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Impact of molecular diffusion on the CO_2 distribution and the temperature in the mesosphere

Simon Chabrillat, Gaston Kockarts, and Dominique Fonteyn
Belgian Institute for Space Aeronomy, Brussels, Belgium

Guy Brasseur
Max Planck Institute for Meteorology, Hamburg, Germany

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[1] Modelling the energy budget in the mesosphere and lower thermosphere requires a precise evaluation of CO_2 distribution in this region. This distribution is primarily determined by competition between vertical eddy diffusion and molecular diffusion. A simple algorithm is proposed to take into account both processes, at all altitudes. Using the SOCRATES bi-dimensional model of the middle atmosphere, we show that molecular diffusion has a direct impact on CO_2 vertical distribution down to approximately 80 km altitude, *i.e.* well into the mesosphere and below the turbopause altitude. A sensitivity study with regard to different aeronomical processes shows that molecular diffusion has the deepest influence in the mesospheric polar night region. Our model shows that molecular diffusion of CO_2 is responsible for a polar night mesopause 12 K warmer than if this process was neglected. Hence, dynamical models should take this process in account across the whole mesospheric altitude range. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 3332 Meteorology and Atmospheric Dynamics: Mesospheric dynamics; 3367 Meteorology and Atmospheric Dynamics: Theoretical modeling

1. Introduction

[2] The importance of carbon dioxide for the radiative budget of the middle atmosphere, through its infrared emission at 15 μm, is well known. Many modelling studies have focused on the evaluation of the cooling in the mesosphere and lower thermosphere (MLT) due to the anthropogenic increase in CO_2 [*Berger and Dameris*, 1993; *Portmann et al.*, 1995; *Thomas*, 1996; *Akmaev and Fomichev*, 2000]. Due to the absence of important chemical sources and sinks, eddy (turbulent) diffusion leads to a nearly constant volume mixing ratio (vmr) for CO_2 in the troposphere and stratosphere. This homogeneity of CO_2 distribution has often been assumed to extend up to the *turbopause*, a conventional boundary often confused with the *homopause*. Although this long-standing confusion has already been pointed out by *López-Puertas et al.* [2000], it deserves further clarification.

[3] The homosphere is the region of the atmosphere where eddy diffusion is important enough to distribute homogeneously the major atmospheric constituents. Above this region is the heterosphere, where molecular diffusion separates these constituents depending on their molecular (or atomic) mass. The limit between these two regions is the homopause, above which the molecular diffusion cannot be neglected. The turbopause is a related, but different concept: it is the altitude where the coefficients of molecular diffusion and vertical eddy diffusion are equal. The value of the vertical, eddy diffusion coefficient K_{zz} depends primarily on the parameterization chosen to estimate the breaking of gravity waves, because this process cannot be computed exactly by chemical models of the atmosphere within their current framework. Hence, the altitude of the turbopause cannot be precisely estimated. Furthermore, this altitude is not univocally defined, because the molecular diffusion coefficient is different for each chemical species.

[4] This explains why the conventional altitude of 100 km, often presented as the approximate location of the turbopause, should be viewed only as a general indication. Many coupled models of the dynamics and the chemistry in the mesosphere/lower thermosphere (MLT) seem to neglect molecular diffusion, or to take it in account only above 90 or 100 km altitude. The previous version of the SOCRATES model [*Brasseur et al.*, 1990] and the GS-2D model [*Garcia and Solomon*, 1994] do not include molecular diffusion, the latter assuming instead a large eddy diffusion coefficient near the upper boundary.

[5] Few recent observational studies include model comparisons [*López-Puertas et al.*, 2000; *Kaufmann et al.*, 2002]. While our work is part of this research, its main goal is to show that the competition between vertical eddy diffusion and molecular diffusion is easy to evaluate, and that the latter has non-negligible effects in the mesosphere.

