The natural greenhouse effect of atmospheric oxygen (O$_2$) and nitrogen (N$_2$)

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[1] The effect of collision-induced absorption by molecular oxygen (O$_2$) and nitrogen (N$_2$) on the outgoing longwave radiation (OLR) of the Earth’s atmosphere has been quantified. We have found that on global average under clear-sky conditions the OLR is reduced due to O$_2$ by 0.11 Wm$^{-2}$ and due to N$_2$ by 0.17 Wm$^{-2}$. Together this amounts to 15% of the OLR-reduction caused by CH$_4$ at present atmospheric concentrations. Over Antarctica the combined effect of O$_2$ and N$_2$ increases on average to about 38% of CH$_4$ with single values reaching up to 80%. This is explained by less interference of H$_2$O spectral bands on the absorption features of O$_2$ and N$_2$ for dry atmospheric conditions.

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1. Introduction

[2] It is a widespread notion that both main constituents of the atmosphere, molecular nitrogen (N$_2$) and molecular oxygen (O$_2$) ‘exert almost no greenhouse effect’ [Le Treut et al., 2007]. Their contribution is mainly ascribed to indirect effects like the pressure-broadening of CO$_2$-lines in the infrared [Lacis et al., 2010; Goldblatt et al., 2009]. Thus, N$_2$ and O$_2$ are sometimes not considered as natural greenhouse gases even in case of low water vapor conditions [Lacis et al., 2010].

[3] Due to their symmetry, homonuclear diatomic molecules like N$_2$ and O$_2$ do not exhibit a static electric dipole moment, such as H$_2$O, nor is there the possibility to induce vibrationally a dipole moment, as in the case of CO$_2$. Thus, there are no strong infrared absorption bands due to dipole transitions as in the case of the major greenhouse gases. However, as discovered by Crawford et al. [1949], collision-induced absorption leads to weak absorption features of N$_2$ and O$_2$ in the infrared [e.g., Hartmann et al., 2008].

[4] Due to the atmospheric concentration of atmospheric N$_2$ (O$_2$) that is about 2000 (550) times higher than that of CO$_2$ and about $4.4 \times 10^5$ ($1.2 \times 10^7$) times more abundant than CH$_4$, even the weak infrared absorption of N$_2$ (O$_2$) can become radiatively important.

[5] The collision-induced fundamental vibration-rotation band at 6.4 µm is the major absorption signature of O$_2$ in the thermal infrared. Timofeyev and Tonkov [1978] reported that at distinct wavelengths near the band center, O$_2$ absorption may affect the atmospheric zenith transmission by up to 9% for dry atmospheric conditions. This effect is strongly modulated by the atmospheric water vapor content since the O$_2$ spectral signature is situated in the same spectral region as one of the most important H$_2$O infrared absorption bands ($\nu_2$ bending). In the atmosphere the infrared signal of O$_2$ has first been detected through balloon-borne limb-sounding observations [Rinsland et al., 1982].

[6] N$_2$ has two major bands influencing the infrared radiation: the collision-induced rovibrational fundamental band at 2400 cm$^{-1}$ and the collision-induced rottotranslational band at 100 cm$^{-1}$. In the atmosphere, the mid-infrared absorption of N$_2$ was first observed by Susskind and Sears [1977] by use of ground-based FTIR measurements. Rinsland et al. [1981] confirmed these observations by analysis of balloon-borne limb solar occultation spectra. A further detailed analysis of the mid-infrared continuum signals of O$_2$ and N$_2$ has been performed on basis of space-borne observations by Rinsland et al. [1989].

[7] The N$_2$ absorption band in the sub-mm range has been analysed in atmospheric measurements by Parado et al. [2001]. They used ground-based Fourier transform spectroscopy at Mauna Kea to determine the continuum like absorption up to frequencies exceeding 1 THz.

[8] In various line-by-line radiative transfer calculations for the validation of radiation codes used within climate models [e.g., Fomin et al., 2004; Collins et al., 2006; Iacono et al., 2008] or for the exact modeling of outgoing longwave radiation [Buehler et al., 2006] the effects of collision-induced continua of N$_2$ and O$_2$ have mostly been taken into account by use of continuum parameterizations like the Mlawer, Tobin, Clough, Kneizys, and Davis (MT CKD) model [Clough et al., 2005]. However, we are not aware of any publications on the quantification of the effect of O$_2$ and N$_2$ on the outgoing longwave radiation flux (OLR). In the following, after a description of the used radiative transfer model we show spectrally resolved typical simulations of atmospheric transmission and OLR for a standard atmospheric situation. Then, the globally resolved net effects of O$_2$ and N$_2$ on OLR are discussed and at the end a comparison with an independent line-by-line model is presented.

2. Radiative Transfer Simulations

[9] For the simulation of broadband infrared spectra at the top of the atmosphere the radiative transfer model KOPRA [Stiller, 2000] has been applied. KOPRA is an accurate and
fast line-by-line model being used for the analysis of spectrally high resolved satellite remote sensing observations like the IR-limb emission sounder MIPAS [Fischer et al., 2008] or the IR-nadir instrument IASI [Keim et al., 2009]. Beside the indirect model validation via the validation of the retrieved atmospheric parameters, KOPRA has successfully been compared to various independent radiative transfer models [e.g., Tjemkes et al., 2003]. For the calculations shown within this paper we have used spectroscopic data from HITRAN 2008 [Rothman et al., 2009]. Continuum contributions for water vapor and CO$_2$ are parameterized according to the MT_CKD model version 2.5.2 [Clough et al., 2005]. The collision induced continuum by O$_2$ is based on the empirical model by Thibault et al. [1997]. The continuum by N$_2$ near 2300 cm$^{-1}$ is calculated according to Lafferty et al. [1996]. The collision induced rovibrational absorption by N$_2$ at around 100 cm$^{-1}$ is taken from the MT_CKD version 2.5.2 implementation which is based on Borysow and Frommhold [1986] and Boissoles et al. [2003]. All following KOPRA radiative transfer calculations have been performed on a spectrally high resolved variable wavenumber grid with a grid width down to 0.0005 cm$^{-1}$ [Kuntz and Höpfner, 1999]. For the figures the high-resolved spectra have been smoothed with a 2 cm$^{-1}$ wide boxcar function.

3. Calculation for a Standard Atmosphere

[10] Figure 1a shows the atmospheric zenith transmission between 10 cm$^{-1}$ and 2500 cm$^{-1}$ (4 μm–1000 μm) for single gases H$_2$O, CO$_2$, O$_3$, N$_2$O, CH$_4$, O$_2$ and N$_2$ and their combination for a typical atmospheric mid-latitude situation [Remedios et al., 2007] as calculated with KOPRA. It is obvious that in case of O$_2$ a maximum reduction of the atmospheric transmission by 40% (around 1550 cm$^{-1}$) and in case of N$_2$ by 50% at 2330 cm$^{-1}$ and 80% at 100 cm$^{-1}$ is reached. The mean zenith transmission of single gas atmospheres is reduced by 2.6% due to O$_2$ and by 8.3% due to N$_2$, in comparison to 1.9% by e.g. CH$_4$. For a zenith angle of 80° an atmosphere consisting only of N$_2$ and O$_2$ would even be opaque by O$_2$ absorption between 1500–1650 cm$^{-1}$ and by N$_2$ absorption in the regions 20–200 cm$^{-1}$ and 2230–2470 cm$^{-1}$. The mean transmission would be reduced by 14.2% due to O$_2$ and by 25.7% due to N$_2$, compared to 6.9% by CH$_4$ and 92.5% by H$_2$O.

[11] The effect of O$_2$ and N$_2$ on the outgoing longwave radiation flux (OLR) at the top of the atmosphere (assumed at
80 km altitude) is estimated by integrating radiance calculations at different nadir angles (0°, 20°, 40°, 60°, 81°) taking into account Earth’s sphericity. (The radiances between 81° and 90° have been neglected since those lines-of-sight do not hit the earth any more but correspond to limb views).

[12] In the following we discuss the net contribution to the OLR by different gases with respect to an atmosphere composed of the full set of species. This means that a gas with an absorption band in the same spectral region as a strong band of another species has less effect on the OLR than in case of less overlapping spectral signatures. As can be seen in Figure 1a, the collision induced absorption band of O\textsubscript{2} is covered by the $\nu_2$ H\textsubscript{2}O absorption, the rovibrational band of N\textsubscript{2} at 2400 cm$^{-1}$ by the strong 4.3 $\mu$m CO\textsubscript{2} absorption and the roto translational band of N\textsubscript{2} at 100 cm$^{-1}$ by absorption mainly due to H\textsubscript{2}O.

[13] Results are presented in Figure 1b as the difference between OLR calculations where a single gas has been omitted and the OLR values where all gases are included ($\Delta$OLR(gas x) = OLR(all without gas x)−OLR(all)). Mind that ‘omitted’ and ‘without gas x’ here mean that the gas is set to be infrared-inactive but still contributes to the atmospheric density and pressure.

