“NEGATIVE TEMPERATURES” IN REVERSIBLE PHOTOCHEMICAL REACTIONS

1963

SovietRxiv

Abstract

Full Text

Physical Chemistry

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"NEGATIVE TEMPERATURES" IN REVERSIBLE PHOTOCHEMICAL REACTIONS

(Presented by Academician N. N. Semenov, 18 IV 1963)

The chemical properties of molecules in electronically excited states differ substantially from the properties of the ground state ([1,2]). In particular, there is a series of very rapid reversible reactions for which the equilibrium constants in the ground (K) and excited (K^*) states differ by several orders of magnitude ([2–7])

$$\begin{aligned} \mathrm{A}^* \rightleftarrows \mathrm{B}^* \qquad K^* &= \frac{[\mathrm{B}^*]}{[\mathrm{A}^*]}, \\ \mathrm{A} \rightleftarrows \mathrm{B} \qquad K &= \frac{[\mathrm{B}]}{[\mathrm{A}]} \end{aligned} \tag{1}$$

Such a scheme corresponds to the four-level system shown in Fig. 1 (B may be either a singlet or a triplet state). This opens up the possibility of obtaining "negative temperatures" in solutions of the corresponding compounds when they are irradiated with light of sufficient intensity. For a negative temperature to arise with respect to the transition $\mathrm{B} \rightleftarrows \mathrm{B}^*$ or $\mathrm{A} \rightleftarrows \mathrm{A}^*$, it is necessary that

$$[\mathrm{B}^*] > [\mathrm{B}] \quad \text{or} \quad [\mathrm{A}^*] > [\mathrm{A}]. \tag{2}$$

Consider the first case, realized when $K \ll K^*$ (when $K \gg K^*$, we obtain the second case, symmetric to the first). We have

$$[\mathrm{B}] = K[\mathrm{A}], \quad [\mathrm{B}^*] = K^*[\mathrm{A}^*]. \tag{3}$$

If $K \ll 1$, while $K^* > 1$ (which for the most part can be achieved by choosing the appropriate conditions), then almost all unexcited molecules will be in the form A, and the excited ones in the form B^*. Then, for an effective lifetime of the excited molecules τ, an excitation rate w_0 (equal to the number of quanta absorbed by substance A per unit volume per second), and a quantum yield of excitation φ ($\varphi \approx 1$ for singlet states and $\varphi < 1$ for triplet states), we have

$$[\mathrm{B}^*] \simeq [\mathrm{B}^*] + [\mathrm{A}^*] = w_0 \tau \varphi.$$

Fig. 1. Four-level system with chemical equilibria

Figure 1: Fig. 1. Four-level system with chemical equilibria

To have $[B^*] > [B]$, it is necessary that

$$w_0 \tau \varphi > K[A]. \tag{4}$$

Inequality (4) is the condition for obtaining a "negative temperature."In practice (see below), $[A] \sim 10^{-4}$ mol/l $\simeq$

Fig. 1. Four-level system with chemical equilibria

$\simeq 10^{17}$ molecules/cm^3. For singlet excited states $\tau \sim 10^{-8}$ sec and $K^*/K \sim 10^6$ ($K^* \sim 10$, $K \sim 10^{-5}$); then $w_0 > 10^{20}$ molecules/sec $\cdot$ cm^3. For triplet states $\tau \sim 10^{-3}$–10 sec*, $K^*/K \sim 10$–10^2, and $w_0 > 10^{19}$–10^{17} molecules/sec $\cdot$ cm^3. Such excitation rates are quite feasible, both in a continuous regime and, all the more, in a pulsed regime.

It is necessary to emphasize that the absorption and emission spectra of A, A* and B, B* differ substantially from one another. The difference of the frequencies of the luminescence maxima is equal to (2)

$$\nu_A - \nu_B = \frac{\ln K^* - \ln K}{hRT_1}$$

(since the entropies of the transformations $A \rightleftarrows B$ for the ground and excited states are approximately the same).

For singlet–singlet transitions in molecules of organic compounds, the oscillator strengths are sufficiently large ($\tau_{\text{rad}} \sim 10^{-8}$ sec, $\gamma \sim 10^{-2}$ cm^{-1}). Therefore, despite the large width of the spectral bands ($\Gamma \sim 10^3$ cm^{-1} $\neq 3 \cdot 10$ sec^{-1}), the absorption coefficients are very large ($\varepsilon \sim 10^4$–10^6 l/mol $\cdot$ cm). All this may make it possible in practice to realize conditions under which such systems enter the regime of light generation. The coefficient of negative absorption (amplification) can be estimated from formula (8)

$$k = \frac{\lambda^2}{8\pi\Gamma} \frac{w_0}{1 + w_0 \tau / N}.$$

For $w_0 \sim 10^{21}$ molecules/sec $\cdot$ cm^3, $\lambda \sim 500$ mμ $\neq 5 \cdot 10^{-5}$ cm and a sample length $l = 10$ cm, we obtain $kl = 0.035$, i.e., 3.5%.

The amplification coefficient can be determined more accurately by using experimental data on absorption coefficients. The optical density of the system is equal to:

$$D = \lg \frac{I_0}{I} = \{\varepsilon_B([B] - [B^*]) + \varepsilon_{B^*}[B^*] + \varepsilon_A[A]\}l, \tag{5}$$

where I_0 is the intensity of the incident light and I that of the outgoing light; ε_B, ε_{B^*}, and ε_A are the absorption coefficients, respectively, of the forms B, B*, and A. The coefficient of stimulated emission of B* is equal to the absorption coefficient ε_B to within the ratio of the statistical weights of B* and B; ε_A at the frequency of the emission maximum of B is usually sufficiently small ($< 10^{-1}$). Then, for $\varepsilon_{B^*} \ll \varepsilon_B$ and

$$w_0 \gg \frac{K[A]}{\tau\varphi}$$

$$D = -\varepsilon_B w_0 \tau\varphi l. \tag{6}$$

Substituting typical values of the quantities, we obtain $D \simeq -10^{-23} w_0$. For $w_0 = 10^{21}$ molecules/sec $\cdot$ cm^3, $D = -0.01$, i.e., the amplification coefficient $\dfrac{I - I_0}{I} = 2.3\%$.

If the sample is placed between two parallel mirrors (a Fabry-Perot interferometer), then, when the losses in the optical system are smaller than this value, self-excitation will be observed.

The most essential condition is $\varepsilon_{B^*} \ll \varepsilon_B$. There are no experimental data on the magnitude of ε_{B^*} for singlet excited states, and it does not seem possible to estimate it sufficiently accurately for specific molecules. However, one may expect that there exist compounds in which absorption by excited molecules in the region of the emission maximum will be sufficiently small.

The principal requirements imposed on systems for using them for the purpose of generating stimulated radiation will be the following: rapidity

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* In the absence of radiationless deactivation.

establishment of equilibria ($k, k^* > 1/\tau$) and a large difference between the equilibrium constants in the ground and excited states ($K/K^* > 10^5$ or $K/K^* < 10^{-5}$); sufficient narrowness of the emission band ($\Gamma < 10^3$ cm^{-1}) and a large value of the absorption coefficient ($\varepsilon > 10^4$ l/mol $\cdot$ cm); small absorption by the excited molecules in the region of the emission maximum ($\varepsilon_{B^*} > \varepsilon_B$); a large quantum yield of luminescence and the absence of side photochemical reactions. As reversible reactions (1) one may use rapid reactions of electrolytic dissociation, isomerization, oxidation-reduction, addition-elimination, complex formation, dimerization, and polymerization. As an example, Table 1 gives the dissociation constants, measured by Förster, Weller, Jackson, and Porter ([2–7]), for several organic compounds in aqueous solutions in the ground (K_g), singlet

Fig. 2. Absorption (1, 2) and fluorescence (3, 4) spectra of various forms of α-naphthol. 1, 3 –naphthol, 2, 4 –naphtholate ion

Figure 2: Fig. 2. Absorption (1, 2) and fluorescence (3, 4) spectra of various forms of α-naphthol. 1, 3 –naphthol, 2, 4 –naphtholate ion

(K_g^s), and triplet (K_g^t) excited states, as well as the dissociation rate constants (k). As can be seen, by choosing a suitable value for the concentration of hydrogen ions ($\mathrm{pH} = -\lg[\mathrm{H}^+]$), it is easy to achieve

$$k^* = \frac{[\mathrm{B}^*]}{[\mathrm{A}^*]} > 1, \qquad k = \frac{[\mathrm{B}]}{[\mathrm{A}]} < 10^{-5}.$$

Fig. 2. Absorption $(1, 2)$ and fluorescence $(3, 4)$ spectra of various forms of α-naphthol. 1, 3 –naphthol, 2, 4 –naphtholate ion.

