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Model studies on vibrationally-rotationally excited hydroxyl molecules in the mesopause region

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Introduction

Near-infrared emissions of vibrationally-rotationally excited hydroxyl molecules can be used to remotely sense the temperature of the mesopause region. Rotational temperatures are derived from Boltzmann distributions fitted to observed spectra.

For the interpretation of the retrieved temperatures, the aspect of rotational thermalization is of great importance.

We present results of a kinetic population model of vibrationally-rotationally excited hydroxyl molecules which accounts for chemical production and loss processes as well as radiative and collision-induced vibrational-rotational transitions.

The model results are compared and fitted to measurement data from the UVES echelle spectrograph at Cerro Paranal in Chile (Presentation EGU2020-3169).

Introduction

Considered are electronic ground state hydroxyl molecules $\text{OH}(X^2\Pi_\Omega)$ which consist of a spin-doublet ($\Omega = \frac{3}{2}$, and $\Omega = \frac{1}{2}$).

Nomenclature / quantum numbers:

$\Omega = \frac{3}{2}$ is labeled F=1, and $\Omega = \frac{1}{2}$ is labeled F=2.

The quantum number of the total angular momentum apart from spin is labeled N (= 1,2, ... for both F).

The total angular momentum quantum number is labeled J ($J = N + \frac{1}{2}$ for F=1, and $J = N - \frac{1}{2}$ for F=2).

The vibrational quantum number is labeled v.

Model approach

The temporal change of the number density $[OH]$ of hydroxyl molecules of state (F,v,N) is given by

$$\frac{d}{dt}[OH] = P + \underline{M}[OH]$$

where P is the production rate vector of $OH(F,v,N)$, and \underline{M} is the matrix of the rate coefficients of the conversions of states $(F_i,v_i,N_i) \rightarrow (F_f,v_f,N_f)$. \underline{M} also includes the chemical loss terms of OH .

The model calculates steady state number densities:

$$[OH] = -\underline{M}^{-1} P$$

Modelled processes

Process		References/remarks
Chemical production	$\text{H} + \text{O}_3 \rightarrow \text{OH}(F, v, N) + \text{O}_2$	Nascent v (von Clarmann et al., 2010) Nascent N (Dodd et al. 1994)
Radiative decay	$\text{OH}(F_i, v_i, N_i) \rightarrow \text{OH}(F_f, v_f, N_f) + h\nu$	Brooke et al. (2016)
Quenching	$\text{OH}(F_i, v_i, N_i) + \text{N}_2 \rightarrow \text{OH}(F_f, v_f, N_f) + \text{N}_2$ $\text{OH}(F_i, v_i, N_i) + \text{O}_2 \rightarrow \text{OH}(F_f, v_f, N_f) + \text{O}_2$ $\text{OH}(F_i, v_i, N_i) + \text{O} \rightarrow \text{OH}(F_f, v_f, N_f) + \text{O}$ $\text{OH}(F_i, v_i, N_i) + \text{O} \rightarrow \text{OH}(F_f, v_f, N_f) + \text{O}^*$	$v_f = v_i - 1$ (von Clarmann et al., 2010) von Clarmann et al. (2010) von Clarmann et al. (2010) Panka et al. (2017)
Chemical loss	$\text{OH}(F_i, v_i, N_i) + \text{O} \rightarrow \text{H} + \text{O}_2$	von Clarmann et al. (2010)

Free model parameters (used for fitting):

- Rate coefficients for collision-induced pure rotational transitions.
- Rotational state changes in vibrational quenching.

Model set up

Model domain

16 altitude levels (79–98 km).

Background atmosphere

Prescribed profiles (temperature, density, O, O₃) from the SABER instrument (Russell et al., 1999) for the Cerro Paranal region.

Measurement data for fitting

OH level populations for $v = 4 - 9$ derived from high-resolution spectra originating from the VLT/UVES echelle spectrograph at Cerro Paranal, Chile. See Noll et al. (2015, 2018), as well as the presentation EGU2020-3169 in this session.

Model data, measurement data, and fit parameters

The model was used to calculate hydroxyl column densities col-OH.

For the model-measurement comparison, the logarithmised population is considered:

$$y = \ln \left(\frac{\text{col-OH}}{g} \right)$$

with g being the statistical weight of the quantum state. In case of a Boltzmann distribution, y is a linear function of the rotational energy, and its slope is $-1/\text{Temperature}$.

