Toward an understanding of the nonlinear nature of atmospheric photochemistry: Essential dynamic model of the mesospheric photochemical system

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Abstract. We present the essential dynamic model of the mesospheric photochemical system (PCS) and suggest a step-by-step procedure for elaborating such a model of an arbitrary atmospheric PCS. The model demonstrates the same possibilities of nonlinear dynamic behavior and qualitatively the same dynamic characteristics as the corresponding original model, but is much simpler than the latter. We show the adequacy of the essential model compared with the original one in bifurcation diagrams, equilibrium states, and such new characteristics as correlation dimension and minimum embedding dimension of a chaotic attractor. The model can be used both for identifying and studying the mechanisms of the nonlinear dynamic behavior of the mesospheric PCS, as well as for solving a number of problems aimed at revealing nonlinear photochemical phenomena in the actual mesosphere.

1. Introduction

1.1. Nonlinear Phenomena in Atmospheric Photochemical Models

Atmospheric photochemical systems (PCSs) determining the behavior of the minor constituents of the atmosphere are essentially nonlinear. It is well known that nonlinear systems can possess a number of qualitative dynamic properties which are impossible in linear systems Among these are such nontrivial properties as the existence of multiple equilibrium states, self-oscillations, and chaos. Thus, there are good reasons for believing that atmospheric PCSs can also possess similar properties Indeed, there are some papers which discuss the existence of the multiple equilibrium states in models of tropospheric [White and Dietz, 1984; Kasting and Ackerman, 1985, Kleinman 1991, 1994; Stewart, 1993], stratospheric [Prather et al., 1979; Fox et al., 1982], and mesospheric [Yang and Brasseur, 1994] photochemical systems. Madronich and Hess [1994], Krol [1995], Stewart [1995], and Poppe and Lustfeld [1996] discuss the presence of selfoscillations in a tropospheric PCS model. The presence of selfoscillations in a model of the Antarctic stratospheric PCS and their role in the ozone hole phenomenon are considered by Konovalov [1993], Konovalov and Feigin [1995], and Feigin and Konovalov [1995, 1996]. Fichtelmann and Sonnemann [1992] report the presence of multiperiodic and chaotic regimes in a model of the mesospheric PCS, which are thoroughly analyzed by Sonnemann and Fichtelmann [1997]. We have grounds to assume that the listed nonlinear properties not only are inherent for photochemical models under investigation, but also may be manifested in the real atmosphere. These grounds are discussed in the following subsection.

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Paper number 98JD01569. 0148-0227/98/98JD-01569\$09.00

1.2. Relevancy of the Model Results to the Real Atmosphere

It is well known that a number of significant atmospheric phenomena (such as cyclones/anticyclones, circumpolar vortexes, sudden stratospheric warming, etc.) exist due to basic hydrodynamic nonlinearities, which are reflected in the model equations describing those phenomena. In contrast, the possibility that basic chemical nonlinearities associated with twoand three-molecule and heterogeneous reactions may cause photochemical nonlinear phenomena significantly affecting the composition of the atmosphere is not taken into account in the majority of studies. The tradition to neglect the potential role of nonlinearities in the atmospheric PCSs is grounded in the long-standing experience of elaboration and verification of the atmospheric models. However, it has not been proven that nonlinear dynamic phenomena (similar to that well-known in nonatmospheric chemistry (see, for example, review by Field and Burger [1985]) are impossible in atmospheric PCSs. Though the current state of knowledge about the nonlinear dynamic properties of the atmospheric PCS does not allow unambiguous conclusions regarding the role of nonlinear photochemical phenomena in the real atmosphere (in fact, the necessary investigations are only now beginning), we can point to two recent studies arguing that photochemical nonlinear phenomena indeed take place under real atmospheric conditions. Kleinman [1994] has clearly demonstrated that the multistability revealed in models of the tropospheric PCS [White and Dietz, 1984; Kasting and Ackerman, 1985] is the reason for observed strong seasonal variations in the chemical composition of the troposphere. Feigin and Konovalov [1996] adduce serious arguments in favor of a significant role of a nonlinear self-oscillating regime in the process of the Antarctic ozone hole formation.

It should also be emphasized that even if some atmospheric PCSs do not manifest any nonlinear dynamic phenomena at present, changes of some atmospheric parameters may cause bifurcations (that is, abrupt changes in the system's behavior under small, smooth changes of the system parameters), which lead to the existence of the nonlinear phenomena in the future. In the mentioned cases of the tropospheric and Antarctic stratospheric PCSs, for example, the changes of atmospheric parameters leading to bifurcations are anthropogenic in origin and associated with increasing emissions of nitrogen oxides and man-made halogens into the atmosphere, respectively.

We consider the results of the previously mentioned studies as evidence that the possible appearance of the nonlinear phenomena in real atmospheric PCSs cannot be neglected without special study.

1.3. The Role of Studies on the Nonlinear Nature of Atmospheric PCSs

In our opinion, the possibility of strong changes in the composition of the atmosphere associated with nonlinear phenomena dictates the necessity and usefulness of special investigations of the atmospheric PCSs with the purpose of revealing any possible nonlinear phenomena which may be manifested under a variety of conditions both at present and in the future. We believe that such investigations would help (1) to define how, when, and where the possible geophysical phenomena caused by photochemical nonlinearities can be observed (possibly, some nonlinear phenomena taking place in the actual atmosphere have not yet been observed because their observations require special conditions or special methods which could be determined by these investigations), and (2) to increase the reliability of the conclusions of studies on prediction of future changes in atmospheric composition. Examples of predictive studies are rather numerous (see, for example, World Meteorological Organization (WMO) [1995, and references therein]). The possibility of incorrect predictions principally exists because these studies take into account rather restricted ranges of parameter values and initial conditions. However, bifurcations could occur under some distinct combinations of parameter values. The realization of such combinations can be either a result of some perturbations not taken into account in the employed models or an unexpected deviation of the parameters' trends from the assumed values. Of course, special attention should be devoted to PCSs demonstrating chemical instabilities. An example of such PCS is the Antarctic stratospheric PCS [Feigin and Konovalov, 1996]. A problem concerning the possible future recovery of the Antarctic ozone hole has been raised recently by Hoffmann et al. [1997]. For their predictions the authors have taken into account possible trends only of stratospheric chlorine. However, because of the complex structure of the Antarctic PCS state space, revealed by Feigin and Konovalov [1996], even small trends of other parameters of the stratosphere, for example, methane concentration, can lead to transition of the Antarctic PCS to another state which may differ from both the present and past states and may be associated with significantly different ozone concentrations. To insure more accurate predictions, the boundaries between qualitatively different regimes in the space of parameters of the Antarctic PCS should be determined and analyzed together with possible parameter trends.

