

Answer to Anonymous Referee #1

Received and published: 18 April 2019

General comments:

This manuscript deals with an interesting effect not properly addressed by previous studies on the population of rotational levels of hydroxyl radicals in the mesosphere / lower thermosphere region of the Earth's atmosphere. The simple fact that kinetic temperature varies within the altitude range of the OH emission layer (for a wave or tidal perturbation possibly dramatically) will lead to an apparent deviation of the population of higher rotational states from LTE in ground-based observations. While this effect may not explain the majority of observed non-thermal populations of higher rotational levels, it certainly is an interesting effect that should be reported and considered in future studies. For this reason this manuscript is of interest to the aeronomy community and should eventually be published in my opinion. I ask the authors to consider the (mainly minor) comments below.

We thank the referee for all comments and helpful feedback. We address each comment in turn below.

Specific comments:

Page 3, line 15: "from the empirical model of the US Naval Research Laboratory Mass Spectrometer and Incoherent Scatter radar (NRLMSISE-00)" sounds a little odd and is misleading. I suggest something like: "from the US Naval Research Laboratory's Mass Spectrometer and Incoherent Scatter radar model (NRLMSISE-00)"

The text has been changed as suggested.

Page 4, line 1: "The temperature dependent rate coefficients for THESE reactions" Should this perhaps be ".. for THIS reaction"? The statement seems to refer to reaction (2) only.

The text has been changed as suggested.

Page 5, line 16: "Where $A_w(z)$ is a function of altitude" Please provide more information on the altitude dependence of the wave amplitude, perhaps show a plot.

We follow here the wave breaking mechanism of (Holton, 1982). To clarify the amplitude behaviour with altitude, we have added the following passage and figure to the text:

“Where φ_w is the wave’s phase, and $A_w(z)$ is a function of altitude so as not to exceed the dry adiabatic lapse rate. The lower edge of the model is 74 km altitude. The wave amplitude as a function of altitude is shown in Figure 2 for the case of a wave with an amplitude of 10 K at 74 km altitude and a vertical wavelength of 15 km. This example is given for an isothermal atmosphere of 200 K (Figure 2 (a), dashed-black). The wave grows in amplitude with altitude to conserve energy (dashed-blue), but at regions where the lapse rate exceeds the dry adiabatic lapse rate (here between 90 and 95 km, and between 110 and 115 km), the wave loses energy and the amplitude decreases (Holton, 1982). The breaking wave is shown in red in Figure 2 (a). Figure 2 (b) shows the instantaneous lapse rate (change in temperature with altitude) of the non-breaking wave (dashed-blue) and the breaking wave (red), which never crosses the dry adiabatic lapse rate of -10 K/km (dashed-black). Figure 2 (c) shows the amplitude of the non-breaking wave (dashed-blue) which increases exponentially and for the breaking wave (red), which decreases at the altitudes where the wave dissipates energy.

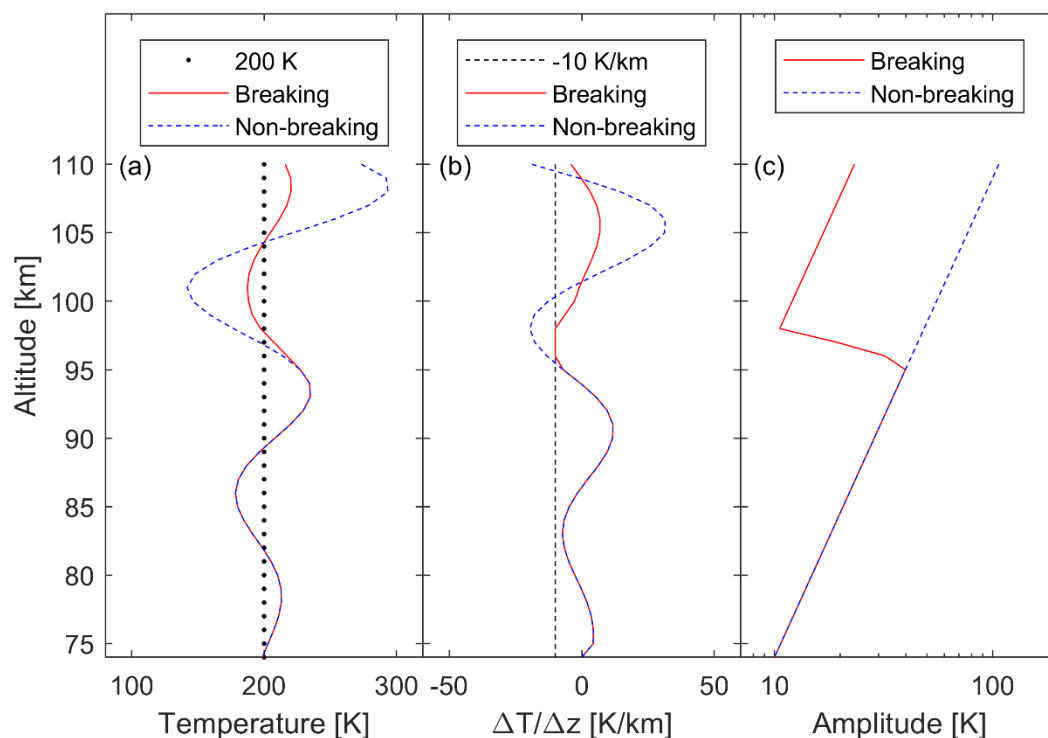


Figure 2: (a) Example of a wave of amplitude 10 K at 74 km altitude perturbing an isothermal atmosphere at $T = 200$ K (dotted-black). The dashed-blue line represents the wave without any breaking, and the red line is the breaking wave as used in the model. (b) The rate of change of temperature with altitude for the wave shown in (a). When the temperature changes faster than -10 K/km (dashed-black) the wave breaks. (c) At these altitudes, the amplitude of the breaking wave (red) decreases, while the non-breaking wave continues to grow exponentially (dashed-blue).”

Page 5, same line: “and φ_w for this example is defined as zero at an altitude of 74 km” This statement suggests that the phase is altitude dependent. Is this really the case? I assume it is constant – then the reference to a specific altitude (74 km) can be removed.

The phase shift ϕ_w is not altitude dependent, as the referee said. The text has been changed to be less confusing. It now reads:

“Where ϕ_w is the wave’s phase (constant with altitude), and $A_w(z)$ is a function of altitude so as not to exceed the dry adiabatic lapse rate. The lower edge of the model is 74 km altitude.”

Page 5, same paragraph: It would be good to state here already, whether the assumed wave perturbation may really occur in the atmosphere, or whether this is an extreme case that essentially never occurs.

We agree that it is good to state this already here. We have added the following sentence to the text.

“Waves with similar amplitudes have been observed at these altitudes (Picard et al., 2004)”.

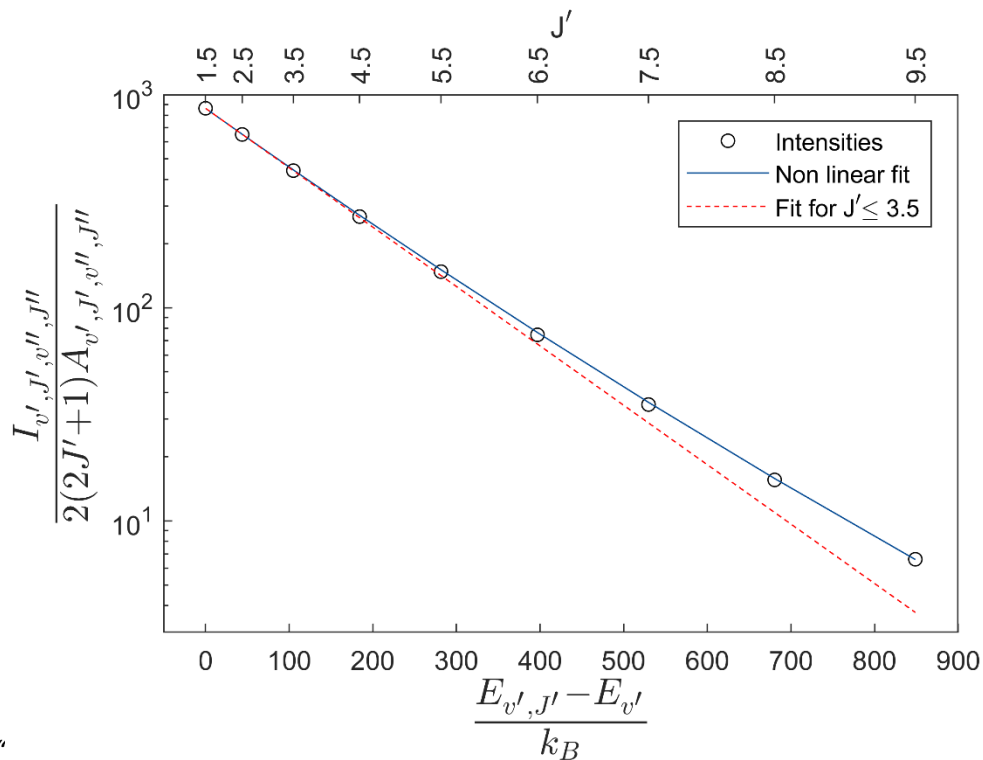
Page 6, line 12: “Where $N_{v'}$ is the integral of the vibrational band VER” Is this really the case? I think $N_{v'}$ is not an integrated VER, but rather the total (integrated) population of the v' level. Otherwise the units don’t fit.

$N_{v'}$ is indeed the integral over the population, or in terms of VER, you can also put the integral as $N_{v'}(z) \cdot \omega_{v'v''} / \tau_{v'}$. We clarified this in the text. It now reads:

“Where $N_{v'}$ is the integral of the vibrational population $N_{v'}(z)$ over altitude, and T is the effective rotational temperature of the altitude-integrated spectrum.”

Page 7, Figure 3, upper abscissa legend: Please add a space between “1.5” and “2.5”

We have rotated the labels by 90 degrees to increase readability. The new figure now looks like this:



Page 8, line 7: “the original background profile is retrieved” I suggest replacing “retrieved” by “obtained”. For me as a “retrieval person” “retrieved” here means the temperature retrieval using the OH technique.”

The text has been changed as suggested.

Page 8, line 8: only a minor comment, but “higher and lower temperatures” is perhaps more accurate than “warmer and colder temperatures”, because temperature cannot really be warm/cold. I leave it up to the authors to decide, whether they want to change this.

The text has been changed as suggested.

Page 9, Figure 4: It would be good to separate the two panels a little, add some space between panel a and b.

We have added some space between these two panels. The figure now looks like this:

“

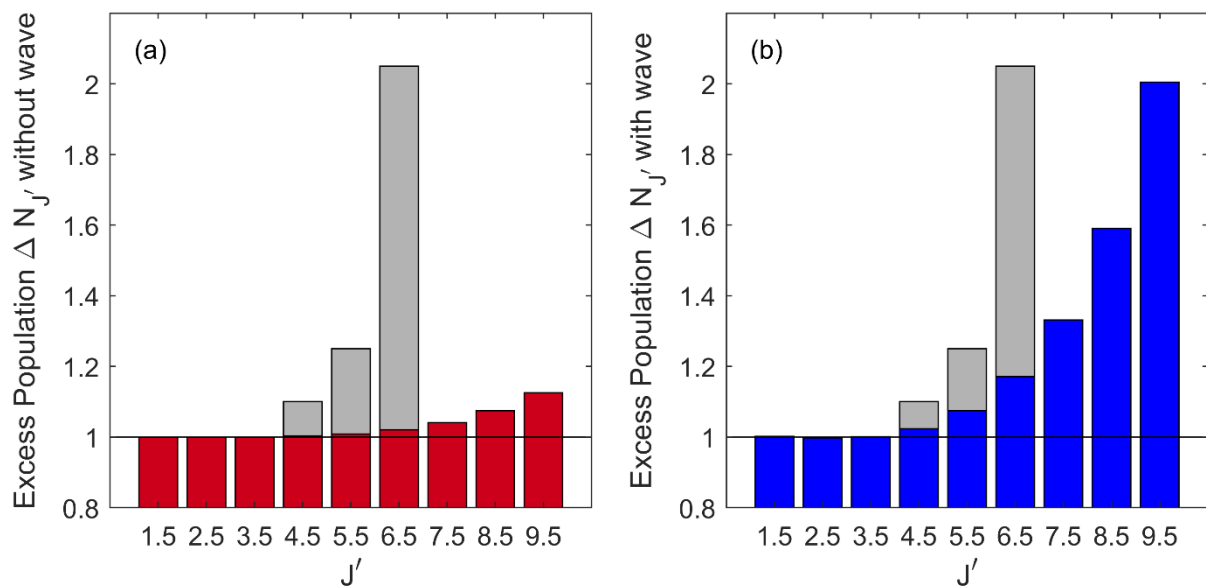


Figure 5: The calculated apparent excess population of the OH (7,4) P(J') lines relative to the Boltzmann population of the fitted temperature to the lowest three lines. Red on the left is calculated with the climatological temperature gradient shown from NRLMSISE-00 above Boulder, Colorado (40.0° N; 105.6° W) in mid-July. Blue on the right is calculated with a wave of $A_w = 30$ K at 90 km, $\lambda_w = 30$ km and a phase that yields the maximum effect, $\varphi_w = 4.9$ rad. This is the same wave as presented in Figure 4. The distribution has a $\beta = 1.9$ %. The grey bars represent the measurements ascribed to NLTE effects from Pendleton et al. (1993).”