2. Solving the Vertical Diffusion Equation at All Altitudes

[6] The vertical flux of any chemical species is the sum of the molecular diffusion flux, the vertical eddy diffusion flux, and the flux due to advection by the vertical component of the winds. While our focus is on CO_2, we describe here a general algorithm to solve the time-dependent vertical diffusion equation for all chemical species. We will avoid any assumption on the altitude range where eddy diffusion dominates over molecular diffusion.

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[7] Let $F_{i,D}$ be the molecular diffusion flux ($\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$) of the chemical species i at altitude z and time t. To compute this flux, we use the classical expression [*Banks and Kockarts*, 1973]

$$F_{i,D} = -n_i D_i \left[\frac{1}{n_i}\frac{\partial n_i}{\partial z} + \frac{1}{H_i} + \frac{1+\alpha_{T,i}}{T}\frac{\partial T}{\partial z} \right], \tag{1}$$

where n_i, D_i, $H_i = kT/m_i g$ and $\alpha_{T,i}$ are respectively the number density, the molecular diffusion coefficient, the scale height and the thermal diffusion factor of species i. T, k, m_i and g represent respectively the temperature, the Boltzmann constant, the molecular mass of species i and the acceleration of gravity, which we will consider as a constant. Let us note that the thermal diffusion factor $\alpha_{T,i}$ is negligible for CO_2. The computation of the molecular diffusion coefficients D_i has been summarized by *Banks and Kockarts* [1973]. Since the original reference can be difficult to find, the method to compute D_i is reported again by *Chabrillat* [2001, p.134].

[8] Molecular diffusion tends to separate the chemical species, depending on their mass. It results in a negative vertical gradient of the vmr for species such as CO_2, which are heavier than air. This process *competes* with the eddy diffusion, which leads to a constant vmr, independently of the mass of the species.

[9] The vertical eddy diffusion flux $F_{i,K}$ is defined by a formulation analogous to (1):

$$F_{i,K} = -n_i K_{zz} \left[\frac{1}{n_i}\frac{\partial n_i}{\partial z} + \frac{1}{H} + \frac{1}{T}\frac{\partial T}{\partial z} \right] \tag{2}$$

where $H = kT/mg$ is the scale height of the atmosphere, m is the (altitude-dependent) averaged molecular mass of air, and K_{zz} is the eddy diffusion coefficient. We see that the competition between the two processes depends entirely on the relative values of their diffusion coefficients.

[10] We use here a version of the bi-dimensional model SOCRATES [*Khosravi et al.*, 2002] specifically optimized for mesospheric and lower thermospheric processes [*Chabrillat*, 2001]. SOCRATES calculates interactively the wind field, the chemical composition and the temperature between 85°South and 85°North, and from $z^* = 0$ km to $z^* = 120$ km. z^* is the log-p vertical coordinate defined by $z^* = H_* \ln\frac{p_0}{p}$ where $H_* = 7$ km is the conventional height scale, p_0 the pressure at ground level and p the pressure at log-p altitude z^*.

[11] Figure 1 shows the two vertical diffusion coefficients, evaluated by the SOCRATES model at equinox, mid-latitudes. The eddy diffusion coefficient is calculated by a Doppler-spread parameterization of gravity-wave momentum deposition [*Hines*, 1997]. This coefficient is proportional to the inverse of the Prandtl number, which can be arbitarily set between 0.1 and 1, and was set at 0.15 for the baseline model. The two coefficients are equal at $z^* = 109$ km, which is slightly above the mesopause $z^* = 103$ km (at this latitude and season). We will show that even though the molecular diffusion coefficient of carbon dioxide is twenty times smaller than the eddy diffusion coefficient at $z^* = 85$ km, the effect of molecular diffusion is not negligible in the mesosphere.

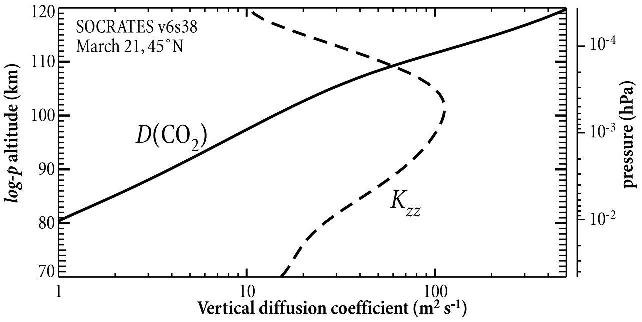

Figure 1. Vertical profiles of the eddy diffusion coefficient and the CO_2 molecular diffusion coefficient, using the SOCRATES baseline model. Latitude 45 North, equinox (March 21), solar minimum conditions.

[12] Thanks to the common "operator splitting" method, SOCRATES solves separately the advection, the chemistry, the vertical diffusion and the horizontal diffusion. The vertical diffusion equation is a second-order equation based on the mass continuity principle:

$$\frac{\partial n_i}{\partial t} = -\frac{\partial}{\partial z}\left(F_{i,K} + F_{i,D}\right) \tag{3}$$

For numerical reasons, we formulate (2) in terms of volume mixing ratios, $X_i = n_i/n$, where n is the total number density of air. Using the perfect gas law and hydrostatic equilibrium, one obtains the classical expression [*Brasseur et al.*, 1990]

$$F_{i,K} = -n K_{zz} \frac{\partial X_i}{\partial z}. \tag{4}$$

[13] Using a first-order implicit method and a staggered z^* grid, the general equation for vertical diffusion (3) is rearranged into a linear and tri-diagonal system, its dimension being equal to the number of vertical levels in the model (121 in SOCRATES). This system is then solved by a classical lower/upper decomposition method, for each chemical species computed by the model. Since this algorithm is based on a flux formulation, it is strictly conservative, *i.e.* the vertical column content for each species remains strictly constant.

[14] The upper and lower boundary conditions are imposed either as volume mixing ratios (vmr) or as fluxes. If, as in SOCRATES, the lower boundary is the surface, one also has the possibility to impose a deposition velocity at the surface. The boundary conditions for CO_2 are imposed as follows: at the surface, $X(CO_2) = 356$ ppm and at the upper boundary ($z^* = 120$ km), a null flux.

[15] The Fortran90 routine developed to solve simultaneously molecular and eddy diffusion can be obtained from the first author.

3. Impact on Carbon Dioxide Distribution and Mesospheric Temperature

[16] To assess the importance of molecular diffusion on CO_2 distribution in the mesosphere, we have run six simulations of the SOCRATES model. The first one (base-

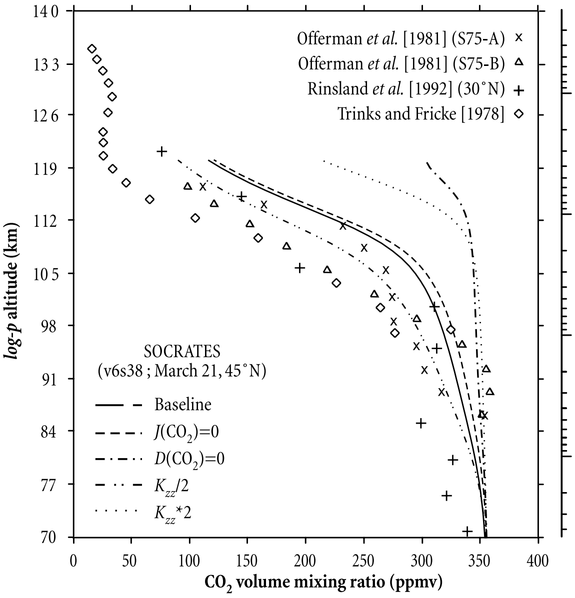

Figure 2. Observed and modelled vertical profiles of the CO_2 vmr, in mid-latitude regions at equinox.

line) takes in account all the processes affecting CO_2 distribution. The second, third and fourth simulations omit, respectively, the effect of photolysis ($J(CO_2) = 0$ where J is the photodissociation coefficient); the effect of molecular diffusion ($D(CO_2) = 0$) and the effect of CO_2 transport by the mean meridional circulation (no advection). Since there is a large uncertainty on the evaluation of the eddy diffusion coefficient, we also perform a sensitivity test with the two last simulations, where K_{zz} is halved ($K_{zz}/2$) or doubled ($K_{zz}*2$). In order to keep the focus on CO_2 distribution, K_{zz} is not modified when calculating the other chemical species. All the simulations were run at solar minimum conditions.

