Chemical Oscillations Based on Photoautocatalysis of Ozone

Pavel Jungwirth*

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic and Center for Complex Molecular Systems and Biomolecules, Dolejškova 3, 18223 Prague 8, Czech Republic

Abstract

A novel oscillating system with no dark oscillations, possessing a single photochemical autocatalytic feedback loop triggered by VUV photolysis of ozone, is proposed. This gas phase photochemical oscillator is extremely simple, involving only ozone, triplet oxygen radical, molecular oxygen, and one additional species, which provides the necessary destabilizing exit reaction. The phase diagram for the suggested system is constructed, and experimentally realistic values of rate constants and light intensity corresponding to the oscillatory regime are found.

* e-mail: jungwirt@jh-inst.cas.cz, FAX: ++420-2-8582307

I. INTRODUCTION

Oscillatory reactions represent arguably the most interesting manifestation of non-equilibrium thermodynamics in chemistry. The nature of chemical oscillations is well understood today and their basic classification has been completed during the last decade [1-3]. Despite this fact, the number of known oscillatory chemical reactions is severely limited and there are still many unsolved problems. One of the remaining open questions concerns the effect of radiation on oscillating chemical systems, which has attracted a considerable interest recently [4-12].

Light represents a very convenient tool, which allows to investigate oscillating chemical systems by continuously changing the irradiation frequency and intensity. Typically, radiation is used to inhibit or amplify existing oscillations via a photochemical reaction, which produces or consumes essential species in the positive or negative feedback loop. This is, for example, the case of photoinduced bifurcations in the $[Ru(bpy)_3]^{2+}$-catalyzed Belousov-Zhabotinsky system, where the catalyst strongly absorbs in the visible region [8-9]. Photoinduced multistability or broadening of the oscillatory region can also occur due to the screening effect, when light is absorbed by more than one species and there is a nonlinear competition in the absorption [11-12].

In principle, radiation can also directly cause chemical oscillations by providing a positive feedback. In such a photoautocatalysis [6], a photochemical process is involved as a key step in the autocatalytic loop. The resulting chemical oscillator has unique properties in the sense that its behavior could be most directly controlled by the light properties (i.e., intensity and/or frequency). Although no evidence on a purely photoautocatalytic oscillatory system has been reported yet, an additional photochemical feedback loop has been described recently for the Briggs-Rauscher system, and the appearance of an additional oscillatory state and multiple stability have been demonstrated [6]. In this Letter, we suggest and explore a novel photochemical oscillatory system with no dark oscillations, possessing a single autocatalytic loop triggered by radiation. Namely, we consider a two-step autocatalytic process, in which ozone is photolyzed by VUV radiation into three triplet oxygen radicals to reform back O_3 in a standard atmospheric Chapman reaction with molecular oxygen [13]. We show, that upon adding one more essential species this gas phase photochemical process exhibits oscillations for realistic values of rate constants, and we discuss a possible experimental realization of the system.

II. MODEL

UV photolysis of ozone in the stratosphere proceeds dominantly towards the ${}^3O +{}^3 O_2$ and ${}^1O +{}^1 O_2$ exit channels [14]. However, at 198 nm a fragmentation channel into three triplet oxygen radicals opens [15-16]. Due to this fact, the total photochemical yield of oxygen radicals (triplet or singlet) exceeds unity for wavelengths shorter than 198 nm. For example, at 157.6 nm this yield reaches 1.9, out of which the yield of production of ${}^3O$ is 1.35 [17]. Once the latter yield becomes larger than 1, ozone can be reformed autocatalytically. This is due to a combination of VUV photolysis and the Chapman reaction [13]:

$$O_3 + h\nu \xrightarrow{k_1} 3{}^3O \tag{1}$$

$$3({}^3O +{}^3 O_2 + M \xrightarrow{k_2} O_3 + M) \tag{2}$$

We mention by passing, that we have considered the above processes with the intense solar Lyman-α line at 121.6 nm as a possible additional source of triplet oxygen radicals to produce ozone in the upper stratosphere and mesosphere. However, due to a low ozone concentration (around 1 ppm at these altitudes [14]) reaction (1) cannot compete with the standard ${}^3O$ production initiated by photolysis of molecular oxygen. Therefore, within a simple atmospheric model the new mechanism leads only to a minor increase of less than 0.1% of the ozone concentration.

