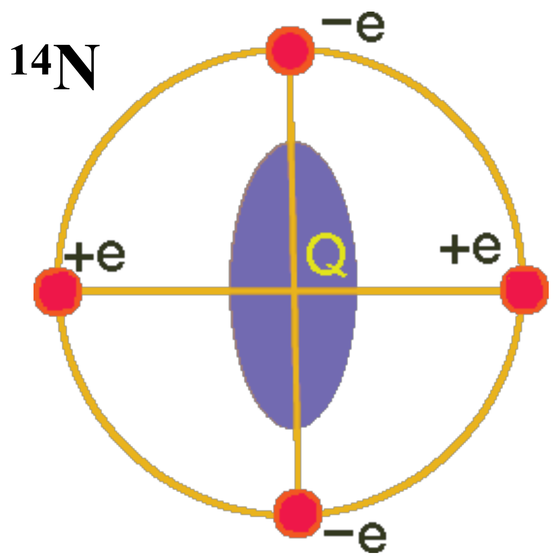
Specific chemical reactions of *para* and *ortho* water



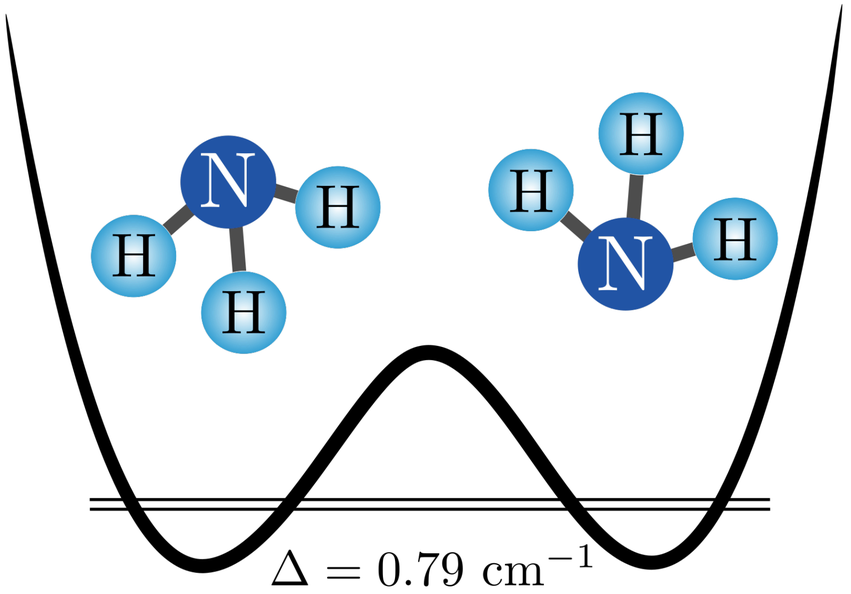
$$H_2O + N_2H^+ \rightarrow N_2 + H_3O^+$$

Kilaj, Gao, Rösch, Rivero, Küpper, Willitsch, *Nat. Commun.* **9**, 2096 (2018)

Why ammonia first?