1.4. Essential Dynamic Models and Their Purposes

Obviously, any investigation of dynamic system properties under a variety of conditions assumes the use of a model of that system. Thus, the crucial question is which model to use. When an investigation concerns the photochemistry of the atmosphere, a natural tendency would be to use a complete photochemical model. However, such models are constructed with the purpose of achieving the best quantitative agreement with observations and, as a rule, are rather bulky and involve too many dynamic variables (here, concentrations of chemical species) and parameters. As a result, numerical calculations give a small probability of revealing the regions of parameter values where the particular PCS exhibits nontrivial dynamic properties. We have suggested another way: to use special models [Feigin and Konovalov, 1996, p. 26,023], 'which combine simplicity with a good correspondence to observed processes', and which we have introduced as the basic models. The good correspondence to the observed processes assumes, first of all, qualitative correspondence of the dynamic behavior of the model to the behavior of the real atmospheric PCS. In this paper we develop this approach and, in particular, we present the general procedure to elaborate this type of model from the corresponding complete photochemical model. (We thus implicitly assume that complete photochemical models can adequately describe the behavior of the real PCSs.) Using the suggested procedure, one obtains a model which satisfies the following basic requirements: (1) the greatest possible simplicity, (2) the lowest order of the system of differential equations involved in the model, and (3) a consistency between qualitative dynamic properties of the simplified and the original complete models of the atmospheric PCS. Following from the fact that the discussed models should present just the essence, that is, the minimum number of actual photochemical processes which carry the essential qualitative features of the dynamic behavior of the considered atmospheric PCSs, hereinafter we refer to these simplified models as 'essential dynamic models'. Note that simplified photochemical models have been already used, in particular, for studying the dynamics of the tropospheric PCS [Stewart, 1995; Poppe and Lustfeld, 1996]. We would like to emphasize that the essential dynamic model is not only a simplified model, but meets the above three requirements also.

The essential dynamic model seems to be very useful not simply for solving the problem of the existence of nontrivial dynamic properties in the considered PCS, but, especially, for understanding the causes and mechanisms determining the existence of these properties. Understanding of the reasons for the existence of the nontrivial dynamic properties leads to, particularly, an identification of both the most important chemical processes determining these properties and critical (bifurcation) parameters. Consequently, this understanding promotes investigations aimed at predicting the ways and conditions under which the nontrivial dynamic properties may manifest themselves in the real atmosphere.

1.5. Objectives of the Paper

This paper deals with a twofold task. On the one hand, as mentioned above, the paper suggests a procedure of obtaining the essential dynamic model. As an example we use the photochemical dynamic model of the mesospheric PCS analogous to the model used by *Fichtelmann and Sonnemann* [1992] and *Sonnemann and Fichtelmann* [1997] (referred below as to FS and SF, respectively). The main advantage of this model is that it demonstrates a rich assortment of nontrivial dynamic regimes (FS, SF). This provides an opportunity to compare the essential and original models over a large number of characteristics and thus to show more clearly the validity and potential of the suggested procedure.

On the other hand, we consider our study as a contribution to the understanding of the nonlinear nature of the real mesospheric PCS. Our interest in this region of the atmosphere has arisen from studying FS, who have revealed that the zerodimensional dynamic model of the mesospheric PCS enforced by the diurnal variations of the photolysis rates possesses a rich assortment of subharmonic oscillations and exhibits chaos. In connection with our statements above about the inconvenience of a complete model for investigations of nonlinear dynamic properties, it seems natural that FS have used for their study a rather simplified model. However, using the simplified model poses the question of whether these properties are an artifact of the simplified treatment or are inherent properties of the real mesospheric PCS. This question is discussed briefly by FS and SF, and according to this discussion it appears that an unambiguous resolution cannot be given at present. Evidently, to solve this question, further investigations using both theoretical and experimental approaches should be done. Taking into account that those investigations may reveal a qualitatively new and unusual geophysical phenomenon, and, in any case, may significantly advance the understanding of the physics and chemistry of the mesopause region, we believe that such investigations deserve to be carried out.

The successful resolution of the posed question implies, in particular, an understanding of the impact on the discussed nonlinear phenomena of different processes, both chemical and nonchemical in origin, which are present in the real mesosphere, but not taken into account in the simplified photochemical models. In parallel with, or even prior to, studying these factors within the framework of more complex models, it appears to be extremely useful to understand the mechanisms of the impact of these factors and to estimate their associated possible changes in the dynamic behavior. By doing so, one gets the opportunity to foresee the results of numerical calculations, as well as to define conditions when changes caused by different factors can either be negligible or provide desirable effects. This would finally lead to an increase in the degree of reliability of the results obtained by means of complex models and allow one to make the studies more comprehensive.

We see only one method to achieve this desired understanding. This method requires the determination of the mechanisms for the appearance of nonlinear effects in the chosen model of the mesospheric PCS and a further analysis of how and to what degree a factor of interest perturbs or changes those mechanisms. We consider the elaboration of the essential dynamic model of the mesospheric PCS presented in this paper as a necessary first step in the suggested method. We note, for example, that in our recently finished study (I. B. Konovalov and A. M. Feigin, manuscript in preparation) the essential dynamic model is used as an instrument for revealing both chemical and dynamical mechanisms for the appearance of nonlinear dynamic phenomena found by FS. Also, using the essential dynamic model, we have made estimations of the impact of the eddy diffusion which show that the subharmonic oscillations can be retained, at least when the value of the eddy diffusion is assumed to be at or less than 10^5 cm²s⁻¹.

Even without a further analysis of the mechanisms for the appearance of nonlinear effects, the essential dynamic model itself presents the assemblage of the most significant chemical processes responsible for the appearance of nonlinear phenomena in the considered model and shows, in the simplest manner, how these processes contribute to the evolution of the considered species. Namely, these processes should be compared with any additional processes which are not included in the original model with the purpose of estimating the impact of those additional processes on the dynamic behavior of the mesospheric PCS.

The original model of mesospheric PCS and its dynamic properties are discussed in section 2. Particularly, in this section we determine characteristics unaccustomed in aeronomy such as correlation and minimum embedding dimensions of a chaotic attractor. In section 3 we describe the procedure of elaborating the essential dynamic model and compare the dynamic properties of the original and essential dynamic models of the mesospheric PCS.

2. The Original Photochemical Model of the Mesospheric Photochemical System and Its Basic Dynamic Properties

2.1. Description of the Original Photochemical Model

As an original photochemical model for elaborating the essential dynamical model of mesospheric PCS we use a model similar to the one investigated by FS. The list of reactions and reaction rate coefficients calculated for mesopause conditions (an altitude of about 82 km) according to *Atkinson et al.* [1989] is given in Table 1. The model simulates the behavior of five minor constituents: O, H, O₃, OH, and HO₂. The concentrations of these constituents are denoted below as x_1 , x_2 , x_3 , x_4 , and x_5 , respectively. The model includes the following set of differential equations describing dynamics of the photochemical system:

$$\frac{dx_1}{dt} = -(a_0 + 2a_{11}x_1 + a_{10}x_3 + a_4x_4 + a_5x_5)x_1 + a_1x_2x_5 + a_{15}x_4^2 + a_{10}s(t)x_3 + 2a_8s(t)$$
(1)

$$\frac{d x_2}{dt} = -(a_0 + a_{12}x_3 + (a_1 + a_2 + a_{14})x_5)x_2 + a_4x_1x_4 + a_7s(t)r$$
(2)

$$\frac{d x_3}{dt} = -(a_{10}x_1 + a_{12}x_2 + a_{13}x_4 + a_{16}s(t))x_3 + a_9x_1$$
(3)

$$\frac{d x_4}{dt} = -(a_4 x_1 + 2a_{15} x_4 + a_3 x_5 + a_{13} x_3) x_4 + a_5 x_1 x_5 + a_{12} x_2 x_3 + 2a_{14} x_2 x_5 + a_7 s(t) r$$
(4)

$$\frac{d_{x_5}}{dt} = -(a_5x_1 + a_3x_4 + (a_1 + a_2 + a_{14})x_2)x_5 + a_5x_2 + a_{13}x_3x_4$$
(5)

Here a_1-a_{16} stand for rate coefficients of the reactions (R1)-(R16) respectively; r denotes a mixing ratio of H₂O (in ppmv), which is a control parameter in the model, since we consider changes in dynamics of the system when this parameter changes while all other parameters of the model remain unchanged. The values of r for each calculation are given below. In the real mesosphere the mixing ratio of H₂O varies significantly, approximately in the range from about 1 to 10 ppmv [*Grossmann et al.*, 1985; *Peter et al.*, 1988; *Bevilacqua et al.*, 1996; *Summers et al.*, 1996]. The function s(t) parameterizes diurnal variations of photolysis rates. Here we assume that s(t) is a stepwise function defined as follows:

$$(t)=1, t\in[Tn;Tn+T/2],$$

and s(t)=0, $t \in [Tn+T/2;T(n+1)]$, n=1,2...