An autocatalytic feedback loop, such as that given by Eqs. 1-2, is a necessary but not sufficient condition for an oscillating chemical system. Actually, since reactions 1-2 represent a critical cycle with respect to the ^3O radical, and additional species Y involved in a destabilizing exit reaction is needed to create oscillations [1]. We have found that four additional reactions listed below form with reactions 1-2 an oscillatory chemical system:

$$^3O + Y \xrightarrow{k_3} \tag{3}$$

$$\xrightarrow{k_4} {}^3O_2 \tag{4}$$

$$\xrightarrow{k_5} Y \tag{5}$$

$$Y \xrightarrow{k_6} \tag{6}$$

Although reactions 1-6 are sufficient for creating oscillations, additional three processes concerning the ^3O, $^3O_2$, and O_3 species and VUV radiation necessarily occur and should, therefore, be included [14]:

$$^3O + ^3O + M \xrightarrow{k_7} {}^3O_2 + M \tag{7}$$

$$^3O_2 + h\nu \xrightarrow{k_8} {}^3O + ^3O \tag{8}$$

$$^3O + O_3 \xrightarrow{k_7} 2^3O_2 \tag{9}$$

Finally, we add exit reactions for the O_3 and $^3O_2$ species.

$$O_3 \xrightarrow{k_{10}} \tag{10}$$

$$^3O_2 \xrightarrow{k_{11}} \tag{11}$$

Although the last two reactions are not essential for the oscillations in the present photochemical system, they remove divergences in concentrations in the non-oscillatory region of the parameter phase space corresponding to small values of light intensity.

Thus, the present model of an oscillating chemical system based on photoautocatalysis of ozone is defined by Eqs. 1-11. Several simplifications have been made, which, however, can in principle be dropped without qualitatively changing the model. First, we have assumed that ozone photolysis at the employed VUV frequency proceeds solely via reaction 1. This certainly exaggerates ^3O production. However, for the photoautocatalysis to take place it is sufficient that the production of triplet oxygen radicals exceeds unity, which is fulfilled for wavelengths shorter than 160 nm [17]. Second, we have neglected the channel leading to singlet species in reaction 8, and triplet to singlet conversions of oxygen radicals in general. This is well justified, since these conversions are generally very slow, moreover, reaction 8 is non-essential and rather unimportant with respect to the oscillatory behavior.

The differential equations 1-11 have been solved numerically using an integrator for stiff systems of ordinary differential equations written by Deuflhard et al. [18-20]. Bifurcation analysis has been performed with the use of the program CONTENT [21].

III. RESULTS AND DISCUSSION

Out of the eleven reactions presented in the previous section, three (2, 7, and 9) have unambiguously defined rate constants assuming ambient conditions [14]. For reactions 3-6 there is a certain degree of flexibility due to the fact that neither the species Y nor the source of molecular oxygen is exactly specified, however, the values of rate constants should remain within chemically reasonable margins. The same degree of flexibility is present also for rate constants for reactions 10-11, the value of which can be tuned by a suitable choice of O_3 and $^3O_2$ exit processes. Reactions 1 and 8 proceed photochemically, therefore, their rate constants are given as products of light intensity and the corresponding absorption cross-section of a given species (O_3 or $^3O_2$) for a chosen VUV wavelength. For example, at wavelengths of 121.6 nm, which we have considered here, O_3 absorption cross-section is $10^{-17} cm^{-2}$, while that of O_2 is three orders of magnitude smaller, amounting to $10^{-20} cm^{-2}$

[22-23]. Thus, assuming experimentally accessible, non-destructive light intensities smaller than say $1kWcm^{-2}$, we get for the 121.6 nm wavelength for k_1 possible values from 0 to $6 \times 10^4 s^{-1}$, with k_8 being thousand times smaller.

