On the influence of diffusion upon the nonlinear behavior of the photochemistry of the mesopause region

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Abstract. The photochemical system of the mesopause region is a nonlinear driven oscillator enforced by the diurnal-periodic solar radiation. Under idealized conditions this oscillator can display nonlinear effects such as period doubling cascades or chaos. We investigate what happens if this system is subjected to atmospheric diffusion. A high-resolution one-dimensional chemical system of the mesopause region has been established in order to answer this question. Strong diffusion destroys nonlinear effects, but for the lower values of the diffusion coefficient which are still of the order of magnitude of real values, different nonlinear effects occur. The most important effect consisted of the creation of a 2-day subharmonic oscillation. Such a 2-day oscillation of the concentration of chemical active species entails a corresponding oscillation of the chemical heating rates which feeds back to the dynamics of this region. The zonal wind influences the period of the oscillation so that the periods differ from the exact 48-hour value by a few hours depending on the wind velocity and its direction. We call this phenomenon the photochemical Doppler effect.

1. Introduction

The mesopause region is one of the most interesting and most important regions of the upper atmosphere. Above this region, within the thermosphere, the variations caused by the alteration of the extraterrestrial solar shortwave spectrum (EUV and X ray) and particle precipitation dominate. Below this layer the meteorological influences predominantly determine variability. The mesopause is the transition region. Just under conditions of highest solar irradiance in summer the lowest natural temperatures in the atmosphere occur. On the basis of this low temperature, noctilucent clouds (NLCs) appear in high to mean latitudes in summer. They are connected with the phenomenon of the polar mesospheric summer echoes (PMSEs) of radar remote sensing [Nussbaumer et al., 1996]. In this region, different atmospheric waves, such as gravity or planetary waves, dissipate and contribute to the diabatic heat input. Simultaneously, the dissipation of waves causes the turbulence to grow strongly, and the eddy diffusion coefficient takes on maximum values. The eddy or turbulent diffusion is extraordinarily variable, both with time and space. Published values of the eddy diffusion coefficient vary by more than 1 order in magnitude (as in the work of Hocking [1990]). The turbulent transport gives rise to a transport of active chemical species, like atomic oxygen, from the thermosphere into the mesopause region. Atomic oxygen is an efficient carrier of latent chemical energy which is converted into heat after its recombination into molecular oxygen. The chemical heating rates peak within the mesopause region and lead to a diabatic heat input comparable with other sources like dissipating grav-

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ity waves [Riese et al., 1994; Meriwether and Mlynczak, 1995; Sonnemann et al., 1997, 1998].

Atomic hydrogen formed by photolysis of predominantly water vapor is, in contrast to atomic oxygen, usually transported upward and leaves the Earth atmosphere as hydrogen escape flux. At about 90 km and below, hydrogen is also transported downward. All influences cause a high variability of the temperature of the mesopause region which feeds back to the dynamics, and this in turn modulates the transport of chemically active species. The thermic regime, for example, the bistable behavior [von Zahn et al., 1996] of the mesopause height, has only been poorly understood thus far. The so-called 2-day wave of different atmospheric parameters like prevailing winds or the temperature are most marked in the domain of the mesopause. It was shown by Sonnemann and Fichtelmann [1987], Fichtelmann and Sonnemann [1987], Sonnemann [1992], Fichtelmann and Sonnemann [1992], Yang and Brasseur [1994], Montecinos-Geisse [1996], Sonnemann and Fichtelmann [1997], Feigin et al. [1998], Johnson et al. [1998], and Konovalov and Feigin [1999] that the chemistry of the mesopause tends toward a nonlinear response. The chemistry can approximately be described as an odd oxygen-odd hydrogen system.

Nonlinear response means that the system creates phenomena like bistable behavior (trigger solution), self-oscillation, subharmonics (i.e., oscillations with periods of an integer multiple of the fundamental period like, e.g., a 2-day wave) and chaos. Under very idealized conditions the occurrence of subharmonics and chaos [e.g., *Fichtelmann and Sonnemann*, 1992; *Sonnemann and Fichtelmann*, 1997] and under consideration of thermospheric fluxes, bistable behavior [*Yang and Brasseur*, 1994] has been found. The cause for the occurrence of subharmonics and chaos consists in the fact that the mesopause chemical system can be considered a damped parametric driven (enforced) nonlinear chemical oscillator [*Sonnemann* 30,592

and Fichtelmann, 1987, 1997] which operates near chemical resonance. The driving force is the diurnal periodic excitation by solar radiation. The characteristic chemical system time, if one considers the decay of small perturbations, ranges in the order of magnitude of the exciting period of 1 day. Konovalov et al. [1997] and Feigin et al. [1998] showed that the essential components of the photochemical system (PCS) are atomic oxygen and atomic hydrogen. In order to reduce the chemical code they used a procedure which focused on the most important reactions, and they derived their so-called essential model which entails a nonlinear response similar to that of the original model. A similar procedure was discussed by Johnson et al. [1998]. From these results one can infer that neglected reactions, like those including nitrogen oxides, have only a minor influence on the behavior of the system. Other conditions and parameters such as the actual value of the temperature, the most recent values of the chemical reaction rates, the real amount of the dissociation rates, the number of daylight hours (meaning season and geographical position), and the concrete diurnal variation of the exciting radiation (if using a step function or the real diurnal variation) of course will shift the borders of the H₂O-control parameter range or the height range of the nonlinear response; but they usually do not prevent such a reaction if the parameters vary within their natural boundaries. We will discuss these problems in more detail later.

