**Atmospheric
Chemistry
and Physics**

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

T. von Clarmann[1], **F. Hase**[1], **B. Funke**[2], **M. López-Puertas**[2], **J. Orphal**[1], **M. Sinnhuber**[1,3], **G. P. Stiller**[1], and **H. Winkler**[3]

[1]Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, Karlsruhe, Germany
[2]Instituto de Astrofísica de Andalucía, CSIC, Granada, Spain
[3]Bremen University, Institute of Environmental Physics, Bremen, Germany

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 $OH(v=0...9)+O_3$ and $OH(v=0...9)+O$ to estimate the effective (i.e. population weighted) reaction rates for various atmospheric conditions. We have found that the effective rate coefficient for $OH(v=0...9)+O_3$ can be larger by a factor of up to 1470 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 1.5% for polar winter and 2.5% for midlatitude night conditions). For $OH(v=0...9)+O$ the effective rate coefficients are

lower by up to 11% than those involving OH in its vibrational ground state. The effects on the odd oxygen sink are negative and can reach -3% (midlatitudinal nighttime lowermost thermosphere), i.e. neglecting vibrational excitation overestimates the odd oxygen sink. The OH sink is overestimated by up to 10%. After a solar proton event, when upper atmospheric OH can be enhanced by an order of magnitude, the excess relative odd oxygen sink by consideration of vibrational excitation in the reaction of $OH(v=0...9)+O_3$ is estimated at up to 0.2%, and the OH sink by $OH(v=0...9)+O$ can be reduced by 12% in the thermosphere by vibrational excitation.

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 O_2 (e.g. Slanger et al., 1988; Toumi et al., 1991; Toumi, 2008; Shi and Barker, 1992; Mlynczak and Solomon, 1993; Slanger, 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.,

Correspondence to: T. von Clarmann
(thomas.clarmann@kit.edu)

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 (also referred to as non-local thermodynamic equilibrium, non-LTE) into account for radiative cooling 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 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-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 $OH(v = 0...9) + O_3$ (Sect. 2) and $OH(v = 0...9) + O$ (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

$$OH + O_3 \rightarrow O_2 + HO_2 \qquad (R1)$$

is an important atmospheric 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 upper mesospheric OH is

$$H + O_3 \rightarrow O_2 + OH(v \leq 9) \qquad (R2)$$

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 Reaction (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 and radiative de-excitation using Einstein coefficients calculated from HITRAN version 2004 (Rothman et al., 2005). While GRANADA usually calculates reactive quenching of OH with atomic oxygen with a rate constant by 10% higher than proposed by Adler-Golden (1997) (2.2×10^{-10} cm^3 molecule^{-1} s^{-1}), for this study for reasons of consistency rate coefficients as suggested by Varandas (2004a) were used for reactive and non-reactive quenching of vibrationally excited OH with O. Details of modelling the collisional processes are compiled in Table 1. Up to 35% and 74% of OH were found to be vibrationally excited for quiescent sunlit and dark atmospheres, respectively. After a solar proton event (SPE) the fraction of OH in its vibrational ground state becomes negligibly small in altitudes above 90 km. It should be mentioned that the use of the reactive quenching rate coefficient as suggested by Adler-Golden (1997) instead of Varandas (2004a) results in only up to 21% of OH vibrationally excited. Under local thermodynamic equilibrium conditions, the fraction of vibrationally excited molecules 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.

Table 1. Collisional processes included in the OH non-LTE model.

No.	Process	Rate coefficients (cm^3molecule^{-1}s^{-1})	Reference
1	$H + O_3 \rightarrow OH(v) + O_2$	$1.4\times10^{-10}\exp(-470/T)$ ($\Phi(v)=$ 0, 0.01, 0.01, 0.01, 0.02, 0.04, 0.19, 0.28, 0.38, 0.06 for v=1-10)[1].	Makhlouf et al. (1995)
2	$OH(v) + N_2 \rightarrow OH(v-1) + N_2$	(0.058, 0.10, 0.17, 0.30, 0.52, 0.91, 1.6, 2.7, 4.8, 6)$\times10^{-13}$ for v=1-10.	Adler-Golden (1997)
3	$OH(v) + O_2 \rightarrow OH(v-1) + O_2$	(0.13, 2.7, 5.2, 8.8, 17, 30, 54, 98, 170, 300)$\times10^{-13}$ for v=1-10.	Adler-Golden (1997)
4	$OH(v) + O(^3P) \rightarrow H + O_2$	(2.72, 2.91, 3.22, 3.38, 3.30, 3.51, 4.22, 4.27, 5.07)$\times10^{-11}$ for v=1-9 at 210 K; (2.36, 2.44, 2.93, 3.45, 3.10, 3.28, 3.88, 4.19, 4.78)$\times10^{-11}$ for v=1-9 at 255 K;	Varandas (2004a)
5	$OH(v) + O(^3P) \rightarrow OH(v-1) + O(^3P)$	(2.49, 2.49, 2.77, 3.09, 2.59, 2.88, 2.33, 2.29, 1.77)$\times10^{-11}$ for v=1-9 at 210 K; (2.09, 2.43, 2.19, 2.57, 2.44, 2.67, 2.23, 1.96, 1.75)$\times10^{-11}$ for v=1-9 at 255 K;	Varandas (2004a)