By scanning the rate constants k_3 - k_6, k_{10} - k_{11}, and the light intensity we have allocated the oscillatory region of the system defined by reactions 1-11. Typical values of rate constants giving chemical oscillations are presented in Table 1. Note, that rate constants k_2, k_7, and k_9 are held at their experimental values corresponding to 300 K [14,24-25]. Photochemical rate constants k_1 and k_8 correspond to a light intensity of $0.17Wcm^{-2}$, which is a relatively small value easily accessible by UV lamps or lasers. Finally, rate constants k_3 - k_6 and k_{10} - k_{11} acquire chemically reasonable values, which should make the search for a suitable species Y and exit processes for O_3 and $^3O_2$ relatively straightforward.

For the rate constants given in Table 1, the oscillatory behavior of the four species involved, O_3, ^3O, $^3O_2$, and Y, is depicted in Figure 1. All these chemical species oscillate with a period of approximately 8 s. The average concentration of $^3O_2$, which is the dominant species in the system under given conditions, amounts to $4 \times 10^{18} cm^{-3}$. This corresponds at 300 K to a pressure of 15 kPa, about 15% of the normal value corresponding to ambient conditions. We also note, that the present oscillatory system is, putting aside the photochemical character of its feedback loop, of the type of models studied by Franck [26], or of the 1CX system from Ref. 1.

Figure 2 depicts an equilibrium diagram, i.e. the dependence of the equilibrium O_3 concentration on the rate constant k_1 (which is proportional to the light intensity), for values of the remaining rate constants k_2 - k_{11} taken from Table 1. For values of k_1 larger than 0.1 s^{-1} the equilibrium O_3 concentration is inversely proportional to the light intensity, while for $k_1 \rightarrow 0$ the ozone concentration sharply drops to zero, too. Most importantly, at a point $k_1 = 3.243 s^{-1}$ and $O_3 = 1.744 \times 10^{17} cm^{-3}$ a Hopf bifurcation occurs.

A further insight into the system under investigation is obtained by following the above Hopf bifurcation in two significant rate constants. Figs. 3a and 3b show such a phase diagram in rate constants $k_1 \mid k_4$ and $k_1 \mid k_5$. We have chosen k_1, since it is directly proportional to the light intensity, and the inflow rates k_4 and k_5 of the two species $^3O_2$ and Y, which are pumped into the system. Both phase diagrams depicted in Fig. 3 shows three distinct regions. The most important and interesting is the oscillatory region, which is bound from below, i.e. disappears for small values of the light intensity. Regions of stable solutions for all species involved lie both above and below the oscillatory region (see Fig. 3). Stable solution I, which corresponds to a small O_3 equilibrium concentration, occurs for small values of k_4 or large values of k_5, while the opposite is true for stable solution II with a large value of the equilibrium value of ozone.

The above described phase behavior is demonstrated also in Fig. 4, which depicts the evolution of the O_3 concentration for three values of the influx of species Y, corresponding to the three distinct regions of the phase diagram. First, for intermediate values of the rate constant k_5 sustained oscillations develop. Second, for low values of k_5 the O_3 concentration initially grows rapidly, but levels off for longer times. Finally, for high values of this rate constant a stable solution corresponding to a low concentration of O_3 is reached fast after few dumped oscillations.