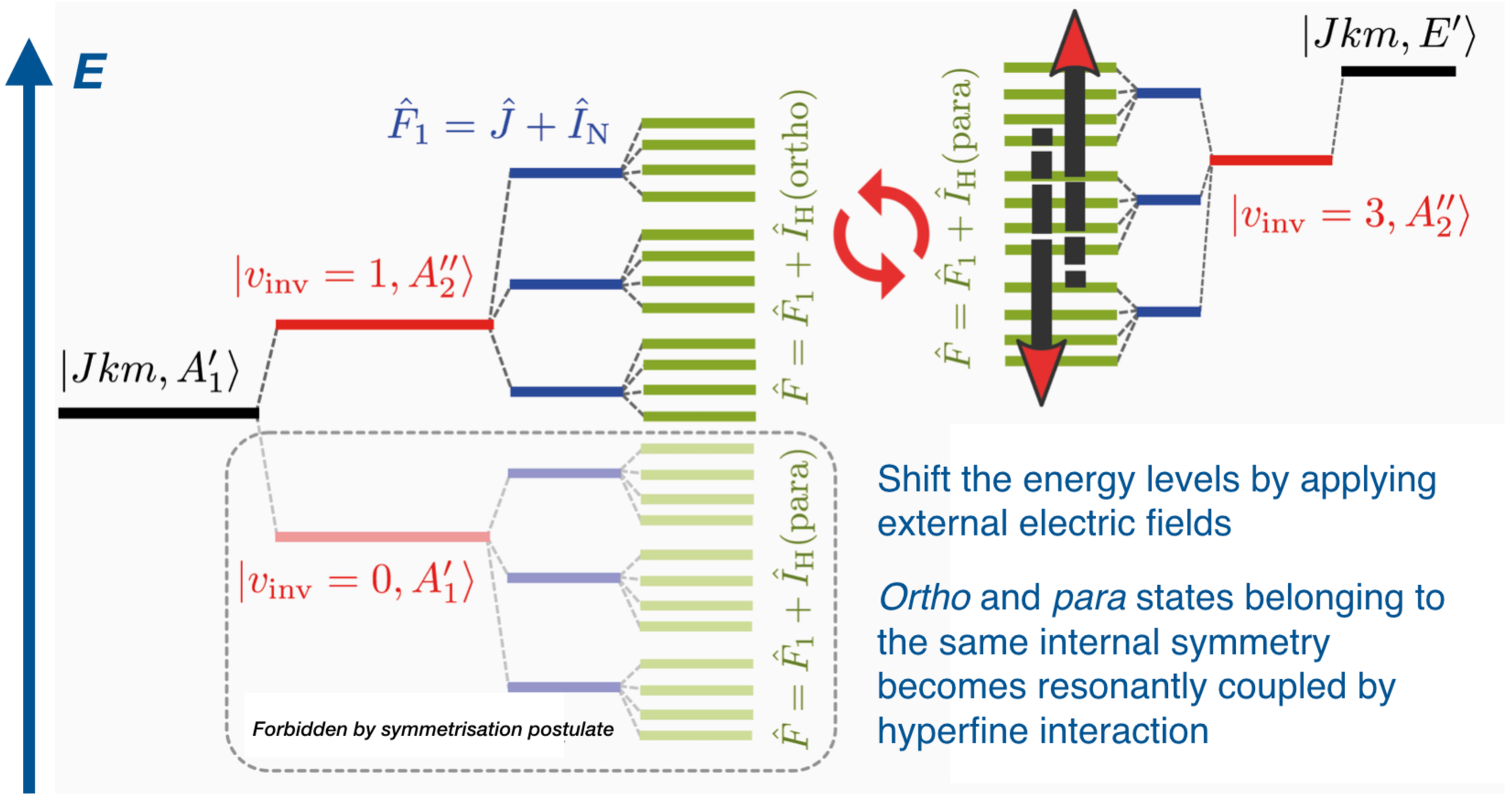


More complex hyperfine structure due to the nuclear quadrupole moment on the N atom.



Low barrier double-well potential: high sensitivity to external and induced internal electromagnetic field perturbations.

Hyperfine interactions between rovibrational states



Shift the energy levels by applying external electric fields

Ortho and *para* states belonging to the same internal symmetry becomes resonantly coupled by hyperfine interaction

Methodology

- Theoretical predictions for kHz-precision experiment
- High-quality (SNR, frequency accuracy, intensity accuracy) spectrum of ammonia
- Cover the whole branch with 15 MHz frequency spacing
- Narrowband with 1 kHz frequency spacing
- Select the most promising rovibrational levels for observations of *para-ortho* transitions

Rigorous variational approach

Spin-rovibrational Hamiltonian

$$H = H_{\mathrm{rv}} + \sum_{l}^{L} \mathbf{V}(l)\hat{\mathbf{Q}}(l) + \sum_{l}^{L} \hat{\mathbf{I}}(l)\mathbf{D}_l\hat{\mathbf{J}} + \sum_{ll'}^{L} \hat{\mathbf{I}}(l)\mathbf{C}_{ll'}\hat{\mathbf{I}}(l')$$

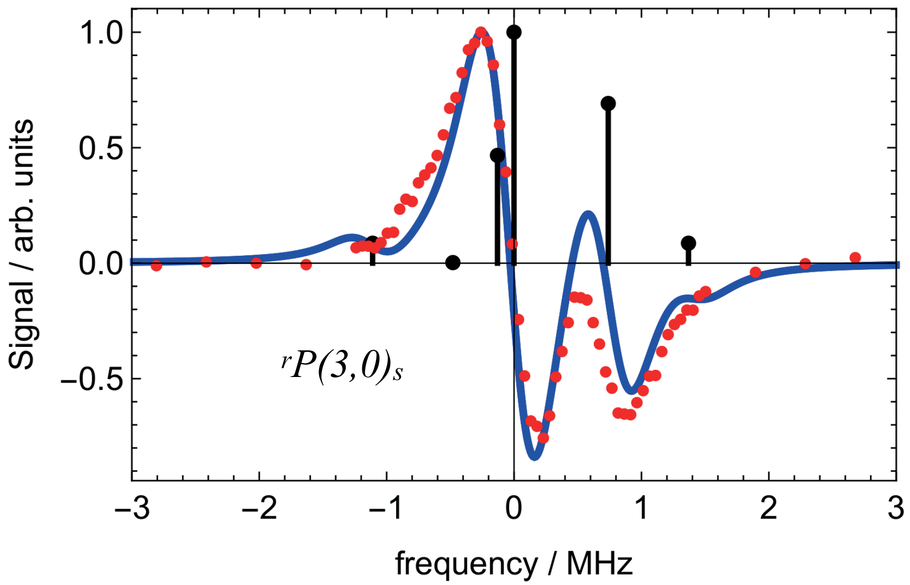
rotations-vibrations ground electronic state

