ABSTRACT The influence of external noise on the steady-state properties of a chemical system with very simple kinetics was studied. We dealt with an isomerization reaction, in a closed system, coupled to a light absorption and radiationless deexcitation process involving only one of the isomers. The theoretical analysis established that external noise deeply modified the macroscopic properties of the system and even induced transition phenomena that are totally unexpected from the usual deterministic description.

1. Introduction

Our objective in this paper is twofold. (i) We want to show that the properties of illuminated chemical systems strongly depend on the magnitude of the intensity fluctuations of the light source. When these fluctuations grow in amplitude, various transition phenomena can be predicted that are unexpected from a deterministic point of view. They correspond to situations in which the systems no longer adjust their macroscopic behavior to the average properties of the environment. Even in first approximation, the usual bifurcation diagrams, obtained for nonfluctuating environments, then become irrelevant. (ii) We want to investigate the manner in which the theoretical predictions that we derived recently (1-3) for model systems apply for illuminated chemical reactions that seem particularly well suited for experimental studies. Compared with other chemical systems that have already been used experimentally in order to test the influence of external noise (4), the systems considered here have the advantage of kinetic simplicity. A thorough theoretical analysis is therefore possible.

The situation studied corresponds to an isomerization reaction in which one of the isomers absorbs light of a given frequency and restores this energy to the system in the form of heat. When the formation of the light-absorbing isomer is exothermic, the rise of the system’s temperature and the light absorption process become autocatalytically coupled: the more isomer present, the more light can be absorbed, the more the temperature rises, and the temperature variations due to the energy fluxes in the form of light and of heat exchanged with the external reservoir. I is a positive or negative feedback effect on the temperature of the system according to whether $\Delta H$ in Eq. 3 is negative or positive.

Nitzan and Ross (5) demonstrated that this kind of system can exhibit bistability phenomena and limit cycle behavior comparable to those usually described in isothermal chemical reaction–diffusion systems (8). The concentration of A and the temperature $T$ inside the system obey the kinetic equations:

$$\frac{dA}{dt} = -(k_1 + k_2)A + k_2A$$

$$\frac{dT}{dt} = \alpha A + \beta(T - T_0) - \lambda \frac{dA}{dt},$$

with $\alpha = A + B = \text{constant}$. The first two terms in Eq. 5 describe the temperature variations due to the energy fluxes in the form of light and of heat exchanged with the external reservoir. $I$ is the light intensity. The third term in Eq. 5 describes the heat generated by the chemical reaction itself. $\alpha$, $\beta$, and $\lambda$ are proportionality constants characteristic of the reaction and of the experimental setup considered. In the following we assume that the time scale of Eq. 4 is fast compared with that of Eq. 5, which allows the adiabatic elimination of $A$ from Eq. 5. Introducing the dimensionless variables

$$x = T/T_0, \quad \alpha = \alpha A/\beta T_0, \quad \Delta T = -\Delta H/RT_0, \quad \tau = \beta t,$$

exothermic reactions, the domain of parameter values for which a phase transition takes place is considerably enlarged; and (iii) this latter domain contains a region in which a “secondary” type of phase transition can be observed. This phenomenon corresponds to the appearance of a trinomial probability density for the temperature of the system and has no equivalent under constant illumination.

2. Nitzan–Ross system and its deterministic steady-state properties

2.1. The Model. We consider a closed chemical system in which an isomerization reaction of the form

$$A \leftrightarrow B$$

is coupled with a light absorption and radiationless deexcitation process

$$A + hv \rightarrow A^* \rightarrow A + \text{heat}$$

involving only one of the components. We are interested in the case in which process 2 is fast compared to process 1 and we suppose that the system as a whole is uniform. The energy absorbed in the form of light and transformed into heat keeps the system out of thermal equilibrium with respect to an external reservoir having a constant temperature $T_e$. The chemical transformation of B into A exerts, through the temperature dependence of the equilibrium constant

$$k_1/k_2 = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) = \epsilon K(T),$$

a positive or negative feedback effect on the temperature of the system according to whether $\Delta H$ in Eq. 3 is negative or positive.