[17] Analysis of CRISTA measurements allowed, very recently, the first global-scale observations of the CO_2 distribution in the MLT [*Kaufmann et al.*, 2002]. Most other CO_2 measurements have been conducted at midlatitudes. *Fomichev et al.* [1998] have compiled a set of observations obtained by mass spectrometer technique [*Trinks and Fricke*, 1978; *Offerman et al.*, 1981] and by the ATMOS/Spacelab 3 instrument [*Rinsland et al.*, 1992], and have reduced them to the vmr of CO_2 as a function of *log-p* altitude. This reduction decreases the variability in the observations and allows an easy comparison with SOCRATES results.

[18] We compare this observational dataset with the model results at equinox (March 21) and at 45° latitude North (Figure 2). The baseline model reproduces the observed vertical gradient in a very satisfactory way. The simulations [$J(CO_2) = 0$] and [$D(CO_2) = 0$] show that this negative vertical gradient is almost entirely due to molecular diffusion. Doubling the eddy diffusion coefficient [$K_{zz}*2$] allows complete mixing of CO_2 in the whole mesosphere, but this result is not consistent with observations. Finally, halving K_{zz} leads to a comparatively small decrease of the vmr, and an even better fit to the observations. This result is consistent with the findings of *López-Puertas et al.* [2000].

[19] Let us now study the annual variations in the abundance of CO_2 predicted by the SOCRATES model, at the same latitude (45°N) at a *log-p* altitude of 100 km, *i.e.* in the mesopause region. Figure 3 shows that, around the mesopause, CO_2 is subject to a rather large annual variation: the minimum is reached at winter solstice and the maximum at summer solstice. The results from the simulations [no advection] and [$D(CO_2) = 0$] show that this is a combined effect of molecular diffusion and transport by the winds. Mesospheric circulation at solstice is characterized by upwelling in the high latitudes of the summer hemisphere, meridional circulation to the winter hemisphere, and downwelling in the high latitudes of the winter hemisphere. Thus, at midlatitudes and during winter, transport by the winds allows the CO_2 -poor thermospheric air masses to reach the mesopause. The reverse is true during summer. In both cases, advection shifts the CO_2 abundance away from the solution of the vertical diffusion equation. Lower K_{zz} values lead to even greater annual variations.

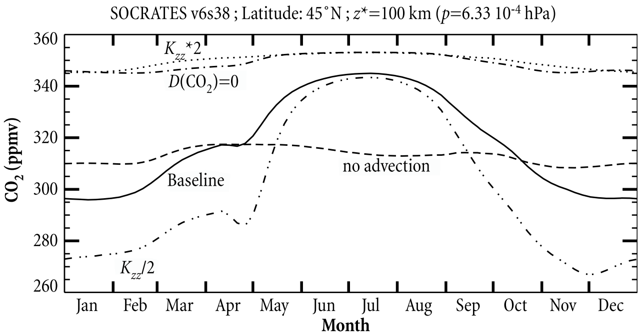

Figure 3. Annual variations of the CO_2 vmr at $z^* = 100$ km and 45° latitude North.

[20] This transport process has important implications for the distribution of CO_2 in the polar night region. Due to the descent of upper mesospheric air masses, the decrease of CO_2 vmr starts at altitudes as low as 55 km (Figure 4). In this particular region, molecular diffusion has an impact in the whole altitude range of the mesosphere.