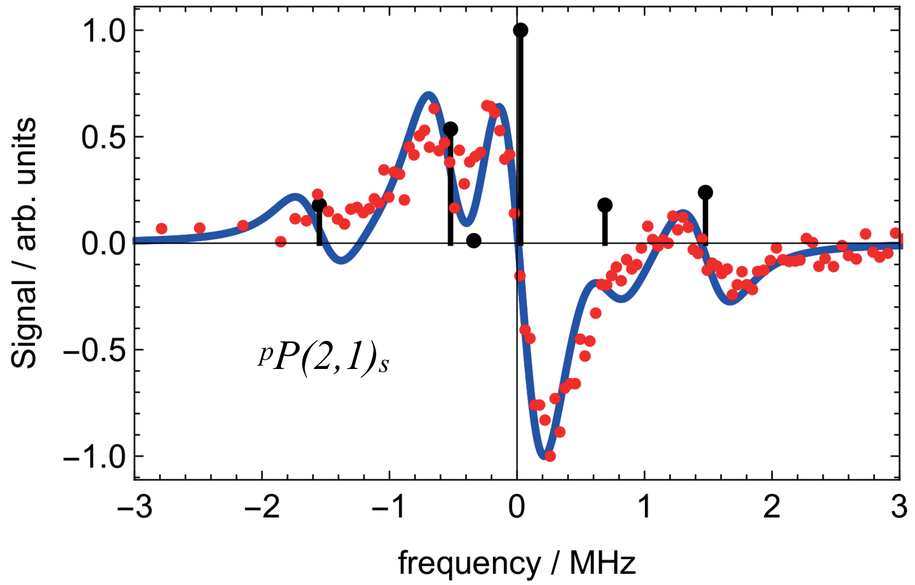
nuclear quadrupole interaction

nuclear spin-rotation interaction

nuclear spin-spin interaction

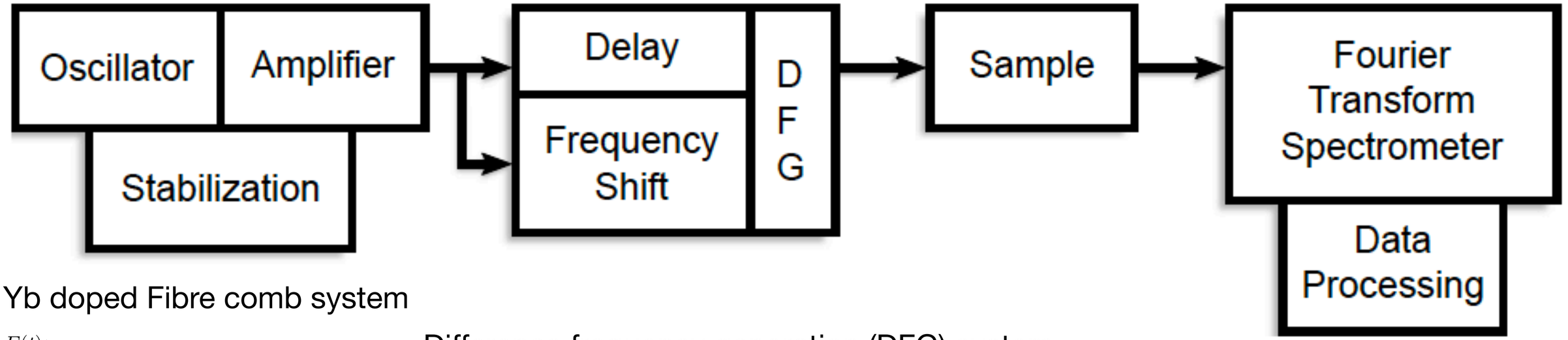
Sub-Doppler saturation dip profiles in the $\upsilon_1+\upsilon_3$ band of NH_3



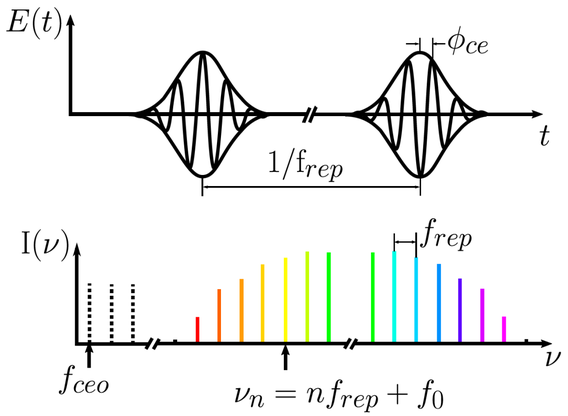


Experiment: Twagirayezu, Hall, Sears, *J. Chem. Phys.* **145**, 144302 (2016)
Theory: Yachmenev, Küpper, *J. Chem. Phys.* **147**, 141101 (2017)