[14] As indicated in Figure 1b, $\Delta$OLR(O\textsubscript{2}) = 0.05 Wm$^{-2}$ and $\Delta$OLR(N\textsubscript{2}) = 0.11 Wm$^{-2}$. Thus, the natural greenhouse effect of oxygen and nitrogen together are about 10% of that of CH\textsubscript{4} ($\Delta$OLR(CH\textsubscript{4}) = 1.55 Wm$^{-2}$). Mind that the mean tropospheric concentration of CH\textsubscript{4} used in these calculations was 1.8 ppmv.

[15] To evaluate the effect of overlapping spectral signatures on the relative contribution to OLR reduction we simulated the pure hypothetical case of single gas atmospheres. Here, compared to the flux for an infrared-inactive atmosphere (365.7 Wm$^{-2}$), each of N\textsubscript{2} and O\textsubscript{2} reduces the OLR by 2.8 Wm$^{-2}$ and CH\textsubscript{4} by 4.3 Wm$^{-2}$. The effect of both major atmospheric constituents together would exceed the

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**Figure 2.** Cloud-free global distribution of the values of OLR reduction due to (top) O\textsubscript{2} and (bottom) N\textsubscript{2} relative to that of CH\textsubscript{4} for realistic all-gas atmospheres: $\frac{\Delta$OLR(O\textsubscript{2} or N\textsubscript{2})}{\Delta$OLR(CH\textsubscript{4})} \times 100$. 

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Table 1. Cloud-Free Global and Antarctic (70°–90°S) Means of the OLR, the Absolute OLR Reduction and the OLR Reduction Relative to That of CH₄ for Realistic All-Gas Atmospheres

<table>
<thead>
<tr>
<th></th>
<th>OLR (Wm⁻²)</th>
<th>ΔOLR (Wm⁻²)</th>
<th>ΔOLR/ΔOLR(CH₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All gases</td>
<td>259.1</td>
<td>63.7</td>
<td>34.1</td>
</tr>
<tr>
<td>No gas</td>
<td>381.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>All w/o H₂O</td>
<td>322.8</td>
<td>11.9</td>
<td>17.7</td>
</tr>
<tr>
<td>All w/o CO₂</td>
<td>185.5</td>
<td>6.3</td>
<td>12.8</td>
</tr>
<tr>
<td>All w/o H₂O</td>
<td>177.3</td>
<td>0.4</td>
<td>0.646</td>
</tr>
<tr>
<td>All w/o N₂O</td>
<td>177.6</td>
<td>0.7</td>
<td>1.12</td>
</tr>
<tr>
<td>All w/o CH₄</td>
<td>177.7</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>All w/o O₂</td>
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<td>0.161</td>
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<td>All w/o N₂</td>
<td>177.0</td>
<td>0.15</td>
<td>0.219</td>
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<tr>
<td>Antarctic</td>
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<tr>
<td>All gases</td>
<td>176.8</td>
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<tr>
<td>No gas</td>
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<tr>
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<td>177.0</td>
<td>0.15</td>
<td>0.219</td>
</tr>
</tbody>
</table>

ΔOLR(gas x) = OLR(all without gas x)−OLR(all), ΔOLR/ΔOLR(CH₄) = ΔOLR(gas x) / ΔOLR(CH₄).

OLR-reduction due to CH₄ by a factor of 1.3. This drop from a factor of 1.3 to 10% in relative importance of N₂ and O₂ compared to CH₄ is caused by the overlapping bands of H₂O and CO₂ in a real atmosphere. To demonstrate how strong this importance is modulated by temperature and water-vapor content of the atmosphere a realistic global situation is described in the following.

4. Global Picture

In this section we investigate the OLR reduction by N₂ and O₂ in relation to CH₄ globally for a real atmospheric situation. As an example, October 16th, 2007 has been chosen arbitrarily. ECMWF T106 analysis for 6 UT of temperature and humidity has been applied to produce altitude profiles at cloud-free locations. To reduce the number of broad-band line-by-line calculations globally a 5° longitude × 5° latitude grid has been used. Within each grid-cell we have chosen the cloud-free profile nearest to the grid center. In case there has been no cloud-free situation, no calculation has been performed for the related grid cell. For all other gases (CO₂, O₃, N₂O, CH₄, O₂, and N₂), standard profiles have been used [Remedios et al., 2007].

The calculations for an atmosphere containing the full set of gases are presented in Figure 2 and in Table 1. In Figure 2 (top) the OLR reduction due to oxygen relative to that of methane ΔOLR(O₂)/ΔOLR(CH₄) is shown, and Figure 2 (bottom) demonstrates the similar effect for nitrogen ΔOLR(N₂)/ΔOLR(CH₄). With exception of the southern polar region the values vary around 6% for O₂ and 9% for N₂.