In Section 2 we summarize the steady-state properties of the Nitzan–Ross system under constant illumination. We then incorporate in Section 3 the influence of light intensity fluctuations into the description. Three effects are shown to occur solely by changing the variance of these fluctuations: (i) hysteresis may be induced even when the formation of the light-absorbing chemical component is endothermic; (ii) in some cases bistability and limit cycle behavior can be observed and (iii) these fluctuations can lead to the appearance of a “secondary” type of phase transition.
Eqs. 4 and 5 then reduce to the simple one-variable system

\[
\frac{dx}{d\tau} = \frac{\alpha}{1 + \epsilon \exp(\Delta r/x)} - x + 1. \tag{7}
\]

2.2. Steady-State Properties under Deterministic (Constant) Illumination. In Fig. 1 we have sketched the steady-state solutions \(x_s\) of Eq. 7 as a function of \(\alpha\) for different values of \(\Delta r\) and a fixed value of \(\epsilon\). According to the sign of \(\Delta r\) one observes:

(i) For \(\Delta r < 0\) (i.e., for endothermic reactions), the steady-state curves \(\alpha = \alpha(x_s)\) are monotonously increasing functions of \(x_s\). When the light intensity increases, the slope of the curves increases continuously from \(1 + \epsilon \exp(\Delta r)\) (for \(x_s = 1\)) towards \(1 + \epsilon\) (for \(x_s \rightarrow \infty\)). Whatever the values of \(\alpha\) and \(T_o\), one has \(d\alpha/d\tau > 0, d^2\alpha/d\tau^2 > 0\) (for \(x_s > 1\)).

(ii) \(\Delta r = 0\) is a transition point beyond which there always exists in the interval \([1, \infty)\) a value of \(x_s\) at which \(d^2\alpha/d\tau^2\) changes sign. At this point, a simultaneous change of sign occurs for \(d\alpha/d\tau\) provided \(\alpha\) and \(\epsilon\) verify the equality

\[
\frac{4}{\beta T_o} = \frac{\alpha}{\alpha - 2}; N = \frac{4}{\alpha - 4}. \tag{8a}
\]

3. Steady-state properties for a fluctuating light source

For the sake of mathematical convenience we shall, in this first approach, describe the effect of a white noise kind of fluctuating light source. This idealization is justified if the correlation time of the intensity fluctuations is short compared to the characteristic time of the macroscopic evolution of the system. We thus assume that \(\epsilon \ll \sigma^2\) and \(\sigma^2\) is the variance of the fluctuations. In the white noise case, the system is described by a diffusion process and we associate to Eq. 7 the stochastic differential equation (9, 10):

\[
\frac{dx}{d\tau} = \left(\frac{\alpha}{1 + \epsilon \exp(\Delta r/x)} - x + 1\right) + \frac{\sigma}{\sqrt{\tau}} dW, \tag{9}
\]

\[
= f(x) d\tau + G(x) dW, \tag{10}
\]

in which \(\alpha\) now represents the value corresponding to the mean \(I\). We interpret Eq. 10 as an Itô equation. The associated Fokker–Planck equation reads

\[
\frac{\partial p(x, \tau)}{\partial \tau} = -\frac{\partial}{\partial x} \left(f(x)p(x, \tau) + \frac{1}{2} \frac{\partial^2}{\partial x^2} G^2(x)p(x, \tau)\right). \tag{11}
\]

In view of finding a physically acceptable steady-state solution to Eq. 12, we first notice that the realizations of the process \(x\) must be restricted to the semiclosed interval \([1, \infty)\). At \(\infty\) this condition is ensured. Indeed, the analytical condition that \(\infty\) be a natural boundary is that

\[
L = \int \exp \left(-\frac{\sigma^2}{2} G^2(z) dz\right) \frac{dx}{x} \geq 0 \tag{12a}
\]

be infinite. It is easily seen that this is the case. On the contrary, the equivalent condition for \(x = 1\) to be a natural boundary is not fulfilled. This is a consequence of the facts that it is not an intrinsic boundary of the problem and that the white noise idealization allows negative realizations for \(I\). We shall remedy this difficulty by imposing the condition that the solution of \(x\), of Eq. 10 be always bigger than or equal to 1. This implies that the process \(x\) undergoes a delayed reflection on the boundary \(x = 1\), meaning that it spends a positive length of time on this boundary.