Block diagram of state-of-the-art frequency comb spectrometer

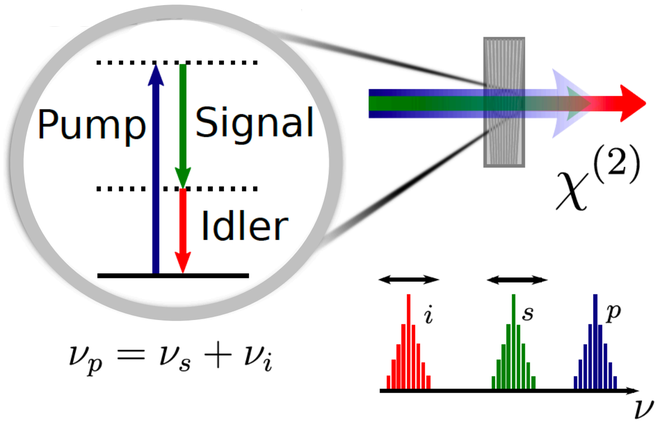


Yb doped Fibre comb system

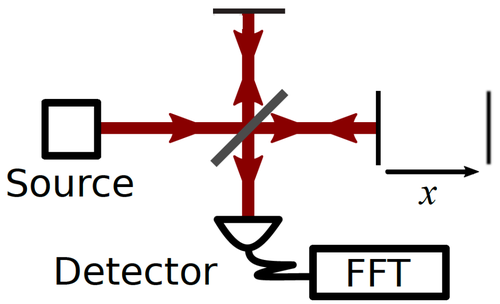


Central wavelength: 1050 nm
Repetition rate: 150 MHz
Pulse duration: ~100 fs

Difference frequency generation (DFG) system

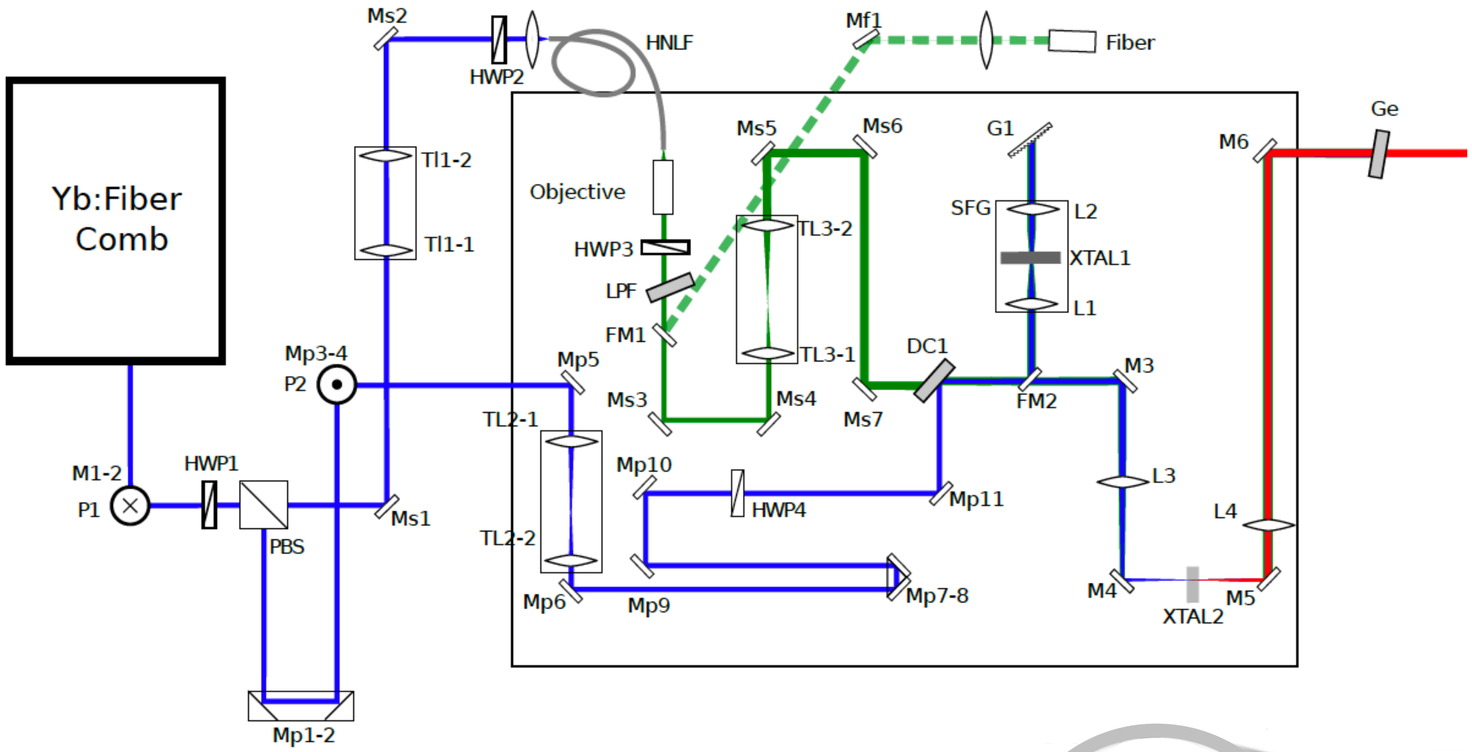


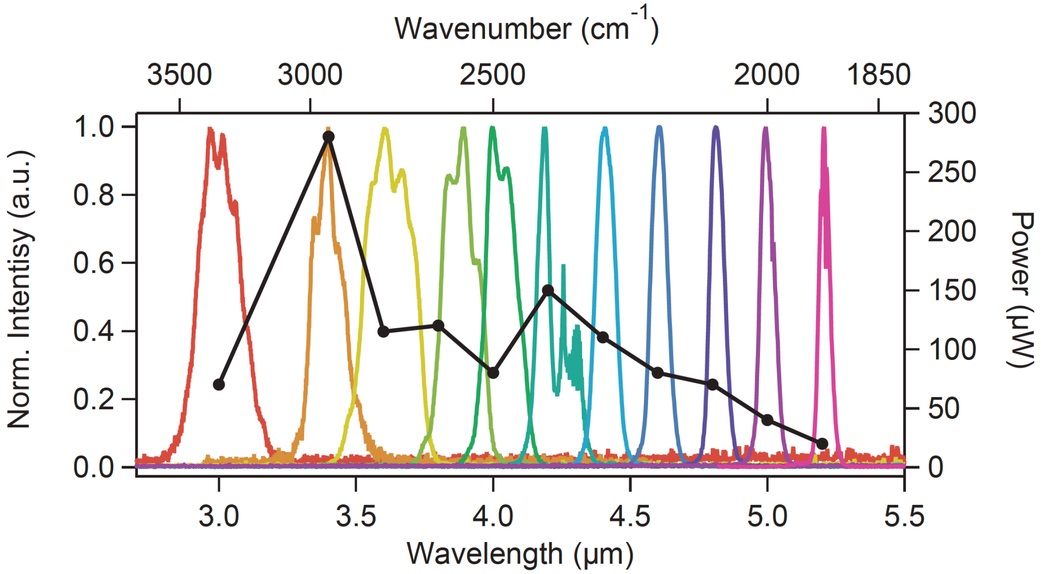
Fourier transform infrared (FTIR) system