Global mean relative OLR reductions are 6.0% and 9.2% for O₂ and N₂, respectively (Table 1).

Over Antarctica, maximum values for ΔOLR(O₂)/ΔOLR(CH₄) of around 30% and for N₂ of up to 50% are reached. Mean values for latitudes poleward of 70°S are 16.1% for O₂ and 21.9% for N₂ as listed in Table 1. This large contribution to the natural greenhouse effect relative to the one exhibited by CH₄ is due to the extremely low humidity over the southern polar region, such that spectral signatures of water vapor interfere less with those of O₂ and N₂.

5. Model Evaluation

The accuracy of KOPRA simulations of the OLR reduction due to O₂ and N₂ relative to CH₄ has been evaluated by comparison with independent calculations performed with the ARTS radiative transfer model [Buehler et al., 2005; Eriksson et al., 2011]. Like KOPRA, ARTS is a line-by-line model which has been applied recently for the modeling of OLR at the top of the atmosphere [Buehler et al., 2006]. For nadir view, a comparison dataset has been calculated on basis of 42 altitude profiles of pressure/temperature and trace gases (H₂O, O₃, CO₂, N₂O, CH₄, O₂, N₂) [Garand et al., 2001]. Figure 3 shows the comparison for ΔOLR(O₂)/ΔOLR(CH₄), ΔOLR(N₂)/ΔOLR(CH₄) and the sum of both.

In general both models compare reasonably well: the mean values for O₂ are 6.4%(KOPRA) vs. 6.1%(ARTS) and for N₂ 8.1%(KOPRA) vs. 6.0%(ARTS), respectively. Differences are explained by different set-ups of the two models. First, the frequency grid of the ARTS simulations has been coarser (0.3 cm⁻¹) than that of KOPRA (min 5 × 10⁻⁴ cm⁻¹). A sensitivity analysis using a degraded frequency grid of 0.3 cm⁻¹ for KOPRA showed a reduction of the total effect from 14.5% to 13.5%, thus approaching the lower values of ARTS. Remaining differences are likely due to the application of different spectroscopic databases.

![Figure 3](image-url)
continuum in the $0-111$ range [Pardo et al., 2001; Boissoles et al., 2003; Pardo et al., 2005]. This probably explains the stronger relative effect of $N_2$ compared to that of $O_2$ within the KOPRA simulations compared to ARTS. In summary, the model intercomparison confirms the relative large effects on OLR by $O_2$ and $N_2$ as deduced from KOPRA simulations.

6. Conclusions

This work challenges a common perception on the negligible role of $O_2$ and $N_2$ as natural greenhouse gases in the Earth’s atmosphere compared to species like $CH_4$ or $N_2O$. It is in fact the large abundance of oxygen and nitrogen which compensates for their only weak interaction with infrared radiation through collision-induced absorption bands. We have shown that for hypothetic atmospheres consisting of only single gases the natural greenhouse effect of $O_2$ and $N_2$ together would be larger than that of $CH_4$ by a factor of around 1.3. For a realistic atmospheric composition this effect is reduced through shading of $O_2$ and $N_2$ absorption bands mainly by spectral signatures of $H_2O$ and, to a less extend, by $CO_2$. Still the net global OLR reduction of oxygen and nitrogen together is with 0.28 Wm$^{-2}$ about 15% of that due to $CH_4$. However, for dry atmospheric situations like over the Antarctic continent the effect of $O_2$ and $N_2$ even reach up to 80% of the influence of $CH_4$ for a realistic atmospheric composition.

An atmospheric situation with increased values of $N_2$ has been proposed as possible solution for the ‘Faint Young Sun’ paradox by Goldblatt et al. [2009]. Repeating their calculation of longwave radiative forcing we obtained similar values for a doubling of $N_2$ concentrations ($\approx 12$ Wm$^{-2}$). We investigated this effect for single absorbers and found reductions of the OLR by 9.4, 5.1, 4.6 and 1.9 Wm$^{-2}$ for $H_2O$, $CO_2$, $N_2$, and $CH_4$. The relatively large value in case of $N_2$ is due to collision-induced continuum absorption which scales with the square of concentration while the dependence of strong absorption bands on line-width is much smaller. Thus, we object to the view that the radiative forcing of $N_2$ increase operates only indirectly by broadening the absorption lines of other gases [Goldblatt et al., 2009]. Actually it is a combination of this indirect effect and the direct impact through collision-induced absorption.

Finally we would like to stress that this work concerns only the contribution of $N_2$ and $O_2$ to the natural greenhouse effect. In no way does it affect the importance of $CH_4$ and other anthropogenically affected gases with respect to global climate change.

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References


