Single vs multi-level quenching of the hydroxyl airglow

C. Franzen[1,2], R.E. Hibbins[1,2], P.J. Espy[1,2], A.A. Djupvik[3]

(1) Norwegian University of Science and Technology (NTNU), Trondheim, Norway.
(2) Birkeland Centre for Space Science (BCSS), Norway. (3) Nordic Optical Telescope (NOT), E-38700 Santa Cruz De La Palma, Spain

ABSTRACT

The reaction in the upper mesosphere between atomic hydrogen and ozone produces hydroxyl (OH) in excited vibrational levels 6 through 9, giving rise to the strong near-infrared airglow emission. The interpretation of the emission for remote sensing of the mesopause region relies on accurate knowledge of the population and quenching of the upper states, and open questions remain as to whether the quenching takes place through single- or multi-quantum deactivation. Here we use spectral observations of OH (9,7) and (8,6) airglow emissions that are available as background measurements during standard K-band astronomical observations from the Nordic Optical Telescope (18°W, 29°N). These emissions, together with a steady-state model, have been used to estimate the ratio of single to multi-quantum quenching efficiency.

BACKGROUND AND METHOD

The OH Airglow

The exothermic $H+O_3$ reaction produces vibrationally excited OH* in quantum levels as high as v'=9. From there, the OH* can radiate through vibrational-rotational transitions that form the OH airglow or be collisionally quenched. The quenching can occur in two different modes. Sudden death quenching deactivates the OH* directly into the ground state, whereas stepwise quenching brings the OH* into lower vibrational quantum levels, where it can again radiate or be quenched. However, the ratio of these two quenching processes is not well determined.

In addition, recent work has shown how the temperatures derived from the v'=8 vibrational level appear to be anomalous. Figure 1 (from Franzen 2015) shows the OH rotational temperature derived from near-simultaneous NOT observations of Meinel bands v'=9 down to v'=3 on the night of 19.02.2013 in comparison with a simultaneous MSIS temperature profile, shown as the black line in the figure. Rotational temperatures were fit to the individual bands using the HITRAN line strengths, and their altitudes were estimated using a steady state model based on an MSIS background atmosphere. Temperatures for bands arising from the v'=8 level are consistently found to be too warm in comparison to the expected temperature profile from MSIS.
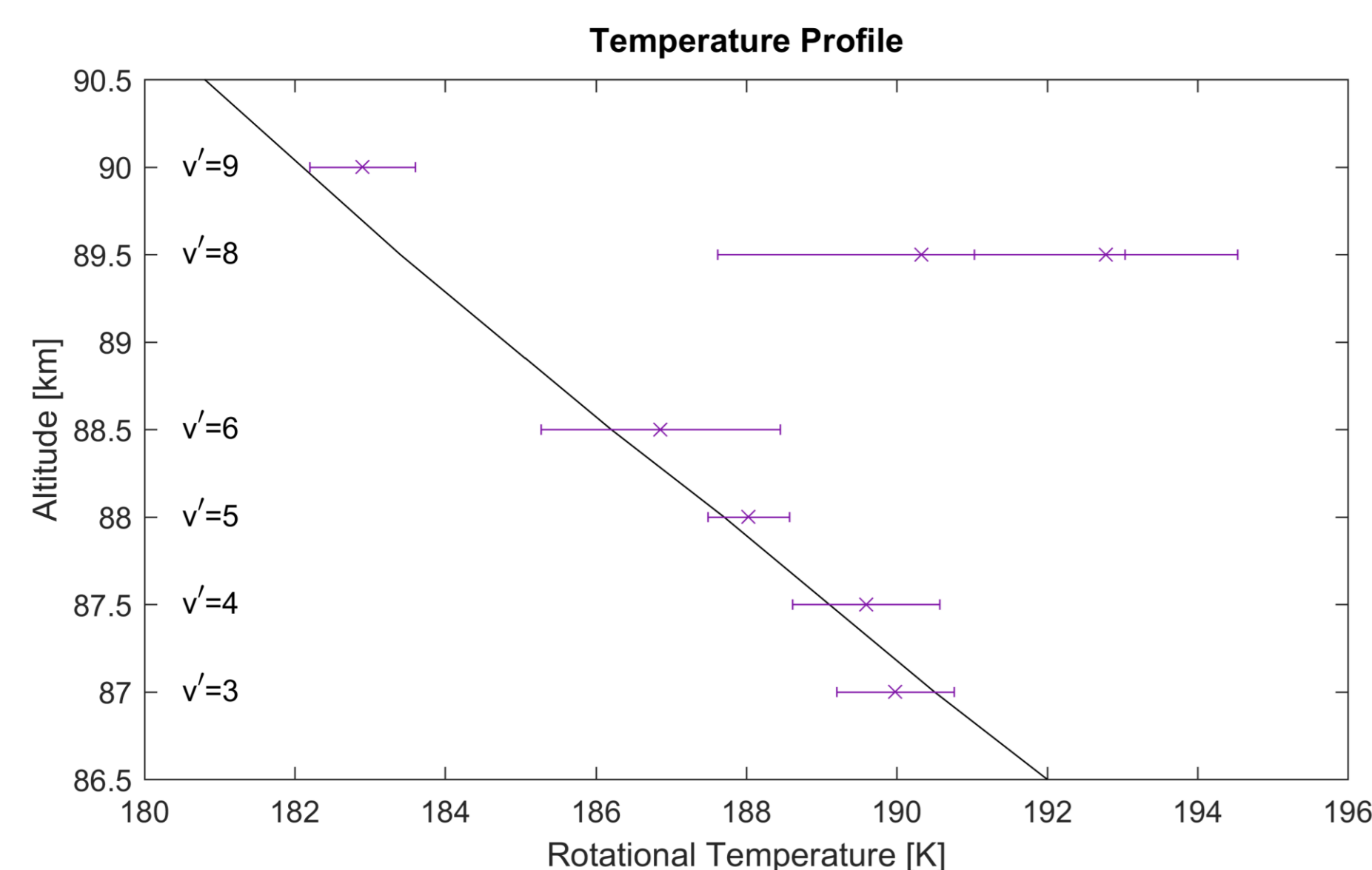