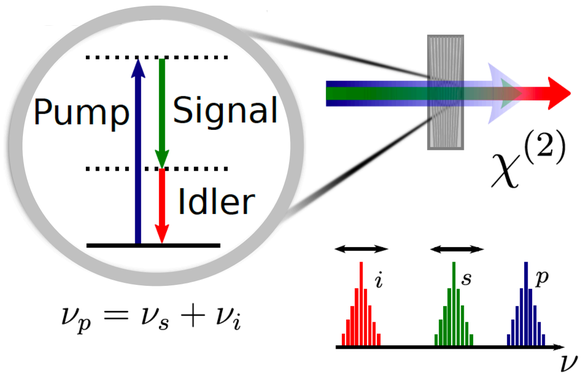
Rutkowski, Masłowski, Johansson, Khodabakhsh, Foltynowicz, *J. Quant. Spectrosc. Radiat. Transf.* **204**, 63 (2018)
Silva de Oliveira, *University of Hamburg*, PhD dissertation (2018)

Difference Frequency Generation (DFG)



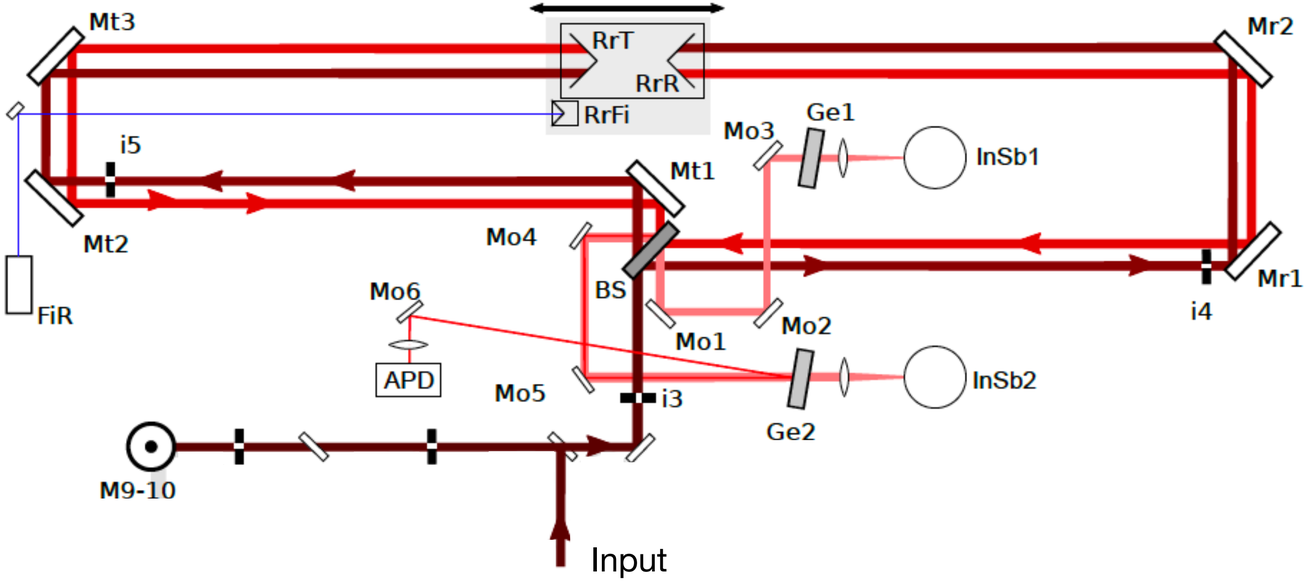


Crystal: Periodically poled lithium niobate (PPLN)
Crystal structure: Fan-out
Poling-periods: from 26.15 µm to 30.65 µm



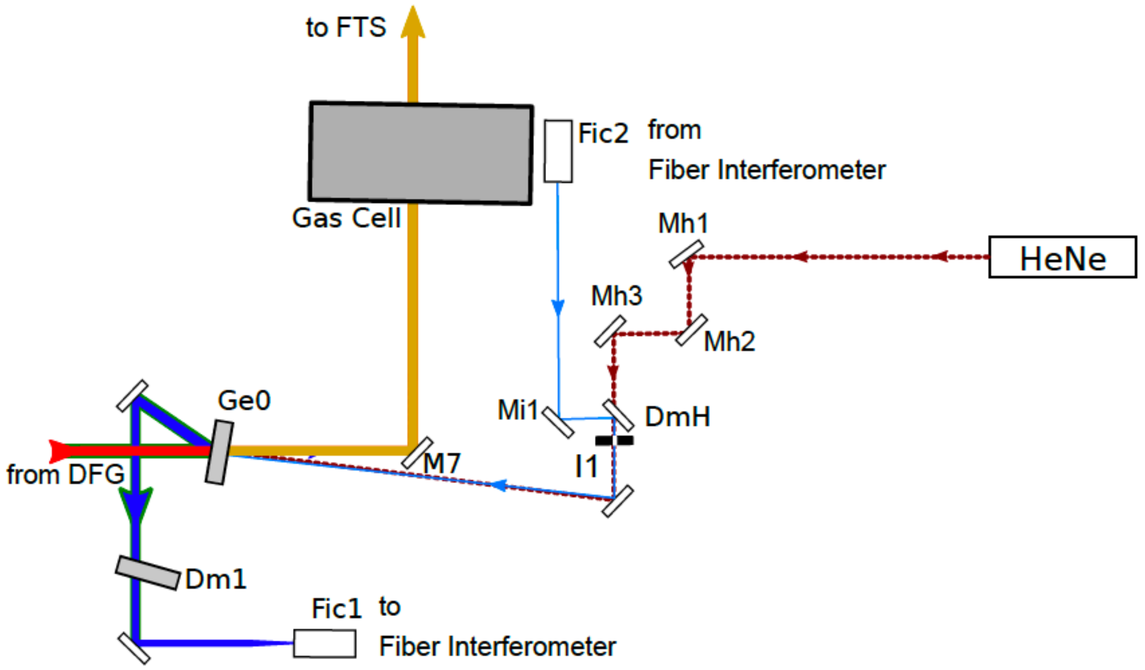
Tuning range: 3 µm to 5.1 µm

Fourier transform spectrometer (FTS)