Page 9, line 18: “The first three rotational levels reproduce the same population as an atmosphere in LTE characterised by a single temperature” It’s not entirely clear, whether this statement refers to the results of Pendleton et al. (1993). I think this is the case and suggest stating this explicitly.

This statement refers to both this paper and the one of Pendleton et al. (1993). We have changed this sentence to clarify this. It now reads:

“The first three rotational levels in this study and in Pendleton et al. (1993) have populations that follow a Boltzmann distribution characterized by a single temperature, and above that, there is excess population.”

Page 10, line 7: “In Fig. 5(a) the non-linearity of the temperature fit increases with both wave strength and vertical wavelength” Looking at the Figure, this statement is not generally correct, is it? There are different regimes showing different behavior, e.g., for a vertical wavelength of 10 km, beta decreases with increasing amplitude. Please rephrase this sentence.

The referee is correct. We have clarified this in the text. It now reads:

“Figure 6 (a) shows that for vertical wavelengths above about 20 km the non-linearity of the temperature fit increases with both wave strength and vertical wavelength approaching 2% of the linear temperature variation (see Equation 10). For shorter vertical wavelengths, the non-linearity is smaller (at about 0.5 %) and decreases with increasing wave amplitude.”

Page 10, line 9: “Figure 5 (b) shows the phase that yields the highest : : :” The Figure does not show the phase, but the apparent excess population for the phase with : : : Please rephrase.

The figure shows the apparent excess population for a wave with a given wavelength and amplitude using the phase that yields the greatest effect. We have now clarified this in the text, which reads:

“Figure 6 (b) shows the apparent excess populations for a wave with a phase that yields the highest apparent excess population for a given wave amplitude and wavelength.”

Page 11, line 10: “Instead it is due to the” It’s not clear, what “it” refers to in this sentence. I assume it is “the difference in the apparent excess population” mentioned a few sentences above. Please state it explicitly.

The “it” refers to the difference in the apparent excess population between the (3,1) and (7,4) bands. This has been clarified and the sentence now reads:

“Instead, the difference in the apparent excess population between the (3,1) and (7,4) bands is likely to be due to the compressed rotational energy structure of the higher vibrational levels that lie closer to the dissociation limit.”

Page 12, line 9: “The simulations executed here show that these temperature profiles can change the populations of the different rotational lines” I have two comments on this sentence: 1) it is not surprising that temperature affects the rotational population of a vibrational state and I think this is not what you actually intend to say. The important point is that the vertical temperature variation leads to an apparent non-thermal population for an observer on the ground, right? 2) can “rotational lines” be populated? The rotational “states” or “levels” are populated and they give rise to the emission.

We agree with the referee on both points. We have changed the sentence to clarify the apparent non-thermal population and exchanged "line" with "level". The whole sentence now reads:

"The simulations executed here show that these temperature profiles can create an apparent non-thermal population of the rotational levels in a given Meinel (v' , v'') band."

Typos etc.:

General: The section titles are all upper cases, which – I believe – is not the ACP standard.

The section titles have been changed as suggested.

Page 1, reaction (1): The "-" sign inside the parentheses may be interpreted as a minus sign and I think it is not really necessary.

The minus sign was supposed to indicate that this energy is the excitation of the OH^ . We agree however that it might be confusing and have deleted this sign.*

Page 3, caption of Figure 1, line 1: "red- dashed" -> "red-dashed" ?

The text has been changed as suggested

Page 4, line 3: "Loss processes include losses DUE to O" ?

The text has been changed as suggested

References:

Holton, J. R.: The Role of Gravity Wave Induced Drag and Diffusion in the Momentum Budget of the Mesosphere, *J Atmos Sci*, 39, 791-799, 1982.

Pendleton, W. R., Espy, P. J., and Hammond, M. R.: Evidence for non-local-thermodynamic-equilibrium rotation in the OH nightglow, *J Geophys Res-Space*, 98, 11567-11579, 1993.

Picard, R. H., Wintersteiner, P. P., Winick, J. R., Mertens, C. J., Mlynczak, M. G., III, J. M. R., Gordley, L. L., Ward, W. E., She, C. Y., and O'Neil, R. R.: Tidal and layer structure in the mesosphere and lower thermosphere from TIMED/SABER CO₂ 15- μ m emission, SPIE, 2004.

Answer to Anonymous Referee #2

Received and published: 22 April 2019

General comments:

This study focusses on the impact of kinetic temperature gradients in the OH airglow emission layer on column-integrated rotational level population distributions. As the populations of high rotational levels tend to originate from altitudes with higher kinetic temperatures than those related to low rotational levels, the rotational level population distribution of a fixed vibrational level cannot be described by a single temperature. The temperature tends to increase with rotational level, which looks like a non-LTE effect. The authors simulated different wave-perturbed temperature profiles combined with a chemical model for the OH emission layer (depending on the vibrational level) to estimate the magnitude of the effect. A comparison with measured OH populations from Pendleton et al. (1993) then showed that this pseudo-non-LTE effect can significantly contribute to the apparent non-LTE deviations in the rotational level population distribution if the wave amplitudes are large.

There has not been a detailed study of the investigated effect in the literature, so far. Hence, it is justified to publish a paper on this topic, although I guess that the effect appears to be negligible in most cases. As the study does not discuss the distribution of true temperature gradients (either from satellite or lidar data), I would appreciate an extension of the analysis in order to better understand the relevance for observed rotational level population distributions like those from Pendleton et al. (1993) or more recent studies. For OH-based estimates of the kinetic temperature, rotational temperatures are usually derived from the first three or four rotational lines. Hence, it would also be interesting to know whether a noteworthy contribution of the discussed effect is possible. OH modelling results in the literature should not be affected as such models are calculated altitude-dependent. Only the interpretation of the column-integrated populations may change slightly.

Apart from the desired clarifications concerning the impact of the effect, the quality of the discussion needs to be significantly improved. In particular, due to the lack of precision in the use of scientific terms, the paper is often confusing and misleading (see detailed comments). Thus, this paper needs a major revision to be acceptable for publication in ACP.

We thank the referee for their extensive and helpful comments.

This study uses a temperature profile from the reanalysis NRLMSIS-00, which is based on “realistic temperature gradients”. We have also been careful to ensure that the waves we present have been reported in the literature using a variety of observational techniques and are therefore physical (Hagan et al., 1999; Oberheide et al., 2011; Picard et al., 2004; She et al., 2002; Shepherd and Fricke-Begemann, 2004; Zhang et al., 2006). The results presented here describe the temperature gradients that arise over the range of these observed waves. We believe that a systematic scan of different waves spanning the range of temperature gradients arising from observed waves presents a stronger argument than a calculation of a specific observation from satellite or lidar, each of which has specific observational bias.

The referee is right that OH temperatures are typically derived from lines with $N < 5$, which are the first three (for the P-branch) or four (for the Q- and R-branches) lines. These lines are not affected, or are only marginally affected, by the findings presented in this paper as is clearly stated in the manuscript. The focus of this paper is not to argue an impact on the majority of OH temperature

calculations, but rather to highlight the impact on attempts to quantify other contributions to the excess populations observed in the higher lying rotational levels.

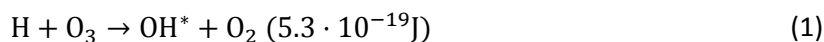
We have responded to all comments in order below and hope that the scientific precision is now acceptable to the referee and that we have cleared up any confusing or misleading text. Again, we thank the referee for their comments and for their help in improving the quality of the paper.

Specific comments:

P.1, L.23: "kcal" is an old-fashioned physical unit. The SI equivalent would be "KJ".

We deleted the kcal unit and use kJ now instead. The whole passage now reads:

"The 8-km thick airglow layer is created at about 90 km altitude (Baker and Stair, 1988; Xu et al., 2012) by the highly exothermic reduction of ozone:



The excess heat of reaction, $\sim 5.3 \cdot 10^{-19}\text{J}$, produces the OH^ in excited vibrational quantum levels of $v'=6-9$ (e.g. Mlynchak and Solomon (1993))."*

P.1, L.29-30: The rotational temperature fits for the OH nascent populations used by Dodd et al. (1994) originate from Llewellyn & Long (1978).

The $v' = 9$ temperature is indeed from Llewellyn & Long (1978), while the $v' = 6$ temperature is from Dodd et al. (1994). This has been corrected. The text now reads:

"Llewellyn & Long (1978) reported a nascent temperature of 760 K for $v'=9$, whereas others report temperatures as high as 9000-10000 K (Dodd et al, 1993; Oliva et al., 2015; Kalogerakis et al., 2018)."

P.1, L.30-31: Khomich et al. (2008) do not report rotational temperatures of about 10,000 K. They refer to such values only in the context of vibrational temperatures. Nevertheless, rotational temperatures of this magnitude have already been measured (Oliva et al. 2015, Kalogerakis et al. 2018).

We have changed the references here as suggested.

P.1, L.32 - P.2, L1: In general, it cannot be stated that low rotational levels (the rotational quantum numbers could be mentioned) are in LTE. In the case of very low vibrational levels, this might be close to reality, but for higher vibrational levels, there appears to be a significant excess even for the lowest states (e.g. Noll et al. 2018). The problem is that the full thermalisation is not achieved due to an insufficient number of thermalizing collisions in the especially short lifetimes of the high vibrational levels. Without the vibrational level changes by collisions and photon radiation, LTE would be possible.

We use the term LTE loosely in the sense that the distribution of radiation from the levels can be describes by a single temperature Boltzmann distribution. For low rotational levels $N \leq 4$, there is evidence that this temperature is consistent with the atmospheric temperature (Oberheide et al., 2006; von Zahn et al., 1987). As such, we have taken the approach that at each altitude, the temperature characterizing the Boltzmann distribution is the local atmospheric temperature, and examine only the deviations to that temperature caused by integrating each rotational line intensity through the temperature gradients across the layer.

We have made this passage clearer, adding specifically which levels we are discussing and that the studies referenced find a single temperature describes the Boltzmann distribution. We have also added a reference to the paper of Noll et al. at the end of this paragraph. Since our study however uses strict LTE conditions in the model and has no NLTE effects programmed in the model, this paragraph remains quite short, since its intention is to give an overview of the general research done in the field rather than to discuss or make inferences on the impact of NLTE effects on the lower rotational levels.

The new paragraph now reads:

“Low rotational levels (with $N \leq 4$) with energy separations less than kT , the amount typically exchanged during collisions, have been observed to have efficient energy transfer in the thermalisation process (Maylotte et al., 1972; Polanyi and Sloan, 1975; Polanyi and Woodall, 1972). Thus, emission from these states has been observed to be characterised by a single temperature Boltzmann distribution (Harrison et al., 1971; Harrison et al., 1970; Pendleton et al., 1993; Perminov et al., 2007; Sivjee et al., 1972; Sivjee and Hamwey, 1987). However, emission observed from the higher rotational levels ($N > 4$), where the energy separation exceeds kT , has indicated an anomalous, non-thermalized population that cannot be described using the same Boltzmann temperature that characterizes the lower rotational levels (Cosby and Slinger, 2007; Dodd et al., 1994; Kalogerakis, 2019; Noll et al., 2015; Pendleton et al., 1989; Pendleton et al., 1993). In keeping with the terminology employed by Pendleton et al. (1993), these two conditions are referred to as Local Thermodynamic Equilibrium (LTE) and Non-Local Thermodynamic Equilibrium (NLTE), respectively. The term LTE as used here is not technically correct as it does not account for radiative effects. Instead it relates only to the collisional distribution of the rotational levels being characterized by the temperature of the surrounding gas, as has been done in Pendleton et al. (1993). Work is currently underway to use observations of the excess populations in the high rotational levels of the OH airglow to determine state-to-state quenching coefficients and to understand the thermalisation process in OH (Kalogerakis et al., 2018).”

P.2, L.8: There are additional relevant studies by Kalogerakis et al. published in ACP and Science Advances in 2019.

See new text in the previous comment.

P.2, L.10: "the OH is in LTE": This statement is wrong. As the authors use an OH kinetic model involving non-LTE chemistry and radiation to derive the OH layer depending on vibrational level, LTE is only true for the rotational populations of a fixed vibrational level in the model. In the case of full LTE, most OH molecules would be in the vibrational ground state. Also note that a difference in the effective emission altitude for the different vibrational levels is a strong indicator of non-LTE effects. Larger non-LTE excesses are related to higher emission altitudes.

