

Do vibrationally excited OH molecules affect atmospheric chemistry?

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Do vibrationally excited OH molecules affect middle and upper atmospheric chemistry?

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Abstract

Except for a few reactions involving electronically excited molecular or atomic oxygen or nitrogen, atmospheric chemistry modelling usually assumes that the temperature dependence of reaction rates is characterized by Arrhenius law involving kinetic temperatures. It is known, however, that in the upper atmosphere the vibrational temperatures may exceed the kinetic temperatures by several hundreds of Kelvins. This excess energy has an impact on the reaction rates. We have used upper atmospheric OH populations and reaction rate coefficients for $\text{OH}(\nu = 0\dots 9) + \text{O}_3$ and $\text{OH}(\nu = 0\dots 9) + \text{O}$ to estimate the effective (i.e. population weighted) reaction rates for various atmospheric conditions. We have found that the effective rate coefficient for $\text{OH}(\nu = 0\dots 9) + \text{O}_3$ can be larger by a factor of up to 1020 than that involving OH in its vibrational ground state only. At altitudes where vibrationally excited states of OH are highly populated, the OH reaction is a minor sink of O_x and O_3 compared to other reactions involving, e.g., atomic oxygen. Thus the impact of vibrationally excited OH on the ozone or O_x sink remains small. Among quiescent atmospheres under investigation, the largest while still small (less than 0.1%) effect was found for the polar winter upper stratosphere and mesosphere. The contribution of the reaction of vibrationally excited OH with ozone to the OH sink is largest in the upper polar winter stratosphere (up to 4%), while its effect on the HO_2 source is larger in the lower thermosphere (up to 1% for polar winter and 1.7% for midlatitude night conditions). For $\text{OH}(\nu = 0\dots 9) + \text{O}$ the rate coefficients differ by plus/minus a few percent only from those involving OH in its vibrational ground state. The effects on the odd oxygen sink are negative and can reach -0.7% (polar summer lowermost thermosphere), i.e. neglect of vibrational excitation overestimates the odd oxygen sink. The OH sink is overestimated by up to 2%. After a solar proton event, when upper atmospheric OH can be enhanced by an order of magnitude, the excess relative odd oxygen sink by $\text{OH}(\nu = 0\dots 9) + \text{O}_3$ is estimated at up to 0.2%, and the excess relative OH sink by $\text{OH}(\nu = 0\dots 9) + \text{O}_3$ can exceed 4% in the thermosphere.

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1 Introduction

Mainly in the 1970s and early 1980s a large number of studies were performed to assess reactions involving vibrationally excited molecules (e.g. Wieder and Marcus, 1962; Coltharp et al., 1971; Worley et al., 1972; Gordon and Lin, 1976; Hui and Cool, 1978; Kneba and Wolfrum, 1980). Atmospheric chemistry modeling, however, then was not an issue as it is now. Furthermore, our knowledge on the vibrationally excited populations in the atmosphere has dramatically improved since then (López-Puertas and Taylor, 2001, and references therein). The impact of vibrational excitation on atmospheric chemistry has been investigated extensively for vibrationally excited O₂ (e.g. Slinger et al., 1988; Toumi et al., 1991; Toumi, 2008; Shi and Barker, 1992; Mlynczak and Solomon, 1993; Slinger, 1994; Miller et al., 1994; Patten Jr. et al., 1994; Toumi et al., 1996; Zipf and Prasad, 1998) but only occasionally for less abundant species (e.g. Lunt et al., 1988; Hierl et al., 1997; Delmdahl et al., 1998; Varandas and Zhang, 2001; Varandas, 2002, 2004a,b; Chen and Marcus, 2006; Vadas and Fritts, 2008; Prasad and Zipf, 2008), and results were in some cases under heavy dispute (Smith and Copeland, 2004; Varandas, 2005). Atmospheric chemistry models, particularly those developed for stratospheric ozone chemistry and later extended towards the upper atmosphere, usually neglect this effect (e.g., SLIMCAT, Chipperfield, 1999; MOZART, Horowitz et al., 2003; MESSy, Jöckel et al., 2005; REPROBUS, Lefèvre et al., 1994; CLAMS, McKenna et al., 2002). Some further models (e.g. KASIMA, Kouker et al., 1999; HAMMONIA, Schmidt et al., 2006; WACCM-3, Garcia et al., 2007) take local thermodynamic disequilibrium for radiative cooling into account but not for chemistry. As a standard approach, the temperature dependence of the reaction rates involved are estimated as a function of kinetic temperature on the basis of the Arrhenius equation. It is assumed that the thermal energy of a molecule is Boltzmann-distributed over all active degrees of freedom and that the total energy of a molecule (translational, rotational, vibrational and electron spin) is well represented by the kinetic (translational) energy of the molecules. In the upper atmosphere, however, due to low collision rates, quenching happens not

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frequently enough to redistribute the vibrational energy that molecules may have via the *status nascendi* or via absorption of a photon, thus leading to non-local thermodynamic equilibrium (non-LTE) (López-Puertas and Taylor, 2001). While it has become a standard procedure to consider non-LTE radiative processes associated with vibrational and rotational excitation in radiative transfer modeling and remote sensing data analysis whenever appropriate (e.g. Funke et al., 2001a,b; Kaufmann et al., 2003; Yankovsky and Manuilova, 2006), consideration of these effects in chemistry modelling is by far no standard today, although it is quite plausible that excess energy in the form of vibrational excitation will make it easier for the reactants to reach the activation energy. This paper tries to estimate whether or not the local thermodynamic equilibrium assumption is a valid approximation for middle atmospheric chemistry applications. Since larger populations of excited molecules are found for species whose excess populations are driven by their *status nascendi* rather than the radiance field, we focus this study on the reactions $\text{OH}(\nu = 0\dots 9) + \text{O}_3$ (Sect. 2) and $\text{OH}(\nu = 0\dots 9) + \text{O}$ (Sect. 3). The need to include vibrational state dependent OH chemistry has already been suggested by Pickett et al. (2006). As a first step we estimate the effective (i.e. population weighted) rate coefficients for various atmospheric conditions (Sects. 2.1 and 3.1). Then we assess the relevance of this reaction relative to other sinks of odd oxygen (Sects. 2.2 and 3.2). Finally, we discuss the limitations of this study and identify necessary future work (Sect. 4).