Frequency stabilised helium-neon (HeNe, SIOS SL4)
Wavelength: 632.9909178 nm
Frequency: 473612436.6 MHz

Frequency spacing (resolution): 15 MHz



Summary and outlook

Have done in first step:

- Theoretical predictions for kHz-precision experiment
- Experimental setup preparation

Next steps:

- 15 MHz spectrum of ammonia in room temperature and cold condition
- Refinement and addition of theoretical predictions
- 1 kHz spectrum of cold beam of ammonia
- Predict and search for *para-ortho* transitions.

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Nicolai Pohlmann
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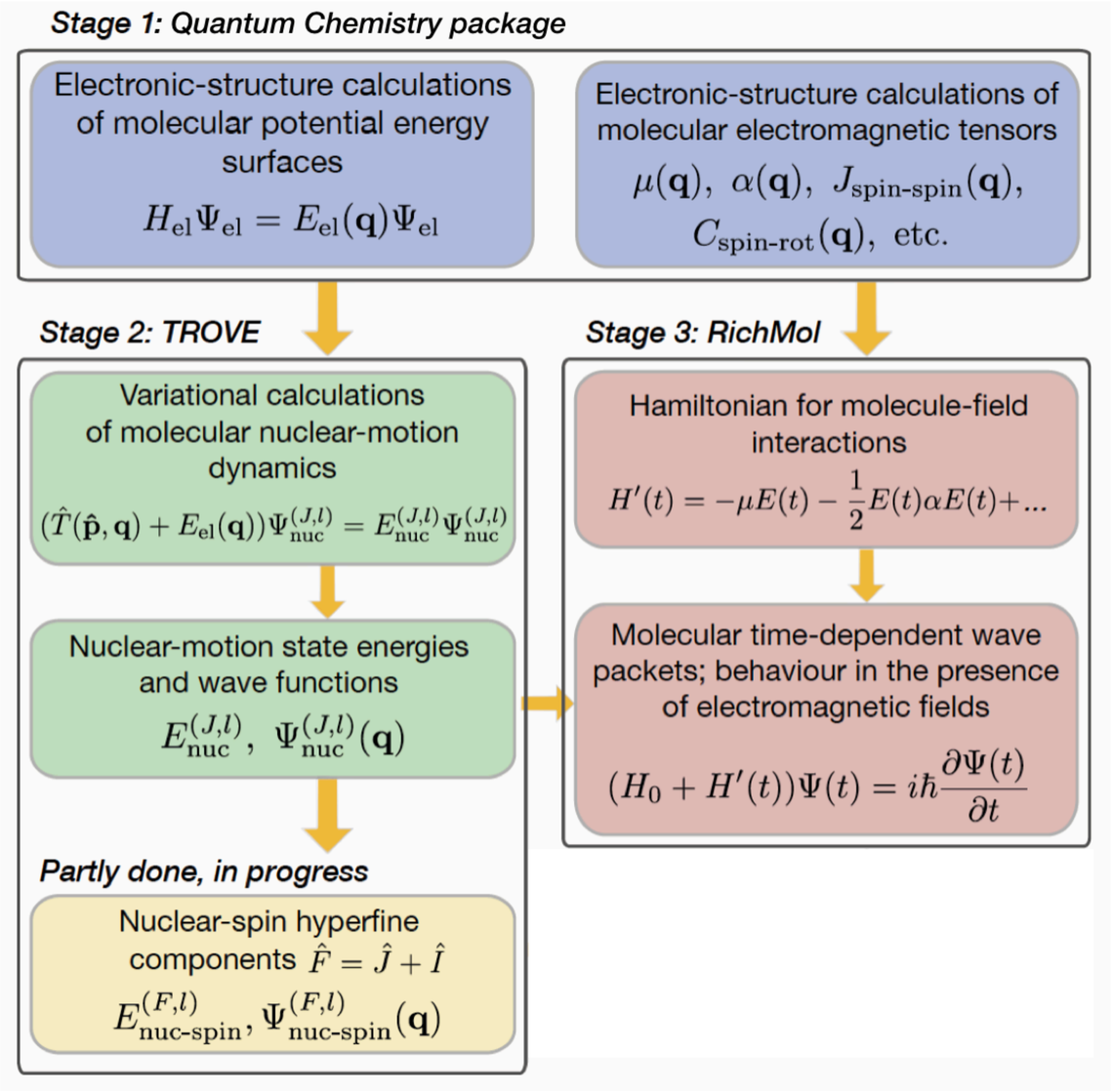
Overview of the theoretical approach