(6)

s

	Reaction	Reaction rates
(R1)	H+HO ₂ →H ₂ O+O	2.40×10^{-12}
(R2)	$H+HO_2 \rightarrow H_2+O_2$	5.6×10 ⁻¹²
(R3)	$OH+HO_2 \rightarrow H_2O+O_2$	1.80×10^{-11}
(R4)	OH+O→H+O ₂	4.15×10 ⁻¹¹
(R5)	$HO_2+O\rightarrow OH+O_2$	8.64×10 ⁻¹¹
(R6)	$H+O_2+M\rightarrow HO_2+M$	3.83×10 ⁻⁴
(R7)	H ₂ O+hv→H+OH	8.50×10^{2}
(R8)	$O_2^+ h\nu \rightarrow 2O$	2.43×10 ⁵
(R9)	$O+O_2+M\rightarrow O_3+M$	5.90×10 ⁻⁶
(R10)	$O+O_3 \rightarrow 2O_2$	1.48×10 ⁻¹⁶
(R11)	$O+O+M \rightarrow O_2+M$	2.00×10 ⁻¹⁸
(R12)	$H+O_3 \rightarrow OH+O_2$	1.16×10 ⁻¹¹
(R13)	$OH+O_3 \rightarrow HO_2+O_2$	1.11×10 ⁻¹⁴
(R14)	H+HO ₂ →2OH	7.20×10 ⁻¹¹
(R15)	OH+OH→H ₂ O+O	1.18×10 ⁻¹³
(R16)	$O_3+hv \rightarrow O_2+O$	1.00×10 ⁻²

 Table 1. Reactions and Their Rate Coefficients Taken Into

 Account in the Original Model

The rate coefficients of bimolecular reactions are given in units of cm^3s^{-1} . The rate coefficients of termolecular reactions are calculated for conditions typical for the mesopause (concentration of air molecules (M)=1.7×10¹⁴ cm⁻³, temperature t=189 K); the rate coefficients of (R6) and (R9) are given in units of s⁻¹, the rate coefficient of reaction (R11) is given in units of cm³s⁻¹. The photolysis rate coefficients (R7) and (R8) are given in units of cm⁻³s⁻¹, and that of (R16) in units of s⁻¹

Thus, we assume that the photolysis rates are constant during the whole daytime, then drop to zero at sunset, and return to the constant value again at sunrise. The real dependence of the photolysis rates on time is smoother; nevertheless, it is much closer to dependence (6) than, for example, to a sinusoidal variation Test calculations show that using a smoother function s(t) instead of (6) does not cause qualitative changes in the system behavior. We have assumed that the transition between extreme values of s(t) (0 and 1) takes time of the order of 10^4 s (or less). The same result has been obtained by FS. Note that the stepwise specification of s(t) allows us to present the evolution of the system (1)-(5) with time-dependent parameters as sequential time intervals, during each of which the system parameters do not depend on time. As a result, we can reduce the analysis of the behavior and dynamic properties of the nonautonomous (timedependent) system to the analysis of those of two autonomous (time-independent) subsystems corresponding to day and night conditions. Within the framework of this description the nonautonomous character of the system is focused on the sunset and sunrise moments. For clarity we assume here that the durations of a day and a night are equal.

2.2. Dynamic Properties of the System (1)-(6) for the Original Model

2.2.1. Bifurcation diagram. The dynamic properties of a system are traditionally presented by a bifurcation diagram, which is referred to as a dependence of dynamic variable values (here, the concentrations of the chemical components) chosen in a definite way on a value of a control parameter. When the response of a system to periodic external forcing is considered, the most informative diagram is formed by the variable values taken in subsequent moments of time separated by the period T of external forcing. In that case the single-valued dependence of the corresponding variables on a

control parameter corresponds to the simplest 'stable' response of the system to periodic forcing; that is, the system exhibits periodic oscillations with period T. As the control parameter changes, the qualitative changes in the dynamic behavior of a system called bifurcations can occur. The presence of bifurcations corresponding to changes of a solution periodicity is reflected in the bifurcation diagram as a nonuniqueness; that is, several variable values correspond to the same parameter value. For example, the two-valued dependence corresponds to the double-periodic solution, that is, the solution with a minimum period equal to 2T. If a certain value of the control parameter corresponds to an infinite number of variable values, then there are some grounds to believe that this value of the control parameter corresponds to a chaotic behavior of the system. Note that both multiple-periodic and chaotic behaviors are referred to in this paper as nonlinear dynamic behaviors, because the possibility of such behaviors arises from the nonlinearity of the system.

The bifurcation diagram of the set (1)-(5) is presented in Figure 1a. The diagram demonstrates the dependence of the night-end concentration of atomic oxygen (x1) on the H2O mixing ratio (r). To obtain this diagram, we made the sequence of calculations with both increasing and decreasing values of r. As the initial values for the dynamic process with given r, we use the night-end values found in the dynamic process with the previous value of r. The calculations are performed using a fifth-order Runge-Kutta method with a relative precision of 10⁷s. To avoid transients, the first 100 periods are neglected; the next 100 periods form the bifurcation diagram. The r step used for bifurcation diagram formation is equal 10⁻³ ppmv. As shown in Figure 1a, when the H₂O mixing ratio is either small enough ($r < r_1 = 1.5$ ppmv) or large enough ($r>r_2=5.3$ ppmv) the bifurcation diagram is singlevalued; that is, the variations of the chemical species have a 1day period. Figures 2a and 3a show examples of diurnal variations of the atomic oxygen (solid curve) and atomic hydrogen (dashed curve) concentrations calculated for low (r=1 ppmv) and high (r=7 ppmv) values of the H₂O mixing ratio, respectively. The asterisks and circles along the abscissa mark the moments corresponding to sunrise and sunset, respectively. A typical feature of the simulated diurnal variations of the chemical species is an increase in concentrations of both the atomic oxygen and all the hydrogen compounds during the daytime and their decrease during the nighttime. The reason for this is that the main source of the hydrogen compounds and atomic oxygen is the photolysis of the H_2O (reaction (R7)) and O₂ (reaction (R8)), respectively, which is absent during the nighttime. For intermediate values of the H₂O mixing ratio $(r_1 < r < r_2)$ we find different multiperiodic regimes and three regions of chaotic behavior, which can be seen in Figure 1a. An example of a double-periodic solution (with r=4.3 ppmv) is presented in Figure 4a. It should be mentioned that the bifurcation diagram also reflects an interesting effect, that two different dynamic regimes can correspond to the same value of the control parameter. In particular, from Figure 1a and, much more clearly from Figure 1c, where the abscissa scale is stretched, it follows that near the left boundary of the region of nonlinear dynamic behavior $(r \approx r_1)$ the single-periodic regime coexists with a triple-periodic regime and, with increasing r, a six-periodic regime. For greater r, we obtain successively (1) a double-periodic regime coexisting with six- to twelve-periodic regimes (the accuracy of our calculations does not allow us to resolve subharmonics of a higher order) and a chaotic regime,



Figure 1. Bifurcation diagrams for (a) the original and (b) the essential dynamic models, and enlarged projections of corresponding pieces of (c) Figure 1a and (d) Figure 1b.