For a possible experimental realization of the proposed oscillatory system based on ozone photoautocatalysis a suitable species Y should be chosen. Since the triplet oxygen radical is a highly reactive species, there is a plethora of molecules which could be involved with it in a exit process analogous to reaction 3. Out of these, molecules which react with ^3O with a rate constant similar to k_3 (see Table 1), should be considered. We stress here again, that the required value of the rate constant k_3 is chemically very realistic. Finally, reactions 4-6, which supply $^3O_2$ and Y, and remove Y from the system, can proceed either chemically or photochemically. The right values of the corresponding rate constants (see Table 1) can be adjusted by a proper choice of the precursors and the Y species.

IV. CONCLUSIONS

In this Letter we have proposed a novel oscillatory gas phase chemical system based on photoautocatalysis of ozone. Only four essential chemical species are necessary to create oscillations - ozone, triplet oxygen radical, molecular oxygen, and an additional species Y, which provides a negative feedback and is characterized by required values of rate constants. This is probably the first oscillatory system with no dark oscillation, possessing a single autocatalytic feedback loop, triggered by radiation. Finally, we have shown, that oscillatory behavior appears for realistic values of chemical rate constants and VUV light intensity, which should enable experimental realization of the process.

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Table 1

Values of rate constants $k_1 - k_{11}$ corresponding to photochemical oscillatory presented in Fig. 1.

k_1	$10s^{-1}$
k_2	$6.2 \times 10^{-34} cm^6 s^{-1}$ [23]
k_3	$10^{-13} cm^3 s^{-1}$
k_4	$6 \times 10^{17} cm^{-3} s^{-1}$
k_5	$4 \times 10^{18} cm^{-3} s^{-1}$
k_6	$10s^{-1}$
k_7	$4.8 \times 10^{-33} cm^6 s^{-1}$ [24]
k_8	$10^{-3} k_1$
k_9	$8.3 \times 10^{-15} cm^3 s^{-1}$ [24]
k_{10}	$10^{-1} s^{-1}$
k_{11}	$10^{-2} s^{-1}$

FIGURE CAPTIONS

Fig. 1: Oscillations of the a) O_3, b) ^3O, c) $^3O_2$, and d) Y species. Values of the corresponding rate constants are given in Table 1. Initial concentrations have been set to $O_3(0) = 10^{17} cm^{-3}$, $^3O(0) = 10^{14} cm^{-3}$, $^2O_2(0) = 10^{18} cm^{-3}$, and $Y(0) = 10^{17} cm^{-3}$.

Fig. 2: Equilibrium diagram in rate constant k_1 (proportional to the light intensity) and O_3 concentration with a Hopf bifurcation. Values of the remaining rate constants are given in Table 1.

Fig. 3: Hopf bifurcation separating the oscillatory region from those corresponding to one or the other stable solution in coordinates k_1 (proportional to the light intensity) and a) k_4 (influx of $^3O_2$), or b) k_5 (influx of Y). Values of the remaining rate constants are presented in Table 1.

Fig. 4: Time evolution of the O_3 concentration in the oscillatory ($k_5 = 4 \times 10^{18} cm^{-3} s^{-1}$), stable with small O_3 concentration ($k_5 = 8 \times 10^{18} cm^{-3} s^{-1}$), and stable with large O_3 concentration ($k_5 = 8 \times 10^{17} cm^{-3} s^{-1}$) regime of the investigated system. Values of the remaining rate constants are printed in Table 1.