$$H = H_{\rm rv} + \sum_l^L \mathbf{V}(l)\hat{\mathbf{Q}}(l) + \sum_l^L \hat{\mathbf{I}}(l)\mathbf{D}_l\hat{\mathbf{J}} + \sum_{ll'}^L \hat{\mathbf{I}}(l)\mathbf{C}_{ll'}\hat{\mathbf{I}}(l')$$

rotations-vibrations ground electronic state — nuclear quadrupole interaction — nuclear spin-rotation interaction — nuclear spin-spin interaction

$$\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{J}}$$

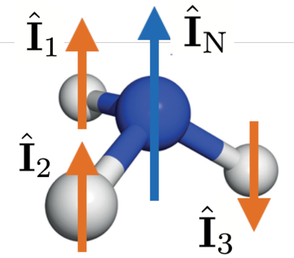
total angular momentum = overall rotation (J) + all nuclear spins (I)

$$\Psi_{\rm int} = \sum_{\mathcal{I}IJ} c^{(F)}_{\mathcal{I}IJ}\Psi^{(\mathcal{I},I,J,F,m_F)}_{\rm rvns}$$

total wavefunction couples different **rovibrational** and **spin** (*ortho* and *para*) states

$$\Psi^{(\mathcal{I},I,J,F,m_F)}_{\rm rvns} = \sum_m\sum_{m_I}(-1)^{J-I+m_F}\sqrt{2F+1}\begin{pmatrix} J & I & F \\ m & m_I & -m_F\end{pmatrix}\Psi^{(J,m)}_{\rm rv}\,\Psi^{(\mathcal{I},I,m_I)}_{\rm ns}$$

$$\left.\begin{aligned}\hat{\mathbf{I}}_{12} &= \hat{\mathbf{I}}_1 + \hat{\mathbf{I}}_2 \\ \hat{\mathbf{I}}_{13} &= \hat{\mathbf{I}}_{12} + \hat{\mathbf{I}}_3\end{aligned}\right\}\mathcal{I}$$
$$\hat{\mathbf{I}} = \hat{\mathbf{I}}_{13} + \hat{\mathbf{I}}_{\rm N}$$
$$\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$$



Yurchenko, Thiel, Jensen, *J. Mol. Spectrosc.* **245**, 126 (2007)
Yachmenev, Küpper, *J. Chem. Phys.* **147**, 141101 (2017)

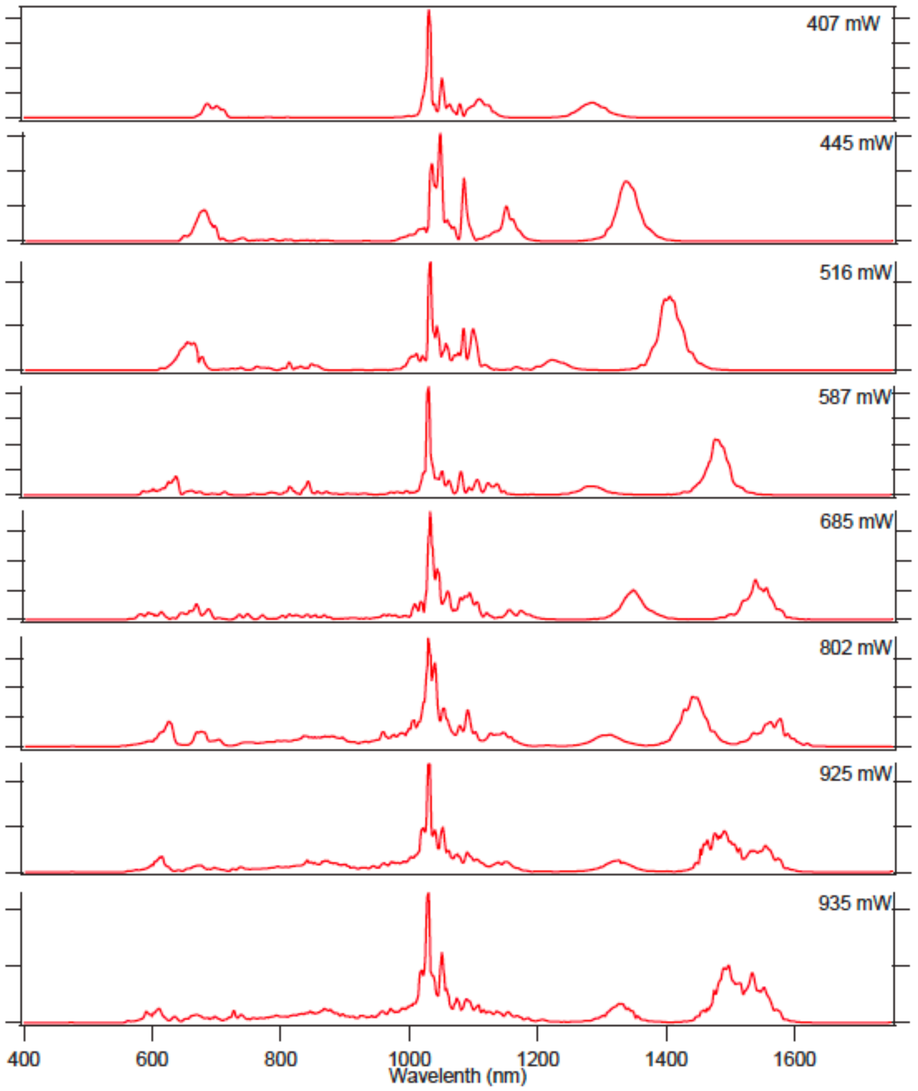
Vibrational transition in ammonia

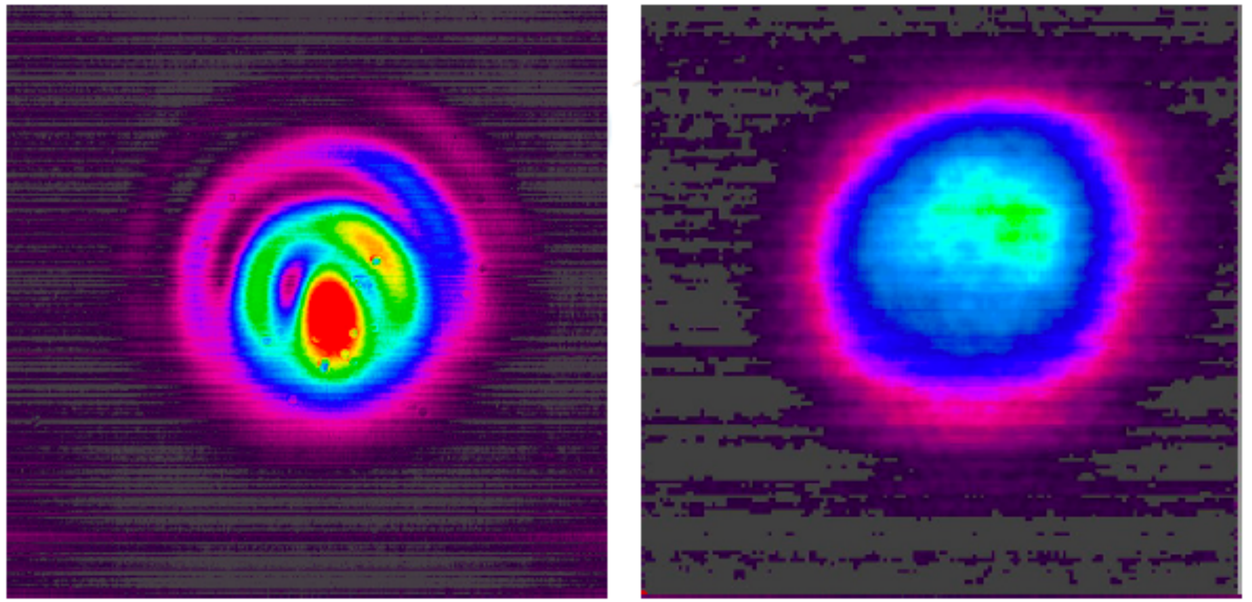
TABLE 3: Band Centers ν_{fi} and Vibrational Transition Moments μ_{fi} for NH_3; Transitions Originating in the Vibrational Ground State

states		ν_{fi}/cm^{-1}		μ_{fi}/D		
f	i	obs.[a]	obs.[b]	ref.[c]	ATZfc[d]	AQZfc[e]
0^-	0^+	0.79	1.47193(1)	45	1.4564	1.4638
ν_2^+	0^-	931.64	0.248(7)	75	0.2445	0.2467
ν_2^-	0^+	968.12	0.236(4)	75	0.2347	0.2366
$2\nu_2^+$	0^-	1596.68	0.02036(25)	67	0.0202	0.0210
ν_4^+	0^+	1626.27	0.08408(34)	67	0.0828	0.0841
ν_4^-	0^-	1626.58	0.08408(34)	67	0.0827	0.0840
$2\nu_2^-$	0^+	1882.18	0.003256(35)	67	0.0026	0.0030
$3\nu_2^+$	0^-	2383.35	0.00496(13)	68	0.0054	0.0053
$(\nu_2 + \nu_4)^+$	0^+	2540.53	0.002358(36)	68	0.0091	0.0085
$(\nu_2 + \nu_4)^-$	0^-	2894.73	0.002182(82)	68	0.0094	0.0089
$3\nu_2^-$	0^+	2895.52	0.002856(40)	68	0.0027	0.0027
$2\nu_4^{0,+}$	0^-	3215.31	0.00920(6)[f]	70	0.0073	0.0064
$2\nu_4^{0,-}$	0^+	3217.58	0.00920(6)[f]	70	0.0074	0.0066
$2\nu_4^{\pm 2,+}$	0^+	3240.16	0.00920(6)[f]	70	0.0091	0.0089
$2\nu_4^{\pm 2,-}$	0^-	3240.82	0.00920(6)[f]	70	0.0090	0.0088
ν_1^+	0^-	3335.31	0.0262(1)	70	0.0269	0.0260
ν_1^-	0^+	3337.11	0.0262(1)	70	0.0270	0.0261
ν_3^-	0^-	3443.19	0.0182(1)	70	0.0180	0.0201
ν_3^+	0^+	3443.63	0.0182(1)	70	0.0181	0.0202
$(\nu_1 + \nu_2)^+$	0^-	4293.74	0.0079	76	0.0087	0.0088
$(\nu_1 + \nu_2)^-$	0^+	4320.04	0.0079	76	0.0083	0.0084
$(\nu_2 + \nu_3)^+$	0^+	4416.92	0.0206	76	0.0246	0.0250
$(\nu_2 + \nu_3)^-$	0^-	4434.65	0.0206	76	0.0244	0.0248

Yurchenko, Barber, Yachmenev, Thiel, Jensen, Tennyson, *J. Phys. Chem. A.* **113**, 11845 (2009)

Raman soliton





MIR beam profiles recorded after collimation.
Left: focussing lens of 40 mm focal length,
the beam waist is about 30 µm.
Right: focussing lens with 250 mm focal length,
the beam waist is about 200 µm.