(2) four- and eight-periodic regimes coexisting with the chaotic regime, and, finally, (3) two different coexisting chaotic regimes. This behavior is known as a hysteresis effect because the changes of the control parameter in opposite directions (either increasing or decreasing) are accompanied by different sequences of the bifurcations. The last feature of the bifurcation diagram that we note is the character of bifurcation for $r=r_1$ (that is, at the left boundary of the multiperiodic region) in the case of decreasing magnitude of r. A return of the system from multiperiodic to single-periodic regime follows a reverse succession of period doubling. As r decreases from r=r₃≅1.7 to r=r₁≈1.6 (see Figure 1c), we first obtain a change-over from the chaotic regime to a twelve-periodic regime, and, further, to a six-, a three-, and finally, a one-periodic regime. An irregular vertical dotted line on the left side of the bifurcation diagram, confining the region of the multiperiodic regimes, is a reflection of a very long (much longer than 100 periods) transitional process. We would like to emphasize that the time interval equal to 100 periods used for formation of the bifurcation diagram was found to be long enough to suppress the transition processes for all other regimes reflected in the bifurcation diagram.

It is very important that most significant dynamic properties of the set (1)-(5) are similar to those of the system investigated by FS and SF. Both systems (1) possess an identical set of the possible forms of dynamic behavior, (2) exhibit a doublingperiod cascade; (3) have the immediate neighborhood of the triple-periodic and chaotic regimes in the bifurcation diagram, and (4) demonstrate the hysteresis effect. Naturally, because of a significant difference between the parameter values involved in the models, full coincidence of the dynamic properties could not be expected. In particular, the bifurcation diagram of our system has (1) slightly different regions of magnitudes r, corresponding to the multiperiodic and chaotic behavior, (2) more chaotic bands, and (3) specific succession of the dynamic regimes when r is both increasing and decreasing in the band from r=1.5 to r=2.1.

2.2.2. Correlation dimension. As we have mentioned above, the considered system can exhibit chaotic behavior. It is known that the chaotic behavior of the system allows us to define some invariant characteristics for this system which do not depend on a particular dynamic process (see, for example, the review by *Abarbanel* [1997]). These characteristics can be used for classification and comparison of various dynamic systems. Furthermore, they provide valuable information for simplifying the given dynamic system. For the mesospheric PCS we consider two such characteristics: a fractal dimension, or more specifically a correlation dimension, and a minimum embedding dimension, which are discussed in this and the next sections, respectively.

An arbitrary chaotic phase trajectory fills a definite region of the phase space, called a chaotic, or strange attractor.



Figure 2. Diurnal variations of the atomic oxygen (x_1) (solid line) and atomic hydrogen (x_2) (dashed line) in a 1-day period regime with r=1 ppmv for (a) the original and (b) the essential dynamic models. The asterisks and circles along the abscissa mark the moments corresponding to sunrise and sunset, respectively.

(Recall that the phase space of the dynamical system refers to an imaging space, whose coordinates are dynamic variables, that is, concentrations of the chemical species in our case. A phase trajectory is a curve formed in the phase space by points corresponding to consecutive instantaneous states of the system during a given dynamic process.) A fractal dimension of the chaotic attractor is a characteristic of the geometric shape of the attractor and relates to the way points of the attractor are distributed in the phase space. Generally, the fractal dimension d satisfies the following relation

where ε is small. Here $N(\varepsilon)$ is a characteristic of the number of attractor points inside a cube with edge length ε . There are several types of fractal dimension according to the $N(\varepsilon)$ defi-

nition [Moon, 1987] and, in particular, a correlation dimension. A correlation dimension (ν) is defined by the equation

$$\nu = \frac{\log(C(\varepsilon))}{\log(\varepsilon)},$$

where $C(\varepsilon)$ is known as the correlation integral and is defined by

$$C(\varepsilon) = \lim_{N \to \infty} \frac{1}{N^2} \sum_{i,j=1}^{N} \theta \left(\varepsilon - \left\| X_i - X_j \right\| \right)$$

Here $\theta(x)$ is the Heaviside function, which is equal to either 0 for $x \le 0$, or 1 for x > 0, $||X_i - X_j||$ denotes the distance between the points X, and X_j of the chaotic attractor, and N is the number of points. It is clear that the magnitude of the correlation integral is proportional to the number of attractor points that are separated by a distance which does not exceed ε . A value of ε is chosen so that $\log(C(\varepsilon))$ is a linear function of $\log(\varepsilon)$. A detailed discussion of the correlation dimension can be found in original papers by *Grassberger and Procaccia* [1983a,b].



Figure 3. The same as in Figure 2, but with r=7 ppmv.



Figure 4. The same as in Figure 2, but for a 2-day periodic regime with r = 4.3 ppmv.

Note that fractal dimensions and, particularly, the correlation dimension give an estimate for the minimum number of coupled equations which are necessary to describe the behavior of the system. The correlation dimension is frequently used in investigations of various dynamic systems [Abarbanel, 1997]. In particular, this characteristic was applied to study the dynamic behavior of atmospheric ozone [Yang et al., 1994] and to the comparison of models describing dynamics of the troposphere [Sundermeyer and Vallis, 1993]. For the nonautonomous system (1)-(5) we calculate the correlation dimension of the chaotic attractor considered in the sixdimensional phase space which includes time as one of the coordinates. Figure 5a shows the calculated dependence of $\log(C(\varepsilon))$ on $\log(\varepsilon)$ for the value r=2.8 ppmv corresponding to the rightmost chaotic region in Figure 1a. The region in Figure 5a where the above values are proportional is marked by a solid straight line. The slope of that line gives the value of the correlation dimension: v=1.93±0.02. Our calculations yield the same magnitudes of the correlation dimension for two other regions of chaotic behavior shown in Figure 1a. These two regions are separated more clearly in Figure 1c, where the abscissa scale is stretched. The calculations of the correlation dimension for these regions were carried out for r=1.75 and r=1.85 (ppmv).

The value of the correlation dimension which we obtain implies that the chaotic attractor in the considered sixdimensional phase space forms a two-dimensional surface. Consequently, if we consider a 'stroboscopic' section of the attractor in five-dimensional phase space, that is, the attractor points corresponding to a definite moment of a day, we find that this section has a linear fractal structure. Indeed, it is easy to understand that a chaotic attractor of the system with periodically changing parameters is evenly 'smeared out' over the time axis, so the fractal dimension of the 'stroboscopic' section should be less by a unit than the one for the full attractor. The structure of the projection of the attractor 'stroboscopic' section on the plane (x1-x2) for the moments corresponding to the end of the night is shown in the Figure 6a. In other words, the points on Figure 6a depict values of atomic oxygen and atomic hydrogen as they appeared in the chaotic dynamic process at the end of the night



Figure 5. Dependencies of the correlation integral C(s) logarithm on $\log(s)$ (see section 2.2.2) for (a) the original and (b) the essential dynamic models.



Figure 6. The structure of the projection of the attractor 'stroboscopic' section on the plane (x_1-x_2) for the moment corresponding to the end of the night (a) for the original model and (b) for the essential dynamic model.