Pure rotational quenching

Following Noll et al. (2018) the rate coefficient k_{rot} for the transitions $(F_i, v, N_i) \rightarrow (F_f, v, N_f)$ is modelled as

$$k_{rot} = c_1 \frac{1 - c_2 |F_i - F_f|}{2 - c_2} \exp \left(-c_3 \frac{E_i - E_f}{k_b T} \right)$$

with fit parameters c_1 , c_2 , and c_3 . For $c_2=1$ there is no spin-flipping; for $c_2=0$ there is equal probability for both $F_f=1$ and $F_f=2$.

Results

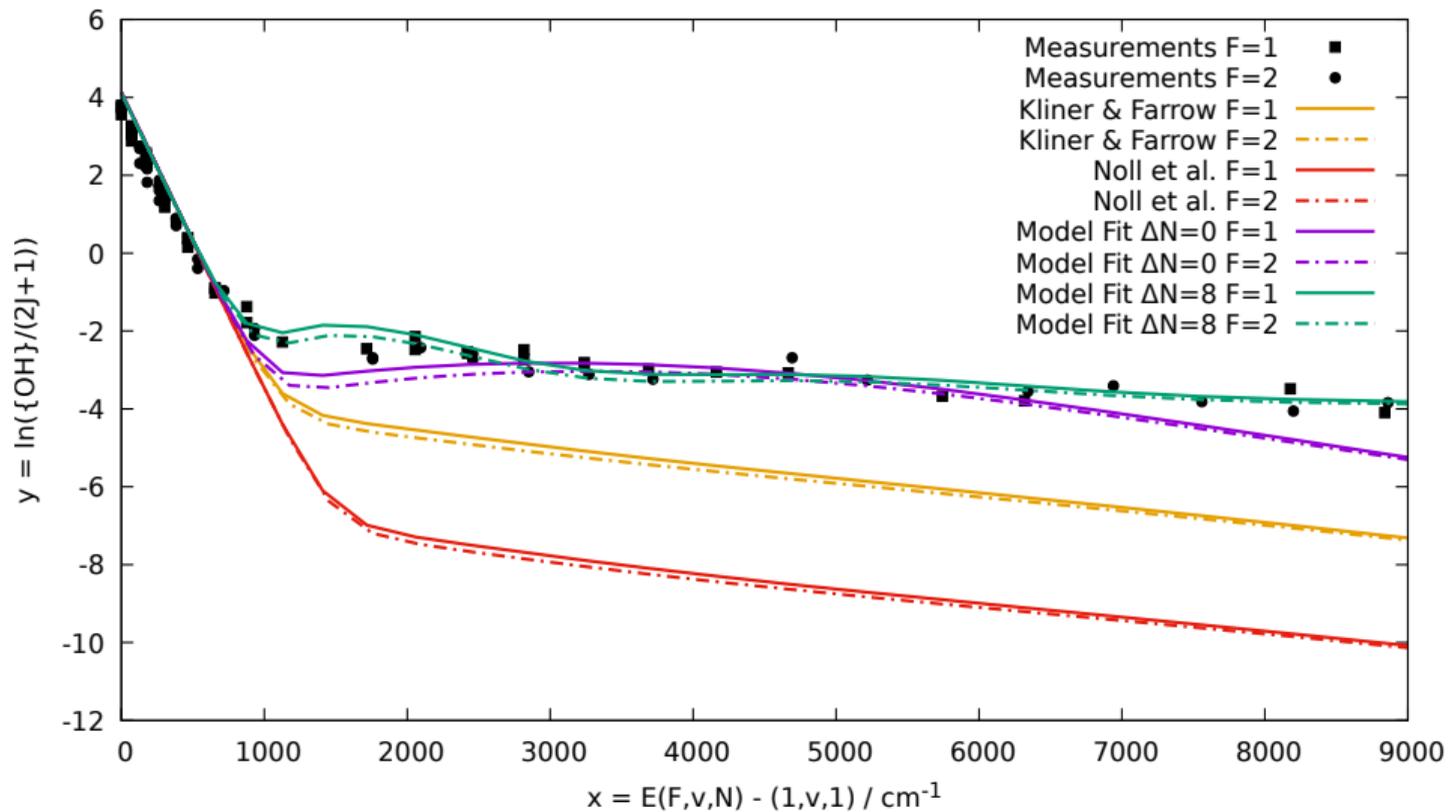
On the following slides, plots show the modelled OH column populations in comparison to measurement data for $v = 4 - 9$. The plots depict y as a function of the energy difference relative to the lowest energy of the vibrational manifold, $E(F,v,N)-E(1,v,1)$.