[1] $\Phi(v)$ is the nascent distribution of state v.
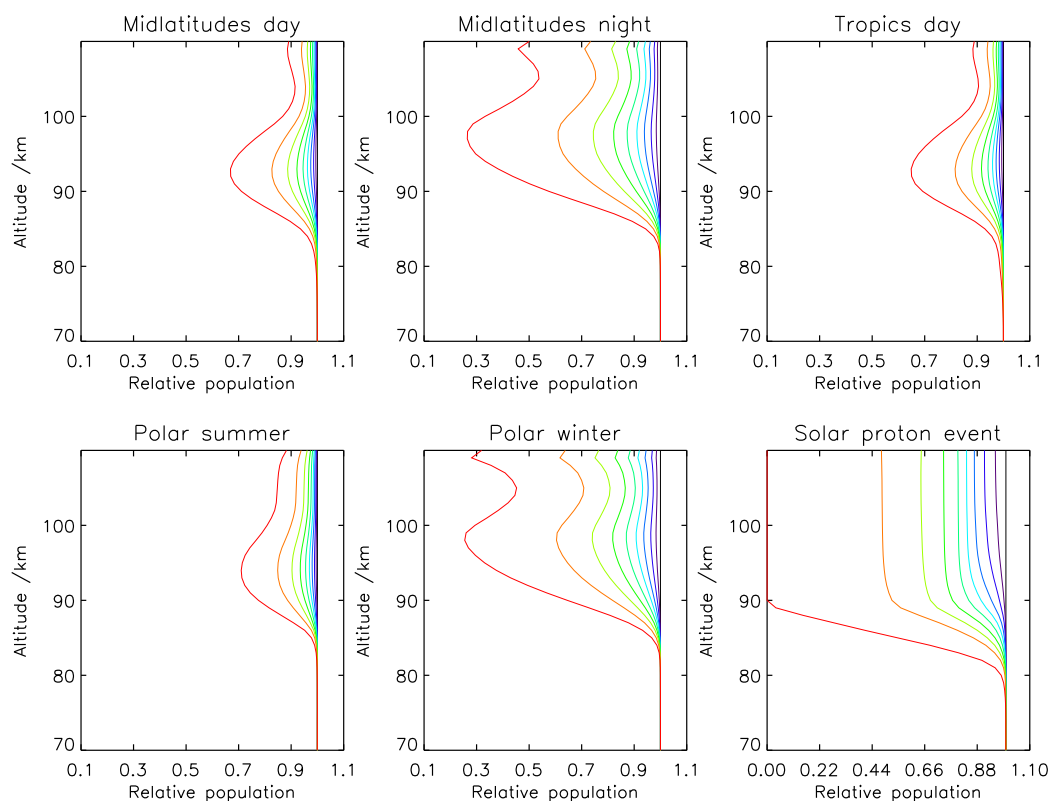
Fig. 1. Cumulative relative populations of the OH vibrational states as a function of altitude from groundstate (leftmost line) to total OH ($v = 0...9$) for various atmospheres. The distances between the lines represent the relative populations of of vibrational levels 1 to 9.
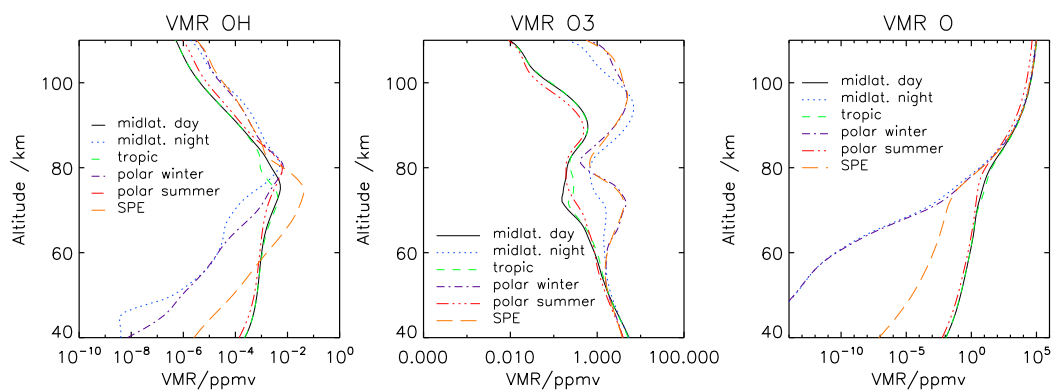
Fig. 2. Assumed mixing ratio profiles of OH, O_3 and O (from left to right) for various atmospheric conditions.

Their rate coefficient for OH in its vibrational ground state at 298 K (6.84×10^{-14} cm^3 molecule^{-1} s^{-1}) agrees reasonably well with that recommended by Sander et al. (2006) (7.25×10^{-14} cm^3 molecule^{-1} 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 population of the respective vibrational level:

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

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 1080. For the SPE atmosphere at 106 km altitude, this factor was found to be as large as 1470. Even in the daytime equatorial atmosphere, where the smallest enhancement is found, the effective rate coefficient reaches a factor of up to 630 at 95 km altitude.
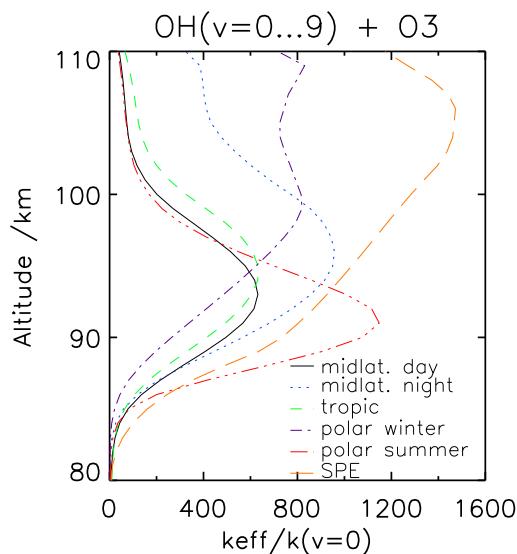
Fig. 3. Relative increase of the total OH($v=0...9$)+O_3 rate coefficients by consideration of vibrational excitation of OH in the reaction OH+O_3 as a function of altitude for various atmospheres.

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 atmospheric conditions (midlatitudes day, midlatitudes night, equator day, polar summer and polar winter, all under quiescent conditions, as well as polar winter under 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
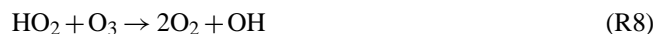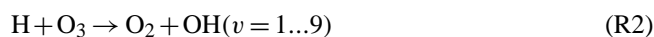
and abundances of constituents were taken from various sources: For the quiescent atmospheres, temperature, pressure, $[N_2]$, $[O_2]$, $[H]$ (above 90 km), and $[O]$ (above 80 km) were taken from MSISE90 (Hedin, 1991); $[HO_2]$ (below 75 km), $[O_3]$ (below 60 km), and $[ClO]$ (below 75 km) were taken 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 reations rates as recommended by Sander et al. (2006). For the SPE case, which represents the situation at 85° North during 29 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 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 ith 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:

$$OH(v=0...9)+O_3 \rightarrow O_2+HO_2 \quad (R1)$$

$$H+O_3 \rightarrow O_2+OH(v=1...9) \quad (R2)$$

$$O_3+O(^3P) \rightarrow 2O_2 \quad (R3)$$

$$O_3+O(^1D) \rightarrow 2O_2 \quad (R4)$$

$$O+O+M \rightarrow O_2+M \quad (R5)$$

$$OH+O \rightarrow O_2+H \quad (R6)$$

$$HO_2+O \rightarrow O_2+OH \quad (R7)$$

$$HO_2+O_3 \rightarrow 2O_2+OH \quad (R8)$$

$$NO+O_3 \rightarrow NO_2+O_2 \quad (R9)$$

$$NO_2+O \rightarrow NO+O_2 \quad (R10)$$

$$Cl+O_3 \rightarrow ClO+O_2 \quad (R11)$$

$$ClO+O \rightarrow Cl+O_2 \quad (R12)$$

$$H_2O_2+O \rightarrow OH+HO_2 \quad (R13)$$

$$NO_2+O_3 \rightarrow NO_3+O_2 \quad (R14)$$

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 even 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, $\Delta s(O_3; OH+O_3)$, might also be of interest. Here we consider sink Reactions (R1–R4), (R8), (R9), (R11), (R14),

$$O_3+h\nu \rightarrow O_2(^3\Sigma_g^-)+O(^3P), \quad (R15)$$

and

$$O_3+h\nu \rightarrow O_2(^1\Delta_g)+O(^1D), \quad (R16)$$
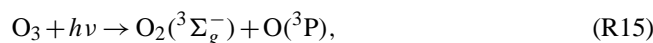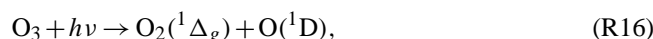
where photolysis rates were calculated with a version of TUV (Madronich and Flocke, 1998) which has been extended to an atmosphere covering altitudes of up to 200 km. The excess relative ozone sink, however, is negligibly small: less than 0.1% in the polar winter upper stratosphere, with a second maximum 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% (Fig. 6).
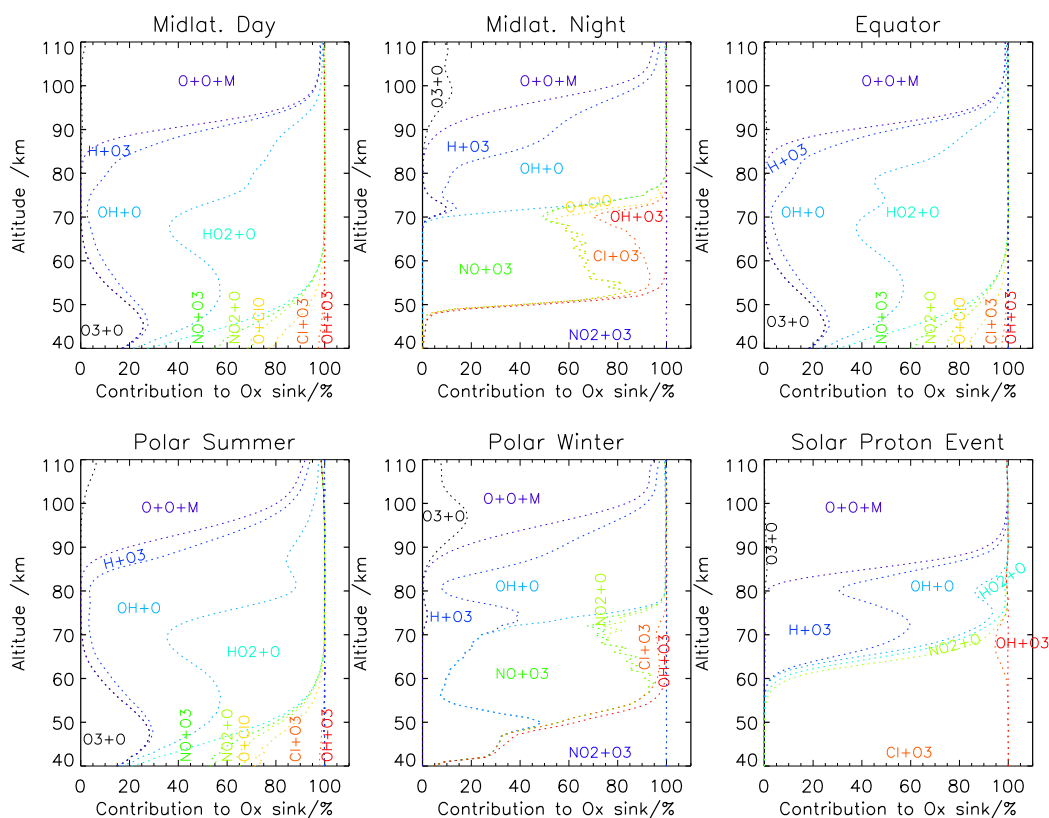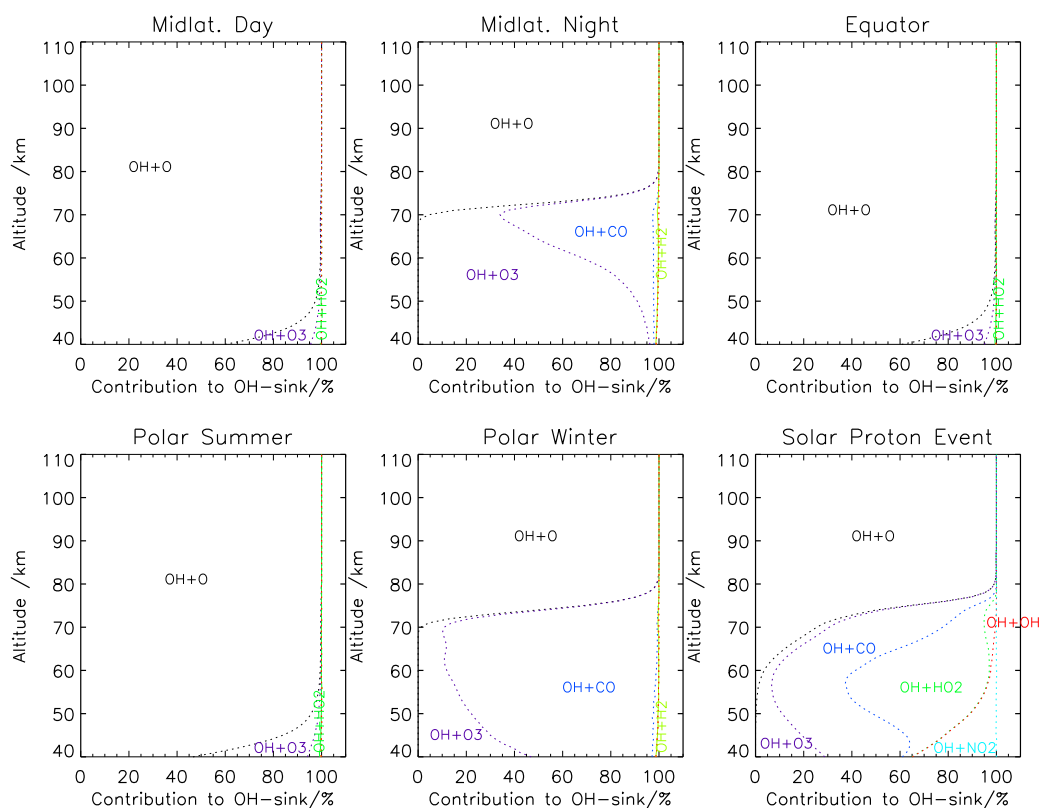
Fig. 4. Cumulative relative contribution to the odd oxygen sink of the leading reactions for various atmospheres.
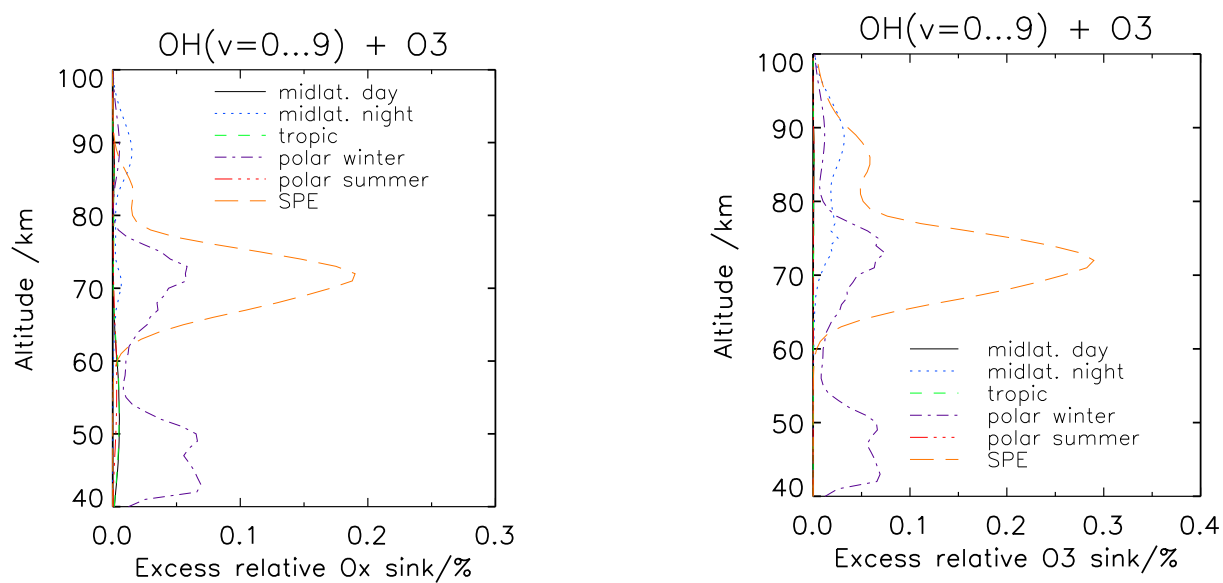
Fig. 5. Excess relative odd oxygen sink by consideration of vibrationally excited OH in the OH+O$_3$ reaction as a function of altitude for various atmospheres.

Fig. 6. Excess relative ozone sink by consideration of vibrationally excited OH in the OH+O$_3$ reaction as a function of altitude for various atmospheres.

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.

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

$$OH + CO \rightarrow CO_2 + H, \tag{R17}$$

$$OH + OH + M \rightarrow H_2O_2 + M, \tag{R18}$$

$$OH + HO_2 \rightarrow H_2O + O_2, \tag{R19}$$

$$OH + H_2 \rightarrow H_2O + H, \tag{R20}$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2, \tag{R21}$$

$$OH + OH \rightarrow H_2O + O, \tag{R22}$$

and

$$OH + NO_2 + M \rightarrow HNO_3 + M, \tag{R23}$$

where for R23 both isomeric variants of the product (HOONO and HONO$_2$) 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($v = 0...9$)+O$_3$ reaction. Besides

$$OH(v = 0...9) + O_3 \rightarrow O_2 + HO_2, \tag{R1}$$

which is reported to produce rotationally and vibrationally excited HO$_2$, two further reaction pathways are proposed:

$$OH(v = 0...9) + O_3 \rightarrow O_2 + O_2 + H \tag{R24}$$
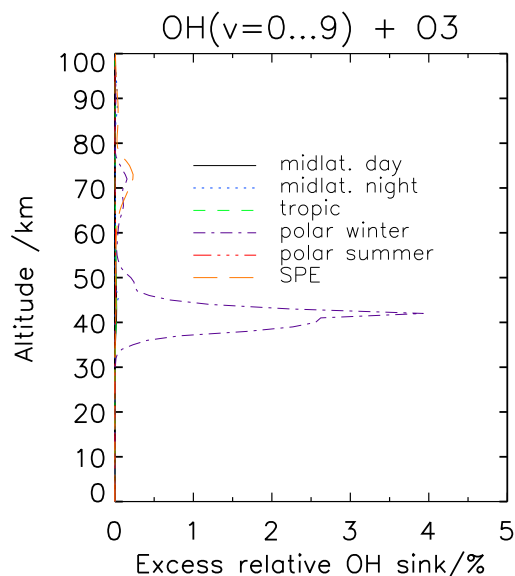
and

$$OH(v = 0...9) + O_3 \rightarrow O_2 + OH + O. \tag{R25}$$
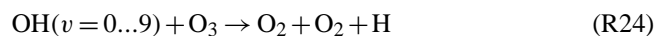
The reason for the latter pathways (Reactions R24 and R25) is that for OH($v \geq 6$) the product HO$_2$ is vibrationally excited

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

Fig. 9. Excess relative HO$_2$ source by consideration of vibrationally excited OH in the OH+O$_3$ reaction as a function of altitude for various atmospheres.

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 that the reactive quenching of OH and O$_3$ always implies OH loss.

2.2.4 HO$_2$ source strength

Finally, we estimate the excess HO$_2$ 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 HO$_2$ sources competing with Reaction (R1) have been considered: Reactions (R13), (R21), as well as
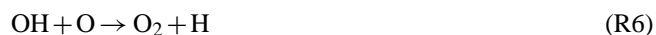
$$H + O_2 + M \rightarrow HO_2 + M, \tag{R26}$$

According to these estimates, in the lower midlatitude nighttime thermosphere the HO$_2$ source is increased by 2.5%, and in the polar winter lower thermosphere by 1.5% (Fig. 9).
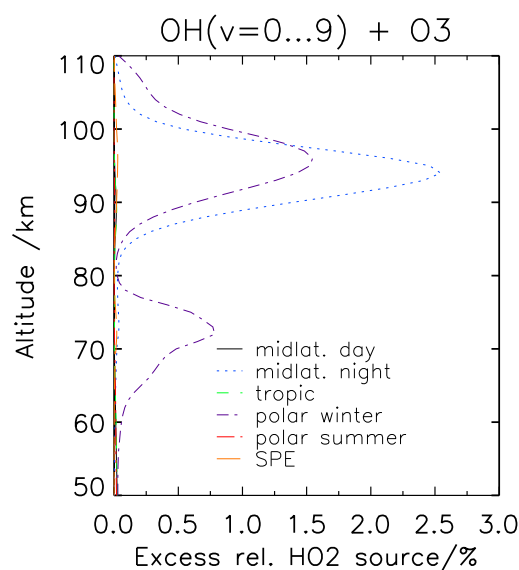
3 The reaction of the hydroxyl radical with atomic oxygen

3.1 Effective rate coefficients

The reaction

$$OH + O \rightarrow O_2 + H \tag{R6}$$

outweighs Reaction (R1) as a sink of odd oxygen in the thermosphere and, depending on illumination, also in the mesosphere and upper stratosphere 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). Contrary to Reaction (R1), the rate coefficients decrease from $v = 0$ to $v = 1$ or $v = 2$ and then increase again for higher vibrational levels. For calculation of the effective rate coefficients according to Eq. (1) we have used pretabulated v-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 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 −5% at 93 km altitude for the sunlit atmospheres under investigation, −9% at 109 km for the polar winter atmosphere to −10% at 96 km for the midlatitudinal night atmosphere (Fig. 10). For the SPE atmosphere deviation reaches −11% at 88 km and 107 km altitude.

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 reaches −3% for the midlatitudinal nighttime atmosphere, and −1 to −2% for all other atmospheres under investigation. The effect is negative at all altitudes for all atmospheres under consideration (Fig. 11). The same competing reactions as for Reaction (R1) have been considered. For quiescent dark atmospheres, the
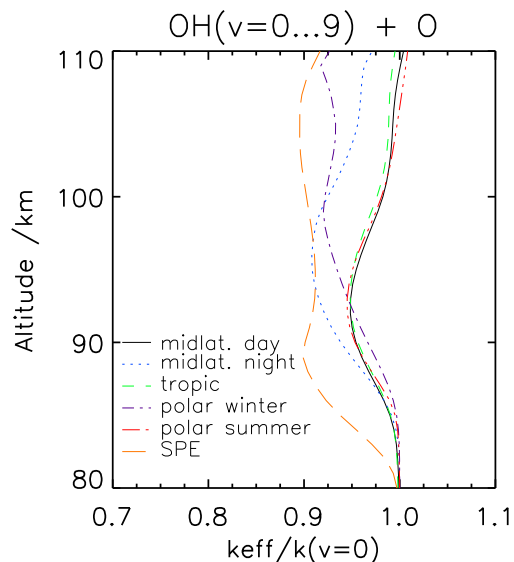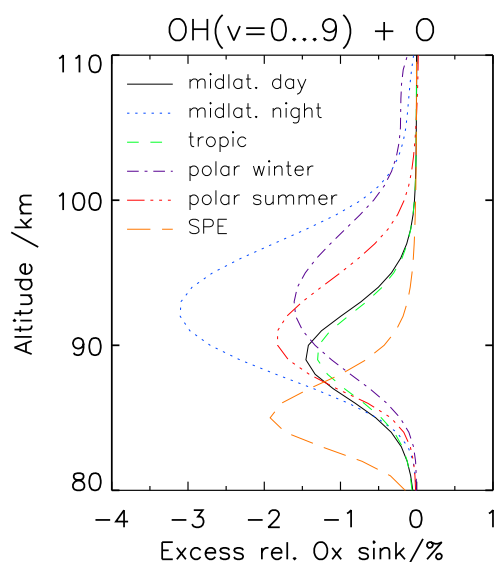
Fig. 10. Relative increase of the total OH($v=0...9$)+O rate coefficients by consideration of vibrational excitation of OH in the reaction OH+O as a function of altitude for various atmospheres.