With these boundary conditions, the stationary distribution function \(F(x)\) reads (10):

\[
F(x) = \begin{cases} \frac{1 + 2f(1)}{N} & \text{if } x < 1 \\ \frac{1}{N} + \frac{2f(1)}{G^2(x)} \int_{x}^{\infty} \frac{\Phi(z)}{G^2(z)} dz & \text{if } x \geq 1 \end{cases} \tag{13}
\]

in which

\[
\Phi(z) = \exp \int_{x}^{\infty} \frac{2f(z')}{G^2(z')} dz' \tag{14}
\]

and

\[
N = 1 + 2f(1) \int_{x}^{\infty} \frac{\Phi(z)}{G^2(z)} dz. \tag{15}
\]

The "probability density" of Eq. 14 is:

\[
p_x(x) = \frac{\delta(x - 1) - 2f(1) \Phi(x)}{N} G^2(x). \tag{16}
\]

The first term is a \(\delta\) function weighted by the factor \(1/N\) and represents the probability density of finding the process on the boundary \(x = 1\). The extrema \(x_m\) of Eq. 17 in the interval \([1, \infty)\), which usually are identified with the macroscopic steady-state values, can be calculated from the relation:

\[
\int_{x_m}^{\infty} \frac{\Phi(z)}{G^2(z)} dz = 0, \tag{18}
\]

which yields, after expressing \(\alpha\) in terms of \(x_m\),

\[
\alpha = \frac{1 + \epsilon \exp(\Delta r/x_m)(x_m - 1)}{\epsilon \exp(\Delta r/x_m)} + \frac{\sigma^2}{x_m^2}(1 + \epsilon \exp(\Delta r/x_m))^2. \tag{19}
\]
Remark that the Stratonovic interpretation of Eq. 10 only amounts to replacement of $\sigma^2$ by $\bar{\sigma}^2/2$ in this expression. Figs. 2 and 3 report the conditions for which the curves, given by the relation 18, admit a critical point—i.e., values of the parameters of $\Delta r$, $\epsilon$, and $\bar{\sigma}^2$ for which there exists on the curve $\bar{\alpha} = \bar{\alpha}(x_m)$ a physically acceptable value at which $d\bar{\alpha}/dx$, and $d^2\bar{\alpha}/dx^2$ vanish simultaneously. The curves in Fig. 2 represent the values of $\Delta r$ and $\epsilon$ for which this condition is realized. The $(\Delta r - \epsilon)$ phase space subdivides essentially into four regions.

(i) In area (a), $P_x(x)$ admits only one extremum (besides the $\delta$ peak at $x = 1$, which in any case is always present) whatever the magnitude of the external fluctuations—i.e., the value of $\bar{\sigma}^2$.

(ii) In (b), despite the fact that $\Delta r < 0$, the probability density $P_x(x)$ is double peaked over a finite range of values of $\bar{\sigma}^2 - 0.5$ $e = 6.34 \times 10^{-13}$ $a^3$