[21] Carbon dioxide has a direct effect on the heat budget of the mesosphere, through infrared radiative cooling in the 15 μm band. To calculate the corresponding cooling rate, the SOCRATES model uses a recent parameterization [*Fomichev et al.*, 1998] which takes in account the decrease of CO_2 abundance in the upper mesosphere and lower thermosphere. We can thus evaluate the thermal impact of CO_2 molecular diffusion in the MLT.

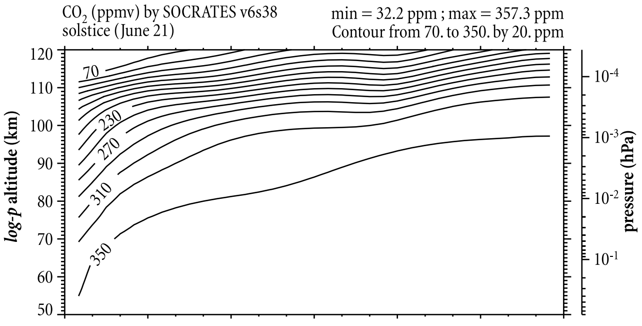

Figure 4. Distribution of CO_2 vmr at solstice (June 21) by the baseline simulation.

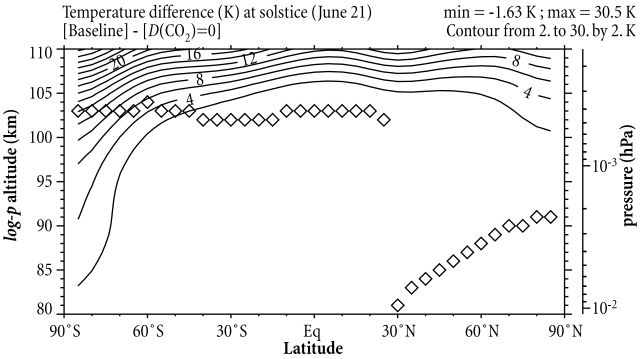

Figure 5. Temperature difference between the baseline and [$D(CO_2) = 0$] simulations, at solstice (June 21). The ◇ show the pressure level of the mesopause (baseline simulation).

[22] Figure 5 shows that, as expected, lower concentrations of CO_2 lead to warmer temperatures in the lower thermosphere. The position and temperature of the mesopause has been the focus of many recent studies [*Berger and von Zahn*, 1999; *Clemesha et al.*, 1999]. In this context, it is particularly interesting to note that the combined effects of molecular diffusion and advection warm the mesopause by up to 12 K in the polar night region, and that this warming even extends into the upper mesosphere.

4. Conclusion

[23] Molecular diffusion is a process easy to take in account in chemical models of the middle atmosphere, and should not be neglected in the mesosphere. Indeed, we have shown that molecular diffusion of CO_2 can have a non-negligible impact on its mesospheric distribution — hence on temperature — even when its coefficient is smaller than K_{zz}. In other words, the homopause must be located *below* the turbopause.

[24] We have focused our study on carbon dioxide, because of its importance for the radiative budget in the MLT. CO_2 is also an excellent tracer in this region, where modelled results are very dependent on the values chosen for the eddy diffusion coefficient and momentum deposition due to gravity wave breaking. The accurate evaluation of these parameters remain an important challenge in modelling of the mesosphere.

[25] The recent launch of the SABER instrument, aboard the TIMED satellite, could bring new insights on these topics. It should measure CO_2 in the middle atmosphere, up to 130 km altitude and for an extended period of time. Comparing these observations with results from global models such as SOCRATES will allow, for the first time, a global evaluation of the transport processes across the mesopause, from a climatic point of view.

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Simon Chabrillat, Institut d'Aéronomie Spatiale, 3 Avenue Circulaire, B–1180, Brussels, Belgium. (simonc@oma.be)

Gaston Kockarts and Dominique Fonteyn, Belgian Institute for Space Aeronomy, Brussels, Belgium.

Guy Brasseur, Max Planck Institute for Meteorology, Hamburg, Germany.