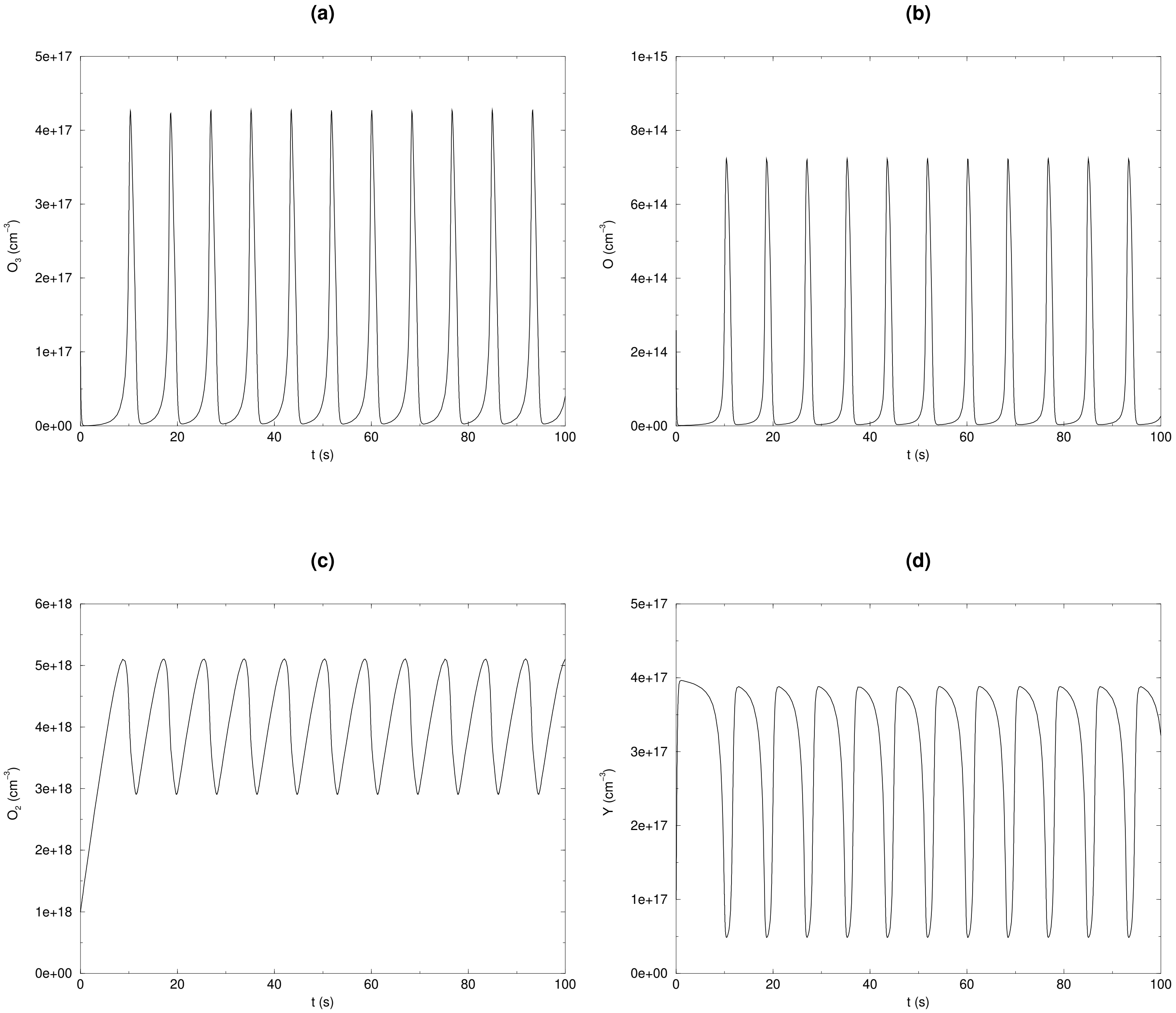
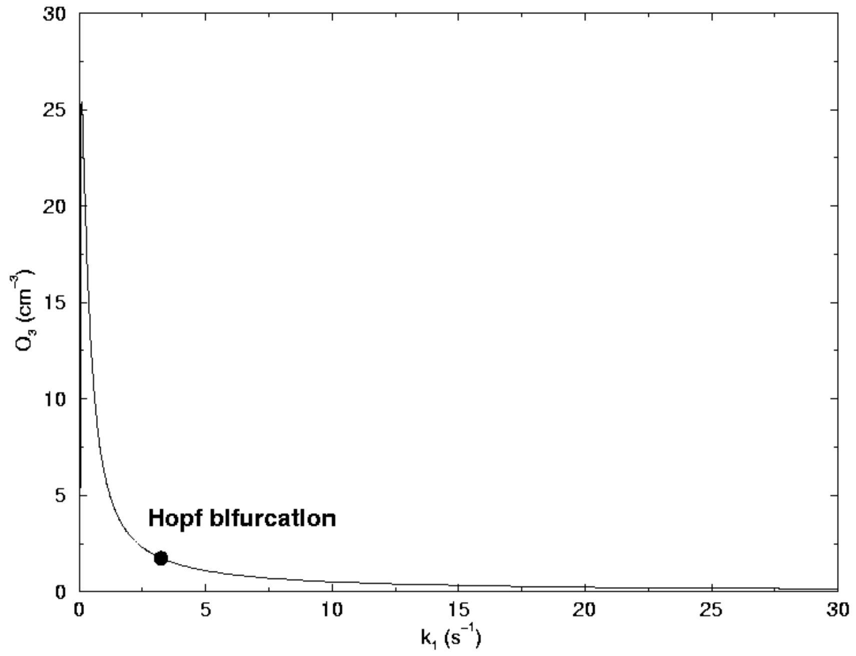