FIG. 4. Location of the extrema of the probability density for an example chosen in domain (b). The curves are plotted for various values of $\bar{\sigma}^2$ and $\bar{\alpha}$. This situation is illustrated in more detail in Figs. 4 and 5. In Fig. 4 the curves of the extrema, as given by Eq. 18, have been plotted for a particular choice of the pair of parameters $(\Delta r, \epsilon)$ and various values of $\bar{\sigma}^2$. Hysteresis occurs for $\bar{\sigma}^2 > 0.2$. When $\bar{\sigma}$ increases beyond this value, this hysteresis phenomenon becomes more and more important and simultaneously shifts towards lower values of $\bar{\alpha}$. Let us point out that the new peak of the distribution, induced by the fluctuations of $I$, corresponds to internal temperatures that are higher than in the deterministic case. This effect is also clearly seen in Fig. 5, where the probability density $P_x(x)$ has been plotted for three values of $\bar{\sigma}^2$ and $\bar{\alpha} = 0.07$. In the case represented, the $\delta$ peak at $x = 1$ grows rapidly while the peak corresponding to the deterministic steady state disappears. As a result, the average

$$Ex = \int_1^\infty xP_x(x)dx$$

changes very little when $\bar{\sigma}^2$ increases, despite the presence of a peak that continuously moves to higher values of $x$—e.g., at $\bar{\sigma}^2 = 0.1$ and $\bar{\sigma}^2 = 1$, one finds, respectively, $Ex = 1.067$ and $Ex = 1.063$.

(iii) In (c), Eq. 18 exhibits hysteresis. However, contrary to what happens in (ii), this hysteresis amounts to the appearance of a peak near $x = 1$. Since this domain contains the deterministic critical curve given by Eqs. 8, it subdivides into two regions: to the left of curve 1 (see Fig. 2) there is no hysteresis under deterministic conditions. When the value of $\epsilon$ is fixed and $\Delta r$ increases from curve 2 to curve 1, hysteresis appears provided that $\bar{\sigma}^2$ is greater than some finite critical value (see $\sigma_1$
FIG. 5. Plot of the probability density for three values of $\sigma^2$, the other parameters being chosen in region (b). The large dots on the ordinate correspond to the probability density on the boundary $x = 1$ for the values of $\sigma^2$ indicated.

curve in Fig. 3). This value tends to zero as $\Delta r$ approaches curve 1. To the right of curve 1, the effect of the fluctuations amplifies a hysteresis phenomenon already existing for $\sigma^2 = 0$ and shifts the hysteresis loop towards larger values of $\alpha$.

(iv) The domain marked (d) has properties that are specific for the fluctuating system and do not show up in any deterministic treatment. Its particularity is to admit a range of values $\sigma_2 < \sigma^2 < \sigma_3$ for which $p_s(x)$ may be trimodal (see Fig. 3) depending on the values of $\alpha$. The behavior of the extrema is displayed in Fig. 6. As can be seen from Fig. 7, where the stationary probability density is represented (for the values of the parameters indicated), the noise-induced middle peak may even dominate the one in the neighborhood of $x = 1$ ($x_m \approx 1.008$). The trimodal behavior might be difficult to detect experimentally for this specific example since the absolute maximum of $p_s(x)$, located near $x = 1.3$, is larger by about two orders of magnitude. Another feature of region (d) is that on increasing $\sigma^2$, the absolute maximum, near $x = 1.3$ for small variances, switches to the peak near the boundary $x = 1$. This shows that the effect of the fluctuations manifests itself not only on the most probable values of the system, but also in a shift of the mean value (Eq. 19), as can be seen from Table 1.

4. Conclusions

An important aspect of the above results is the fact that the region in which hysteresis occurs for deterministic external constraints is for all values of $\Delta r$ and $\epsilon$ entirely contained in the domain in which hysteresis may be observed under fluctuating environmental conditions. This implies that under experimental conditions one may expect a shift of the critical points, corresponding to the onset of a chemical instability, which will be more important the larger the fluctuations of the light intensity. Only if these fluctuations are absolutely eliminated will the transition occur on transition line 1 in Fig. 2.