The water vapor concentrations, for which the nonlinear reactions were revealed, correspond to the natural concentrations in that they have low levels of ppmv, but they seem to be a little bit too high when compared with photochemical model calculations. However, the situation is still controversial. There are hints of unusually high water vapor concentrations within the mesosphere and lower thermosphere [e.g., Radford et al., 1977; Sonnemann et al., 1977; Grossmann et al., 1985]. A possible influx of water vapor from extraterrestrial sources, such as small comets [Frank et al., 1986] and hydrogen-implanted interplanetary dust grains [Parthasarathy, 1977], have been discussed in the past. It is extremely difficult to measure H_2O concentrations above 80 km, and the rate of error rises strongly with increasing height. Generally, higher water vapor concentrations have been found in the mesosphere in summer [e.g., Nedoluha et al., 1996]. This finding has been explained in terms of a stronger advective upward transport. There is also an indication of a semiannual cycle, especially at heights near 80 km which is the altitude of nonlinear response. The water vapor concentrations measured by means of microwave technique can exceed 3 ppmv at 80 km height. von Cossart et al. [1999] inferred from three-color observations of NLCs by means of ground-based lidar a mean water vapor concentration of 4.1 ppmv at about 83 km, which is also a relatively high value. Despite speculation about an enhanced water vapor concentration within the upper mesosphere-lower thermosphere, the basic question remains: is the nonlinear response of the photochemical system of the mesopause a real effect, meaning, does the phenomenon occur, at least temporarily, or is it only an interesting theoretical possibility? In addition, the question of in which height range a nonlinear response can theoretically appear at all is of importance. The question also arises as to which conditions prevent or perhaps even promote the occurrence of nonlinear effects.

Particularly the upper boundary values of the long-lived components atomic oxygen and atomic hydrogen can be strongly subjected to transport. Also, vertical wind can exert a considerable influence on the distribution of minor constituents. However, the strongest probable impact on the system behavior is diffusion. Subjection of the nonlinear behavior of the mesopause photochemistry to diffusion as well as possible appearances of this behavior under real atmospheric conditions are discussed in this paper.

2. Model Description

A simple one-dimensional (1-D) model consisting of 201 layers has been developed and used for a series of model calculations. It comprises the height range between 72 and 92 km. Both of the boundaries, as demonstrated below, are sufficiently far away from the region of nonlinear response. The layer distance amounts to 100 m. For special investigations the layer distance has been reduced to 10, 1, and 0.01 m. The boundary values of the upper border have been fixed for the long-lived components H and O. Neither of the species have a distinct diurnal variation there. The diurnal variations of OH, HO₂, and O₃ have been calculated from these values employing the zero-dimensional equations and use them as timedepending upper boundary values. No values have been fixed at the lower boundary. Here the boundary values correspond to the values of the limit cycle of the system without consideration of diffusion (solution of the zero-dimensional system again). The characteristic diffusion times there [Mange, 1957] are large compared to the chemical system time so that the rate of error is relatively small. The dissociation rates are defined as step functions again. As discussed by Sonnemann and Fichtelmann [1997] and Feigin et al. [1998], the step function is a sufficient approximation of the real diurnal variation. Compared with the chemical reaction time, short-time variations of the radiation or other small-scale impacts will also be smoothed out by the system. The integration procedure uses an automatic time step control. The greatest relative change of any concentration for each time step amounted to 10^{-3} to 10^{-4} (in the figures partly labeled with r). Table 1 lists the rate constants used for the calculations.

Since the time of the first calculations for the investigation of the nonlinear PCS of the mesopause, some chemical rate constants have changed considerably. In order to compare results obtained in the present paper with earlier results, the rate constants have not been made topical for these cases. The second column of Table 1 lists the current chemical rate constants which depend on temperature. Computation employing these values yields a similar nonlinear response.

The dissociation rates correspond to the upper height in the table. In contrast to J_{O_3} , which was taken as constant, J_{O_2} decreases with decreasing height, which has to be considered. Also, J_{H_2O} declines weakly in this height range, but the product $J_{H_2O}[H_2O]$ only acts in the reaction scheme. Therefore a weakly decreasing J_{H_2O} is equivalent to a corresponding weak increase of $[H_2O]$. We employ a constant value of $J_{H_2O} = 2.4 \times 10^{-6} \text{ s}^{-1}$ here and also fix the water vapor concentration for every model run. Lastly, J_{O_2} decreases noticeably with decreasing height. The dependence of J_{O_2} on height is taken into account in accordance with Sonnemann et al. [1998]. All further necessary details will be mentioned at the respective places of the next sections.

3. Consideration of Diffusion, the Onion Bifurcation

Normally, diffusion entails the tendency to destroy structures. This is a consequence of the second law of thermody-

	Rate Constant*	
Reaction	A (Old)	B (New)
$(1) O + O_3 \rightarrow 2O_2$	9.08×10^{-16}	$8.00 \times 10^{-12} \exp(-2060/T)$
(2) O ₃ + H \rightarrow O ₂ + OH	$1.78 imes 10^{-11}$	$1.40 \times 10^{-10} \exp(-470/T)$
(3) O + OH \rightarrow O ₂ + H	4.40×10^{-11}	$2.20 \times 10^{-11} \exp(120/T)$
(4) $O_3 + OH \rightarrow O_2 + HO_2$	2.37×10^{-14}	$1.60 \times 10^{-12} \exp(-940/T)$
(5) $O + HO_2 \rightarrow O_2 + OH$	3.50×10^{-11}	$3.00 \times 10^{-11} \exp(200/T)$
(6) $O + HO_2 \rightarrow O_2 + H_2$	$5.40 imes 10^{-12}$	5.60×10^{-12}
(7) O + HO ₂ \rightarrow 2OH	2.26×10^{-12}	7.30×10^{-11}
(8) $OH + OH \rightarrow O + H_2O$	1.12×10^{-12}	$4.20 \times 10^{-12} \exp(-240/T)$
(9) OH + HO ₂ \rightarrow O ₂ + \overline{H}_2O	4.00×10^{-11}	$4.80 \times 10^{-11} \exp(250/T)$
(10) $HO_2 + HO_2 \rightarrow O_2 + H_2O_2$	2.50×10^{-12}	$2.30 \times 10^{-13} \exp(600/T)$
(11) $O + O_2 + M \rightarrow O_3 + M$	$1.05 imes 10^{-34}$	$6.90 \times 10^{-34} (\hat{300}/T)^{1.25} \times \alpha_1$
		$+ 6.20 \times 10^{-34} (300/T)^2 \times \alpha_2$
$(12) O + O + M \rightarrow O_2 + M$	8.23×10^{-33}	$3.80 \times 10^{-30} \exp(-170/T)/T \times \alpha_1$
		$+4.8 \times 10^{-33} (300/T)^2 \times \alpha_2$
$(13) O + OH + M \rightarrow HO_2 + M$	$1.40 imes 10^{-31}$	$2.00 \times 10^{-32} \times \alpha_2$
(14) O ₂ + H + M \rightarrow HO ₂ + M	$8.08 imes 10^{-32}$	$5.50 \times 10^{-32} (300/T)^{14} \times \alpha_2$
(15) $OH + H + M \rightarrow H_2O + M$	3.31×10^{-27}	$1.38 \times 10^{-24} T^{2.6} \times \alpha_2$
(16) $O_2 + h\nu \rightarrow 2O$	$1.26 imes 10^{-8}$ †	$3.15 \times 10^{-8} (92 \text{ km})$
(17) $H_2O + h\nu \rightarrow H + OH$	2.40×10^{-6}	2.40×10^{-6}
$(18) O_3 + h\nu \rightarrow O_2 + O$	7.10×10^{-3} †	7.10×10^{-3}

Table 1. Rate Constants Used for the Calculations

*Photodissociation constants are in units of s^{-1} , two-body rate constants are in units of cm³ s⁻¹, and three-body rate constants are in units of cm⁶ s⁻¹.

†At 81 (km), $\alpha_1 = [O_2]/[M]; \alpha_2 = [N_2]/[M].$

namics. However, in nonlinear dissipative systems, diffusion can also produce special dissipative structures such as waves or autosolitary patterns. The chemistry of the atmosphere represents such a nonlinear dissipative system when diffusion acts the dynamics of the phase points associated with two neighboring layers are no longer independent of each other. On the assumption that the system operates in the chaotic mode within a certain height range, chaos moves into a spatial order there. In case a bifurcation occurs from one layer to the next the question arises, What influence does the diffusion have on this bifurcation? Obviously, the response depends on the strength of the diffusion characterized by the diffusion coefficient. The upper border for the model with a height resolution of $\Delta z = 100$ m is located at 92 km. Neither of the essential components possess a distinct diurnal variation there, so their amount can be fixed (time-independent). In contrast to this, O_3 , OH, and HO₂ are marked by a strong diurnal variation, but they possess only small concentration values which do not essentially influence the family concentration of their chemical families. They can be considered to be a free varying species, and their concentrations can be inferred from the fixed O and H concentrations solving respective differential equations for O₃, OH, and HO₂ without inclusion of diffusion. This procedure yields their time-dependent upper boundary values.

The characteristic diffusion time can be estimated by the formula $\tau = A(H_p^2/K)$ and corresponds to the time which a molecule needs in order to pass a length of the pressure scala H_p [Banks and Kockarts, 1973]. Commonly, the diffusion time is calculated with A = 1, but it characterizes only the order in magnitude [Banks and Kockarts, 1973]. Employing A = 1 and $H_p = 6$ km for a characteristic diffusion time of 1 day, one can deduce that a required diffusion coefficient K equals 4.17×10^6 cm² s⁻¹. This is a very high value of K, and the real values are essentially smaller within the spatial domain modeled. In other words, the characteristic chemical time of the system.

However, the height range of nonlinear response is usually less than 2 to 3 km (i.e., about $H_p/3$ to $H_p/2$), and in a time close to the characteristic chemical time the diffusion can provide an interdependence of the layers exhibiting different nonlinear response under nondiffusion conditions. Therefore the following question becomes more important: How does the system react at and around the range of nonlinear response when it is subjected to diffusion?

We use the diffusion coefficient K as a control parameter and reduce it step by step starting with a high value of K. This parameter has been fixed for each model run, and the system has been integrated until the transients died away. The initial conditions are the same for the computations of all the Figures 1a-1n. The old set of reaction rates has been used. In this case the model domain has been reduced to 10 km. It ranges from 76 to 86 km; the layer distance amounts to 50 m. The values near the boundary have been excluded from the figures. The individual graphs are independent of each other. The water vapor concentration of 6 ppmv was relatively high for these model runs, but the results are also similar for other lower concentrations.

Figure 1a shows no subharmonic oscillation for $K = 1.25 \times 10^5$ cm² s⁻¹. We display only the atomic hydrogen concentration at sunset in the stroboscopic representation. A very faint bifurcation occurs for diffusion coefficients less than about 1.21×10^5 cm² s⁻¹. Figure 1b exhibits such a faint period 2 for $K = 1.18 \times 10^5$ cm² s⁻¹ that it is not clear thus far whether this faint period 2 is a numerical artifact due to a insufficient accurate integration of the system or not. Obviously, the upper boundary still influences the behavior for the larger diffusion coefficients. Figure 1c depicts a somewhat stronger period 2 oscillation for $K = 1 \times 10^5$ cm² s⁻¹ within a sickle-shaped region. This region has an extension of about 5 km. Compared with the domain of nonlinear reaction without consideration of diffusion, diffusion enlarges this range of nonlinear response. Figures 1d and 1e display the diagrams for $K = 4 \times 10^4$ and



Figure 1. (a-n) The pictures exhibit the "onion bifurcations" using the old rate constants (column A of Table 1) for the calculations. Coming from high values of the diffusion coefficient and reducing it step by step, the diagrams in stroboscopic representation show a cascade of period doublings in the upper part of the domain of nonlinear response. This cascade comes to an end by a transition to small chaotic bands which finally fuse to a chaotic one band. Figures 1h–1l display a higher resolution for small diffusion coefficients. Asterisks connected with straight lines belong to the same sunset. The water vapor concentration amounts to 6 ppmv in this case.



 3×10^3 cm² s⁻¹. The height region of the period 2 oscillation shrinks, but the amplitude difference rises. The amounts of the eddy diffusion coefficient are entirely unrealistic in these cases, but the first one still corresponds to the values of the molecular diffusion coefficient in the domain of nonlinear reaction for Figure 1d. A further lowering of the diffusion coefficient surprisingly yields a cascade of period doublings in the upper part ending in a chaotic two-band region. In the first stage each band of this chaotic two band is probably split into different small subbands. Figures 1e-1g illustrate the cascade for $K = 3 \times 10^3$, 1.6×10^3 , and 8.8×10^2 cm² s⁻¹. The shapes of the diagrams resemble the onion pattern.

Figures 1h-1l show at enlarged resolution the development to the chaotic dynamics. Figure 1h still displays period 16 oscillation for $K = 8.2 \times 10^2$ cm² s⁻¹. The chaotic two band is split into different small bands. The chaotic two band be-



Figure 1. (continued)

comes a one band for even smaller values of the diffusion coefficient. This is showed by Figure 1k for $K = 4 \times 10^2$ cm² s^{-1} . The duration of the transient behavior increases strongly. There is a weak phase coupling between the different layers within the chaotic band. This is, of course, not the case for K = $0 \text{ cm}^2 \text{ s}^{-1}$ (Figure 1n). Already very weak diffusion coefficients of the order of 10^1 to 10^2 cm² s⁻¹ disturb the diagram without consideration of diffusion. The diagram without diffusion shows a period doubling cascade with increasing height, a small chaotic band, and a period 3 band which is led by a catastrophic bifurcation into the fundamental period 1. At the borders of the catastrophic bifurcations an early influence can be observed if a weak diffusion begins to act. Period 3 is not very stable against diffusion in this example. This region will be converted into a chaotic two band after a long transient time as Figure 11 exhibits for $K = 1 \times 10^2$ cm² s⁻¹.

For small diffusion coefficients the behavior strongly depends on the initial values. Starting with relatively arbitrary values, there is no guarantee for a phase synchronous oscillation. In Figure 1m for $K = 2 \times 10^{1}$ cm² s⁻¹ the phase of the lower part of the period 2 region is different from that of the upper part, meaning that when the lower part adopts the low amplitude, the upper part is in the high-amplitude phase and vice versa. At the respective place of phase transition the bifurcation diagram shows a weak intrusion. Obviously, the diffusion is too small for a phase synchronisation of neighboring layers. However, this takes place for stronger diffusion coefficients as used for Figures 1a-1k. Obviously, there is a serious problem. A phase synchronization for very weak diffusion could happen after an extremely long time so that Figures 11 and 1 m may represent only a transient state with a quasistable appearance. Considering the behavior in a constant height at the place of the bifurcation cascade (around 82.8 km) and employing the diffusion coefficient as control parameter, the period doubling cascade does not show the bifurcation behavior as known from the pitchfork diagram. (Whether there is a universal number like the Feigenbaum number characterizing the scaling behavior of the border of bifurcation or not has not yet been investigated. The calculations would be extremely computer time consuming.) For instance, the first bifurcation near K = 1.25 cm² s⁻¹ takes place under an angle of zero or at least near zero (very acute).

Figure 2 shows the result for a water vapor concentration of 4 ppmv without consideration of diffusion for atomic hydrogen, using the latest rate constants again. The model domain now amounts to 20 km (92–72 km). There are different peculiarities of the bifurcation diagram as an included band of period 3 bifurcating into a period 6 band. A broad period 4 band jumps into a period 3, and that jumps into a period 5 band. The transition from one subharmonic state to another could take place via very small chaotic bands, smaller than the height resolution of dz = 100 m here. Such special features are very common, and they will appear if the parameters are changed only slightly.

Generally, the height of nonlinear reaction increases with the new reaction rates, and the concentrations, especially of ozone, approach more real values. The peak concentration of



Figure 2. Bifurcation diagram without consideration of diffusion for a water vapor concentration of 4 ppmv using the latest reaction rates (see Table 1, column B) for a temperature of T = 180 K. The most pronounced features are the different relatively broad periodic windows of periods 3, 4, 5, and 6. The lower part is marked by a period doubling cascade. There are at least two small chaotic bands.



Figure 3. (a-h) Employing the parameters of Figure 2 and including diffusion, the onion bifurcations differ from those of Figure 1. Reducing the diffusion coefficient again, the system creates a period doubling cascade in the first stage. After reaching a chaotic behavior, the system produces a nonchaotic response anew also including a region of nearly a period 3 (actually a period 6) oscillation. Further decreasing of the diffusion coefficient results in a chaotic three band.

ozone at the secondary maximum is greater than 1×10^8 cm⁻³. The values depend, of course, on the upper boundary values of O and H and on the magnitude of the diffusion coefficient. As already discussed, the influence of diffusion leads to the "onion

bifurcation," called a space bifurcation. Figures 3a-3h illustrate the different system response on varying diffusion coefficients. For low (unreal) values of the diffusion coefficient the initial conditions determine the phase of the oscillation and



also the features of the diagram. For stronger diffusion the final diagram does not depend on the initial values. Obviously, bifurcation behavior is different in this case. The most pronounced features are those of a period 3, indeed a period 6. Beginning with strong diffusion and lessening it step by step, there is a period doubling cascade again ending in a chaotic behavior (as in Figures 3a-3d). Surprisingly, for lower diffusion the dynamics become nonchaotic again (as in Figures 3e and 3f). Lowering the diffusion coefficient further (Figures 3g and 3h), subtle but also different catastrophic bifurcations occur yet again, and a transition to chaos begins. The transition from the period 1 oscillation for strong diffusion into a period 2 oscillation around $K = 1.2 \ 10^5 \ \text{cm}^2 \ \text{s}^{-1}$ takes place by a catastrophic bifurcation in this case (not shown in Figure 3). Evidently, a period 2 oscillation is still maintained for diffusion coefficients corresponding to low values of the real atmosphere.

4. Possible Perturbations and Related Transient Behavior

A system which needs 100 days or more in order to approach a limit behavior cannot approximately reach its limit state in the atmosphere in reality. In the atmosphere there are continuously perturbations of different kinds. Consequently, a manifestation of the transient behavior is more likely than the final one. In the first place, one may think of dynamical impacts such as advective transport of air masses or of diffusive transport, in this connection especially of the vertical transport of minor constituents from remote areas. This transport is particularly efficient within the mesopause marked by strong gradients (partly negative density scale heights) of the most important minor constituents. Both the essential constituents O and H [see Feigin et al., 1998] are extraordinarily variable at the upper boundary of the model. Atomic oxygen can vary by more than 1 order of magnitude [Offermann et al., 1981], and atomic hydrogen varies in a similar way depending, among other things, on the exospheric temperature, which, as far as it is concerned, depends on the strongly changeable solar EUV and X-ray radiation.

The characteristic diffusion times drastically increase below a height of about 80 to 85 km. Below this height, strong perturbations caused by suddenly increased eddy diffusion are rather unlikely. The variation of vertical advection is more important there. Also, the temperature can change relatively quickly, and it influences the chemical rate constants and consequently the distribution of the minor constituents. The eddy diffusion coefficient can alter, depending on the wave activity, in timescales below 1 day, so it can drop from $>10^6$ cm² s⁻¹ to $<10^5$ cm² s⁻¹ in the same volume.

 $J_{\rm H_2O}$ can change suddenly connected with the emergence or disappearance of visible active centers on the Sun surface. As mentioned, this alteration is equivalent to a change of humidity. We have to compare the characteristic time of the perturbations with the characteristic response time of the system and can therefore state that the real behavior of the chemical system of the mesopause region is strongly influenced and determined by the transient behavior of the system. The computations show always transient nonlinear reactions of the system within and around the region of nonlinear limit behavior. The most frequently observed response of the "nondiffusion model" is that of a "transient chaos." Such a transient chaos is shown by Figure 4. Beginning with arbitrary initial values, the system creates transient chaos in the first stage in that region where a period 5 oscillation will be finally established. The transient chaos is closely connected with the phenomenon of the internal crisis [Grebogi et al., 1983]. It will also occur if the final behavior approaches a subharmonic limit cycle.

After a perturbation, the response of the system often consists of an oscillating approach of the new state. This is especially true near the region of nonlinear response also under the influence of diffusion. Strong diffusion destroys a subharmonic or chaotic response of the system. Being in a limit cycle of the fundamental mode of a system which is subjected to strong diffusion and disturbing it, for example, by a drastic change of $J_{\rm H_2O}$, the system reaches its new limit state via a transient attenuating period 2 oscillation around the region of nonlinear response without consideration of diffusion. Figure 5 displays one example of such behavior. The left orbits are depicted in a stroboscopic presentation again after a sudden change of the photolysis rate of H₂O on the fortieth day. The right course represents the atomic hydrogen profile before the perturbation.

5. Photochemical Doppler Effect

Now we assume that a larger coherent air mass is in the same photochemical regime, for example, it is in the subharmonic regime of period 2 without phase shift. This air mass moves in a zonal direction either with or counter to the Earth's rotation. That means an air parcel reaches the same local time condition again earlier or later than 1 day. The period for this air parcel is effectively shorter or longer than 1 day.

As the Earth rotates from west to east, this means that eastward wind moves with the Earth rotation and westward wind moves against it. Figure 6 shows zonally averaged zonal winds for solstice computed on the basis of our 3-D model of dynamic and chemistry of the middle atmosphere [Sonnemann et al., 1998]. The results sufficiently correspond with measurements. They illustrate that the summer is characterized by easterly winds and the winter is characterized by westerly winds in the middle atmosphere with the exception of the equatorial latitudes. The wind speed amounts to some 10 m s⁻¹. For instance, numerical estimations for a geographical latitude of $\varphi = 60^{\circ}$ and $|\nu| = 20 \text{ m s}^{-1}$ (mean zonal wind) show that the day is effectively shortened to 21.96 hours or lengthened to 26.04 hours. Related to 2 days, it amounts to 43.92 hours or to 52.08 hours. For a wind around the equator the deviation from the 48-hour value amounts only to half the time; however, the zonal winds for this numerical example have been chosen very moderately and can also be significantly stronger as Figure 6 demonstrates.

The shift of the frequency can be calculated by a modified Doppler formula

$$\nu_D = \nu_{\text{earth}}^* \left(1 + \frac{u_{\text{zonal}}}{u_{\text{earth}} \times \cos \varphi} \right).$$

Owing to the convention that west winds have a positive and east winds a negative sign, the Doppler formula contains a positive sign within the parenthesises. The velocity of the Earth at the equator using an Earth radius of R = 6378 km and a



Figure 4. Transient chaotic behavior within the period 5 window within the upper part of the model domain using the new rate constants (column B of Table 1). The water vapor concentration amounts to 3.5 ppmv, and the layer distance is 1 m. The regions of denser point covering between about 81.19 and 81.14 km approximately indicate the places of the final period 5 oscillation.



Figure 5. When including diffusion, strong diffusion coefficients finally suppress a nonlinear response of the system, but after a perturbation a transient attenuated period 2 oscillation can occur. The right curve shows approximately a final state for $J_{\rm H_2O} = 2.4 \times 10^{-6} \, {\rm s}^{-1}$ for days 38–40. The left group of curves represents the attenuated period 2 oscillation after cutting the photodissociation rate of H₂O into halves.

height of z = 80 km is $u_{\text{carth}} = 470$ m s⁻¹. In the work of *Fichtelmann and Sonnemann* [1992] a bifurcation diagram was presented employing the control parameter v or T (frequency or duration of an artificial day). In context with the photochemical Doppler effect, such a consideration makes sense.

6. Chemical Heating Rates

As stated in the introduction, the mesopause is the transition region between dominant meteorological influences (below) and prevailing extraterrestrial influences (above) and is marked by different diabatic heating sources. One of the most important sources consists of chemical heating. Particularly, atomic oxygen is transported from the thermosphere into the mesosphere. Its latent chemical energy is converted into heat. This diabatic heat source has an order of magnitude comparable with other sources like energy from dissipating wave



Figure 6. Zonally averaged zonal winds near solstice computed on the basis of our global three-dimensional model of dynamic and chemistry of the middle atmosphere. The order of magnitude of the averaged wind speed amounts to as far as some 10 m s⁻¹.

Reaction	Efficiency Factor	Exothermicity, eV
$(1) H + O_3 \rightarrow OH^* + O_2$	0.6	3.28
(2) HO ₂ + O \rightarrow OH + O_2	1	2.34
$(3) OH' + O \rightarrow H + O_2$	1	0.79
(4) O + O ₃ \rightarrow O ₂ + O ₂	1	4.07
(5) H + $O_2 + M \rightarrow HO_2 + M$	1	1.99
(6) O + O ₂ + M \rightarrow O ₃ + M	1	1.05
(7) O + O + M \rightarrow O ₂ + M	1	5.12

 Table 2.
 Reactions, Efficiency Factors, Exothermicity, and

 Specific Heat Used in Model

Specific heat is in units of J K⁻¹ g⁻¹. $Cp(N_2) = 1.0397 \times 10^6$. $Cp(O_2) = 0.9174 \times 10^6$. $Cp(O) = 1.3696 \times 10^6$.

activity. The mesopause is per definition the region of the temperature minimum indicating the lowest energy input per molecule by absorption of solar irradiance. Especially in the summer, the temperature is extremely low. Thus an additional energy input has a large effect. The chemical heating rate depends on the concentrations of the reacting constituents. As shown in the preceding section, there is at least the possibility of a transient period 2 oscillation after any perturbation of the photochemical system. Such a period 2 oscillation of the constituents leads to a period 2 oscillation of the chemical heating rates. Now we estimate the chemical heating rates for the most important reactions using this simple one-dimensional model for different water vapor concentrations and eddy diffusion coefficients. Table 2 lists the most important reactions and the respective exothermicity of the individual reactions. The reaction $H + O_3 \rightarrow OH^* + O_2$ results in an excited constituent. The chemiluminescence of the excited OH* represents a loss of chemical energy. Mlynczak and Solomon [1993] estimated an efficiency factor of 0.6 for this reaction and of unity for all other reactions. We will use these values in our calculations.

Figures 7a-7f show the results of the computations for 4 ppmv H₂O concentration, T = 180 K and $K = 1 \times 10^5$ cm² s^{-1} using the latest reaction rates. The diurnally integrated values are taken from sunset to sunset. A 2-day periodic oscillation of the heating rate can occur below the absolute peak of the heating rate. Compared with results which were calculated by means of the old reaction rates, the height region of nonlinear response is somewhat raised, and the effect is also a little bit stronger. The magnitude of the difference between 2 successive days amounts to between some tenth K d^{-1} to about 1 K d^{-1} depending on the water vapor concentrations, temperature, and upper boundary conditions. It is, of course, arbitrary to integrate the heating rates from sunset to sunset. An interval of 1 day starting at another time of day may yield a greater difference of the heating rates between two consecutive intervals. The phase of an induced 2-day wave would depend on the phase of the period 2 oscillation of the chemical heating rates.

Considering the individual reactions, one can see that the important reactions $H + O_3 \rightarrow OH + O_2$ and $O + O_2 + M \rightarrow O_3 + M$ are not in sync with the reactions $O + HO_2 \rightarrow OH + O_2$ and $H + O_2 + M \rightarrow HO_2 + M$. Taking into consideration the efficiency factor of the reaction $H + O_3 \rightarrow OH + O_2$, the difference between both the amplitudes of the total chemical heating rate somewhat increases. As mentioned before, the result depends on the upper boundary values of O and H. At 92 km, atomic oxygen had an amount of 1×10^{11} cm⁻³, obviously a low value, and H had an amount of 1×10^9 cm⁻³, a very high value. Consequently, the commonly important re-

action $O + O + M \rightarrow O_2 + M$ has no influence here. Enhancing atomic oxygen and reducing atomic hydrogen at the upper boundary, the weight of the different reactions changes especially within the upper model domain.

The diurnal variation of the chemical heating rates is shown by Figures 8a-8c. There is a nighttime enhancement of the total chemical heating rate. In other words, there is generally a periodic pumping of the dynamic system by chemical heating. The influence of such an exciting mechanism has not been considered in literature thus far. In the region below the mesopause there is an additional periodic excitation with a period of 2 days under favorable conditions such as low turbulence. Such periodic pumping could be able to modulate the vertical wind which itself modulates the transport of chemically active species from the thermosphere into the mesopause region. The necessity of a modulated vertical transport of atomic oxygen was pointed out by Ward et al. [1997]. This conclusion was inferred from a 2-day wave-induced variation in the oxygen green line volume emission rate above 90 km where the chemical lifetime of atomic oxygen is too large in order to create a chemically induced 2-day wave.

The periodic downward transport of atomic oxygen could (resonantly) amplify or trigger the pumping effect. Below about the concentration peak of atomic oxygen around 95 km, the very strong heat-producing reaction $O + O + M \rightarrow O_2 + M$ acts. There is, of course, a phase delay between influx of atomic oxygen and heat response, but there would also be a time delay between excitation below the mesopause and modulation of the vertical wind 10 km above. Whether there is such a mechanism of 2-day wave excitation or not cannot be deduced from these simple imaginations. Calculations will be necessary to prove this on the basis of three-dimensional interactively operating models of dynamic and chemistry of this height region. Such a complex model is not available at present.

7. Conclusions and Summary

The inclusion of diffusion into the PCS of the mesopause region represents a first step to model real nonlinear atmospheric conditions. Generally, high diffusion coefficients destroy all nonlinear effects which appear under nondiffusion conditions. Within the height range of appearing nonlinear effects the real eddy diffusion coefficient may have a scatter of values ranging between about 10^5 and 10^6 cm² s⁻¹. However, Lubken [1997] was the last to publish on very low diffusion coefficients derived from measurements below about 80 to 85 km, low enough to maintain a nonlinear response of the photochemical system. Such small turbulent diffusion has been indirectly confirmed by optical meteor trail observations persisting over many hours. For small real eddy diffusion coefficients of the order of $n \times 10^5$ ($n \le 1.2$) a period 2 oscillation is still maintained. A higher subharmonic oscillation or even chemical chaos does not seem to appear under real conditions. However, there is still the possibility of transient chaos after a perturbation. There is also the possibility that a transient period 2 oscillation occurs after a perturbation although the final state consists in the fundamental period 1 oscillation. A perturbation can be connected, for example, with a sudden change of the Lyman- α radiation due to occurring or vanishing of active centers on the visible surface of the Sun.

The most important conclusion from a 2-day oscillation of the chemical constituents near the region below the mesopause



Figure 7. (a-f) Chemical heating rates for 4 ppmv H₂O concentration and $K = 9 \times 10^4$ cm² s⁻¹ showing a weak period 2 oscillation. The efficiency factor for the reaction H + O₃ \rightarrow OH^{*} + O₂ is $\varepsilon = 0.6$ (according to *Mlynczak and Solomon* [1993]). The heating rates of the different reactions do not act in the same phase. The scale has been changed for the reaction O + O + M \rightarrow O₂ + M and shifted for the total chemical heating rate.

is connected with the modulation of the chemical heating rates. Such a periodic heating weakly modulates the dynamics and the vertical wind in particular. A modulated dynamics feeds back to the transport of chemically active minor constituents from the thermosphere such as atomic oxygen or atomic hydrogen which modulates the chemical heating again. In order to calculate the influence of a chemical-induced periodic excitation one needs at least an interactively operating threedimensional model of the dynamics and chemistry of the mesopause region. Owing to the fact that especially the zonal



Figure 8. (a-c) Diurnal variations of the total chemical heating rate (in K s⁻¹) and the rates of the important reactions O + $HO_2 \rightarrow OH + O_2$ and $H + O_3 \rightarrow OH^* + O_2$ ($\varepsilon = 0.6$) showing the nighttime enhancement of the heating rates. The pictures start at sunset (1800 LT). Parameter is as used for Figure 7, but $K = 1 \times 10^5$ cm² s⁻¹.

wind has an order of magnitude of some 10 m s⁻¹, the period of weak modulation would usually differ from the exact value of 48 hours by few hours. This phenomenon was called the photochemical Doppler effect.

The use of the most recent chemical reaction rates regarding the low mesopause temperature leads to increasing the height range of nonlinear response somewhat and made the effect a little bit more pronounced. During the summer the H_2O concentration is probably higher than in other seasons [*Bevilacqua et al.*, 1985; *Nedoluha et al.*, 1996]. This seems to support the effect of chemical 2-day oscillation in this season.

The enhancement of the Lyman- α radiation acts like a water vapor increase so that one could expect that there would be a dependence on the solar cycle. On the other hand, increasing Lyman- α radiation reduces the water vapor concentration, and this may lessen the effect again. A dependence of the amplitude of the 2-day wave in the prevailing wind in the mesopause region on the solar cycle was found by *Jacobi et al.* [1996]. They found out that the amplitude was greater during solar maximum. A 2-day wave was also discovered in temperature [*Wu et al.*, 1995] and other atmospheric parameters.

The 2-day wave in the prevailing wind is a late summer phenomenon in the middle atmosphere. It occurs mainly in low and middle latitudes. The maximum is reached in late July/ early August in the northern hemisphere and in late January/ early February in the southern hemisphere, but it also occurs in all other seasons with weak amplitudes. The maximum amplitudes are usually attained at heights between 80 and 95 km. The observed modulation of the temperature amplitude is essentially greater (5 K or more according to Wu et al. [1995]) than the amplitude deduced from the chemical heating rates. That is why such a modulation of the chemical heating rates cannot directly explain the variation observed. The only possibility could rest in the fact that a relatively small 2-day oscillation of the chemical heating rate acts as a trigger for windinduced transport of chemically active constituents, in particular, of atomic oxygen. Just such a transport during 2-day wave appearance has been demonstrated by Ward et al. [1997].

"Pure" chemical evidence for a real 2-day oscillation of the chemical system is difficult to obtain because the cause of an observed oscillation cannot be identified. Consequently, a 2-day oscillation should be found in the airglow (Meinelbands) by excited OH* formed by the reaction $H + O_3 \rightarrow OH^* + O_2$ or in the 1.27 μ m band emission of $O_2({}^{1}\Delta_g)$ which is produced, among other things, by the photodissociation of O_3 . However, such an oscillation could also be explained in terms of dynamics being imprinted by transport of minor constituents via vertical wind or by temperature-induced change of the chemical reaction rates which feed back to the chemical heating rate. However, it is difficult to decide what is the cause and what is the response. In any case, complex measurements of different atmospheric parameters are still necessary.

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