In addition to the responses to P1, L32 and P2, L1 we have changed this phrase to "the rotational population distribution of the OH is in LTE" for clarification. The whole paragraph now reads:

"Here we examine the effects of temperature gradients in the OH emission region on the resulting vertically integrated spectrum of the Meinel $\Delta v=2$ sequence. To achieve this, model work was executed, where the model assumes that for each vibrational level, the rotational population distribution of the OH is in LTE at every altitude. The emission in each rotational line is then integrated vertically."

P.2, L.12-13: The use of "excess" is only correct if its definition is related to the lowest rotational levels. In the case of a temperature gradient of zero and an average temperature as the reference, there would also be negative population changes up to a certain rotational level.

We defined the word excess here as relative to the expected Boltzmann population due to a single temperature, which is characterised by the lines with $N \leq 4$. However, because these negative excess populations all are $<1\%$ and very small compared to the effects of higher lines, we decided to keep the term. We agree however that the term should be better defined here (see also comment below) and we have added a further sentence here. The context now reads:

"We find that even if the OH rotational levels are in strict LTE with the surrounding atmosphere, the temperature gradients through the OH emission region will create apparent excess emission in the higher OH rotational lines. Here we calculate the apparent excess population relative to the Boltzmann population expected using the temperature determined by the population of rotational levels with $N \leq 4$. This excess population can be incorrectly interpreted as due to NLTE effects, affecting the subsequent calculations of the thermalisation process."

P.2, L.30: "the OH" should be extended by "rotational level distributions" (see comment on P.2, L.10).

We have changed the text accordingly. The whole sentence now reads:

"Thus the OH rotational level distributions, even if thermalised at each altitude, will be described by different temperatures at each of those altitudes."

P.2, L.30-32: In fact, there is not a single OH layer if non-LTE effects contribute and OH ro-vibrational states are considered separately. Each OH line originates from a different altitude range (even if the upper vibrational level is kept fixed) depending on the non-LTE contribution. Hence, in reality, it will be complicated to separate the temperature gradient effects from the true non-LTE effects.

The referee is of course right in saying that non-LTE effects will make the situation more complex. The aim of this paper is to demonstrate that even without NLTE effects there is an important impact on the rotational distribution of the OH airglow. We agree that it will be complicated to separate the temperature gradient effects from the true non-LTE effects. This paper makes no attempt to explain the observed NLTE effects. However, even with NLTE effects, the sentence in question here would still be true: "Any instrument that integrates through the OH layer will therefore not see rotational line emission resulting from a single, average temperature, but from the whole span of temperatures present in the layer." We do not see that this statement is in conflict with the reviewer's comment, and prefer to keep the sentence as is, but thank the referee for the further explanation.

P.2, L.32-33: "the emission from high rotational lines that occurs in the warm regions": This statement should be softened since a negligible contribution of the cold regions to the high rotational states would require large temperature gradients. In this respect, it would be helpful if such a criterion could be quantified in the paper.

We have added a citation to the paper of Picard et al. (2004), who measured temperature changes of 60 between 85 and 95 km altitude. Additionally, the reported wave amplitudes in the mesopause region are consistent with temperature gradients up to this order. Since such large perturbations due to waves/tides are possible and observed, and even smaller gradients are shown in our results to have a significant impact, this sentence would appear to be accurate.

P.3, L.8: "OH is in LTE" (see comment on P.2, L.10).

See also answer to the comment P.2, L.10. We have also made the wording here more precise. The sentence now reads:

“We utilise a steady-state model of the OH VER, described below, to synthesise individual synthetic rotational spectra at 1 km intervals from 74 to 110 km. The model assumes that for each vibrational level, the rotational population distribution of the OH is in LTE (i.e. a single-temperature Boltzmann distribution) with the local temperature at each altitude.”

P.3, L.11: "excess population" (see comment on P.2, L.12-13).

See also answer to comment P2, L12-13. After already defining the term more clearly, we feel confident in keeping this text.

P.4, L.5-7: The use of hot nascent OH populations stringently leads to non-LTE level populations. Therefore, it should be made clear that these calculations are only used to derive the vertical OH emission distribution for each vibrational level (which neglects the spread of emission heights depending on the rotational level). The rotational level population distributions are arbitrarily set to LTE.

We have specified more clearly that the rotational population calculations are performed for each vibrational level. The text now reads:

“was also used to calculate the production rate of OH for each vibrational level, using the reaction rate coefficient (Sander et al., 2003). Due to the exothermicity of reaction 4, vibrational levels from $v'=6$ to 9 can be populated. The production of each vibrational level OH*(v') is calculated using the branching ratios from Sander et al. (2019).”*

P.4, L.8: The most frequent constituent of the Earth's atmosphere, N₂, is not considered for the collisional loss. Why?

The rate coefficient for OH quenching with N₂ is small, and Knutsen et al. (1996) were only able to provide an upper limit. Since the O₂/N₂ mixing ratio is virtually constant up to the turbopause, the O₂ would be 3 times more effective at quenching than the N₂. Thus, neglecting the N₂ would be well within the uncertainty of the O₂ rate coefficient and would not significantly affect the altitude distribution of the OH.

P.4, L.10: Why is the primitive "sudden death" approach used for all kinds of collisions? This is not state of the art. There are various examples of more sophisticated models in the literature. For example, the model by Adler-Golden (1997) as well as the fast Sharma et al. (2015) process for OH vibrational relaxation by atomic oxygen collisions had a big impact.

We thank the referee for pointing this out. The more sophisticated quenching models primarily change the relative vibrational distributions. However, the altitude profile of a single vibrational level is relatively unchanged, which is the primary consideration in this work. We have compared the vibrational distribution of single vibrational levels generated here with those of Adler-Golden (1997) and found them to be in good agreement. A stronger effect on the altitude profile is the profile of atomic oxygen, which is known from the SABER measurements to be highly variable. However, for MSIS atomic oxygen distributions, we are confident that our simple model reproduces the altitude distribution of a single vibrational level adequately for the purposes of this study. A small addendum was added to the paragraph mentioning the comparison with the Adler-Golden results.

However, a mistake was made in the description of this model. The sudden death criterion is used for the O quenching, while O₂ and CO₂ quench for steps of one vibrational unit. These are the major quenching channels for these species (Chalamala and Copeland, 1993; Dodd et al., 1991; Dyer et al., 1997; Knutsen et al., 1996; McDade and Llewellyn, 1987). We have changed the text here to correct this mistake. It now reads:

“Collisional loss for each OH(v') vibrational level was calculated for collisions with O, O₂ and CO₂ using the rate coefficients of Dodd et al. (1991), Knutsen et al. (1996), Dyer et al. (1997) and Chalamala and Copeland (1993). The model assumes quenching to the ground vibrational state, known as “sudden death” for the O, and stepwise quenching by one vibrational unit for the O₂ and the CO₂ (McDade and Llewellyn, 1987). The relative shape and peak height of the altitude profiles of the individual vibrational levels agree closely with those of the more sophisticated model of Adler-Golden (1997)”*

P.4, L.11: Radiation is also an important source of non-LTE effects, especially if it is not reabsorbed nearby as in the case of OH. This also contributes to the fact that the model in Sect. 2.1 is not able to provide OH in LTE. Hence, one should make clear that there is no consistent OH model that delivers thermalised populations. The investigation of the temperature gradient effect therefore requires the arbitrary manipulation of population distributions. I do not criticise this approach but it should be better communicated.

We now clarify the “misuse” of the terms LTE and non-LTE when we first introduce them in the body of the paper. Please see also the answer to the comment on P1, L32 – P2, L1.

“The term LTE as used here is not technically correct as it does not account for radiative effects. Instead it relates only to the collisional distribution of the rotational levels being characterized by the temperature of the surrounding gas, as has been done in Pendleton et al. (1993). “

P.4, L.11: "z" is not defined.

We have added the definition of z as the altitude. The text now reads:

“The total radiative loss from each vibrational level is given by $N_{\nu}(z) / \tau_{\nu}$, where $N_{\nu}(z)$ is the concentration of the hydroxyl ν' vibrational level at the altitude z and its lifetime, τ_{ν} , are calculated from Mies (1974).”

P.4, L.12: Mies (1974) does not give lifetimes. He provides Einstein-A coefficients. The set of coefficients is already quite old. Better data would be available.

We thank the referee for this comment. It is true that Mies calculated Einstein coefficients rather than lifetimes. We used these to calculate the lifetimes ourselves. This is now written more precisely in the paper. (See new text in the previous comment.) However, while the distribution of line strengths within the rotational levels are different with different authors, primarily due to vibration-rotation coupling, these differences tend to average out. This is because the differences are in different directions for the R- and P- branches, and virtually zero for the Q-Branch. Thus the lifetimes of the vibrational levels (the inverse of the sum of the individual line strengths) is relatively unchanged.

P.4, L.13: Mies (1974) does not introduce $\omega_{\nu\nu'}$.

Mies (1974) does, however, give all the important Einstein coefficients to calculate the branching ratio as the ratio of the sum of A-coefficients for one level divided by the total sum of all A-coefficients. We have specified this in the text, which now reads:

“The total VER of any ν' to ν'' vibrational transition is then given by $V_{\nu\nu''}(z) = \omega_{\nu\nu''} \cdot N_{\nu}(z) / \tau_{\nu}$, where $\omega_{\nu\nu''}$ is the vibrational branching ratio calculated from the Einstein coefficients from Mies (1974).”

P.4, L.26-29: Eq. 5 needs to be revised for several reasons. $N_{J'}$ can only be a relative population as an absolute population is already given by $N_{v'}$ if the descriptions from Sect. 2.1 still hold. A better solution would be to use $N_{v'J'}$ from Eq. 6. As $\omega_{v'v''}/\tau_{v'}$ corresponds to $A_{v'v''}$, the equation shows a product of Einstein-A coefficients, which looks wrong. It would be OK to replace both terms by $A_{v'v''J'J''}$. Moreover, $V_{v'v''J'J''}$ and $N_{J'}$ are also functions of z . Finally, level splitting by spinorbit coupling is not considered (symbol: i or F). This should be included as Fig. 2 proves that it was considered for the model.

We have changed the equation according to the suggestions of the referee. We have also now explained that we only look specifically at the 3/2 electronic subset and drop all further references to the F quantum number for readability. The new passage now reads:

$$V_{v'v''J'J''}(z) = \frac{\omega_{v'v''}}{\tau_{v'}} N_{v'J'}(z) \cdot A_{v',v'',J'J''}, \quad (2)$$

where $A_{J'J''}$ is the Einstein coefficient for the rotational transition and $N_{v'J'}$ is the population of the upper rotational level, J' . We concentrate in this paper on the 3/2 electronic subset of the OH airglow and drop the spin-orbit splitting quantum number F in all equations for readability."

P.4, L.29 - P.5, L.2: Eq. 6 also needs to be revised since the partition function $Q_{v'}(T_{\text{rot}})$ (Mies 1974) is missing. Otherwise the rotational level population distribution is not correctly normalised. It would be better to replace $E_{J'}$ by $E_{v'J'}$ as the level energy also depends on v' . Moreover, the electronic substates are not provided. Finally, the z dependences of $N_{v'J'}$ and $N_{v'}$ are not given.

We have changed the equation according to the suggestions from the referee. The section now reads:

$$N_{v'J'}(z) = \frac{N_{v'}(z) 2(2J'+1)}{Q_{v'}(T(z))} \cdot \exp\left(\frac{-E_{v'J'}}{k \cdot T(z)}\right) \quad (3)$$

Where $N_{v'}$ is the total population of the v' vibrational level from the model, $E_{v'J'}$ is the energy of the v', J' vibration-rotation level, the factor $2(2J'+1)$ is the degeneracy of that level (including Λ -doubling) and $Q_{v'}(T(z))$ is the partition function (Herzberg, 1950). "

P.5, L.4: "the OH is in LTE" (see comment on P.2, L.10).

Please see the answer to that comment. Again, here we state that the model assumes that the OH is in LTE to show that a single-temperature Boltzmann population, at the local temperature of the atmosphere, is used to describe the rotational distribution of emission.

P.5, L.7-8: The statement related to the cool and warm regions should be weakened since a complete separation of the rotational level populations cannot be expected for typical temperature gradients.

We have amended the sentence since, as the referee says, the low lines are not only due to the cooler regions. The whole sentence now reads:

“This results in a net spectrum of low rotational lines whose intensities are enhanced relative to the mean temperature of the emission region when emitted from the cooler regions. Accompanying this are high rotational lines whose intensities are enhanced relative to the mean temperature of the emission region when emitted from the warm regions. Each of these is weighted by the VER of the vibrational transition at each altitude, $N_v(z) \cdot \omega_{v'v''} / \tau_{v'}$.”

P.5, L.11: "assuming LTE" should be extended by "for the rotational level populations".

We agree that this addition makes the text more accurate. The complete sentence now reads:

“As an example, the model described above was used to create a synthetic spectrum of the (7,4) rotational-vibrational band, assuming LTE for the rotational level populations at every altitude level, for mid-July, mid-latitude conditions”.

P.6, L.2: "ergs cm⁻³ s⁻¹" are quite old-fashioned units. Moreover, "s⁻¹" would be correct.