Figure 1:
Temperature measurements from different vibrational quantum levels (purple) and the corresponding MSIS profile (black). The temperatures of the v'=8 level are consistently too warm.

DATA

Spectra from the Nordic Optical Telescope

The Nordic Optical Telescope (NOT) is situated on La Palma (18° W, 29° N). All measurements used in this work were the atmospheric background observations for standard astronomical spectroscopic observations. The reduction methods are described in Franzen (2015). The spectra used in this work contain two Meinel band transitions, the (9,7) and the (8,6). Since both transitions are measured simultaneously, the ratio of their intensities is independent of the absolute calibration of the system. Figure 2 shows a spectrum of the Meinel band transitions taken with a 100-s integration time. This work included 19 observations, of which 18 were from the night of the 06.09.2012 with the remaining observation from 19.02.2013.
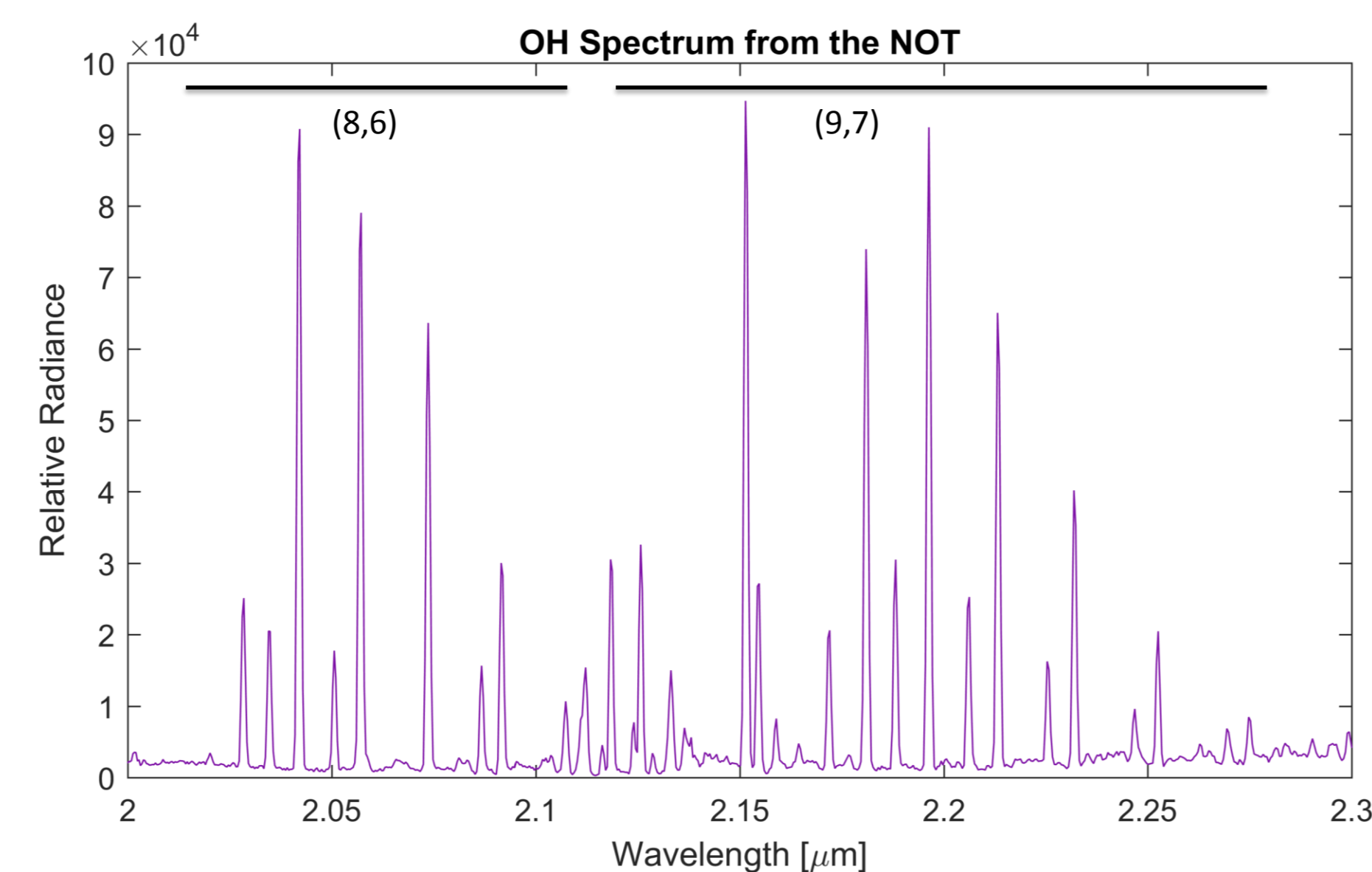

Figure 2:
K-band atmospheric spectrum from the NOT of the OH airglow, containing the transitions (9,7) and (8,6).

Calculation of the f_S

The ratio of the stepwise quenching to the total rate coefficient of all quenching is termed f_S. Here we infer f_S for v'=9 to v=8. Since v'=9 is the highest quantum level produced, the observed intensities of the (9,7) and (8,6) Meinel band transitions, combined with a steady state calculation using a background atmosphere, yield an estimate of f_S in terms of the transition probabilities of Langhoff et al. (1986) and the rate coefficients of the following reactions:

	Reaction	Reference
1	$H + O_3 \rightarrow HO^* + O_2$	Sander et al. (2006); Klenerman and Smith (1987)
2a	$O + O_2 + N_2 \rightarrow O_3 + N_2$	
2b	$O + O_2 + O_2 \rightarrow O_3 + O_2$	IUPAC Gas Kin. Dat. Ev. (2003)
3	$NO + O_3 \rightarrow NO_2 + O_2$	
4	$OH_{n'}^* + O \rightarrow H + O_2$	Lopez-Moreno (1987)
5a	$OH_{n'}^* + O_2 \rightarrow OH_{n-1}^* + O_2$	Dodd (1991); Knutsen (1996); Dyer (1996); Chalamala
5b	$OH_{n'}^* + CO_2 \rightarrow OH_{n-1}^* + CO_2$	(1993)
6	$O + O_3 \rightarrow O_2 + O_2$	Sander et al. (2006)

Table 1:
Reactions used in the background atmosphere with the references for the associated rate coefficients.

RESULTS

Data and error discussion

The values for f_S vary within the data between 0.54 and 0.73. Each individual data point has a statistical error of approximately 0.01 due to uncertainties in the simulated values of the background atmosphere and the statistical noise from the spectroscopic measurement. The average and standard deviation over all values is $\overline{f_S} = 0.64 \pm 0.053$.

Nightly variations

In figure 3, the data are shown against the time of the night, when they were taken. The data taken shortly after midnight yield an average of $\overline{f_{S,1}} = 0.62 \pm 0.028$, while the data taken later in the night have a higher value of $\overline{f_S}$ with a smaller standard deviation: $\overline{f_{S,2}} = 0.69 \pm 0.047$.
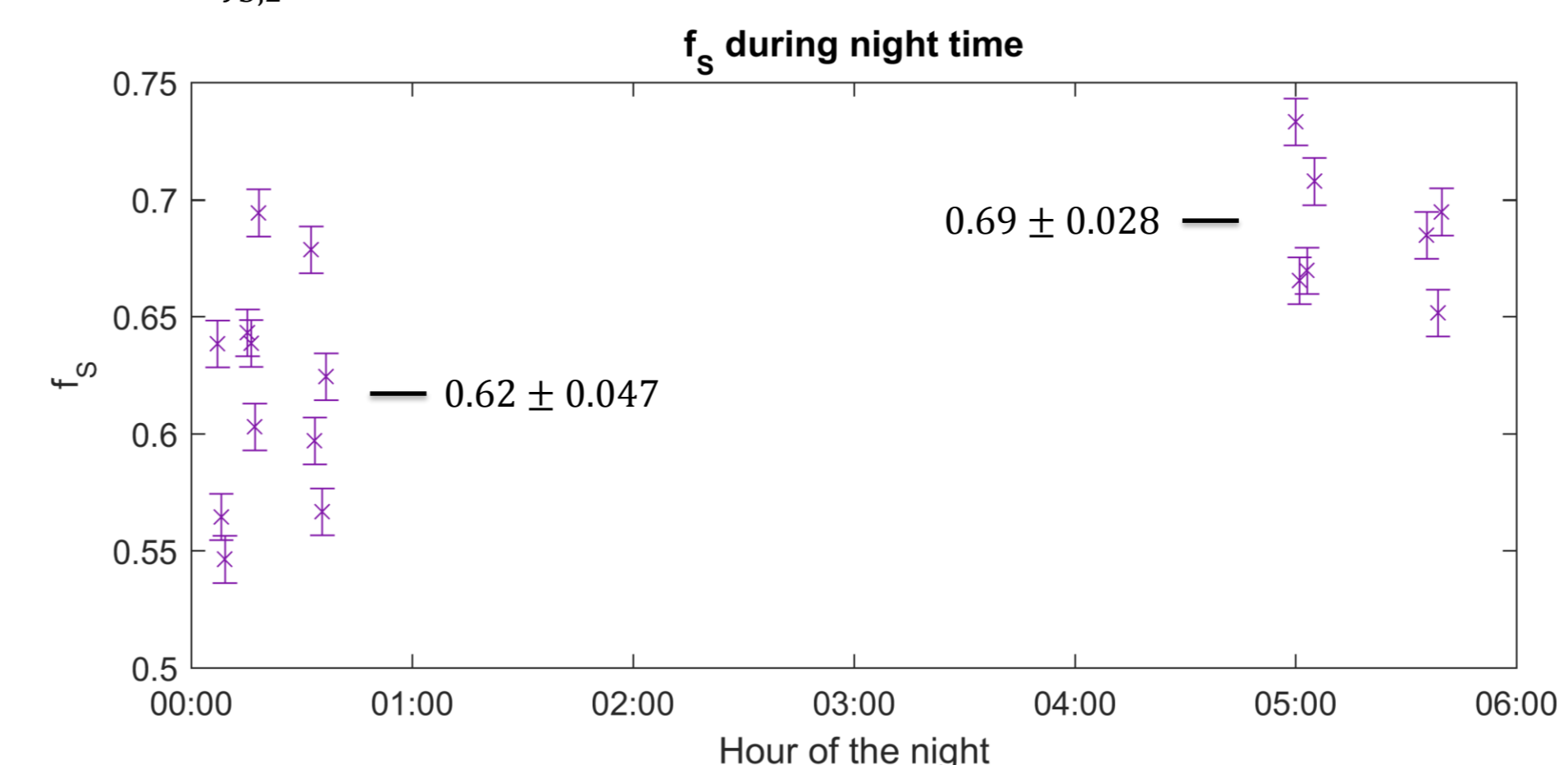

Figure 3:
Measured values of f_S for different times during the night. The value appears larger, with a smaller variation near the end of the night.

Test for Temperature Dependency

The rotational temperature of the OH layer has previously been observed to change during the course of a night (e.g. Parihar et al. 2013), with a typical rise in the temperature near sunrise. The change in f_S shown above could be related to this change in temperature. In figure 4, the data are plotted against the rotational temperature, but no significant correlation can be seen. The calculated correlation coefficient is -0.45. It is therefore unlikely that the temperature causes this change in f_S.
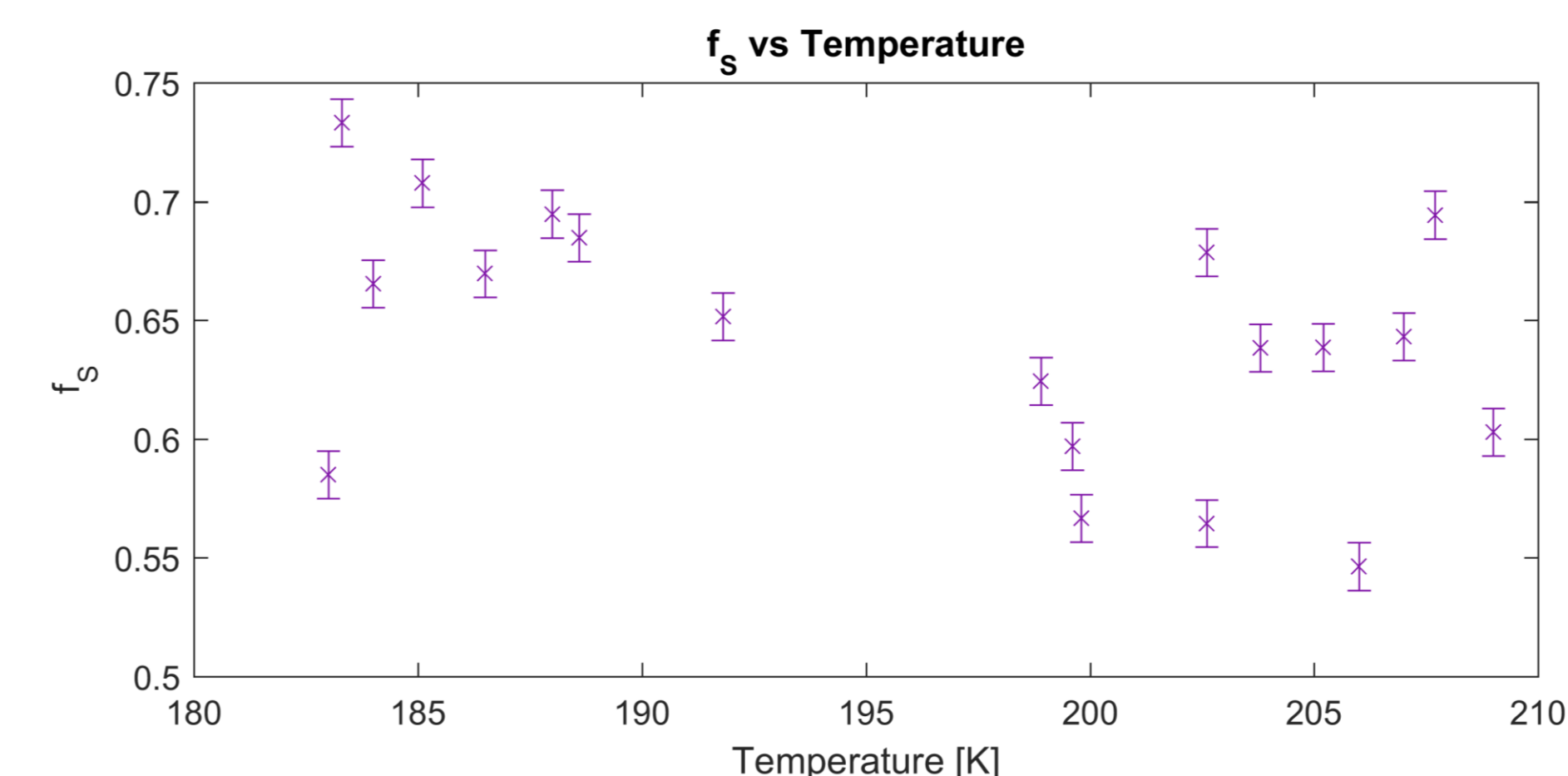

Figure 4:
Measured values of f_S against the rotational temperature of the hydroxyl layer. No clear correlation can be seen.

DISCUSSION

Variations of the results

Even though each measurement of f_S has a relatively small statistical error (~2%), the values of f_S vary over a range of up to nearly 10 times the statistical error. A significant change can be seen at the end of the night, where the value of $\overline{f_{S,2}}$ is 10% bigger than $\overline{f_{S,1}}$ at midnight. This variation could not be explained with the nightly variation of temperature, since no correlation between f_S and the rotational temperature of the OH layer could be found.

Interpretation of f_S

The value of f_S expresses the ratio of the stepwise quenching from the vibrational quantum level v'=9 to v=8 over the total quenching. The data presented in this work show that stepwise deactivation occurs about 64% of the time, with quenching to lower quantum levels, including the ground level, occurring the rest of the time.

SUMMARY & FUTURE WORK

Summary

A value for the quenching ratio $\overline{f_S}$ of single to multiple quantum quenching has been calculated to be $\overline{f_S} = 0.64 \pm 0.012$. A small variation during the night was observed, though no correlation between this value and the rotational temperature of the hydroxyl layer could be found. Additional data from the NOT archive will be used to examine whether the large f_S into v'=8 is unusual and perhaps the cause of the anomalous temperature behavior seen in figure 1.

REFERENCES

R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe Atmos. Chem. Phys. Discuss., 3, 6179-6699, 2003

Chalamala B.R., Copeland R.A., Collision dynamics of OH(X²P,n=9 [J. Chem. Phys. 99 (8), 5807-5811 (1993)]

Dodd J.A., Lipson S.J. and Blumberg W.A.M, Formation and vibration relaxation of OH(X²P,n) by O₂ and CO₂, [J. Chem. Phys. 95 (8), 5752-5762 (1991)]

Dyer M.J., Knutsen K., Copeland R.A., Energy transfer in the ground state of OH: Measurements of OH(n=8,10,11) removal, [J. Chem. Phys. 107 (19), 7809-7815 (1996)]

Franzen, C. (2015). Using Background OH Airglow from astronomical Observations for atmospheric Research: A Proof of Concept. Institutt for fysikk. Trondheim, NTNU. Master.

Klenerman, D and I. W. M. Smith, Infrared chemiluminescence studies using a SISAM spectrometer, [J. Chem. Soc. Faraday Trans. 2, 83, 339-241, 1997] Evaluated kinetic and photochemical data for atmospheric chemistry: part 1 – gas phase reaction of Oₓ, HOₓ, NOₓ, and SOₓ species

Knutsen K., Dyer M.J., Copeland R.A., Collisional removal of OH(X²Pᵢ,n=7) by O₂, N₂, CO₂ and N₂O, [J. Chem. Phys. 104 (15), 5798-5802 (1996)]

Langhoff, S. R., Werner, H.-J. and Rosmus, P., Theoretical Transistion probabilities for the OH Meinel System, [J. Mol. Spec.,118, 507-529 (1986)]

Lopez-Moreno J.J., Rodrigo R., Moreno F., Lopez-Puertas M., Molina A., Altitude distribution of vibrationally excited states of atmospheric hydroxyl at levels n=2 to n=7, [Planet. Space Sci. 35 (8), 1029-1038, 1987]

N. Parihar, A. Taori, S. Gurubaran, and G. K. Mukherjee. *Ann. Geophys.*, 31(2):197–208, 2013.

Sander, S. P., et al. (2006), Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation number 15, JPL Publ.

Turnbull, D. N. and Lowe, R. P., New hydroxyl Transistion probabilities and their importance in airglow studies, [Plant. Space Sci., 37, 6, 723-738 (1989)]

ACKNOWLEDGMENTS

This presentation participates in OSPP

EGU

Outstanding Student Poster & PICO Contest