\footnote{$\sigma_1$ vanishes as a power of the distance from the deterministic critical point.}

The results reported above confirm and further exemplify the importance of taking into account the influence of environmental fluctuations in the description of nonequilibrium systems. It is striking to see that an environment that fluctuates, even if only in a highly incoherent way (i.e., with a very short correlation time and no preferred states), can induce such complex steady-state properties as, e.g., those of region (d) in Fig. 2 in chemical systems whose kinetics is about the simplest one can think of. Under deterministic external constraints, behaviors of the same type are possible only for much more complex reaction schemes [see, for example, the enzymatic systems described by Bunnow and Colton (11)]. This underlines once more that external noise should not in all cases be considered as a nuisance "unfortunately" perturbing an "ideal system," but on the contrary could play an important role by allowing for phenomena that would be impossible in a constant environment. This new viewpoint is of considerable interest.

We would like to express our opinion that it is especially important to explore its relevance in biological systems. Indeed, as a general rule, the natural processes of development and self-organization that take place in living systems are subjected

<table>
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<tr>
<th>$\sigma^2$</th>
<th>$\delta(x - 1)$</th>
<th>$P_s(x_{m1})$</th>
<th>$P_s(x_{m3})$</th>
<th>$E_x$</th>
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<tr>
<td>0.008</td>
<td>$9.35 \times 10^{-13}$</td>
<td>$2.12 \times 10^{-3}$</td>
<td>6.74</td>
<td>1.297</td>
</tr>
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<td>0.01</td>
<td>$7.58 \times 10^{-9}$</td>
<td>$1.15 \times 10^{-1}$</td>
<td>5.63</td>
<td>1.297</td>
</tr>
<tr>
<td>0.013</td>
<td>$9.84 \times 10^{-7}$</td>
<td>1.29</td>
<td>4.85</td>
<td>1.292</td>
</tr>
<tr>
<td>0.0189</td>
<td>$2.50 \times 10^{-4}$</td>
<td>17.4</td>
<td>3.14</td>
<td>1.236</td>
</tr>
<tr>
<td>0.05</td>
<td>$3.89 \times 10^{-2}$</td>
<td>75.1</td>
<td>$3.83 \times 10^{-1}$</td>
<td>1.049</td>
</tr>
</tbody>
</table>

Given are the probability of being at the boundary $x = 1$, the height of the peak closest to 1 ($1.004 < x_m < 1.009$), that of the peak at $x_m \approx 1.3$, and the mean value $E_x$ for $\epsilon = 6.34 \times 10^{-39}$, $\Delta r = 92.2$, and $\sigma = 0.3$. 

Table 1. Parameters of the probability density for different values of $\sigma^2$. 

FIG. 6. Plot of the extrema of the probability density for an example chosen in domain (d).
to extremely complex environmental conditions and are con-
trolled by a multitude of environmental factors (e.g., pH, salt
concentration, light, humidity, and nutrients). Because of this
complexity, fluctuations of the "environmental state" are un-
avoidable and in many instances one may look into the effect
of these fluctuations on the functioning and organization of
biological systems as a whole. Do biological systems feel and
respond only to the average properties of the external world or
is it also possible that some macroscopic manifestations of bi-
ological order are "forced" by environmental randomness? Some
attempts have been made to deal with this question in an eco-
logical context (12). The results that we report here for ex-
tremely simple physicochemical systems suggest, however, that
it is meaningful to consider this problem within a much broader
perspective. Such a variable as light controls a wealth of fund-
damental biological phenomena related to bioenergetics, dif-
ferentiation, motion, and enzyme kinetics. As examples one
may mention the light-induced synthesis of ATP by bacte rio -
rhodopsin in Halobacterium halobium (13), the phototaxis of
Dictyostelium discoideum in which light at some intensities
increases the rate of migration by stimulating the sheath for-
mation while at strong intensities it induces the reverse reaction
(14, 15), the light-stimulated morphogenesis in the fruiting
Myxobacterium stigmatella aurantiaca (16), and the pho-
toenhancement of the specific activity of the enzyme chymo-
trypsin (17). In the analysis of all such problems the question
of the influence of light intensity fluctuations may be raised.

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