The rather small value of the correlation dimension which we obtain allows us to infer that only three coupled equations are necessary to simulate the observed dynamic behavior of the system (1)-(5). Indeed, it is known that systems of dimension less than three can not exhibit deterministic chaotic behavior. This means that the minimum number of coupled equations in the system with periodically changing parameters is two, as the third equation can simply correspond to the time periodic dependence of the parameter values (see, for example, *Moon* [1987]).

2.2.3. Minimum embedding dimension. The minimum embedding dimension is discussed in detail, for example, by *Abarbanel* [1997]. As far as we know, this characteristic has not yet been used for studying the atmosphere. A minimum embedding dimension (d_E) can be defined as the minimum number of coordinates of an arbitrary phase subspace where

the phase trajectory belonging to the chaotic attractor does not have any overlaps. This definition assumes, in particular, that the value of the minimum embedding dimension is always an integer. In other words, once d_E is determined, we obtain immediately the minimum dimension of a system which can describe the considered chaotic motion. To calculate d_E we use a so-called 'false neighbor' method [*Kennel et al.*, 1992]. False neighbors are points belonging to the chaotic attractor which are close in the phase subspace of a relatively low dimension, but well separated in the phase subspace of a higher dimension. The minimum embedding dimension is equal to the dimensionality of the phase subspace where the number of false neighbors is negligible. The procedure of calculating d_E can be briefly described as follows [*Abarbanel*, 1997].

Using the time series of the observed variable x(t) (x₁ in our case), a phase portrait can be reconstructed with delay coordinates, that is, a point on the attractor is given by a data vector $y_k = \{x(t_k), x(t_k+\tau), \dots x(t_k+(d-1)\tau)\}$, where d is a presumed dimension of the phase space and τ is an almost arbitrary chosen delay time. Then the nearest neighbor (in the Euclidean sense) to this point is to be found and will be a vector $y_n = \{x(t_n), x(t_n+\tau), \dots x(t_n+(d-1)\tau)\}$. In going from the d to d+1 dimension the additional component of the vector y_k is $x(t_k+d\tau)$, and that of the vector y_n is $x(t_n+d\tau)$. Comparing the distance between y_k and y_n in a space of dimension d with distance in the dimension d+1 (this should be done for all available pairs y_k and y_n), we can establish the true and false neighbors. The difference between these distances relative to the distance in dimension d is expected to be rather small for the true neighbors, while this value for those vectors whose neighborhood in dimension d is just a result of a projection from a higher dimension, that is, for the false neighbors, is expected to be much greater. The procedure is quite insensitive to the concrete reasonable value of the threshold used to separate the true and false neighbors. A definite threshold value is chosen according to recommendations of Kennel et al. [1992]. It is expected that the percentage of false neighbors will drop from nearly 100% in dimension one to almost zero when the true dimension value, d_E, is reached.

The results of calculations for the system (1)-(5) presented in Figure 7a show that $d_E=3$. This value is in complete agreement with the result for the correlation dimension from section 2.2.2.

2.2.4. Equilibrium state. As mentioned above, the dynamic process simulated for the time-dependent (nonautonomous) system with regard to the stepwise character of (6) can be presented as successive dynamic processes described by the time-independent (autonomous) systems corresponding to the daytime and nighttime situations. The traditional method of investigating the dynamic properties of nonlinear systems is based on studying the structure of the phase space of the system [Andronov et al., 1966]. All qualitative peculiarities of the behavior of the system are reflected in its phase space structure. For example, self-oscillations correspond to a limit cycle in the phase space, and the monotonic transition from the arbitrary initial state to the same equilibrium corresponds to the only equilibrium state of a stable node type in the phase space of the system. The numerical investigation of the phase space of the system for the daytime conditions shows that the structure of the system phase space is determined by a single equilibrium state. So, in this case the qualitative peculiarities of the system behavior are completely determined by the type of the equilibrium state, which in turn is



Figure 7. The dependencies of the false neighbor numbers on the embedding dimension for (a) the original and (b) the essential dynamic models.

determined by the eigenvalues (the roots of the characteristic equations of the linearized system). In our case the set of equations is of the fifth order and has five different eigenvalues. Numerical investigations reveal that we have the equilibrium state of the stable focus-node type. The stable focus behavior of the phase trajectories corresponding to the damping oscillations of the variables is determined by the pair of complex conjugate eigenvalues $\lambda_{1,2}=\operatorname{Re}(\lambda)\pm i\operatorname{Im}(\lambda)$, $\operatorname{Re}(\lambda)$ and Im(λ)=0, where *i* is an imaginary unit. The stable node behavior of the phase trajectories corresponding to the exponential monotonic approach of the system to the equilibrium state is determined by the three real eigenvalues. The magnitudes of the eigenvalues corresponding to the node type are much greater than those corresponding to the focus type. Because of this, the process of adjustment of the system to the equilibrium can be arbitrarily divided into two successive stages. During the first stage the fast responses with typical times of 10^{1} - 10^{2} s corresponding to the real eigenvalues drive the system to a quasi-equilibrium state. After that, in the second stage the slow motions with typical times of 10⁴-10⁵ s corresponding to the complex eigenvalues take place. So, the system behavior visible at the longest timescales corresponds mostly to the 'focus' behavior of the phase trajectories. Figure 8a shows the

parameter r dependencies of values of $(-\text{Re}(\lambda)^{-1})$ (solid line), that is, the characteristic damping time of perturbations in the vicinity of the equilibrium state, and values of $2\pi \text{Im}(\lambda)^{-1}$ (dashed line), that is, the period of oscillations about the equilibrium state.

Both numerical and analytic considerations show that all phase trajectories in the phase space of the system corresponding to the nighttime conditions converge to the equilibrium state of the degenerate stable node type, where $x_{1,2,4}=0$ and x_3 and x_5 are arbitrary constants determined by the initial conditions of the nighttime evolution. The fact that the equilibrium states are stable and unique in both the daytime and nighttime subsystems unambiguously testifies that both subsystems are stable and that the complicated dynamics of the original nonautonomous system cannot be attributed to instability of the autonomous subsystems.



Figure 8. Dependencies on the parameter r of the characteristic damping time of perturbations in the vicinity of the equilibrium state (solid line) and of the period of oscillations about the equilibrium state (dashed line) for (a) the original and (b) the essential dynamic models.

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2.3. Remarks About Suitability of the Chosen Original Model

Note that the previously mentioned specific tasks of our study (see section 1.5) have determined our using as an original model not a complete photochemical model, as suggested in section 1.4 for the most general case, but an already simplified model, described in section 2.1, analogous to that used by FS and SF. As shown below, this model is yet a subject for further significant simplification from both the chemical and mathematical points of view. Due to this, the chosen original model is well suited to the first task of our study.

The chosen original model is also well suited to the second specific task of our study formulated in section 1.5, concerning the investigation of nonlinear effects revealed by FS, since our original model demonstrates those effects. In principle, there is a possibility that if the essential dynamic model were elaborated from the more complete photochemical model taken with the same parameter values, it would differ from the essential model presented below. However, our consideration of the processes involved in the original model, in connection with general notions regarding photochemistry of the mesosphere as they are described, in particular, in the book of Brasseur and Solomon [1984], shows that our original model includes all processes of the mesopause region which provide a major contribution to the dynamics of the species involved in the model. Thus, we consider the mentioned possibility as rather unlikely.