The missing minus sign has been added. We prefer to keep the units in ergs cm⁻³ s⁻¹ for direct comparison with the units system used with the SABER instrument.

P.6, L.7-8: The statement is only correct for the plotted phase of the wave. A phase shift of 180 deg would change the effective sign of the temperature gradient in the OH layer.

This is true. Later in the paper we model all phases to cover such cases. In this figure caption we only refer to the example given in the figure to highlight the general effect. We have changed the sentence to make this clearer and to avoid confusion. It now reads:

“With the example wave given here, the temperature variation increases the VER of the lower rotational lines at 95 km altitude, and of the higher rotational lines at 80 km.”

P.6, L.10-13: In the same way as Eqs. 5 and 6, Eq. 8 needs to be improved. I propose to write $I_{v'v''J'J''}$, $A_{v'v''J'J''}$, $E_{v'J'}$, and $E_{v''}$. This is further modified if the electronic substates are introduced (e.g. by adding i' or F'). Finally, $Q_{v'}(T_{rot})$ is also missing here.

We have updated the equation as suggested. It now reads:

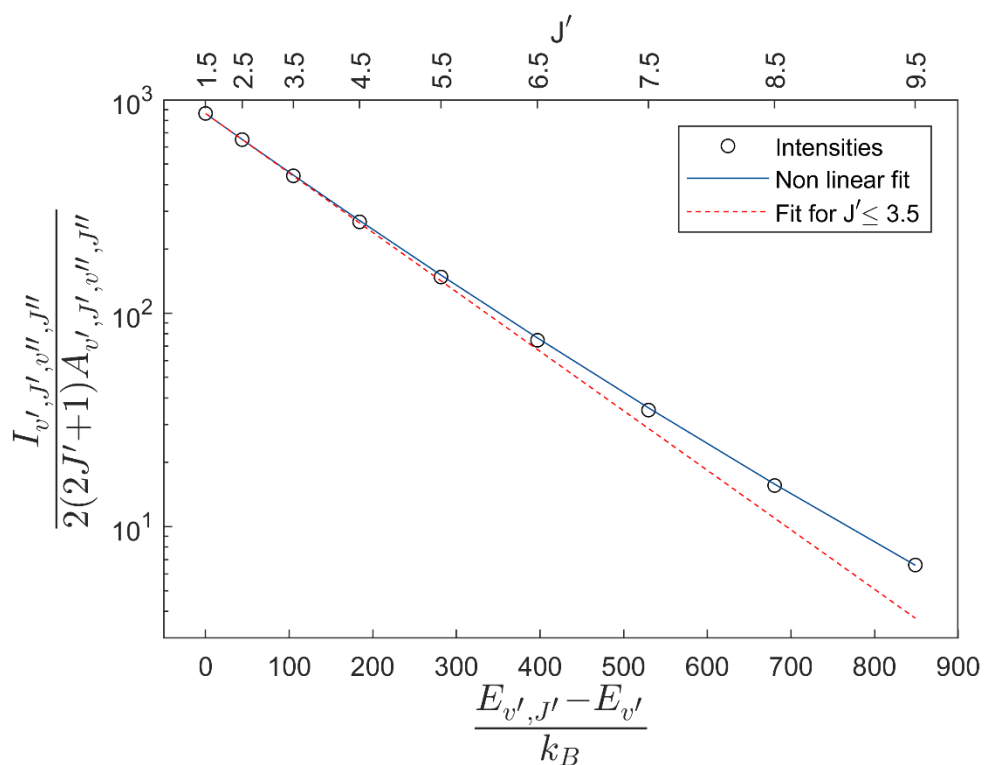
$$\frac{I_{v',v'',J',J''}}{2(2J'+1)A_{v',v'',J',J''}} = Q_{v'}(T)N_{v'} \cdot \exp\left(\frac{-(E_{v',J'}-E_{v'})}{kT}\right)$$

P.6, L.13-16: As Eq. 9 is very similar to Eq. 8, the same proposals are relevant. Depending on the changes, the symbols in Fig. 3 need to be adapted.

We have also updated this equation. It now reads:

$$\ln\left(\frac{I_{v',v'',J',J''}}{2(2J'+1)A_{v',v'',J',J''}}\right) = \ln(Q_{v'}(T)N_{v'}) - \frac{1}{T}\left[\frac{(E_{v',J'}-E_{v'})}{k}\right]$$

We have also updated the symbols in the Figure (which is now Figure 4):



P.7, L.1-2: "the lowest three rotational levels": This obviously refers to the $F = 1$ substates.

This is correct. Since we have now said specifically that we only look at the $F = 1$ sub-state (see comments to P4, L26-29), we keep the text here as it was.

P.7, L.10: The populations are related to P_1-branch lines.

Since we have now said specifically that we only look at the $F = 1$ substates (see comments above), we keep the text here as it was.

P.7, L.16 - P.8, L.1: This is again an equation which should be improved (see comments on previous equations).

We have updated this equation in the same manner. It now reads:

$$\ln \left(\frac{I_{v',v'',J',J''}}{2(2J'+1) \cdot A_{v',v'',J',J''}} \right) = \ln(Q_{v'}(T)N_{v'}) - \frac{1}{T} \left[\frac{(E_{v',J'} - E_{v'})}{k} \right] + \frac{\beta}{T^2} \left[\frac{(E_{v',J'} - E_{v'})}{k} \right]^2$$

P.8, L.1-2: It is stated that the beta parameter was used to improve the fit of the population distribution in Fig. 3. However, the actual value of beta is not provided.

The β factor for this example is 0.019. We have added this to the text. It now reads:

"The retrieved temperature $T_{NL} = 154.9 \pm 0.1$ K, is the same as $T_{1,3}$ within the fitting uncertainties, with a β factor of 0.019."

P.8, L.28-30: beta is also not given for the scenarios in Fig. 4.

The wave used for this figure is the same as used before, so the β -factor is still 0.019. We have added this information to the figure caption. It now reads:

"This is the same wave as presented in Figure 4. The distribution has a $\beta = 0.019$."

P.8, L.32-34: "the distribution of integrated rotational line intensities" for the fitting procedure does not appear to be limited in terms of the rotational levels. If high rotational levels contribute to the fit, the low rotational levels will show under populations. In this case, "excess" will be the wrong term.

The apparent excess population is defined relative to the predicted Boltzmann population of the lowest three rotational lines. This has also been clarified earlier (see comments above). We have also clarified this point in the text here. The text now reads:

"The apparent excess population is the ratio between the calculated intensity of a rotational line integrated in altitude, and the intensity of that line predicted by a Boltzmann distribution fitted to the distribution of integrated line intensities of the lowest three rotational lines using a single, effective temperature"

P.9, L.10: Excess populations for P₁-branch lines are shown. The excess is probably related to the first three rotational levels. This information should be given in the caption.

We agree that this should be stated here. The text now reads:

"The calculated apparent excess population of the OH (7,4) P(*J'*) lines relative to the Boltzmann population characterized by the temperature fitted to the lowest three lines."

P.9, L.14-26: The comparison with the measurements of Pendleton et al. (1993) would be less awkward if the population ratios from their Fig. 16 are also plotted in Fig. 4. It should not be a problem to add histograms of different colour or transparency to the two subfigures.

We agree that this is a sensible addition. We have changed the figure and associated text as follows:

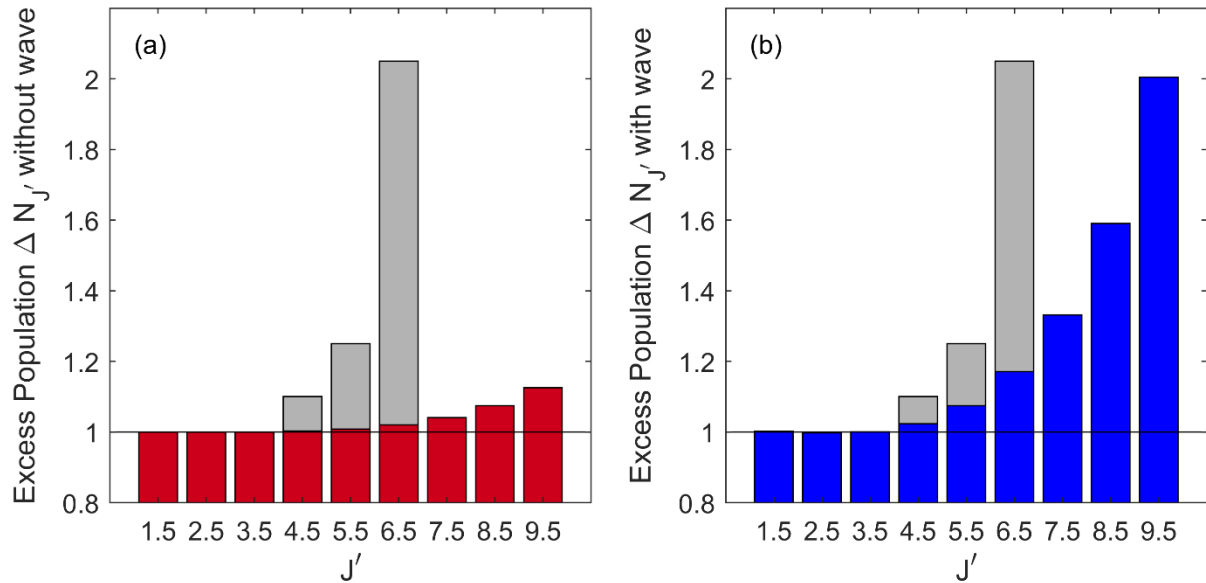


Figure 5: The calculated apparent excess population of the OH (7,4) P(J') lines relative to the Boltzmann population of the fitted temperature to the lowest three lines. Red on the left is calculated with the climatological temperature gradient shown from NRLMSISE-00 above Boulder, Colorado (40.0° N; 105.6° W) in mid-July. Blue on the right is calculated with a wave of $A_w = 30$ K at 90 km, $\lambda_w = 30$ km and a phase that yields the maximum effect, $\varphi_w = 4.9$ rad. This is the same wave as presented in Figure 4. The distribution has a $\beta = 1.9$ %. The grey bars represent the measurements ascribed to NLTE effects from Pendleton et al. (1993).

These results can be compared to the findings from Pendleton et al. (1993) in their Fig. 16, for the (7,4) transition above Boulder, Colorado during mid-summer, the same season and transition as presented here. These results are shown as grey bars in Figure 5 (a) and (b)."

P.9, L.22: This is actually the only place where "P_1" is given. This notation will be understood if the related cases are consistently changed in the paper.

We have removed the 1 subscript, as we now discuss earlier in the paper that we are only discussing the 1 sublevel. The text now reads:

"For example, Pendleton et al. (1993) reported an apparent excess population of around a factor of 2 for the P(N=7) (i.e. J'=6.5) line."

P.9, L.26 - P.10, L.2: This conclusion sounds more dramatic than it is since OH kinetic models are usually resolved in altitude, i.e. the models implicitly include the temperature gradient effect. Hence, comparisons with ground-based measurements should be trustworthy without any change in the modelling approach.

We agree models is the wrong word to use here. We are referring to calculations of kinetic thermalisation based on integrated airglow measurements. We have clarified this by changing the word "models" for "studies". The text now reads:

"Thus, the effect of the atmospheric temperature background has to be considered in addition to NLTE effects whenever the populations inferred from integrated airglow observations of high J' lines are to be used in kinetic thermalisation studies."

P.10, L.5: It is not clear which lines were used for the baseline fit for the derivation of the excess population. It might be helpful to define the term "excess population" at the first occasion and then to state that this definition is used for the rest of the paper.

We have defined "excess population" in response to the P2, L12-13 comment.

P.10, L.6-7: "The figure shows the (7,4) transition" sounds a bit strange. The figure shows results related to the (7,4) band. There are other similar sentences in the paper. As I would primarily expect that "transition" describes a spectral line, "band" or "vibrational transition" appear to be clearer.

We keep the nomenclature of Pendleton et al. (1993), who discuss the (7,4) "transition", as a comparison to our work. We agree however that this sentence is a bit clumsy and have rephrased it as suggested from the referee. It now reads:

"The figure shows results related to the (7,4) vibrational transition, which is the same transition that Pendleton et al. (1993) used."

P.10, L.9-10: The discussion in Sect. 3 only focusses on the "highest apparent excess population" for waves of a given amplitude and vertical wavelength. It would also be helpful to briefly quantify the average effect and the related variation. As already discussed in the context of the general comments, it is also important to know what the real distribution of temperature gradients for the OH layer is (or equivalently: the true frequency of the different simulated waves) in order to estimate the real impact of the temperature gradient effect. These results should be compared to the true non-LTE effects (as for the two examples in Fig. 4).

Such random wave motions can vary with latitude, longitude, season and time of day. We have attempted to give references in the paper indicating that the gradients observed here have been

observed. However, a comprehensive survey of all wave motions present in the mesosphere and their statistics is well beyond the scope of this paper.

However, we have added a short paragraph on the mean effect of waves with different phases as suggested. The mean effect is about 30 % of the maximum, which was presented in the paper, with a range between 20 % and 40 % dependent on the wavelength and amplitude of the wave. The new text is now:

“Figures 5 and 6 show the results for the phase which creates the strongest apparent excess population. The mean effect as a result of all different phases simulated is independent of the transition and varies between 20 and 40% of the maximum effect presented in Figures 5 and 6.”

P.12, L.3: Just writing "The apparent excess population" is incomplete. In fact, it is "The maximum apparent excess population" for the described wave.

We have changed the sentence as suggested. It now reads:

“The maximum apparent excess population of the $J' = 6.5$ upper level for a wave with wavelength 30 km and an amplitude of 30 K at 90 km altitude as a function of vibrational upper level.”

P.12, L.10: "the OH in LTE" (see comment on P.2, L.10).

See the response to that comment. Our simulations only calculate the OH in LTE, regardless of whether or not this happens in the real atmosphere. We changed the text slightly to make this even clearer:

“Even though the simulations calculated the rotational population distribution of the OH to be in LTE with the surrounding gas at every altitude, the integrated intensities of the higher rotational lines indicate an apparent excess population that could be misinterpreted as contributing to the NLTE effects previously reported (Cosby and Slinger, 2007; Noll et al., 2015; Pendleton et al., 1993).”

P.12, L.18: It depends on the research goal and the related significance of the effect whether the consideration of the effect is really "necessary". Concerning the estimate of the true impact, the paper should be improved.

We are confident that this paper shows that a considerable part of the ground-based measured excess population of higher rotational lines can be due to the influence of waves and tides. We therefore think it is important to consider this effect whenever rotational distributions are inferred

from ground-based airglow observations. This is exactly what the sentence in questions states. We have no intention to imply that these findings are “necessary” for anything other than this specific research goal. We are confident that the impact presented in this paper is a “true impact”, as the waves simulated in this paper have been observed before and could therefore be present in any ground-based measurement. Please see also the next comment.

P.12, L.18: "the rotational distribution of the OH" might be replaced by "OH rotational level population distributions", which sounds better.

We have changed the sentence as suggested. It now reads:

“We conclude that it is necessary to consider the temperature profile in order to infer OH rotational level population distributions from ground-based airglow observations.”

Technical corrections:

Whole paper: I have identified four different styles for the vibrational level symbol "v" (see e.g. P.5). In several equations, it is even an upper case letter. This should be harmonised. Other symbols should be checked in the same way.

We could not find the incident where the vibrational level was upper case. In equation (5), the capital V is referring to the volume emission rate rather than any vibrational level and should therefore be capitalised. We have attempted to harmonise the other instances as suggested by the referee.

P.9, L.2: "rad" should not be in italics.

We have changed this in the text.

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Modelled Effects of Temperature Gradients and Waves on the Hydroxyl Rotational Distribution in Ground-Based Airglow Measurements

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Abstract. Spectroscopy of the hydroxyl (OH) airglow has been a commonly used way to remotely sense temperatures in the mesopause region for many decades. This technique relies on the OH rotational state populations to be thermalised through collisions with the surrounding gas into a Boltzmann distribution characterised by the local temperature. However, deviations of the rotational populations from a Boltzmann distribution characterised by a single temperature have been observed and attributed to an incomplete thermalisation of the OH from its initial, non-thermodynamic equilibrium distribution. Here we address an additional cause for the apparent amount of excess population in the higher rotational levels of the OH airglow brought about by integrating these OH emissions through vertical gradients in the atmospheric temperature. We find that up to 40 % of the apparent excess population, currently attributed to incomplete thermalisation, can be due to the vertical temperature gradients created by waves. Additionally, we find that the populations of the different upper vibrational levels are affected differently. These effects need to be taken into account in order to assess the true extent of non-thermodynamic equilibrium effects on the OH rotational populations.

1 Introduction

The hydroxyl (OH) airglow has been employed for many years for remote sensing of the Mesosphere and Lower Thermosphere (MLT) region (Meinel, 1950a, b). The 8-km thick airglow layer is created at about 90 km altitude (Baker and Stair, 1988; Xu et al., 2012) by the highly exothermic reduction of ozone:



The excess heat of reaction, $\sim 5.3 \cdot 10^{-19} \text{J}$, produces the OH* in excited vibrational quantum levels of $v'=6-9$ (e.g. Mlynczak and Solomon (1993)). Subsequent radiative cascading and collisional-deactivation produces OH* in all vibrational levels ≤ 9 . Radiative de-activation can occur between any two vibrational quantum levels, but transitions with $\Delta v = 2$ are preferred (Langhoff et al., 1986).

The excess energy of reaction (1) also creates rotational excitation within the OH* molecule in addition to the vibrational excitation. The nascent rotational population for high rotational levels, J , shows a distribution characteristic of a temperature far above the local atmospheric temperature. Llewellyn & Long (1978) reported a nascent temperature of 760 K for $v'=9$, whereas others report temperatures as high as 9000-10000 K (Dodd et al, 1993; Oliva et al., 2015; Kalogerakis et al., 2018). Low rotational levels (with $N \leq 4$) with energy separations less than kT , the amount typically exchanged during collisions, have been observed to have efficient energy transfer in the thermalisation process (Maylotte et al., 1972; Polanyi and Sloan, 1975; Polanyi and Woodall, 1972). Thus, emission from these states has been observed to be characterised by a single temperature Boltzmann distribution

(Harrison et al., 1971; Harrison et al., 1970; Pendleton et al., 1993; Perminov et al., 2007; Sivjee et al., 1972; Sivjee and Hamwey, 1987). However, emission observed from the higher rotational levels ($N > 4$), where the energy separation exceeds kT , has indicated an anomalous, non-thermalized population that cannot be described using the same Boltzmann temperature that characterizes the lower rotational levels (Cosby and Slanger, 2007; Dodd et al., 1994; Kalogerakis, 2019; Noll et al., 2015; Pendleton et al., 1989; Pendleton et al., 1993). In keeping with the terminology employed by Pendleton et al. (1993), these two conditions are referred to as Local Thermodynamic Equilibrium (LTE) and Non-Local Thermodynamic Equilibrium (NLTE), respectively. The term LTE as used here is not technically correct as it does not account for radiative effects. Instead it relates only to the collisional distribution of the rotational levels being characterized by the temperature of the surrounding gas, as has been done in Pendleton et al. (1993). Work is currently underway to use observations of the excess populations in the high rotational levels of the OH airglow to determine state-to-state quenching coefficients and to understand the thermalisation process in OH (Kalogerakis et al., 2018). Here we examine the effects of temperature gradients in the OH emission region on the resulting vertically integrated spectrum of the Meinel $\Delta v = 2$ sequence. To achieve this, model work was executed, where the model assumes that for each vibrational level, the rotational population distribution of the OH is in LTE at every altitude. The emission in each rotational line is then integrated vertically.. We find that even if the OH rotational levels are in strict LTE with the surrounding atmosphere, the temperature gradients through the OH emission region will create apparent excess emission in the higher OH rotational lines. Here we calculate the apparent excess population relative to the Boltzmann population expected using the temperature determined by the population of rotational levels with $N \leq 4$. This excess population can be incorrectly interpreted as due to NLTE effects, affecting the subsequent calculations of the thermalisation process.. The deviations in the inferred populations from a single-temperature Boltzmann distribution are compared with observations that include both NLTE and temperature gradient effects. This comparison is made for realistic atmospheric temperature profiles that have been perturbed with realistic atmospheric gravity-waves in order to help quantify the true NLTE content needed to construct a quantitative picture of OH thermalisation. Recent measurements indicate that the Boltzmann distribution of the rotational levels may be characterized by a temperature that is higher than that of the surrounding gas due to incomplete thermalization (Noll et al., 2018). However, the purpose of this paper is to show that even if complete thermalization with the surrounding gas takes place, ground based measurements integrating through temperature gradients within the OH layer will not see a rotational population described by a Boltzmann distribution characterized by a single temperature.

1.1 Overview of the OH emission

Fig. 1 shows an example of the OH airglow volume emission rate (VER) and a temperature profile, measured from the Sounding of the Atmosphere using Broadband Emission Radiometry (SABER) instrument aboard the NASA Thermosphere Ionosphere Mesosphere Energetics Dynamics (TIMED) satellite (Mlynczak, 1997; Russell et al., 1999). This specific measurement is a zonal mean and monthly average from July 2016 between the latitudes of 20 and 30 degrees north. The OH VER from the vibrational levels 8 and 9 is shown in red in the figure, while the black curve shows the temperature profile. It can be seen that the temperature is not constant through the OH layer. In this example the atmospheric temperature changes by over 10 K through the layer. This observed behaviour is similar to other observations, for example from French and Mulligan (2010), who compared TIMED/SABER observations with ground-based observations.

Waves will exacerbate this effect by perturbing both the OH VER and changing the temperature gradient. Thus, the rotational level distribution of the OH, even if thermalised at each altitude, will have different temperatures at each of those altitudes. Any instrument that integrates through the OH layer will therefore not see rotational line emission resulting from a single, average temperature, but from the whole span of temperatures present in the layer. That is, the emission from high rotational lines that occurs in the warm regions will be present in the spectrum along with the predominantly low rotational level lines emitting from the colder regions.

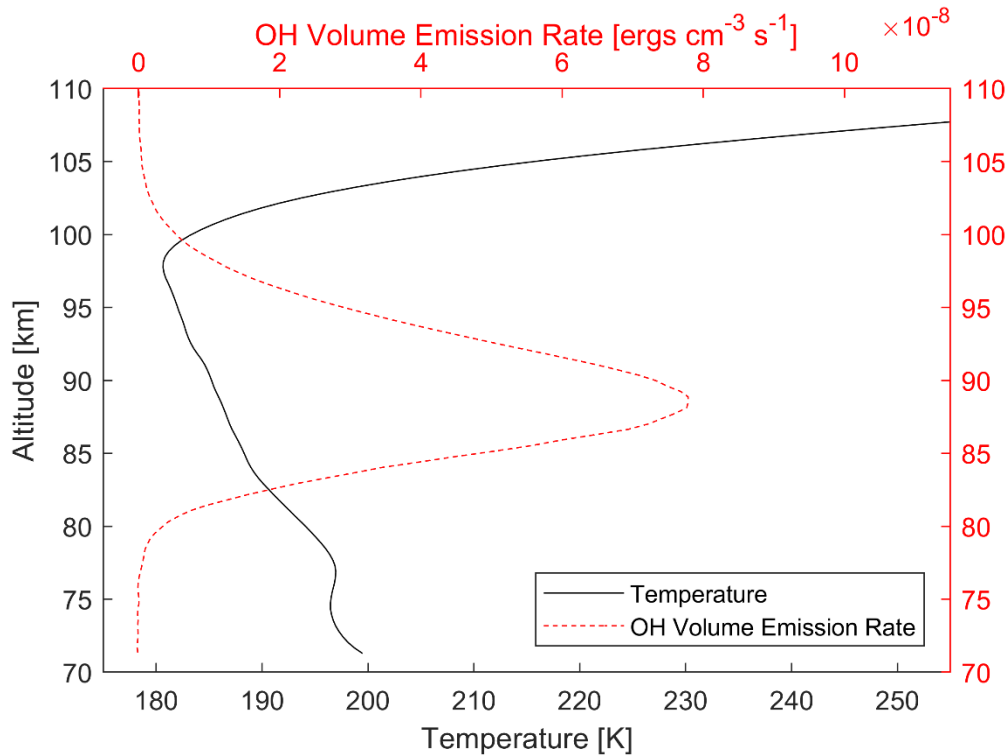


Figure 1: Example of a typical temperature profile (black) of the airglow layer and the VER (red-dashed) from the SABER satellite showing the variation of temperature through the emission region. This specific measurement is a zonal mean and monthly average from July 2016 between the latitudes of 20 and 30 degrees north for the bands from the 8 and 9 upper-state vibrational levels.

2 Method

We utilise a steady-state model of the OH VER, described below, to synthesise individual synthetic rotational spectra at 1 km intervals from 74 to 110 km. The model assumes that for each vibrational level, the rotational population distribution of the OH is in LTE (i.e. a single-temperature Boltzmann distribution) with the local temperature at each altitude. Each rotational line is integrated in altitude to give the net spectrum that would be observed by an instrument integrating through the layer. The distribution of emission in the rotational lines is then used to infer the population of the OH rotational levels, allowing us to quantify the portion of the inferred excess population in the upper levels that is due to the temperature gradients across the OH layer.

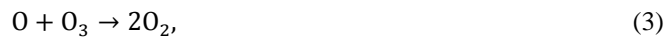
2.1 The OH model

The atmospheric background temperature and concentrations of N₂, O₂, H and O are taken from the US Naval Research Laboratory's Mass Spectrometer and Incoherent Scatter radar model (NRLMSISE-00) (Picone et al., 2002). The steady-state ozone concentration is then calculated from balancing the production and loss processes.

5 The production mechanism is:



where M is a reaction mediator. The temperature dependent rate coefficients for this reactions are taken from the International Union for Pure and Applied Chemistry (IUPAC) Gas Kinetic Database (Atkinson et al., 2004). Loss processes include losses due to O via



using the reaction rate coefficient of Sander et al. (2003). The loss of O₃ to atomic hydrogen,



10 was also used to calculate the production rate of OH* for each vibrational level, using the reaction rate coefficient (Sander et al., 2003). Due to the exothermicity of reaction 4, vibrational levels from v'=6 to 9 can be populated. The production of each vibrational level OH*(v') is calculated using the branching ratios from Sander et al. (2019). Collisional loss for each OH*(v') vibrational level was calculated for collisions with O, O₂ and CO₂ using the rate coefficients of Dodd et al. (1991), Knutsen et al. (1996), Dyer et al. (1997) and Chalamala and Copeland (1993).
15 The model assumes quenching to the ground vibrational state, known as "sudden death" for the O, and stepwise quenching by one vibrational unit for the O₂ and the CO₂ (McDade and Llewellyn, 1987). The relative shape and peak height of the altitude profiles of the individual vibrational levels agree closely with those of the more sophisticated model of Adler-Golden (1997).

The total radiative loss from each vibrational level is given by $N_{v'}(z) / \tau_{v'}$, where $N_{v'}(z)$ is the concentration of the hydroxyl v' vibrational level at the altitude z and its lifetime, $\tau_{v'}$, are calculated from Mies (1974). The total VER of any v' to v'' vibrational transition is then given by $V_{v'v''}(z) = \omega_{v'v''} \cdot N_{v'}(z) / \tau_{v'}$, where $\omega_{v'v''}$ is the vibrational branching ratio calculated from the Einstein coefficients from Mies (1974). This radiative cascade into lower vibrational levels then acts as an additional production term for levels below v'=9. Balancing these production and loss terms at each height yields the steady-state concentration of each OH* vibrational level as a function of
25 height, $N_{v'}(z)$. Such a model has been shown to fit observations, for example TIMED/SABER (Xu et al., 2012).

2.2 The wave model

As mentioned above, the background atmospheric temperature profile can be perturbed by waves. We therefore include wave-induced temperature perturbations in the model. Following Holton (1982), we limited the wave growth with altitude to maintain temperature gradients to below the dry adiabatic lapse rate. The wave has the
30 form

$$A_w(z) \cdot \cos\left(\frac{2\pi z}{\lambda_w} + \varphi_w\right), \quad (5)$$

Where φ_w is the wave's phase, and $A_w(z)$ is a function of altitude so as not to exceed the dry adiabatic lapse rate. The lower edge of the model is 74 km altitude. The wave amplitude as a function of altitude is shown in Fig. 2 for the case of a wave with an amplitude of 10 K at 74 km altitude and a vertical wavelength of 20 km. This example is given for an isothermal atmosphere of 200 K (Fig. 2 (a), dashed-black). The wave grows in amplitude with altitude to conserve energy (dashed-blue), but at regions where the lapse rate exceeds the dry adiabatic lapse rate (here between 90 and 95 km, and between 110 and 115 km), the wave loses energy and the amplitude decreases (Holton, 1982). The breaking wave is shown in red in Fig. 2 (a). Fig. 2 (b) shows the instantaneous lapse rate (change in temperature with altitude) of the non-breaking wave (dashed-blue) and the breaking wave (red), which never crosses the dry adiabatic lapse rate of -10 K/km (dashed-black). Fig. 2 (c) shows the amplitude of the non-breaking wave (dashed-blue) which increases exponentially and for the breaking wave (red), which decreases at the altitudes where the wave dissipates energy.

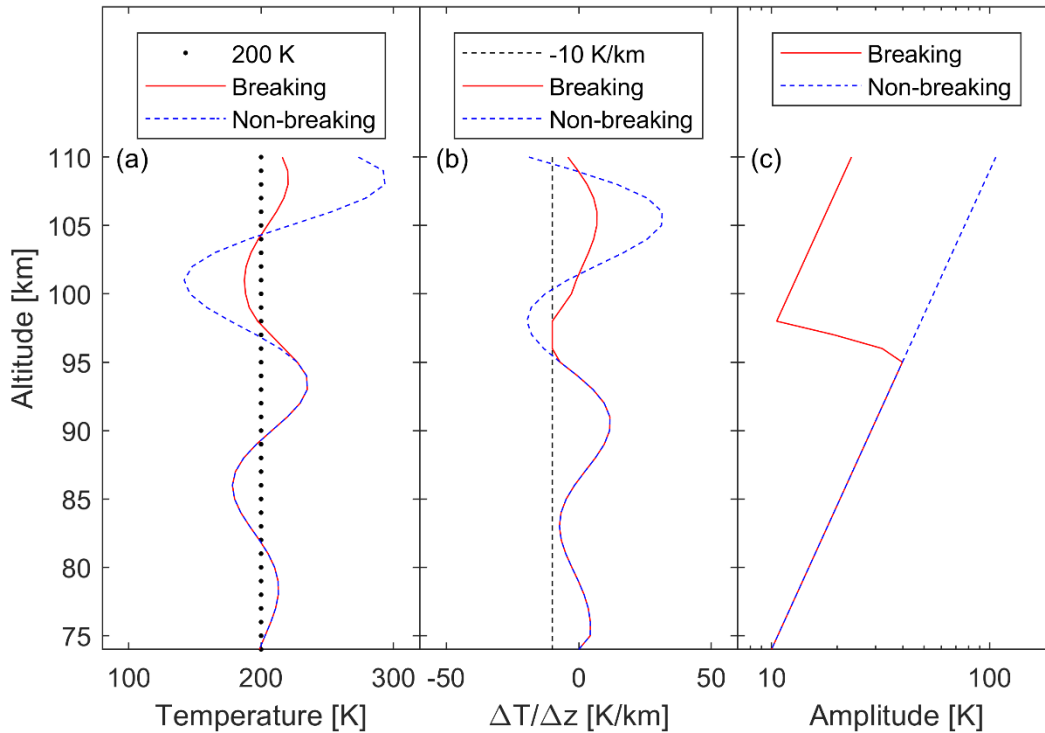


Figure 2: (a) Example of a wave of amplitude 10 K at 74 km altitude perturbing an isothermal atmosphere at $T = 200$ K (dotted-black). The dashed-blue line represents the wave without any breaking, and the red line is the breaking wave as used in the model. (b) The rate of change of temperature with altitude for the wave shown in (a). When the temperature changes faster than -10 K/km (dashed-black) the wave breaks. (c) At these altitudes, the amplitude of the breaking wave (red) decreases, while the non-breaking wave continues to grow exponentially (dashed-blue).

The background atmosphere mixing ratios from the NRLMSISE-00 model were also perturbed using the gravity wave polarisation relations from Vincent (1984). This perturbed background atmosphere and temperature profile were then used in the steady-state model for the OH to yield a new, wave-perturbed $N_{v'}(z)$ for the analysis.

2.3 Simulation of a ground-based measurement

- 5 The VER of a rotational transition for the J' to J'' state from the upper state, v' , of the v' to v'' vibrational band is given by:

$$V_{v'v''J'J''}(z) = \frac{\omega_{v'v''}}{\tau_{v'}} \cdot N_{v',J'}(z) \cdot A_{v',v'',J'J''}, \quad (6)$$

- where $A_{J'J''}$ is the Einstein coefficient for the rotational transition and $N_{v',J'}$ is the population of the upper rotational level, J' . We concentrate in this paper on the 3/2 electronic subset of the OH airglow and drop the spin-orbit splitting quantum number F in all equations for readability. Assuming that collisions have thermalised the closely spaced rotational levels with the surrounding gas at temperature T , their population may be described using a Boltzmann distribution written as:

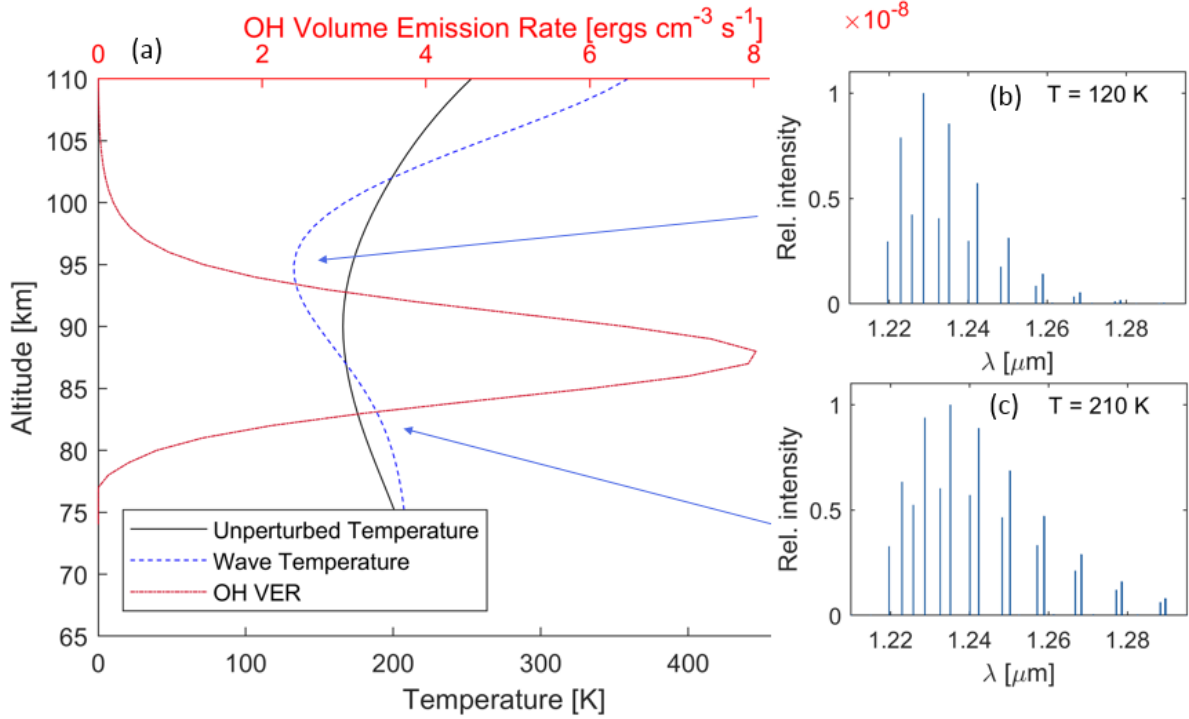
$$N_{v',J'}(z) = \frac{N_{v'}(z)2(2J'+1)}{Q_{v'}(T(z))} \cdot \exp\left(\frac{-E_{v',J'}}{k \cdot T(z)}\right) \quad (7)$$

Where $N_{v'}$ is the total population of the v' vibrational level from the model, $E_{v',J'}$ is the energy of the J' rotational level, the factor $2(2J'+1)$ is the degeneracy of that level (including Λ -doubling) and $Q_{v'}(T(z))$ is the partition function (Herzberg, 1950).

- 15 Using the rotational transition probabilities of Rothman et al. (2013), the rotational line VERs are calculated within a single v' to v'' transition assuming that the OH is in LTE for the rotational level populations with the surrounding gas at each altitude and therefore follows a Boltzmann distribution of population characterised by the local temperature. The VER of each rotational line is integrated through the layer from 74 km through to 110 km to give the intensity of the line, $I_{J'J''}$. This results in a net spectrum of low rotational lines whose intensities are enhanced relative to the mean temperature of the emission region when emitted from the cooler regions. Accompanying this are high rotational lines whose intensities are enhanced relative to the mean temperature of the emission region when emitted from the warm regions. Each of these is weighted by the VER of the vibrational transition at each altitude, $N_{v'}(z) \cdot \omega_{v'v''} / \tau_{v'}$.

- 25 As an example, the OH model was used to create a synthetic spectrum of the (7,4) rotational-vibrational band, assuming LTE for the rotational level populations at every altitude level, for conditions for mid-July for a mid-latitude region. Specifically, the data presented are for Boulder, Colorado (40.0° N; 105.6° W) to make a direct comparison with the findings from Pendleton et al. (1993). The background temperature profile (black line) and the (7,4) VER variation with altitude (red line) are shown in Fig. 3 (a). These are perturbed by the wave with an initial amplitude of 10 K at 74 km altitude, which has grown to about 30 K at 90 km altitude, and a vertical wavelength of 30 km, shown in blue-dashed. Waves with similar amplitudes have been observed at these altitudes (Picard et al., 2004).

The resulting distribution of rotational line intensities as a function wavelength for two altitudes is shown in Fig. 3 (b) and (c). The net spectrum as observed by a ground-based instrument is analysed, as detailed below, to examine the influence of this high-rotational level tail on the fitted temperature.