A global scaling factor (independent of v) is applied to yield the same total number of OH molecules summed over these six bands.

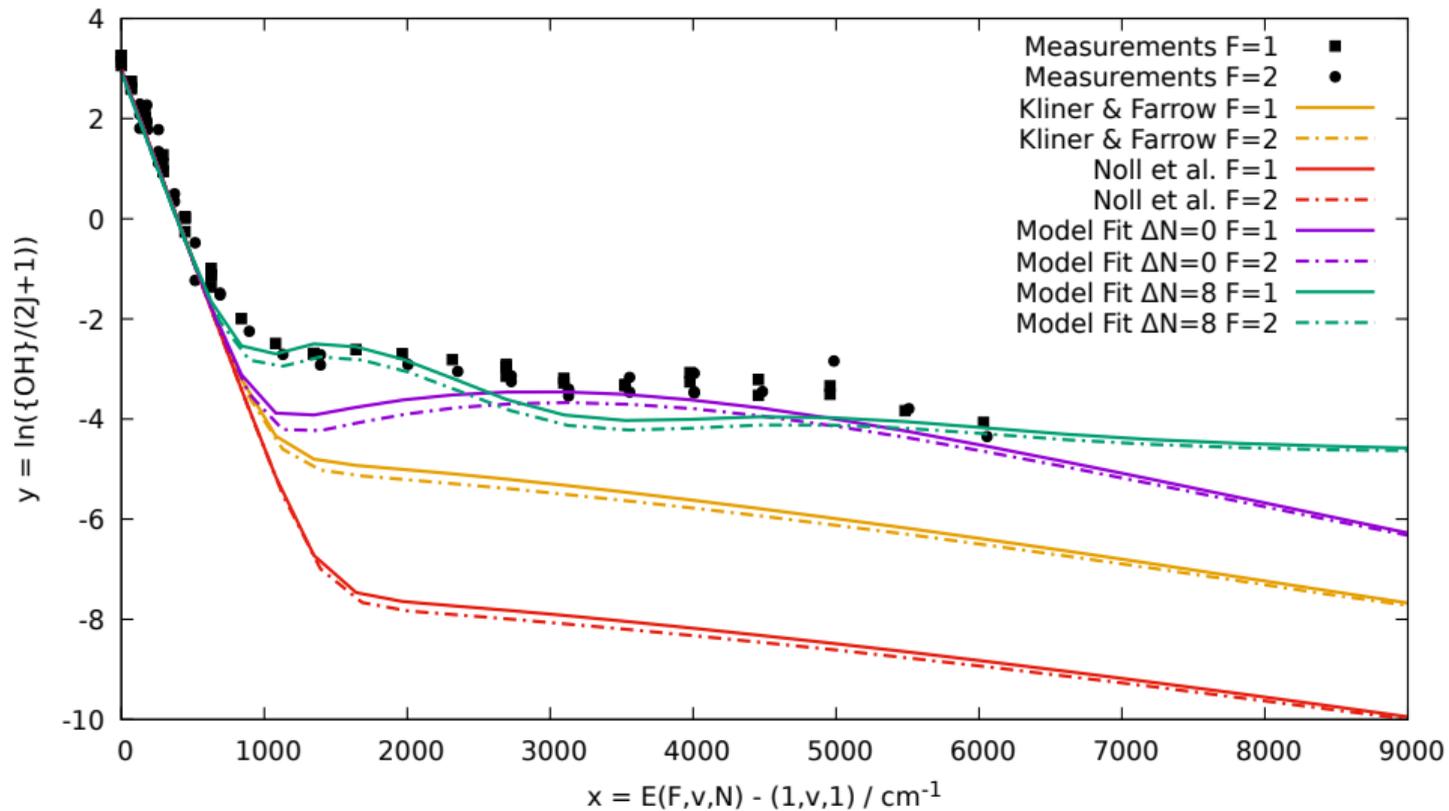
Four different model results are shown, obtained with rate coefficients k_{rot}

- (1) according to laboratory measurements of OH($v=0$) (Kliner and Farrow, 1999).
- (2) according to Noll et al. (2018) obtained from a fit to OH($v=9$) populations.
- (3) fitted to OH($v=4-9$).
- (4) fitted to OH($v=4-9$). Additionally fitted rotational change ΔN in vibrational quenching.

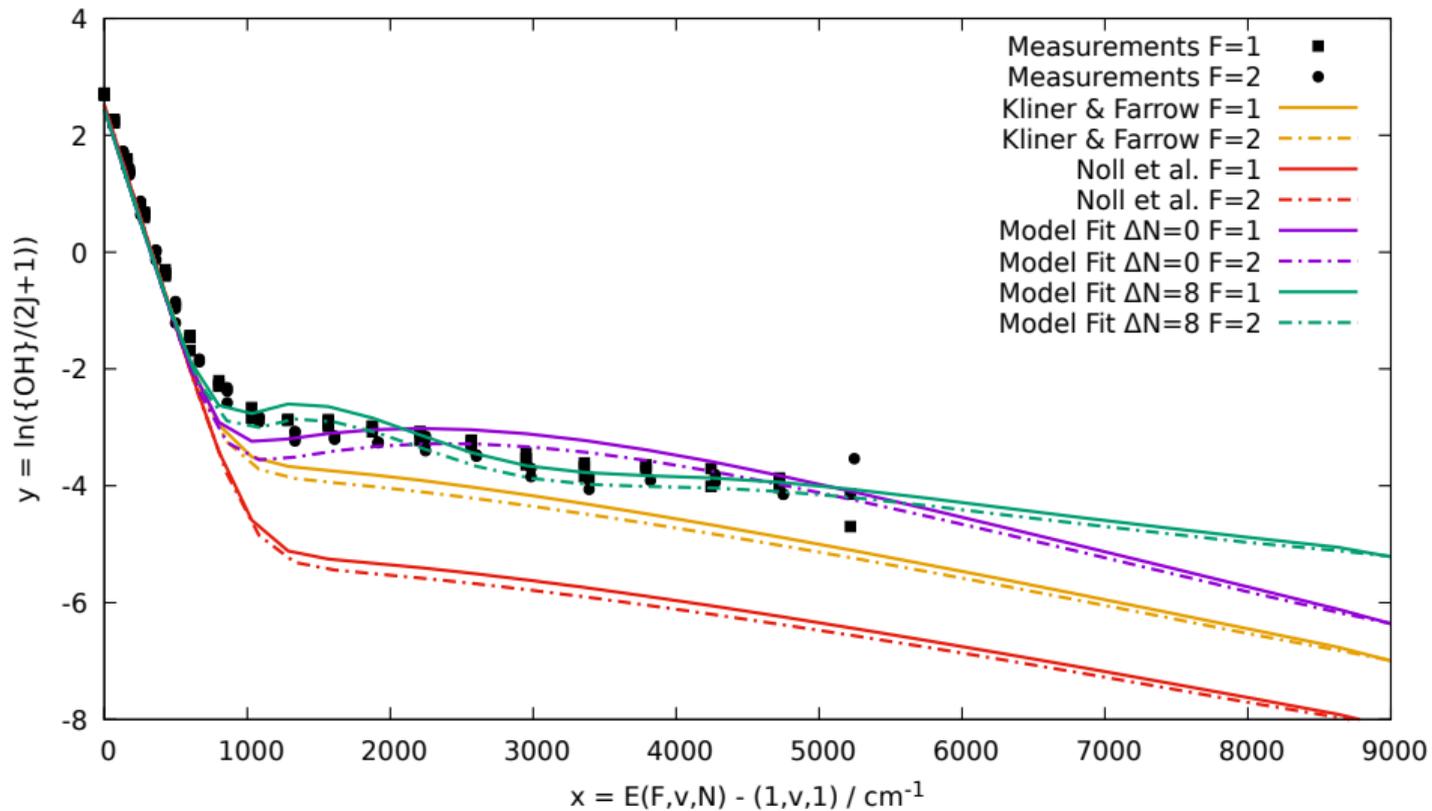
$v = 4$



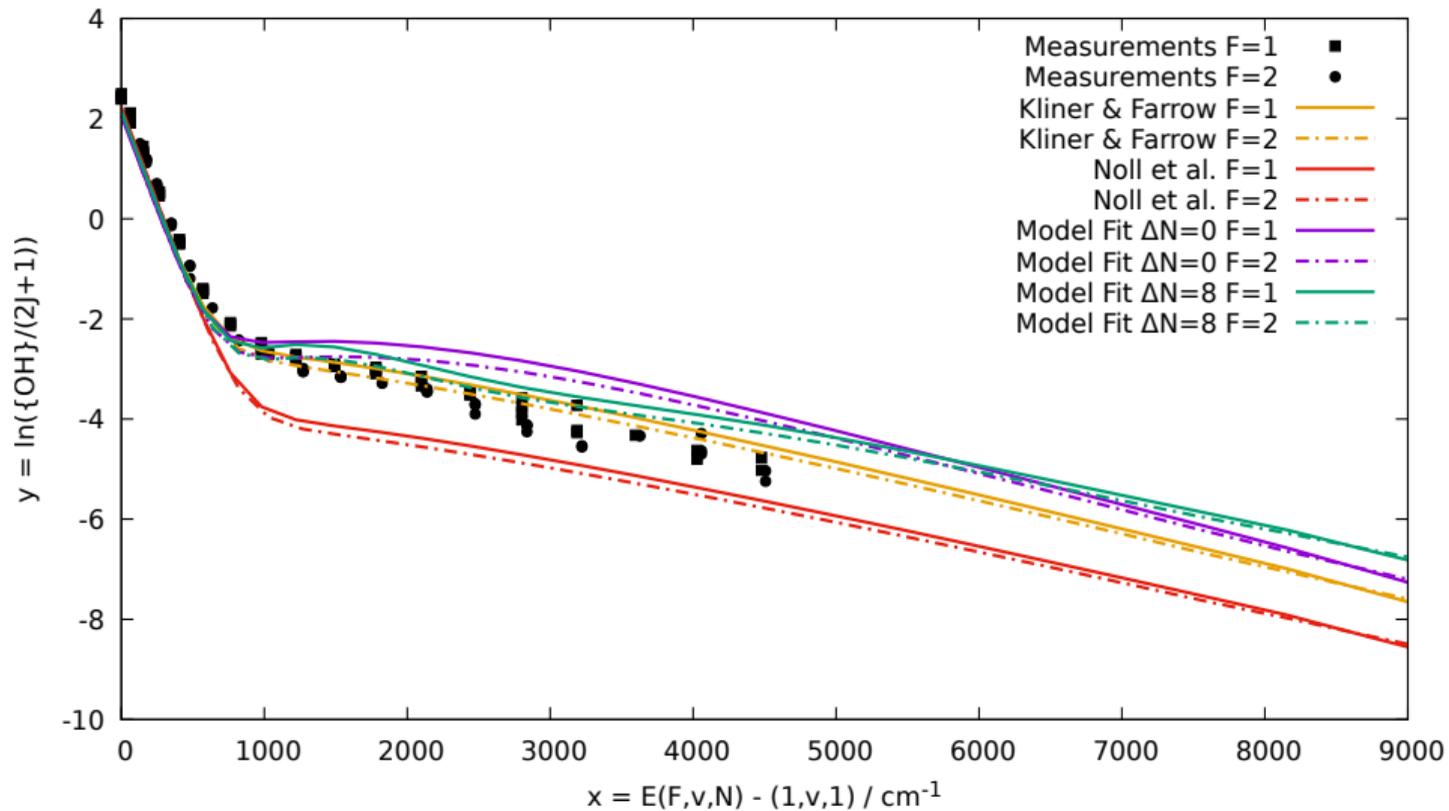
$\nu = 5$



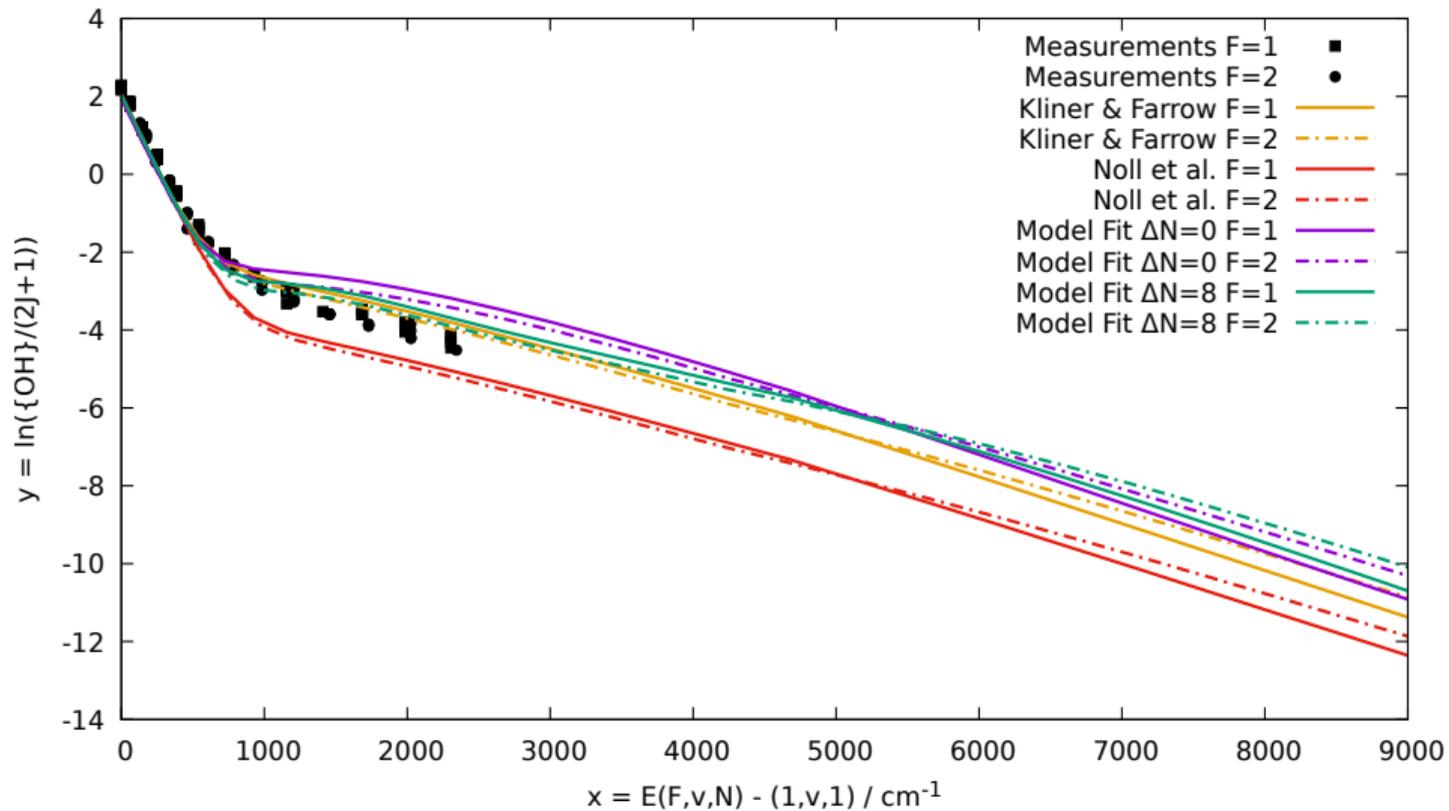
$v = 6$



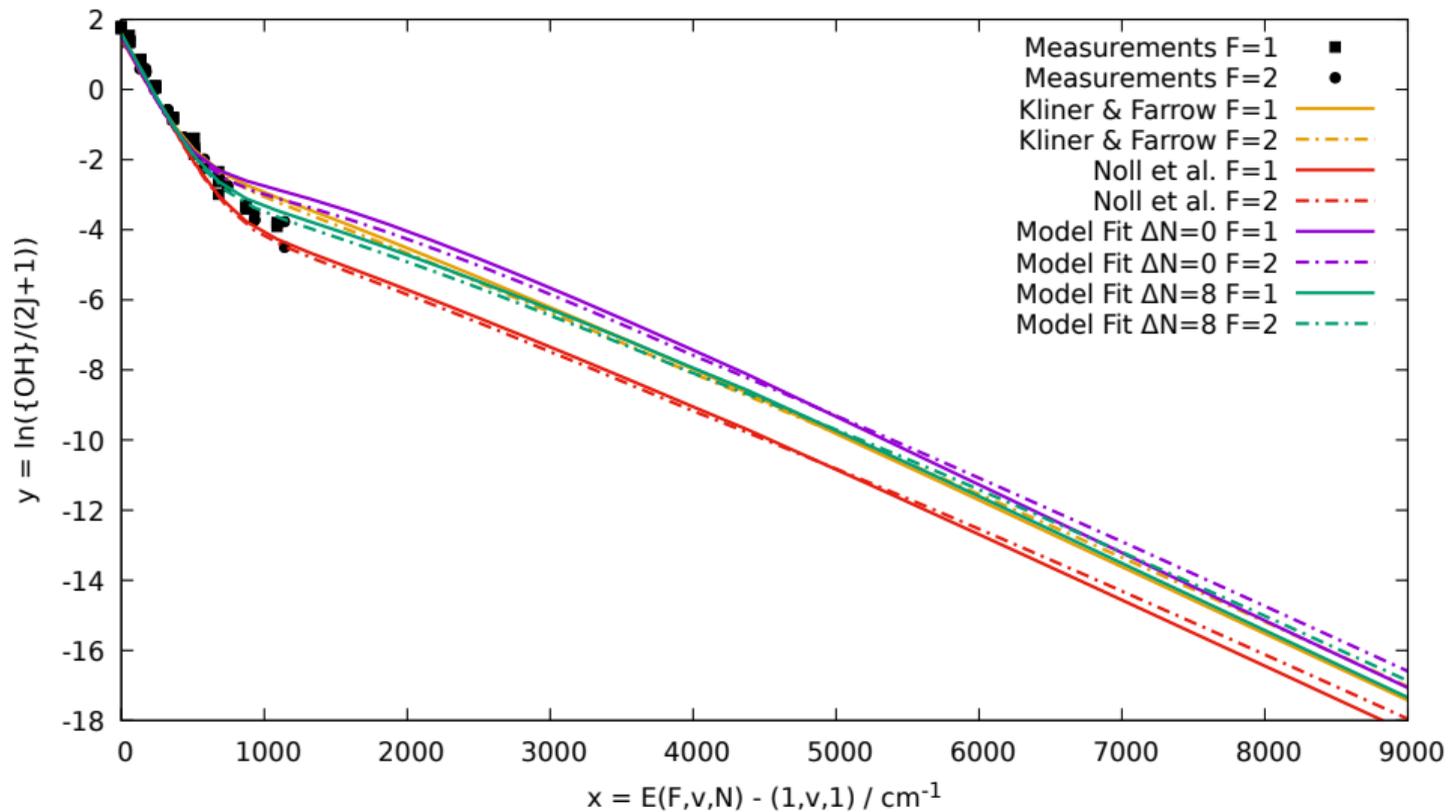
$v = 7$



$v = 8$



$v = 9$



Results

- Generally, the model reproduces the measured bimodal temperature structure of the different vibrational manifolds with apparent colder temperatures for small rotational energies, and higher temperatures for larger rotational energies (Noll et al.. 2020, and presentation EGU2020-3169).
- Especially for low v , the model runs with k_{rot} coefficients taken from the literature underestimate the abundance of molecules at larger rotational energies. Our model fits indicate rate coefficients k_{rot} to be about a factor $\sim 2-3$ larger.
- If only $v=9$ is considered, the best fits are obtained with small values of c_2 in agreement with Noll et al. (2018). However, better global fits ($v=4-9$) are obtained for $c_2 \sim 1$.
- The inclusion of a rotational state change ΔN in the vibrational quenching processes improves the model fits, in particular at low v and high rotational energies, best value $\Delta N = +8$.

References

Brooke et al. (2016), *J. Quant. Spectrosc. Radiat. Transf.* 168, 142–157.

Dodd et al. (1994), *J. Geophys. Res.* 99, 3559–3585.

Kliner and Farrow (1999), *J. Chem. Phys.* 110, 412–422.

Noll et al. (2015), *Atmos. Chem. Phys.* 15, 3647–3669.

Noll et al. (2018), *J. Atmosp. Solar-Terr. Phys.* 175, 87–99 and 100–119.

Noll et al. (2020), *Atmos. Chem. Phys. Discussion*, <https://doi.org/10.5194/acp-2019-1102>.

Panka et al. (2017), *Atmos. Chem. Phys.* 17, 9751–9760.

Russell et al. (1999) in: Larar, A.M. (Ed.) *Optical Spectroscopic Techniques and Instrumentation for Atmospheric and Space Research III*, pp. 277–288.

von Clarmann et al. (2010) *Atmos. Chem. Phys.*, 10, 9953–9964