At the same time, it is possible that the presented essential dynamic model may require some corrections in situations when a significantly different set of parameters is considered (see also related remarks in section 3.1.3). It should be noted also that our study concerns the basic dynamic properties of the photochemistry itself, that is, taken separately from the other atmospheric processes. Other atmospheric factors can be analyzed on the basis of the essential dynamic model as suggested in section 1.5.

3. Essential Dynamic Model of the Mesospheric Photochemical System

3.1. The Procedure of Elaboration of the Essential Dynamic Model for a Photochemical System

3.1.1. Preliminary remarks. The equations of the essential model can be obtained using the conceptually standard approximate procedures which are used for elaboration of adequate mathematical models of various dynamic systems. These procedures are the successive asymptotic expansion of the right-hand sides of the equations in terms of small parameter/parameters and separation of the variables according to their characteristic times. The question of the correctness of the asymptotic expansion in the noted procedures has been considered first by Andronov and Pontryagin [1937]. In particular, they introduced the important notion of the rough dynamic system [see also Debaggis, 1952], that is, the system whose dynamic behavior does not change qualitatively under finite changes of the right-hand (nondifferential) sides of the set of differential equations describing an evolution of variables. The validity of this procedure is proved by means of a series of theorems (see, for example, Andronov et al. [1973]). The main theorem is one stating the continuous dependence of the solution on changes of both the right-hand parts and initial conditions. A detailed description of various definitive methods of an asymptotic expansion for a system with one degree of freedom can be found in the work by *Nayteh* [1981].

The second procedure connected with a successive separation of variables according to their characteristic times has been suggested first by *Feigin* [1955] for description of the socalled discontinuous oscillations in some radio-technical systems. This procedure leads to the maximum decrease of the order of the set of differential equations that still retains its ability to describe adequately the processes investigated. *Andronov et al.* [1966] suggest various examples of using this technique for mechanical and radio-technical systems. *Haken* [1978] uses a particular case of this procedure, which is named by the author as the method of an adiabatic approximation, for analysis of a number of various systems of different nature, and, in particular, for chemical systems.

We discuss in this paper an application of these procedures to the case of the dynamic system describing the evolution of chemically reacting components. To be correctly simplified, such systems, generally, require simultaneous application of both of the above noted procedures. Although we are sure that neglecting some small factors in the right-hand parts of the corresponding equations precedes any application of the variable separation procedure to any real system, we have not yet succeeded in finding any publications describing such combined application. Below we suggest a step-by-step procedure that combines the two particular procedures discussed above in their application to the specific case of atmospheric photochemical systems. It should be noted that in this paper we limit the description of the procedure to the most typical situations in atmospheric photochemistry. The suggested procedure may be advanced for possible specific situations without any principal problems.

3.1.2. Step-by-step procedure. The procedure assumes the following successive steps.

1. The considered system is first converted into dimensionless form. The source system can be written as

$$\frac{d x_i}{dt} = f_i(x_1, ..., x_n, t), \quad i=1, 2, ..., n,$$
(7)

where x_i is the concentration of the reagent *i* and $f_i(x_1, ..., x_n, t)$ is a function describing chemical sources and sinks of the reagent *i*.

$$\tau_1 \frac{d z_1}{dt} = g_{10}(z_1, \dots, z_n, t) + \mu_{12} g_{12}(z_1, \dots, z_n, t) + \mu_{12} g_{12}(z_1, \dots, z_n, t) + \dots$$
(8)

Here $z_i = x/x_{ci}$, where x_{ci} is a characteristic value of the variable x_i ; μ_{i1} , μ_{i2} , ... are dimensionless small parameters, such that $\mu_{y+1} << \mu_y$, $\mu_{i1} << 1$, i=1, ... n. The functions $g_y(z_1, ..., z_n, t)$ have a magnitude of the order of unity. The quantities τ_i represent typical times of changing values of variables z_i . Here, these times are estimated within the framework of a separately considered equation for the reagent *i*. The last is important, as below we show that the typical time of the variable change with evolution of the whole system can significantly differ from τ_i .

2. We next simplify the set of equations. In the majority of cases, but not always, to preserve the relationship of the dynamic properties of the simplified model and those of the original model, it is necessary to take into account only the greatest terms in (8), having assumed $\mu_{ij}=0$ for all *i* and *j*. As a result, we obtain the set of the following equations:

$$\tau_{i} \frac{d z_{i}}{dt} = g_{i0}(z_{i}, \dots z_{n}, t)$$
(9)

Below we refer to these equations as the zero-order equations.

3. We then separate variables z_i into three groups according to values of their typical times τ_i . Let us study the dynamics with typical timescale τ_s . Then, the variables with $\tau_i >> \tau_s$ are considered to be the parameters of the system, so we assume for the corresponding variables z_i =const. The variables with $\tau_i << \tau_s$ are considered to be fast and are supposed to be in a state of instantaneous equilibrium. Values of the fast variables are found from the set of algebraic equations obtained from equations (9) for z_i under the condition $dz_i/dt=0$. For the slow variables, for which $\tau_i - \tau_s$, we consider (9), in whose right-hand sides we substitute the values of the fast variables as functions of the slow ones, obtained from the derived set of algebraic equations. In doing so, we arrive at the desired simplified equations adequately describing the original system dynamics with typical times $\tau_i - \tau_s$.

4. The zero-order approximation is insufficient in the case where the set of algebraic equations for the fast variables is underdetermined because some of the equations are linearly dependent. Consequently, the solution of this set of equations depends on one or several constants. For a dimensional form of equations these constants are equal to the sum of concentrations of a minimum number of linearly dependent fast components with integer (positive or negative) weight factors. Specifying the constants as x_f and numbering them by index *j* we can write

$$x_{j} = \sum_{k=1}^{m} \alpha_k x_{i_k}, \qquad (10)$$

where *m* is the number of linearly dependent equations for the fast variables which determine the constant/constants, i_k are indexes of variables in the original system, and α_k are weight factors, which must satisfy the condition

$$\sum_{k=1}^{m} \alpha_k x_{c_{lk}} \tau_{lk}^{-1} g_{lk^0} = 0$$
 (11)

Note that usually $\alpha_k = 1$. Obviously, the magnitudes of x_{ij} can be considered as constants during the time $\tau \leq \tau_{iq}$, where i_q is the index of the slowest of the *m* fast components. So, values x_{ij} can vary at timescales greater than τ_{iq} . A temporal evolution of x_{ij} is described by the equations derived from the original dimensionless set of equations (8) as the result of summing *m* equations for concentrations of the corresponding components z_{ik} with the weight factors $\alpha_k x_{cik} \tau_{ik} t^{-1}$ (see (10) and (11)). In (8) one has to take into account the terms proportional to $\mu_{i,i}$, since the greatest terms are canceled due to the linear dependence of the zero-order approximation equations. The equations for a dimensionless value $z_{ij} = x_{ij} / x_{cij}$, where

$$x_{cfj} = \sum_{k=1}^{m} x_{cij}$$

is a characteristic value of x_{f} , are

$$r_{fj} \frac{d z_{fj}}{dt} = g_{fj}(z_1, \dots z_n, t).$$
 (12)

Clearly, the typical time τ_{fj} of z_{fj} changes is of the order of τ_{iq}/μ_{iql} . The new variables also should be separated in accordance with their typical times (see item 3). If some of these new variables are relatively fast (when $\tau_{iq} < \tau_{fj} << \tau_s$), then we

have to solve the set of corresponding algebraic equations for these variables. It is possible that again some equations for x_{ff} are linearly dependent. In this case, consideration of the equations which include the terms proportional to μ_{r2} is required. These equations can be obtained using a procedure analogous to the one described in item 4. Such an iterative procedure should be continued until all newly defined variables are either (1) fast and linearly independent ($\tau_{ff} < \tau_s$), (2) slow ($\tau_{ff} \approx \tau_s$), or (3) parameters ($\tau_{ff} >> \tau_s$). The desired essential dynamic model includes all simplified equations for the slow variables.

3.1.3. Some concluding remarks. We make three observations concerning the above suggested procedure.

1. Note that the validity and possible application of the above suggested procedure do not depend on the number of species or chemical processes involved in the zerodimensional photochemical models which are subjects of simplification. Indeed, neither the combined procedure nor the separate procedures assume any restrictions on complexity or number of degrees of freedom of the system to be simplified. Our choice of a comparatively simple version of the original model is discussed in the introduction.

2. The suggested procedure may require a special correction, if fast variables perpetually oscillate and the amplitude of their oscillation is comparable with their equilibrium values. In dissipative systems (in particular, chemical ones), such oscillations can be either self-oscillations (examples of selfoscillations in the atmospheric PCSs models are discussed, in particular, by Krol [1995], Stewart [1995], and Feigin and Konovalov [1996]) or forced oscillations, discussed, in particular, in this paper. It should be emphasized that in the case of forced oscillations, no correction is necessary for the typical atmospheric photochemistry situation where the characteristic times of the fast variables are much less than the period of oscillations In particular, such a situation takes place in the case of diurnal variations of atomic oxygen in the stratosphere, which indeed exhibits very strong oscillations, but does not stray far from equilibrium (either daytime or nighttime) during a major part of its diurnal course. In the opposite situation (when the characteristic times of fast variables are much greater than the period of oscillations), a correction is also not necessary because the amplitude of the oscillations cannot be significant under such conditions. A special consideration is indeed necessary in the intermediate situation, which appears to be rather rare in the atmosphere. An example of such a situation is shown to take place in the case of the diurnal variations of N₂O₅ [Brasseur and Solomon, 1984]. Note that different methods of handling fast oscillations in the equations for slow variables have been well studied in classical mechanics [Landau and Lifshits, 1973]. It should be particularly emphasized that an analysis of oscillations themselves does not require any correction of procedure; an example of such an analysis is given in this paper. Note also that the basic ideas of the suggested procedure, such as an asymptotic expansion of the right-hand sides of the differential equations and a separation of variables according to their characteristic times, are, no doubt, completely applicable for an analysis of the specific cases mentioned.

3. The suggested procedure assumes a priori estimation of characteristic values of reagent concentrations. Those values are used to convert the system to dimensionless form (see item 1 of subsection 3.1.2). The estimation can be carried out based on either observed data or model results. Naturally, the obtained characteristic values depend on values of the control pa-

rameters. Indeed, changes of the parameters may lead to quantitative changes of the characteristic values due to changes in the terms of equations containing the parameters. Especially strong changes of the characteristic values may occur when the corresponding changes of parameters cause bifurcations. Correspondingly, each given essential dynamic model adequately describes the dynamical properties of the original model for some limited region of the control parameters' values, which includes the control parameters' values used for estimation of characteristic variable values. Determination of the limits of applicability of an essential dynamic model can be done by directly comparing the dynamic properties of the essential and original models using, first of all, their bifurcation diagrams. An example of such a determination is given below in section 3.3.

3.2. Application of the General Procedure to Elaborating the Essential Dynamic Model of the Mesospheric PCS

Following the procedure described above, we find for the mesospheric PCS that according to the zero-order equations, the only slow variable is x_1 and the other variables are fast. However, the zero-order approximation equations for variables x_2, x_4 , and x_5 turn out to be linearly dependent. Thus, we have to consider equations of the higher approximation for the newly defined variable $x_{i}=x_{2}+x_{4}+x_{5}$ (see (10)). A solution of the corresponding set of zero-order algebraic equations for x_2 , x_4 , and x_5 (it is enough to take any two of the three available equations) shows that $x_{4,5} << x_2$, and, consequently $x_2 \approx x_f$. The last approximate equality means that the equation for x_f actually determines the dynamics of x_2 when the fast dynamics of both x_4 and x_5 are taken into account. The typical time of x_2 (or x_{f} according to (12) is shown to be 10⁴ s. Thus, the variable x_2 , which is a fast variable according to the zero-order equations, turns out, under a correct consideration, to be as slow as x_1 . Finally, the essential dynamic model of the mesospheric PCS describing dynamic processes with the typical timescales of 10⁴-10⁶ s includes two equations for the slow variables x_1 and x_2 :

$$\frac{d x_1}{dt} = -\alpha x_2 - (1 - s(t))\mu \alpha_1 + \delta s(t), \qquad (13)$$

$$\frac{dx_2}{dt} = -\beta x_2^2 / x_1^2 - \sigma x_2^2 / x_1 + \gamma s(t)r.$$
(14)

Here s(t) is a stepwise function determined according to (6), $\alpha = 2a_0, \mu = a_0, \delta = 2a_3, \beta = 2a_3a_0^{2}/(a_5a_4), \sigma = 2a_0(a_1+a_2)/a_5, \gamma = 2a_7.$

We would like to emphasize again that (13) and (14) involve fast dynamics of the fast variables x_3 , x_4 , and x_5 . These fast variables are connected with the slow ones via the following expressions: $x_4 \approx a_6 x_2/(a_4 x_1)$, $x_5 \approx a_6 x_2/(a_5 x_1)$, $x_3 = a_9 x_1/a_{16}$ (daytime), and $x_3 = \text{const}$ (nighttime).

A definite value of x_3 at nighttime cannot be found in the framework of the essential model, and, in fact, is not significant for the evolution of both x_1 and x_2 . As a consequence, the rather strong reactions (R12) and (R16), which significantly influence ozone concentration, do not contribute to the evolution of the essential model, and thus, to that of the original model. It should be noted that the overall result of a 'chemical' simplification of the original model is that the essential model incorporates only nine reactions (R1)-(R9) of 16 considered in the original one.

Applying the procedure described above to the particular case of our system, we choose the typical variable values to be

close to equilibrium values in the daytime system for r=2.8 ppmv: $x_{c1} \approx 10^{10} \text{ cm}^{-3}$, $x_{c2} \approx 10^8 \text{ cm}^{-3}$, $x_{c3} \approx 10^8 \text{ cm}^{-3}$, $x_{c4} \approx 10^7 \text{ cm}^{-3}$, $x_{c5} \approx 10^{6}$ cm⁻³. However, as follows, in particular, from the results of numerical calculations presented in Figures 3a and 4a, the system can go far from its daytime equilibrium state during its diurnal variations. Such a strong variation of chemical components can change relations between the typical times of the components and result in the necessity to correct the model. Our estimations show that the approximations used for obtaining the simplified equations become quantitatively incorrect only during deep 'drops' of the variable magnitudes at the end of the nighttime evolution. A special investigation reveals that the dynamic behavior of the essential model during these drops does not differ qualitatively from that of the original model. Moreover, a duration of the nighttime 'drops' smaller than 1 hour is negligible compared to the duration of a day (24 hours). Inasmuch as the elaborated essential model is intended to reproduce the qualitative dynamic properties of the original system, we assume that the equations obtained with the above characteristic values of variables can be used for an approximate description of the evolution of the whole system. The validity of this assumption, within certain limits, is supported by a comparison of the dynamic properties of the original system with those of the simplified one (section 3.3).