5 Figure 3: (a) Illustration of the change in the OH airglow spectrum with altitude due to the temperature profile. The red line shows a modelled VER profile of the OH in $\text{ergs cm}^{-3} \text{s}^{-1}$. The black line shows the background temperature profile retrieved from the NRLMSISE-00 model. The blue dashed line shows the same temperature profile but perturbed by a wave with an amplitude which has grown to about 30 K at 90 km altitude and a vertical wavelength of 30 km. The insets (b) and (c) on the right show the P-branch of OH spectra of the (7,4) transition at different altitudes for the wave case. With the example wave given here, the temperature variation increases the VER of the lower rotational lines at 95 km altitude, and of the higher rotational lines at 80 km.

2.4 Temperature fitting

After integration through the layer, the relative population of the J' state relative to the lowest rotational energy level, E_0 , is now given in terms of the line intensity by:

$$\frac{I_{v',v'',J',J''}}{2(2J'+1) \cdot A_{v',v'',J',J''}} = Q_{v'}(T) N_{v'} \cdot \exp\left(\frac{-(E_{v',J'} - E_{v'})}{kT}\right) \quad (8)$$

15 Where $N_{v'}$ is the integral of the vibrational population $N_{v'}(z)$ over altitude, and T is the effective rotational temperature of the altitude-integrated spectrum. From this, the observed line intensities from rotational levels of known quantum number, energy, and transition probability may be used to define the relative total population and temperature using:

$$\ln\left(\frac{I_{v',v'',J',J''}}{2(2J'+1) \cdot A_{v',v'',J',J''}}\right) = \ln(Q_{v'}(T)N_{v'}) - \frac{1}{T} \left[\frac{(E_{v',J'} - E_{v'})}{k}\right] \quad (9)$$

Fig. 4 shows the result in terms of Equation (9), of integrating each rotational line in the (7,4) Meinel band for the atmospheric perturbation of a wave with an amplitude of 30 K at 90 km altitude and 30 km vertical wavelength. This is the same wave as shown in Fig. 3. Following Pendleton et al. (1993), fitting a temperature to the lowest three rotational levels of the OH spectrum yields the dashed red curve shown in Fig. 4. It may be seen that the lowest three rotational levels are well characterized by a single, Boltzmann rotational temperature, $T_{1,3} = 155.8 \pm 0.8$ K, as has been observed in nightglow spectra (Espy and Hammond, 1995; Franzen et al., 2017; Harrison et al., 1970; Noll et al., 2015). However, there is excess emission in the higher rotational lines which could be interpreted as populations exceeding that expected from a thermalised Boltzmann distribution. This apparent excess population occurs even though the OH distribution was constrained to be a Boltzmann distribution with a single temperature at each altitude.

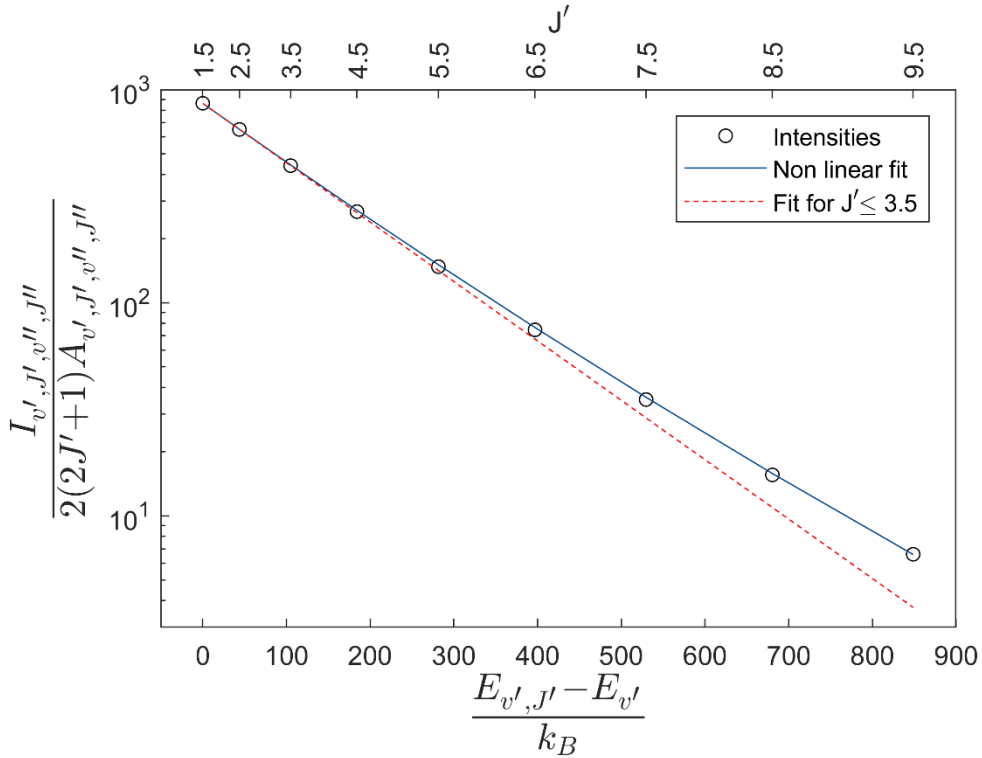


Figure 4: Population of P-branch lines of the (7,4) Meinel band as calculated with an atmospheric background profile containing the wave shown in Fig. 3. The energies given on the x-axis are relative to the lowest rotational energy. An exponential fit to the lowest three rotational levels (red dashed line) underestimates the populations at higher levels. A non-linear fit as presented in Equation (10) can fit the intensities of rotational levels as high as $J' = 9.5$, while reproducing the same temperature as the fit to the lowest three levels.

A non-linear formulation can be used in order to characterise this excess population. This non-linear fit is of the form:

$$\ln\left(\frac{I_{v',v'',J',J''}}{2(2J'+1) \cdot A_{v',v'',J',J''}}\right) = \ln(Q_{v'}(T)N_{v'}) - \frac{1}{T} \left[\frac{(E_{v',J'} - E_{v'})}{k}\right] + \frac{\beta}{T^2} \left[\frac{(E_{v',J'} - E_{v'})}{k}\right]^2 \quad (10)$$

Here β is a non-linearity parameter, which is a free parameter in the non-linear fit. This non-linear fit is also presented in Fig. 4 as a solid blue line, showing that the intensity in rotational lines as high as $J' = 9.5$ is now fitted. The retrieved temperature $T_{NL} = 154.9 \pm 0.1$ K, is the same as $T_{1,3}$ within the fitting uncertainties, with a β factor of 0.019.

5 2.5 Expansion to arbitrary waves

So far, we have considered only a single wave with one given amplitude, wavelength and phase as an example. Different wave amplitudes A_w will, of course, change the populations seen in Fig. 4. In the limiting case, where $A_w = 0$, the original background temperature profile is obtained. Different wavelengths λ_w will also change the shape of the atmospheric temperature profile. Short λ_w waves can change the temperature toward both higher and lower temperatures within the OH layer. Thus, their effect can be small when integrated over the whole layer. Longer λ_w waves, especially with λ_w on the order of, or longer than, the thickness of the OH layer, can introduce a temperature change that only warms one end of the layer and cools the opposite end. When such gradients reinforce the background temperature change with altitude, they can change the total integral over the OH layer substantially, as seen in Fig. 4. Lastly, the wave phase φ_w can change the influence of the wave on the total integral of the OH layer. The same wave would have the opposite temperature perturbation if φ_w was shifted by half a wavelength. In this case, the wave would work against the natural temperature gradient of the background atmosphere without a wave, resulting in a smaller effect than that shown in Fig. 4.

All three wave parameters - A_w , λ_w and φ_w - should therefore be considered when modelling different waves to examine their influence on the total integrated OH spectrum. In this research, the three parameters were adjusted in equidistant steps. The amplitude A_w was varied between 0 K and 40 K at an altitude of 90 km, spanning a range of previously observed semi-diurnal tide amplitudes (Hagan et al., 1999; Oberheide et al., 2011; Picard et al., 2004; She et al., 2002; Shepherd and Fricke-Begemann, 2004; Zhang et al., 2006). The vertical wavelength λ_w was varied between 2 km and 80 km, spanning the range of gravity waves, tides and planetary waves (Davis et al., 2013). The phase φ_w was varied between 0 and 2π .

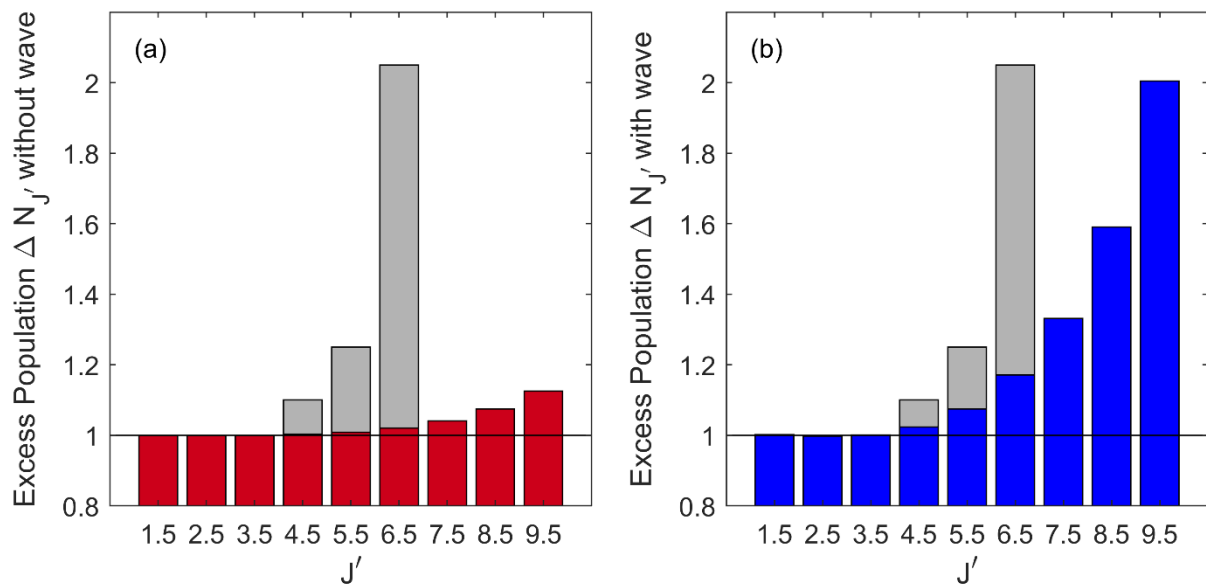
25 3 Results and discussion

Fig. 4 shows that a large atmospheric temperature gradient can produce higher populations in the higher J' rotational lines than would be expected from a strict LTE fit with only one effective temperature. We now want to quantify how large this apparent excess population can become and compare it to the study by Pendleton et al. (1993). An ensemble of waves was simulated as described above. The apparent excess population and the non-linearity parameter, β , were calculated for each wave-perturbed temperature background profile.

Fig. 5 shows two different wave scenarios for the (7,4) transition. The red plot (with the axis on the left-hand side) shows a no-wave scenario, where the atmospheric background temperature profile from the NLRMSISE-00 model is used. The apparent excess population is the ratio between the calculated intensity of a rotational line integrated in altitude, and the intensity of that line predicted by a Boltzmann distribution fitted to the distribution of integrated line intensities of the lowest three rotational lines using a single, effective temperature. It is clear that the first

three lines with $J' \leq 3.5$ can be characterised by a single, effective Boltzmann temperature. However, all higher lines show populations in excess of that expected from a single effective temperature. The effective overpopulation approaches approximately 12.5% for $J' = 9.5$, even though the OH molecule is thermalised with the local temperature at every altitude.

5 The blue bars (with the plot on the right side) show a scenario with a wave perturbing the atmosphere. This specific wave has an amplitude $A_w = 30$ K at 90 km altitude, $\lambda_w = 30$ km and $\varphi_w = 4.9$ rad. This would be a large amplitude gravity wave, but still within the range of atmospheric tidal observations. Although different J' levels are affected differently, the general shape is similar to that observed with the no-wave scenario. However, the magnitude of the effect is much greater. The first three lines show the populations expected in a single temperature
 10 LTE case, while higher J' levels yield increasingly higher apparent excess populations. For the highest line considered in this paper with $J' = 9.5$, the apparent excess population is twice that expected for a Boltzmann distribution with a single effective temperature, despite the OH being in LTE for the rotational level populations at every altitude.



15

Figure 5: The calculated apparent excess population of the OH (7,4) P(J') lines relative to the Boltzmann population of the fitted temperature to the lowest three lines. Red on the left is calculated with the climatological temperature gradient shown from NRLMSISE-00 above Boulder, Colorado (40.0° N; 105.6° W) in mid-July. Blue on the right is calculated with a wave of $A_w = 30$ K at 90 km, $\lambda_w = 30$ km and a phase that yields the maximum effect, $\varphi_w = 4.9$ rad. This is the same wave as presented in Fig. 3 and 4. The distribution has a $\beta = 0.019$. The grey bars represent the measurements ascribed to NLTE effects from Pendleton et al. (1993).

20

These results can be compared to the findings from Pendleton et al. (1993) in their Fig. 16, for the (7,4) transition above Boulder, Colorado during mid-summer, the same season and transition as presented here. These results are shown as grey bars in Fig. 5 (a) and (b). Although the measurement from Pendleton et al. (1993) included NLTE effects, the overall shape of the distribution is similar to the LTE for the rotational level populations simulations

25

presented here. When comparing these results, note that Pendleton et al. (1993) use the lower-state quantum number N , which corresponds to our $J' + \frac{1}{2}$. The first three rotational levels in this study and in Pendleton et al. (1993) have populations that follow a Boltzmann distribution characterized by a single temperature, and above that, there is excess population. The difference between the absolute numbers we observe and those of Pendleton et al. (1993) indicates the portion of the NLTE effect that might be due to the temperature gradients modelled here. For example, Pendleton et al. (1993) reported an apparent excess population of around a factor of 2 for the P($N=7$) (i.e. $J'=6.5$) line. However, for the two cases presented here in Fig. 5, there is less apparent excess population. While the no-wave scenario yields an apparent excess population of 1.02, a background profile with a wave yields 1.17 times the population. These numbers mean that up to about 17 % of the effect Pendleton et al. (1993) observed could be due to wave activity and not NLTE effects. Thus, the effect of the atmospheric temperature background has to be considered in addition to NLTE effects whenever the populations inferred from integrated airglow observations of high J' lines are to be used in kinetic thermalisation studies.

This calculation of the apparent excess population can now be repeated for waves of different amplitudes, wavelengths and phases. Fig. 6 shows the non-linearity in terms of the β -value of the temperature fit (from Equation (10)) and the corresponding apparent excess population of the sixth rotational line with $J' = 6.5$ ($N = 7$), the highest line reported by Pendleton et al. (1993) in their NLTE study of the OH. The figure shows results related to the (7,4) vibrational transition, which is the same transition that Pendleton et al. (1993) used. Fig. 6 (a) shows that for vertical wavelengths above about 20 km the non-linearity of the temperature fit increases with both wave strength and vertical wavelength approaching 2% of the linear temperature variation (see Equation 10). For shorter vertical wavelengths, the non-linearity is smaller (at about 0.5 %) and decreases with increasing wave amplitude. Fig. 6 (b) shows the apparent excess populations for a wave with a phase that yields the highest apparent excess population for a given wave amplitude and wavelength. There are small but observable effects in the limiting case of no waves (background atmosphere, see Fig. 5 (a)), and the apparent excess population increases for longer wavelengths and stronger waves similarly to the non-linearity of the fit. Extreme waves with 40 K amplitude at an altitude of 90 km can cause up to 30 % apparent excess populations in the $J'=6.5$ line.

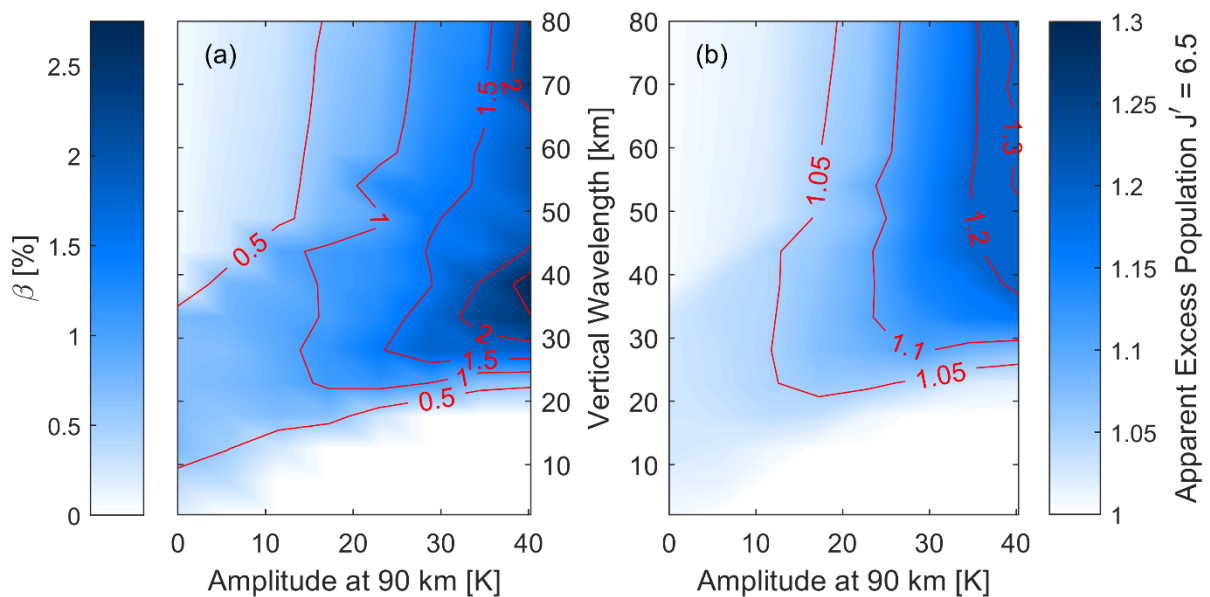


Figure 6: (a) The β -value from the non-linear fit (Equation (10)), and (b), the apparent excess population of the $J' = 6.5$ ($N = 7$) of the (7,4) Meinel transition for the ensemble wave spectrum. The values are shown as a function of the wavelength, λ_w , and the amplitude, A_w . Each value represents the phase φ_w where the apparent excess population was largest. Extreme waves (tides) can show a non-linearity of about 2% corresponding to an apparent excess population of 30%.

5

While Fig. 6 shows the (7,4) transition, Fig. 7 shows the same analysis for the commonly observed (3,1) transition. Both the β -value and the apparent excess population look qualitatively similar to the (7,4) band, but the effect of waves on the (3,1) transition is about 30 % stronger. That means that the non-linearity exceeds 2.5 % and the apparent excess population of the $J' = 6.5$ level is up to 40 % for the largest waves shown here.

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Fig. 6 and 7 show the results for the phase which created the strongest apparent excess population. The mean effect of all different phases simulated is independent of the transition and varies between 20 % and 40 % of the maximum effect presented in Fig. 6 and 7.

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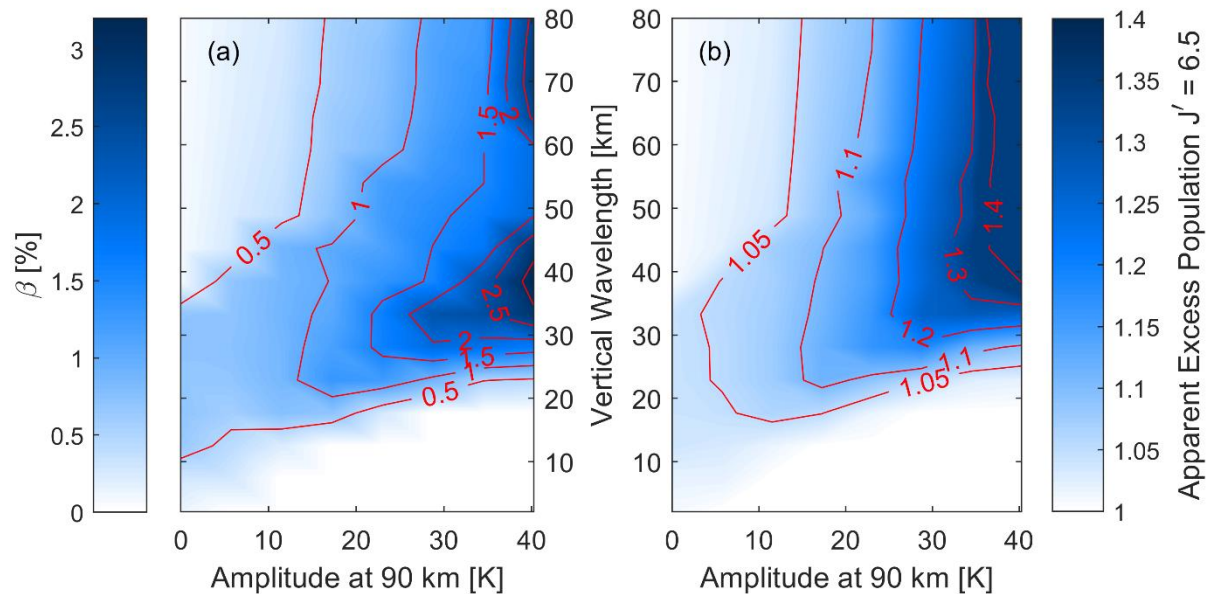


Figure 7: As Fig. 6, but this time for the (3,1) transition. Both the β -value from the non-linear fit in (a) and the apparent excess population of the $J' = 6.5$ upper level in (b) show a stronger effect than seen for the (7,4) transition in Fig. 6.

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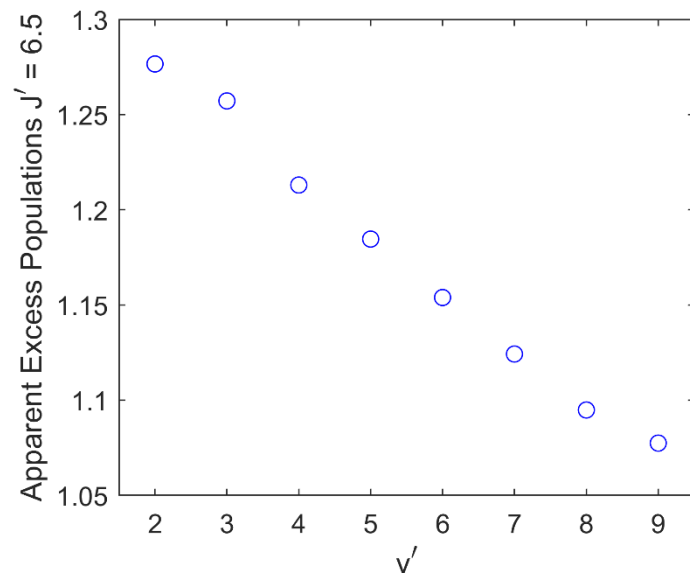
Tests showed that the difference in the apparent excess population between the (3,1) and (7,4) bands is unlikely to be due to the altitude separation of the different vibrational levels in the OH airglow layer (von Savigny et al., 2012). Repeating the analysis and weighting the $v'=3$ and 7 levels with the same VER profile yields essentially the same result; as did performing the analysis in an unperturbed isothermal background temperature profile.

Instead, the difference in the apparent excess population between the (3,1) and (7,4) bands is likely to be due to the compressed rotational energy structure of the higher vibrational levels that lie closer to the dissociation limit.

A given J' level in a low vibrational state will have more rotational energy than one in a high vibrational state. So for a given temperature, higher rotational levels will be thermally populated in the higher vibrational levels. These thermally populated higher rotational levels then make the perturbing effects of waves relatively less important.

Fig. 8 illustrates the dependency of the amount of apparent excess population on the different vibrational upper levels at different altitudes. For consistency, the apparent excess population of the $J' = 6.5$ upper level is again shown. All data points are for the wave presented above as an example, with an amplitude of 30 K at 90 km altitude and a vertical wavelength of 30 km.

- 10 The smallest upper vibrational level of $v' = 2$ shows an apparent excess population of about 28 %, while the highest upper vibrational level of $v' = 9$ only shows an apparent excess population of about 8 %.



- 15 Figure 8: The maximum apparent excess population of the $J' = 6.5$ upper level for a wave with wavelength 30 km and an amplitude of 30 K at 90 km altitude as a function of vibrational upper level. The effect of the waves, creating the apparent excess population decreases with rising vibrational quantum number v' .

4 Conclusions

- 20 Spectroscopic observations of the OH airglow have been commonly used to measure temperatures in the MLT. The OH radiates over an extended, Chapman-like layer that extends over several kilometres, over which the temperature is changing. Strong waves perturbing the MLT can make this change in temperature within the OH layer substantial. The simulations executed here show that these temperature profiles can create an apparent non-thermal population of the rotational levels in a given Meinel (v', v'') band. Even though the simulations calculated the rotational population distribution of the OH to be in LTE with the surrounding gas at every altitude, the integrated intensities of the higher rotational lines indicate an apparent excess population that could be

misinterpreted as contributing to the NLTE effects previously reported (Cosby and Slanger, 2007; Noll et al., 2015; Pendleton et al., 1993).

We have shown in this work that the influence of a wave that has an amplitude of 30 K at an altitude of 90 km can explain between 12 % and 30 % of the effects previously ascribed to NLTE by Pendleton et al. (1993). Smaller waves can also have an impact of up to 10 %, and their impact can not be ignored. Other transitions with lower vibrational quantum numbers show even higher apparent excess populations caused by this temperature-variation effect. We conclude that it is necessary to consider the temperature profile in order to infer OH rotational level population distributions from ground-based airglow observations.

Author contribution

CF modified the chemical model with dynamic inputs, ran the model and interpreted the model output. CF also wrote the paper. PJE supported the analysis process and paper writing. REH gave input on interpretation and paper writing.

Competing interests

The authors declare that they have no conflict of interest.

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