2 The reaction of the hydroxyl radical with ozone

2.1 Effective rate coefficients

The reaction



is an important sink of odd oxygen ($[O_x]=[O_3]+[O(^3P)]+[O(^1D)]$) (see, e.g. Brasseur and Solomon, 2005; brackets represent number densities). However, many open questions with respect to ozone chemistry of the mesosphere and the lower thermosphere are reported in the literature (e.g. Crutzen, 1997). The main source of mesospheric OH is



which produces vibrationally excited OH up to the 9th vibrational level. At upper stratospheric and mesospheric pressures quenching rates are low, and in consequence populations of vibrationally excited OH are large there (Kaufmann et al., 2008; Pickett et al., 2006), giving rise to OH airglow. Figure 1 shows the relative OH populations for vibrational levels 0 to 9 for six different atmospheres as calculated by the generic non-LTE population model GRANADA (Funke et al., 2002). This model includes Eq. (R2) as source of excited OH, and the following de-excitation processes: non-reactive quenching with N_2 and O_2 (Adler-Golden, 1997), reactive quenching with atomic oxygen, with a rate constant by 10% higher than proposed by Adler-Golden (1997), and radiative de-excitation using Einstein coefficients calculated from HITRAN version 2004 (Rothman et al., 2005). Up to 21% of OH is found to be vibrationally excited. The fraction of vibrationally excited molecules in local thermodynamic equilibrium is in the order of magnitude of only 10^{-8} .

Literature on the rate coefficients involving Reaction (R1) for vibrationally excited OH is quite sparse and in partial disagreement (Coltharp et al., 1971; Worley et al., 1972; Finlayson-Pitts et al., 1983; Varandas and Zhang, 2001 and references therein). For our study, rate coefficients as a function of temperature and OH vibrational level as suggested by Varandas and Zhang (2001) are used. Their rate coefficient for OH in its vibrational ground state at 298 K ($6.84 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) agrees reasonably well with that recommended by Sander et al. (2006) ($7.25 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). From the former data we calculate the effective rate coefficient as the weighted mean of the rate coefficient of all relevant vibrational levels, where the weight is the relative

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population of the respective vibrational level:

$$k_{\text{eff}} = \frac{1}{[\text{OH}(v=0\dots 9)]} \sum_{v=0}^9 k_v[\text{OH}(v)]. \quad (1)$$

For quiescent conditions, vertical profiles of the volume mixing ratios of OH are taken from Garcia and Solomon (1983) for altitudes up to 90 km while above photochemical equilibrium with atomic hydrogen from MSISE90 (Hedin, 1991; Picone et al., 2002) is assumed (Fig. 2). To investigate the impact of atmospheric perturbations due to ionisation, a scenario directly after the onset of a large solar proton event (SPE) was also considered. Atmospheric conditions for this scenario were adopted from a model run performed with the University of Bremen Ion Chemistry Model (Winkler et al., 2009), initialised by our polar night atmosphere.

Largest differences between the rate coefficient involving OH only in its vibrational ground state and the effective rate coefficient accounting for vibrational excitation have been found in the lower thermosphere (Fig. 3). The effective rate coefficients exceed those involving only OH($v=0$) by a factor of several hundred for all atmospheric conditions under investigation (midlatitude day and night, equatorial day and polar winter and summer quiescent conditions as well as polar winter after a solar proton event). In the polar summer atmosphere around 90 km altitude consideration of vibrationally excited OH accelerates the target reaction even by a factor of up to 940. For the SPE atmosphere at 108 km altitude, this factor was found to be as large as 1020. Even in the daytime equatorial atmosphere, where the smallest enhancement is found, the effective rate coefficient reaches a factor of up to 400 at 93 km altitude.

2.2 Relevance compared to competing reactions

In order to assess the effect of vibrational excitation of OH in the target reaction on trace gas budgets, its impact on losses and sources of reactants and products has been compared to that of competing reactions. This has been done for six different

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atmospheric conditions (midlatitudes day, midlatitudes night, equator day, polar summer and polar winter, all under quiescent conditions, as well as polar winter under solar proton event (SPE) conditions). The latter scenario was included because SPEs produce large amounts of atomic hydrogen giving rise to excess OH of which a considerable fraction is vibrationally highly excited (Crutzen and Solomon, 1980). Profiles of meteorological state variables and abundances of constituents were taken from various sources: For the quiescent atmospheres, temperature, pressure, $[N_2]$, $[O_2]$, $[H]$ (above 90 km), and $[O]$ (above 80 km) were taken from MSISE90 (Hedin, 1991); $[HO_2]$ (below 75 km), $[O_3]$ (below 60 km), and $[ClO]$ (below 75 km) were taken from SLIMCAT (Chipperfield, 1999); for $[CO]$, $[OH]$ (up to 90 km), $[NO_x]$, $[Cl]$, $[H_2O_2]$ and $[H_2]$ a model by Garcia and Solomon (1983) was used. Photochemical equilibrium of $[OH]$ and $[H]$ (above 90 km), photochemical correction of $[O_3]$ in the mesosphere, $[O(^1D)]$ in photochemical equilibrium with $[O_3]$, $[O]$ in consistency with $[O_3]$, $[O(^1D)]$, and NO_x -partitioning were calculated with a dedicated box model using reaction rates as recommended by Sander et al. (2006). For the SPE case, which represents the situation at 85° North during 29th October 2003 shortly after 00:00 UT, we have adopted the atmospheric composition as simulated with the University of Bremen Ion Chemistry Model (Winkler et al., 2009), using ionisation rates due to proton and electron impact (Wissing et al., 2010). This scenario represents the situation when HO_x has already been enhanced but no significant SPE-induced O_3 reduction had taken place yet.