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.

above also holds for the atomic oxygen sink, while the effect of vibrationally excited OH reaches only about -0.5% for sunlit atmospheres (Fig. 12). For the SPE atmosphere the atomic oxygen sink is not affected at all. Consideration of vibrationally excited OH alters the OH sink by up to -5% for sunlit atmospheres, about -10% for quiescent dark atmospheres and -12% for the SPE atmosphere (Fig. 13).

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 1080 faster if vibrational excitation is considered. For SPE conditions this acceleration factor can even exceed 1400. 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 2.5%). The largest relative impact is found for the dark atmospheres.

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 is larger than that of the reaction of OH with ozone: The odd oxygen destruction is reduced by about up to 3% and the OH sink is reduced by up to 10%. For SPE conditions the effect on the OH sink can reach -12%. 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.
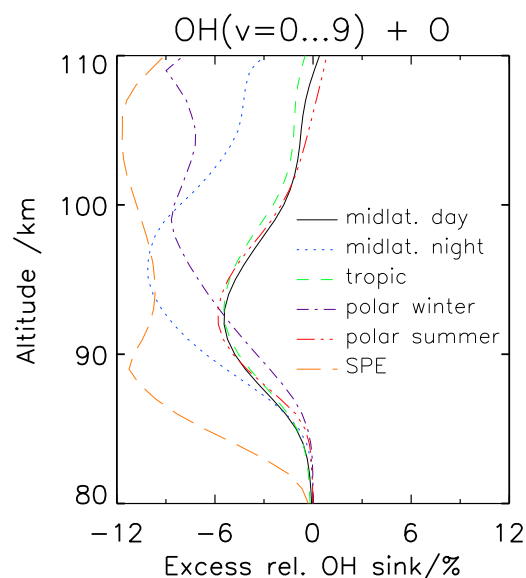
Certainly our study depends on the populations of OH vibrational levels assumed to calculate the effective rate coefficients and thus on the rate constants used in the GRANADA non-LTE model. The rate coefficient for OH($v=1...9$)+O$\rightarrow$O$_2$+H as recommended by Adler-Golden (1997) (2.0×10^{-10}) is nearly an order of magnitude larger than that used here, and even consideration of non-reactive quenching of OH($v=1...9$) and O as suggested by Varandas (2004a) reduces the discrepancy in the total removal of vibrationally excited OH to no less than a factor of about three (cf. Table 1). Use of the rate coefficient as suggested by Adler-Golden and confirmed by Pickett et al. (2006) by means of upper atmospheric measurements leads to much lower populations of vibrationally excited states, and in consequence the effect on chemistry would be even smaller than that reported in this paper. In light of this, our calculations thus can be regarded as upper estimates. On the other hand, the values suggested by Varandas (2004a) are in reasonable agreement with rate coefficients in the JPL
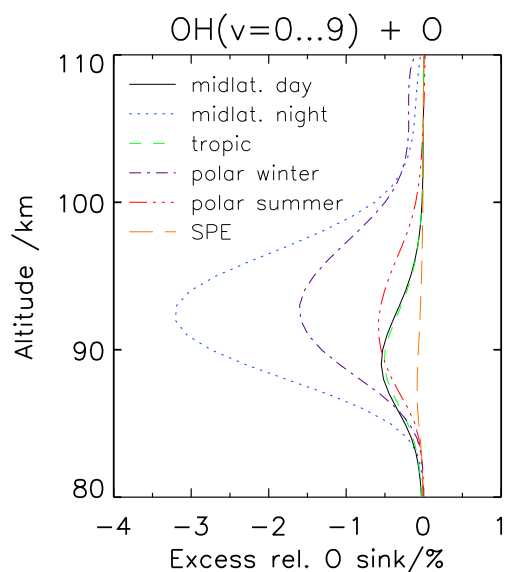
Fig. 12. Excess relative atomic oxygen sink by consideration of vibrationally excited OH in the OH+O reaction as a function of altitude for various atmospheres.

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.

recommendation on chemical kinetics (Sander et al., 2006). Assuming that the v-dependence of this particular reaction rate is as weak as reported by Varandas, the discrepancy between Adler-Golden results and the JPL recommendation cannot be explained by the fact that the latter refers most probably to OH in its vibrational ground state. This discrepancy appears to be an interesting problem in itself, particularly since the uncertainty of the reaction rate coefficients as such clearly outweights the relevance of the title question of this paper.

In summary, 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 in this field, involving further reactions of vibrationally excited O_2, O_3, HO_2, 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 abun-

dances and atomic oxygen abundances change with different speed. And finally, our 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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