Note also that the mentioned possibility that the sum of certain component concentrations may vary much slower than each of these components separately is well known in the chemistry of the atmosphere and provides grounds for the method of chemical families [Turco and Whitten, 1974; Brasseur and Solomon, 1984], which is widely used in modeling of atmospheric processes. This is related to the presence of fast chemical reactions in which the components involved in the chemical family are interconverted, while their total concentration is not changed. In our essential system such fast reactions are (R4), (R5), and (R6). The changes in the total concentration of the chemical family members are determined by the other reactions, which are much slower. In our system, those are, first of all, (R1), (R2), and (R3), which determine the changes in the total concentration of the components OH, H, and HO₂, which form the so-called 'odd hydrogen' family. Previously, we have suggested a more general procedure presenting a 'nonchemical' method, which allows one to obtain the simplified equations, based on the following reasons: (1) The method of chemical families does not provide a maximum possible simplification of the sets of equations of chemical kinetics. (2) The definition of the chemical families is based on a priori knowledge of peculiarities of the chemical processes involved in the system, and we have not succeeded in finding a description of a consistent and justified procedure to extract chemical families from an assemblage of chemical reagents in an arbitrary chemical system. Alternatively, we see that the chemical families which may significantly simplify the consideration of the system dynamics under a given timescale emerge naturally in the asymptotical procedure described above. (3) Since our objective is to create a set of simplified equations which possesses the same dynamic properties as the whole system, it seems reasonable to follow the approach used for that in other branches of physics.

3.3. Dynamic Properties of the Essential Dynamic Model

We study the same dynamic characteristics and properties for the essential model as for the original one. These characteristics and properties are described in section 2.2 and are presented in Figures 1-8, with Figures 1a-8a corresponding to the original model and Figures 1b-8b corresponding to the essential model. In addition, the stretched pieces of bifurcation diagrams for the original and essential models are presented in Figures 1c and 1d, respectively.

In particular, Figure 1b presents the bifurcation diagram (see section 2.2.1) for the essential model. Comparing Figure la and Figure 1b, we can see that the region of the nonlinear dynamic behavior of the original model (1.5 ppmv<r<5.4 ppmv) is close to that of the essential model (1.8 ppmv<r<5.9 ppmv). The main dynamic regimes follow changes of the parameter r in the same sequence for both the original and essential models for both increasing and decreasing magnitudes of 'r' (see also Figures 2-4). Qualitative differences in dynamical properties take place only within two narrow regions of values of the parameter r. For decreasing values of r, the difference takes place for the regions $r_1 < r < r_3$ (Figure 1c) and $r'_1 < r < r'_3$ (Figure 1d). In particular, in the essential model, there is a cascade of period doubling near the left boundary of the pointed region. The cascade leads to the extremely narrow region of chaotic behavior. In the original model, however, the sequence of the dynamic regimes near the boundary value $r=r_1$ is different. The transition from the chaotic regime to the period 1 oscillations goes consequently through the reverse cascade of period doubling and the period 3 regime. For increasing values of r, qualitative differences of the bifurcation diagrams are significantly smaller: There is a region $(r'_4 < r < r'_3)$ of period 4 oscillations in the diagram of the essential model which is absent in the diagram of the original one.

A general reason for the differences between the essential and original models is discussed in section 3.1.3, item 3: The noted difference indicates that the presented essential model is not valid for control parameter values taken from the rather narrow region near the left boundary and that a special version of the essential model should be elaborated with the purpose of an adequate description of that region. The elaboration of that model, of course, can be achieved by using the previously suggested procedure and characteristic values of variables appropriate to the region of interest. We expect that the required special version of the essential model will be only slightly different from the model (13)-(14) discussed above.

The correlation dimension (see section 2.2.2 and Figure 5) of the essential model is found to be 1.23 ± 0.02 . This value is smaller than that for the original model (1.93 ± 0.02). However, both values correspond to the linear structure of the chaotic attractor 'stroboscopic' section shown in Figure 6. The minimum embedding dimensions (see section 2.2.3) for both the original and essential models are exactly equal. This fact is additional evidence of a qualitative similarity of the both models.

A study of the equilibrium state (see section 2.2.4) for the essential model can be done analytically. The single equilibrium state in the daytime subsystem is determined by the following relations:

$$x_{10} = \frac{\sigma x_{20}^2}{2\gamma r} + x_{20} \left[\left(\frac{\sigma x_{20}}{2\gamma r} \right)^2 + \frac{\beta}{\gamma r} \right]^{1/2}, \ x_{20} = \frac{\delta}{\alpha}. \ (15)$$

....

The eigenvalues of the system linearized near the equilibrium state are given by

$$\lambda_{1,2} = -\frac{\alpha \gamma r}{\delta} \left(1 \pm i \left(\frac{\delta^2}{\gamma r \alpha_{\chi_{10}}} \left(\frac{\beta \delta^2}{\gamma r \alpha_{\chi_{10}}^2} + 1 \right) - 1 \right)^{1/2} \right). (16)$$

It is easy to see that the eigenvalues correspond to either the stable node or the stable focus types of the equilibrium state. For conditions considered in this paper the equilibrium state is of the focus type. The results in Figure 8 point to, at least, a qualitative agreement between the equilibrium state properties for the essential and original models.

The comparison between the dynamic properties and characteristics of the original and essential models confirms our guess that the model whose dynamic behavior is described by (13)-(14), can indeed be considered as the essential dynamic model of the mesospheric photochemical system.

4. Conclusions

In this paper we have attempted to elaborate and investigate the essential dynamic model of the mesospheric photochemical system (PCS). As the original model we have used a model which is similar to that investigated by Fichtelmann and Sonnemann [1992] and Sonnemann and Fichtelmann [1997] and possesses a rich assortment of scenarios of dynamic behavior. We have suggested a general way to reduce the original model of an arbitrary atmospheric PCS to the essential model using a step-by-step procedure. Possessing qualitatively the same dynamic properties and characteristics as the original model, the elaborated essential dynamic model is much simpler. In particular, the essential dynamic model of the mesospheric PCS includes a set of only two ordinary differential equations (ODEs) and nine chemical reactions, while the original model includes set of five ODEs and 16 chemical reactions. We have demonstrated the similarity of the essential and original models in their bifurcation diagrams, correlation dimensions, and minimum embedding dimensions, as well as equilibrium state characteristics. We believe that the elaboration of the essential model of an atmospheric PCS is the first step necessary for studying the possibilities and mechanisms of the PCS nonlinear dynamic behavior. The suggested procedure of obtaining the essential model and the model itself can be used for identifying and studying the mechanisms of nonlinear dynamic behavior of the mesospheric PCSs and for solving a number of problems aimed at revealing nonlinear photochemical phenomena in the actual mesosphere.

Acknowledgments. The authors gratefully acknowledge E. V. Suvorov and V. Y. Trakhtengerts for useful remarks, and L. M. Kagan for the kind assistance in preparing the English version of the paper. Useful discussions with G. Sonnemann and his remarks are much appreciated. We would like to thank the anonymous reviewers for their helpful comments and suggestions that improved the manuscript, and R. D. Saylor for valuable help in improving English language usage. One of the authors (Y. I. M.) is grateful to H. D. I. Abarbanel for his kind permission to use the computer code for calculation of the FNN. This work was supported by the Russian Foundation for Basic Research, grant 96-02-19476.

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(Received July 18, 1997; revised May 4, 1998; accepted May 7, 1998.)

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