Let us consider α-naphthol in more detail. Figure 2 shows the absorption and fluorescence spectra ($\tau = 10^{-8}$ sec) of the various forms of α-naphthol.

Table 1

Dissociation constants of organic compounds in the ground and excited states

Reaction	Compound	$\mathrm{p}K_g$	$\mathrm{p}K_g^s$	$\mathrm{p}K_g^t$	$K \cdot 10^{-[[\text{unclear}]]}$
$\mathrm{ROH} \rightleftarrows \mathrm{RO}^-\mathrm{H}^+$	α-Naphthol	9.23	2.0–2.5	–	–
$\mathrm{ROH} \rightleftarrows \mathrm{RO}^-\mathrm{H}^+$	β-Naphthol	9.46	2.8	7.1–8.1	48
$\mathrm{ROH} \rightleftarrows \mathrm{RO}^-\mathrm{H}^+$	2-Naphthol-5-sulfoxylate	9.18	1.6	–	–
$\mathrm{R_3N} + \mathrm{H}^+ \rightleftarrows \mathrm{R_3NH}^+$	α-Naphthylamine	4	−2	–	–
$\mathrm{R_3N} + \mathrm{H}^+ \rightleftarrows \mathrm{R_3NH}^+$	Quinoline	5.1	–	5.8–6.0	–
$\mathrm{R_3N} + \mathrm{H}^+ \rightleftarrows \mathrm{R_3NH}^+$	Acridine	5.45	10.6	5.6	18

Reaction	Compound	pK_g	pK_g^s	pK_g^t	$K \cdot 10^{-[[\text{unclear}]]}$
$R_3N + H^+ \rightleftarrows R_3\overset{+}{N}H$	N,N-Dimethyl-naphthylamine	4.9	–	2.7-2.9	–
$RCOOH \rightleftarrows RCOO^- + H^+$	α-Naphthoic acid	3.7	10-12	3.8-4.6	–
$RCOOH \rightleftarrows RCOO^- + H^+$	β-Naphthoic acid	4.2	10-12	4.0-4.2	–

At a concentration of the aqueous solution $3 \cdot 10^{-5}$ mol/l $= 2 \cdot 10^{16}$ molecules/cm^3 (ensuring sufficiently uniform and effective absorption of the exciting light in a sample 1 cm in diameter) and pH 4 we have:

$$\lg[B^*]/[A^*] = 1.5;$$

$$[B^*] = 30[A^*];$$

$$[B^*] \simeq 10^{-8} w_0$$

$$\lg[B]/[A] = -5.23;$$

$$[B] = 6 \cdot 10^{-6}[A] \simeq$$

$$\simeq 10^{11} \text{ molecules/cm}^3.$$

The condition for obtaining a "negative temperature" is: $[B^*] > 10^{11}$, i.e. $w_0 > 10^{19}$ molecules/sec $\cdot$ cm^3. The optical density of the system (at $l = 10$ cm) for the frequency of the luminescence maximum ($\lambda = 500$ mμ, $\nu = 20000$ cm^{-1}), if absorption by the excited molecules is small, will be equal to:

$$D = \lg I_0/I = -1.5 \cdot 10^{-24} w_0.$$

For an attainable pulsed-regime value $w = 10^{22}$ molecules/cm$^3 \cdot$ sec, $[B^*] = 10^{14}$ molecules/cm^3, $D = -0.015$, and the gain coefficient per pass is 3.5%.

The principle set forth in the present work makes it possible to choose widely among a variety of systems for creating a four-level quantum generator, advantageously distinguished by the absence of any need to transfer the greater part of the initial molecules into the excited state. Changing the structure of the compounds used and introducing various substituents makes it possible to select substances with practically any emission spectrum—from the ultraviolet to the infrared region.

In conclusion, I express my gratitude to V. I. Serdobolsky, I. I. Sobelman, and V. L. Tal' roze for fruitful discussion of the present work.

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Received
1 IV 1963

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Note: Figure translations are in progress. See original paper for figures.