2.2.1 The odd oxygen sink

At altitudes where the effective reaction rate coefficient of $OH(v = 0..9) + O_3$ differs largely from that of OH in its vibrational ground state, this reaction is a negligibly small sink of odd oxygen, while the major sinks are removal of atomic oxygen by the three body reaction involving two oxygen atoms, removal of atomic oxygen by OH and HO_2 , and ozone destruction by atomic hydrogen, the NO_x cycle, atomic chlorine, and the recombination of ozone and atomic oxygen to give molecular oxygen (Fig. 4). This

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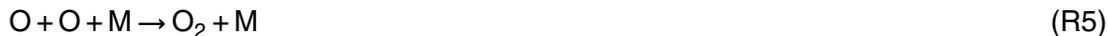
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means that the excess relative O_x sink $\Delta s(O_x; OH + O_3)$ of the target reaction

$$\Delta s(O_x; OH + O_3) = \frac{-(k_{\text{eff}} - k_{v=0})[OH][O_3]}{\sum_i (-k_i n_i \prod_{j=1}^{m_i} [X]_j)} \quad (2)$$

with respect to the combined sink of all O_x removal reactions i under consideration is small, where k_i is the rate coefficient of the i th reaction, n_i is the number of O_x molecules involved, m_i is the total number of reactants, $[X]_j$ are the concentrations of the involved molecules and $k_{v=0}$ is the rate coefficient of the target reaction for OH in its vibrational ground state. The following odd oxygen sinks have been considered:



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All rate constants except those of Reaction (R1) were taken from Sander et al. (2006). Particularly, no non-local thermodynamic equilibrium effects have been considered for Reactions (R3)–(R14).

Thus, although the effect of vibrational excitation of OH on the effective reaction rate is enormous, the effect on the O_x sink strength is negligibly small. For a polar winter atmosphere, the effect is less than about 0.1% and at least an order of magnitude smaller for all other atmospheres under investigation except for SPE conditions (Fig. 5). For the latter condition the excess relative O_x sink reaches nearly 0.2%.

2.2.2 The ozone sink

In altitude regions of interest, O and O_3 are not in a fast equilibrium, hence the sink strength of Reaction (R1) with respect to ozone, $\Delta s(\text{O}_3; \text{OH} + \text{O}_3)$, might also be of interest. Here we consider sink Reactions (R1)–(R4), (R8), (R9), (R11), (R14),



and



where photolysis rates were calculated with a version of TUV (Madronich and Flocke, 1998) which has been extended to an atmosphere covering altitudes of up to 200 km. The excess relative ozone sink, however, is negligibly small: less than 0.1% in the polar winter upper stratosphere, with a second maximum near the mesopause, and substantially smaller for all other altitudes and atmospheres except for SPE-conditions, where the excess relative O_3 sink reaches values slightly less than 0.3%.

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2.2.3 OH sink

Here we assess the impact of consideration of vibrationally excited OH on the OH abundance itself. For calculation of the excess relative contribution to the OH sink, we consider the following OH sinks competing with Reaction (R1) (all assumed not to depend on the vibrational state of OH): Reaction (R6), as well as



and



where for R23 both isomeric variants of the product (HOONO and HONO₂) are considered. The relative weight of OH loss reactions is shown in Fig. 7 for the six atmospheres under assessment. In the middle to upper stratosphere the excess relative sink of OH reaches values up to 4% for polar winter conditions, and a local maximum of 0.2% occurs in the upper mesosphere (Fig. 8). For the SPE atmosphere, the target reaction involving vibrationally excited OH accounts for about 0.25% additional OH loss, and for all other atmospheric conditions the effect of consideration of vibrationally excited OH on the OH sink is negligibly small.

It has to be noted that Varandas and Zhang (2001) report further reaction pathways for the OH($\nu = 0 \dots 9$) + O₃ reaction. Besides



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which is reported to produce rotationally and vibrationally excited HO₂, two further reaction pathways are proposed:



and



The reason for the latter pathways (Reactions R24 and R25) is that for OH($v \geq 6$) the product HO₂ is vibrationally excited above its dissociation limit. Since the efficiency of pathway Reaction (R25) is small compared to that of the total of pathways Reactions (R1) and (R24), we have ignored it when estimating the OH loss, i.e. we assume
10 that the reactive quenching of OH and O₃ always implies OH loss.

2.2.4 HO₂ source strength

Finally, we estimate the excess HO₂ source strength, again under the simplifying assumption that the rate coefficients of the reaction paths Reactions (R24) and (R25) are zero. In this sense our results are upper estimates. The following HO₂ sources competing with Reaction (R1) have been considered: Reactions (R13), (R21), as well as
15



According to these estimates, in the lower midlatitude nighttime thermosphere the HO₂ source is increased by 1.7%, and in the polar winter lower thermosphere by 1% (Fig. 9).

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3 The reaction of the hydroxyl radical with atomic oxygen

3.1 Effective rate coefficients

The reaction



5 outweighs Reaction (R1) in the thermosphere and, depending on illumination, also in the mesosphere and upper stratosphere as a sink of odd oxygen by far (Brasseur and Solomon, 2005, cf. Fig. 4). Also for this reaction a dependence of the rate coefficient of the vibrational level of the reaction OH molecule is reported (Varandas, 2004a). Con-
10 trary to Reaction (R1), the rate coefficients decrease from $\nu = 0$ to $\nu = 1$ or $\nu = 2$ and then increase again for higher vibrational levels. For calculation of the effective rate coefficients according to Eq. (1) we have used pre-tabulated ν -dependent k -values reported in Table 3, “Method II” of Varandas (2004a), linearly interpolated to the actual temperatures. Arrhenius-type exponential estimation led to unrealistic values when
15 temperatures outside the range of pre-tabulated values forced extrapolation. Due to the weak temperature dependence of this reaction, the error due to linear interpolation is considered tolerable. Deviations of the effective reaction rate coefficient from rate coefficients valid for OH in its vibrational ground state range from about -2% in equatorial atmospheres at 90 to 95 km altitude to about $+1-2\%$ in polar summer/winter and mid-latitude night atmospheres above 100 km altitude (Fig. 10). For the SPE atmosphere
20 there deviation reaches $+5\%$ at 110 km altitude.

An interesting feature is that $k(\nu = 0)$ reported by (Varandas, 2004a) is approximately 50% lower than experimental values referenced in their paper and values recommended by Sander et al. (2006). It is speculated that reactants in the laboratory measurements actually were – through their nascent processes – still in non-local ther-
25 modynamic equilibrium. If this was true, atmospheric chemistry modelling would be systematically wrong even for local thermodynamic equilibrium conditions.

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3.2 Relevance with respect to competing reactions

The effect on the odd oxygen sink of Reaction (R6) by consideration of vibrationally excited OH is most pronounced between 85 and 95 km altitude and exceeds -0.7% for the polar summer atmosphere, and reaches -0.2 – -0.6% for all other quiescent atmospheres under investigation. Between 90 and 100 km altitude for the nighttime atmospheres (polar and midlatitude) there is a small positive contribution to the odd oxygen sink (Fig. 11). For the SPE atmosphere the relative relevance is even smaller. The same competing reactions as for Reaction (R1) have been considered. Since at altitudes where vibrational populations of OH are relevant, atomic oxygen is the dominating odd oxygen component, the above also holds for the atomic oxygen sink (Fig. 12). Consideration of vibrationally excited OH alters the OH sink by a fraction of a percent for quiescent atmospheres (Fig 13). For the SPE atmosphere near 100 km altitude, the OH excess sink exceeds 4%.

4 Conclusions

For the reaction of OH with O_3 , the effect of vibrational excitation of OH on the effective reaction rate is dramatic: In a polar summer atmosphere, ozone destruction by OH can be up to a factor of 940 faster if vibrational excitation is considered. For SPE conditions this acceleration factor can even exceed 1000. However, since at altitudes where populations of vibrationally excited OH are large enough to make an important contribution to atmospheric chemistry, the $OH+O_3$ reaction is of minor importance, the effect of considering vibrationally excited OH on odd oxygen and ozone sinks are negligible. More important but still moderate is the effect on the OH sinks (up to 4%) and HO_2 sources (up to 1.7%). The largest relative impact is found for the polar winter atmosphere, where competing reactions are slower.

Although the change of the effective reaction rate through vibrational excitation of OH is much lower for its reaction with atomic oxygen, its impact on atmospheric chemistry

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is larger compared to the reaction with ozone: The odd oxygen destruction is reduced by still less than 1% but the OH sink is altered by ± 1 –2%. Only for SPE conditions there is a pronounced effect on the OH sink which above 100 km can reach 5%. The effect of vibrational excitation of OH on reactions studied in this paper is, in comparison to total sources and sinks of the involved species, by far not large enough to explain the so-called “HO_x-dilemma” (Conway et al., 2000; Summers et al., 1997), although, as already suggested by Varandas (2004b), non-local thermodynamic equilibrium effects might explain a different chemistry in the mesosphere compared to the stratosphere; nor is the effect large enough to solve the so-called “ozone deficit problem” (Jucks et al., 1996; Osterman et al., 1997; Canty et al., 2006), at least when these reactions are studied in an isolated manner without consideration of potential feedback effects.

Our studies suggest that conventional atmospheric chemistry modelling without consideration of non-local thermodynamic equilibrium chemistry should be sufficiently accurate for the range of atmospheric conditions studied here, since the effect is, compared to the importance of competing reactions, only small to moderate. However, these results should not be inappropriately generalized. Firstly, because there are some cases (particularly nighttime mesosphere) where this effect has the potential to contribute noticeably to the odd hydrogen partitioning. Secondly, the assessment of only two particular reactions cannot be more than a first step towards a more comprehensive analysis of this field, involving further reactions of vibrationally excited O₂, O₃, HO₂, NO, CO and other molecules. In this context it should also be mentioned that the products of the target reactions themselves may be vibrationally excited and thus may trigger additional non-local thermodynamic equilibrium chemistry. Thirdly, only sample atmospheric conditions were studied, and results may be different for, e.g., polar twilight conditions, particularly if the competing quantities OH abundances and atomic oxygen abundances change with different speed. And finally, analysis relies on independent treatment of populations and chemistry, i.e. there is no feedback from the subsequent chemistry back to the non-LTE model used to estimate the populations of the vibrational states. While we try to complete our archive of reaction rates

of vibrationally excited molecules, we still have the vision of replacing our approach of effective reaction rates by a fully coupled time-dependent chemistry and non-LTE model, allowing accurate treatment of all feedback mechanisms.

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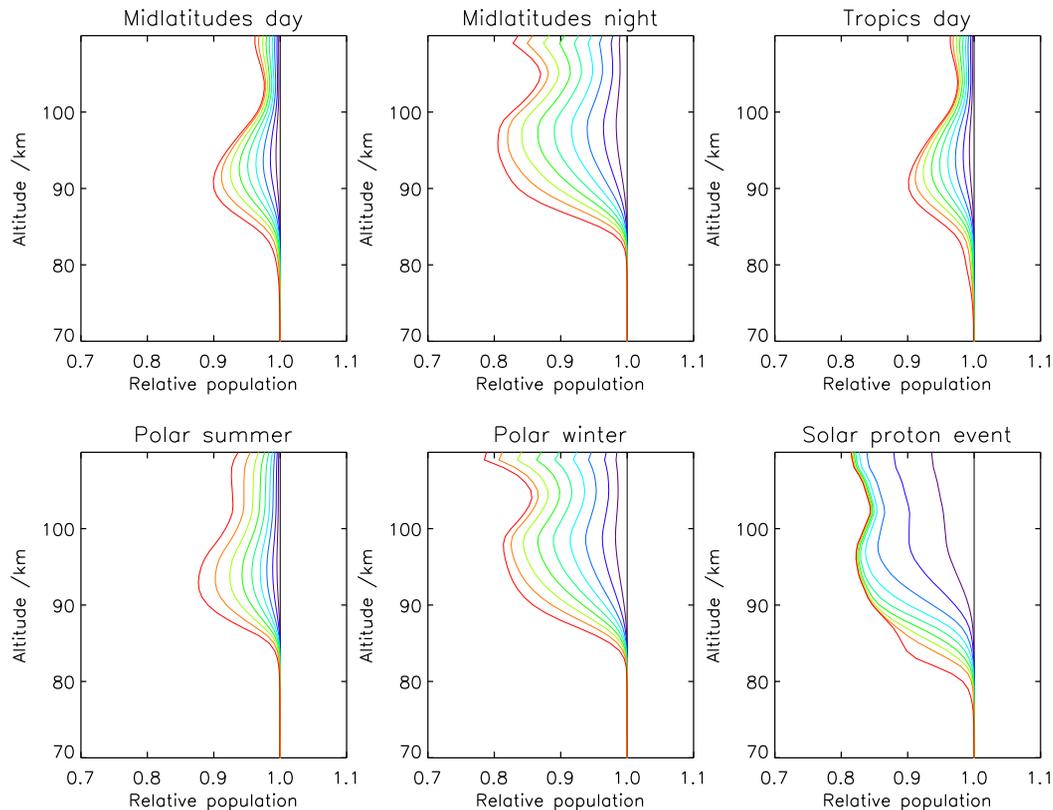


Fig. 1. Cumulative relative populations of the OH vibrational states as a function of altitude from groundstate (leftmost line) to total OH ($v = 0 \dots 9$) for various atmospheres. The distances between the lines represent the relative populations of of vibrational levels 1 to 9.

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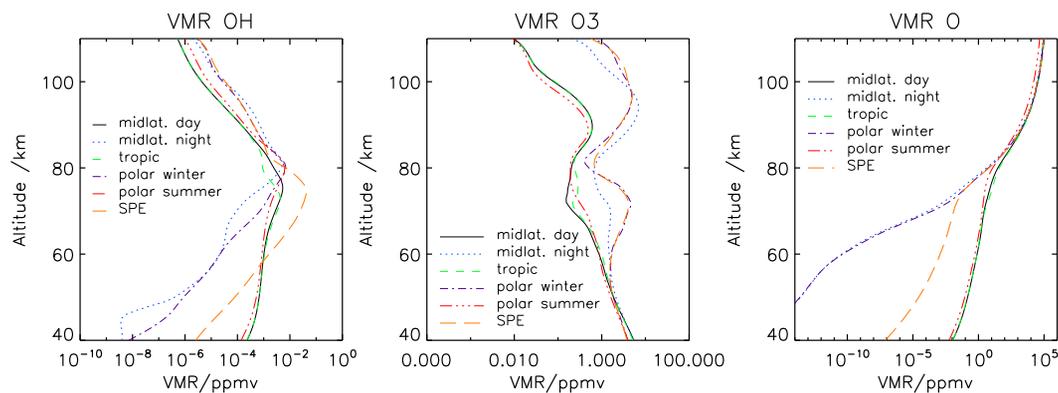


Fig. 2. Assumed mixing ratio profiles of OH, O₃ and O (top to bottom) for various atmospheric conditions.

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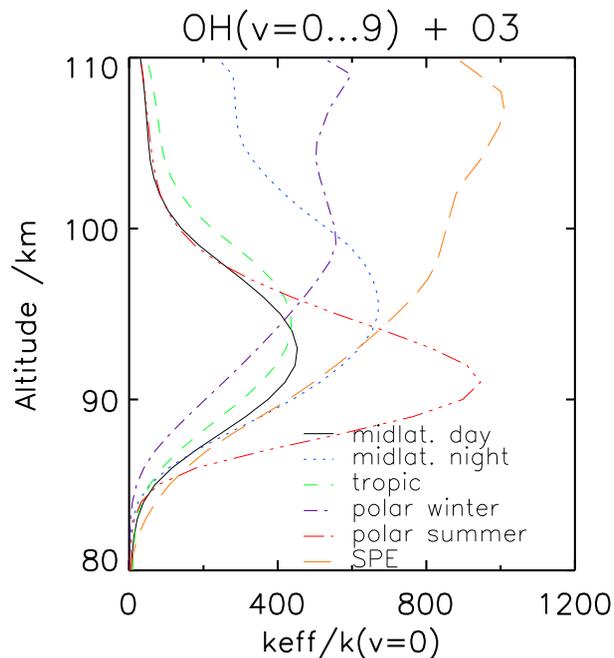


Fig. 3. Relative increase of the total OH($v=0\dots9$)+O₃ rate coefficients by consideration of vibrational excitation of OH in the reaction OH+O₃ as a function of altitude for various atmospheres.

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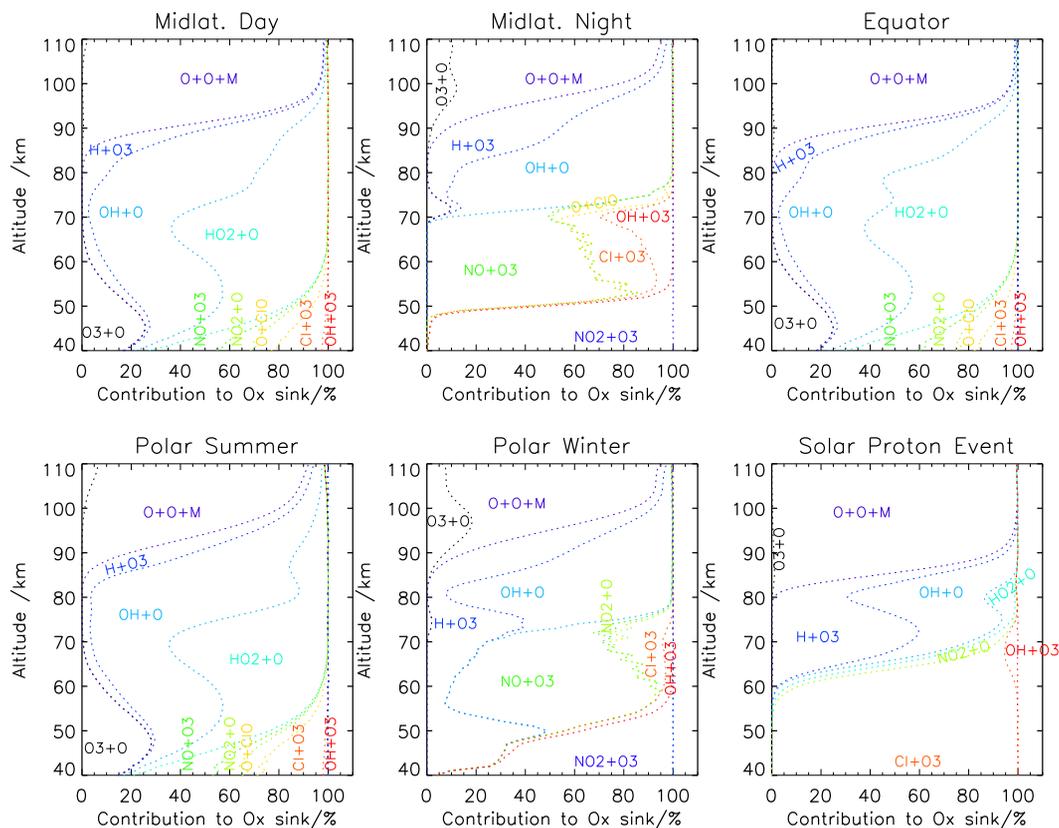


Fig. 4. Cumulative relative contribution to the odd oxygen sink of the leading reactions for various atmospheres.

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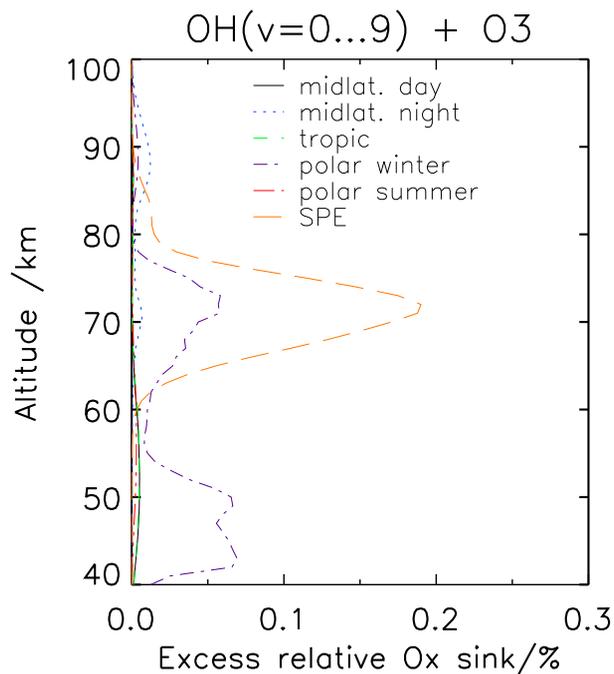


Fig. 5. Excess relative odd oxygen sink by consideration of vibrationally excited OH in the $\text{OH} + \text{O}_3$ reaction as a function of altitude for various atmospheres.

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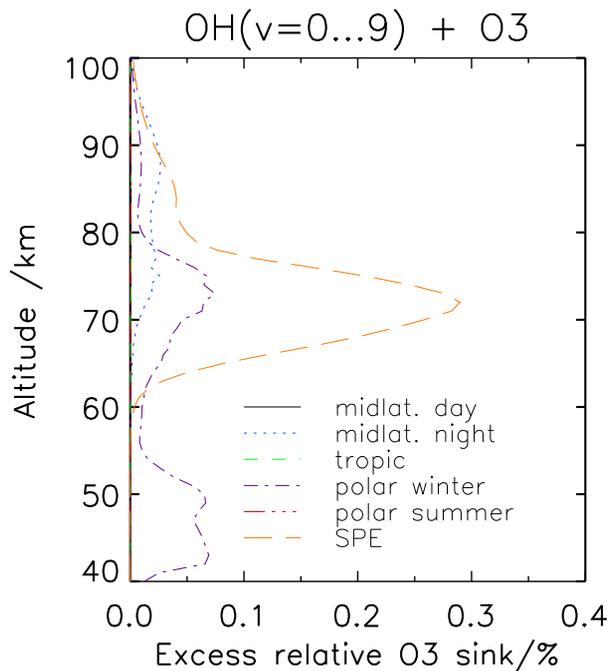


Fig. 6. Excess relative ozone sink by consideration of vibrationally excited OH in the OH+O₃ reaction as a function of altitude for various atmospheres.

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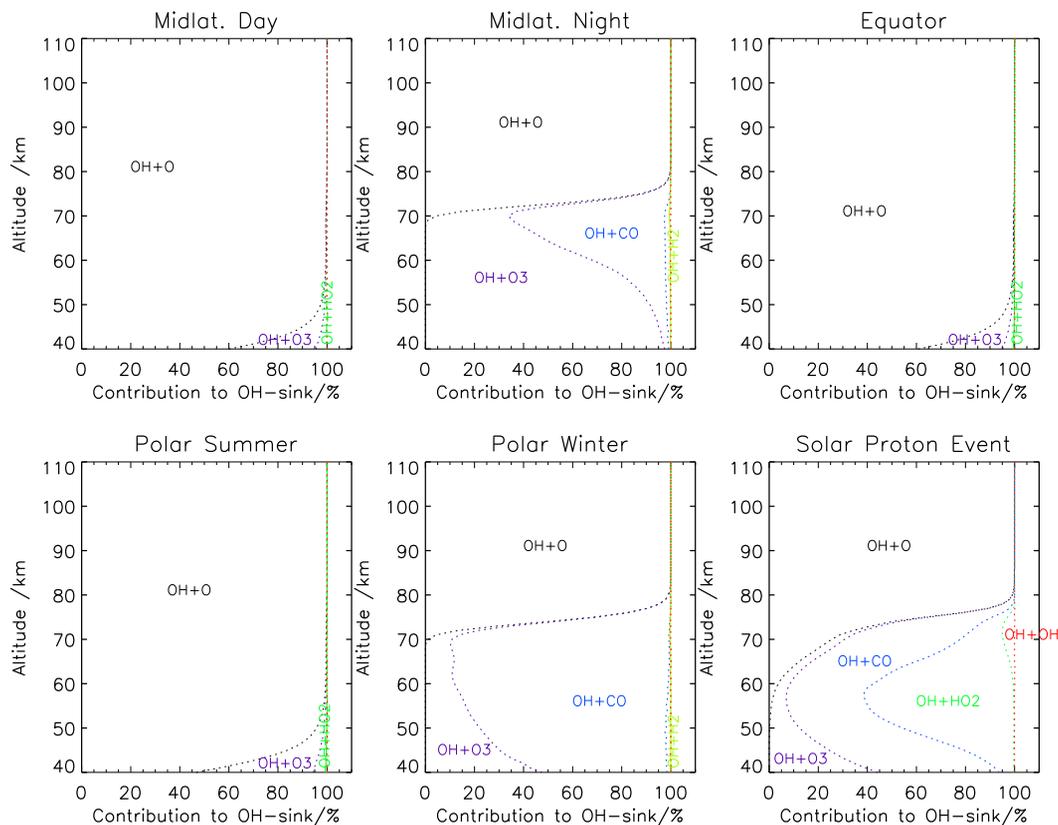


Fig. 7. Cumulative relative contribution to the OH sink of the leading reactions for various atmospheres. The areas between the lines represent the contribution of a particular reaction.

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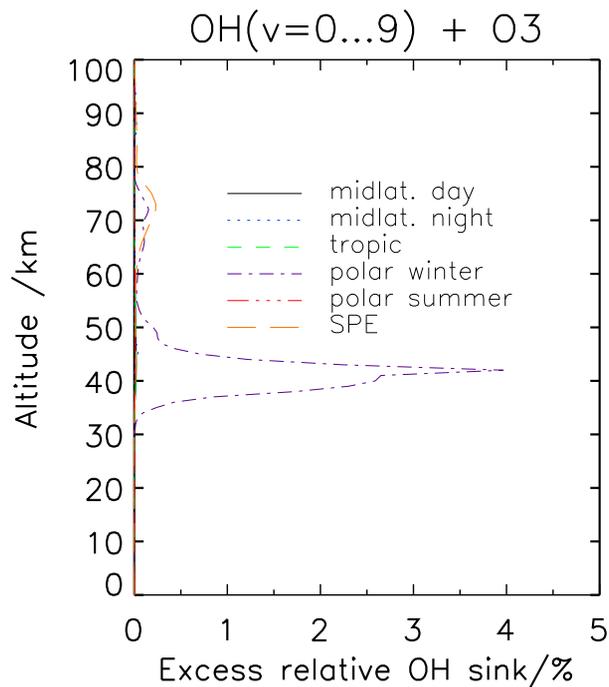


Fig. 8. Excess relative OH sink by consideration of vibrationally excited OH in the $\text{OH}+\text{O}_3$ reaction as a function of altitude for various atmospheres.

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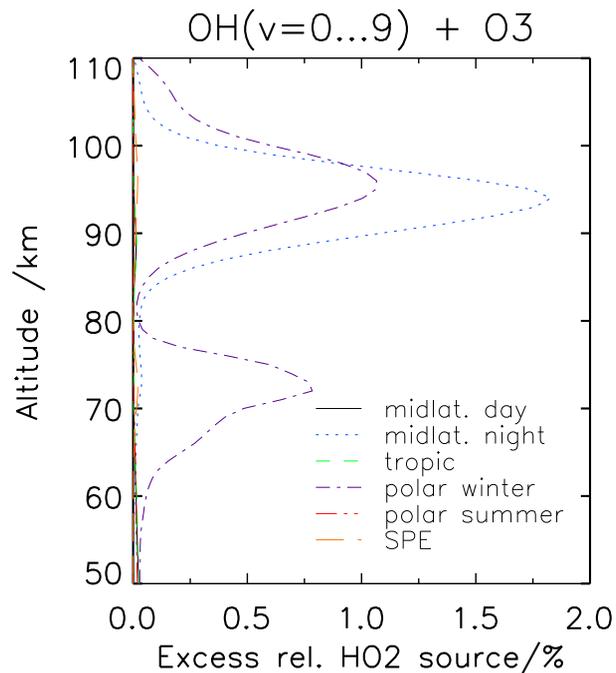


Fig. 9. Excess relative HO₂ source by consideration of vibrationally excited OH in the OH+O₃ reaction as a function of altitude for various atmospheres.

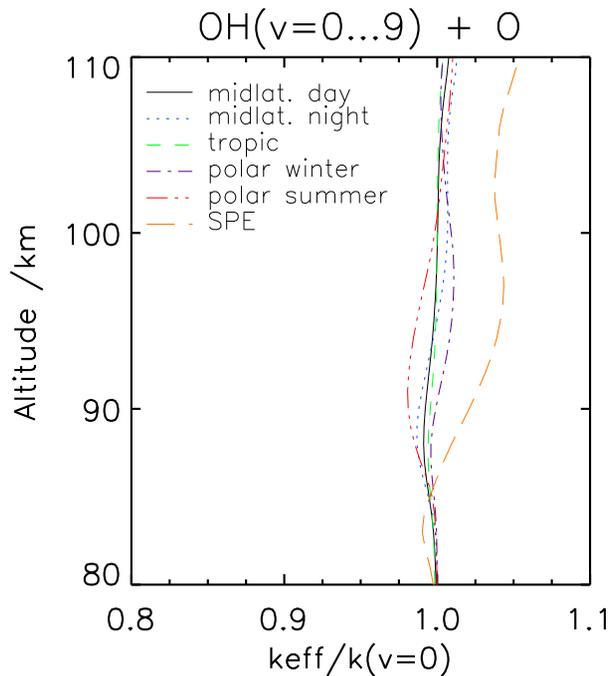


Fig. 10. Relative increase of the total OH($v=0\dots9$)+O rate coefficients by consideration of vibrational excitation of OH in the reaction OH+O as a function of altitude for various atmospheres.

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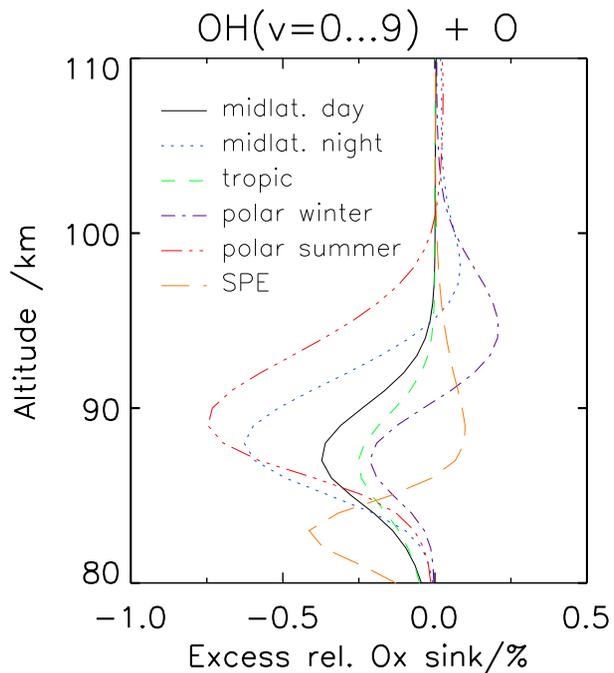


Fig. 11. Excess relative O_x sink by consideration of vibrationally excited OH in the OH+O reaction as a function of altitude for various atmospheres.

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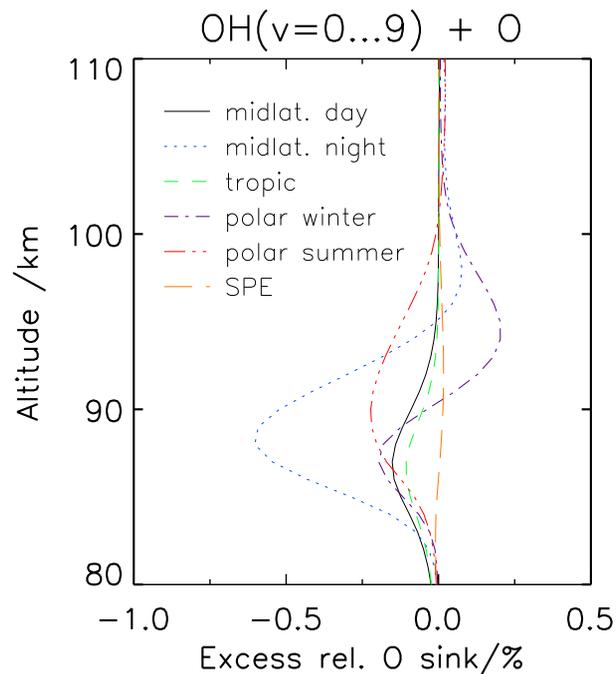


Fig. 12. Excess relative atomic oxygen sink by consideration of vibrationally excited OH in the OH+O reaction as a function of altitude for various atmospheres.

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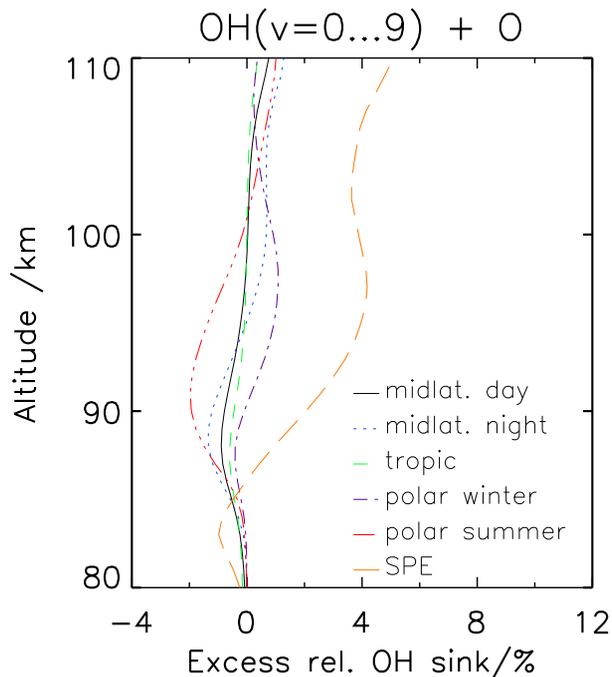


Fig. 13. Excess relative OH sink by consideration of vibrationally excited OH in the OH+O reaction as a function of altitude for various atmospheres.

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