Figure 1, Jungwirth:

Figure 2, Jungwirth:



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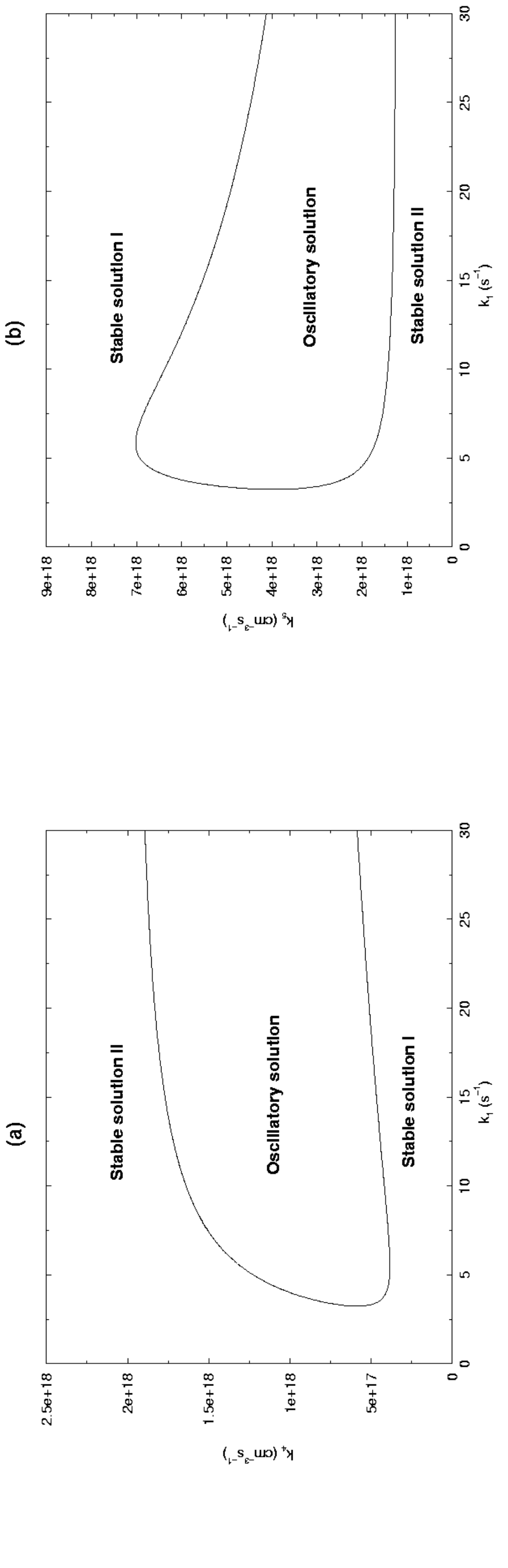

Figure 4, Jungwirth: