Kinetic mechanism of laser-chemical reactions

V. N. Sazonov

P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted 5 December 1979)
Zh. Eksp. Teor. Fiz. **79**, 39–45 (July 1980)

It is suggested that with increasing vibrational energy of a polyatomic molecule the rate of the V-T relaxation increases to a lesser degree than the rate of excitation of the molecule by laser radiation. As a result, the molecules located on the tail of the Gibbs vibrational-energy distribution, despite the collisions, are excited even more strongly and acquire enough activation energy to enter into a reaction. It is stated that recent experimental data on the absorption of radiation by strongly excited molecules do not contradict this assumption. Possible experiments aimed at verifying the proposed mechanism are indicated.

PACS numbers: 82.50. – m, 33.80. – b

1. INTRODUCTION

A chemical reaction can be called laser-chemical when it takes place in a medium in which laser radiation produces a kinetically nonequilibrium state. For example, when the laser radiation, acting on polyatomic resonant molecules in a gas mixture, excites a definite vibrational degree of freedom in these molecules above the thermal level, while the remaining degrees of freedom retain the Gibbs distribution.

Experiments, (see, e.g., Refs. 1–6; a more detailed bibliography is contained in Ref. 7) have shown that pulsed and cw IR laser radiation induce in a gas mixture chemical reactions, some of which are nontrivial because they cannot be obtained by heating the mixture in the usual manner (with a gas burner etc.). The laser-chemical nature of these reactions is still considered to be doubtful.[8] It is proposed to explain the nontrivial results within the framework of a thermal mechanism of the reaction, with account taken of the large temperature difference between the irradiated and shaded parts of the reactor, of the rapid heating and cooling of the gas when the laser is turned on and off, etc. On the other hand, the existence of a kinetically nonequilibrium state is denied in this case on the basis of the following arguments.

Consider the excitation of a resonant molecule by laser radiation. Let the energy of the laser photon be $\hbar\omega_l$, the cross section for the absorption of the photon σ, and the photon flux density J. Then the excitation power is equal to

$$P_{exc}=\hbar\omega_l\sigma J.$$

Taking typical values $\hbar\omega_l=0.12$ eV (CO_2 laser), $J=10^{21}$ phot/cm^2 sec (corresponding to an energy flux $I=\hbar\omega_l J=20$ W/cm^2), and $\sigma=10^{-18}$ cm^2, we obtain $P_{exc}=120$ eV/sec.

To describe the action of the radiation, this quantity must be compared with the thermalization power

$$P_{th}=\hbar\omega_l\tau_{VT}^{-1},$$

where τ_{VT} is the characteristic time of conversion of the vibrational energy (V) into translational energy (T). At a mixture pressure 300 Torr and a temperature $T=500$ K, the time τ_{VT} is usually of the order of 10^{-5} sec. Hence $P_{th}=1.2\times10^4$ eV/sec. We introduce the parameter

$$\varepsilon=P_{exc}/P_{th}. \tag{1}$$

According to the foregoing,

$$\varepsilon=J\sigma\tau_{VT}. \tag{2}$$

Since $\varepsilon=0.01\ll1$, the laser radiation cannot alter the equilibrium population significantly. Its action reduces mainly to thermal heating of the gas.

This reasoning is correct in the sense that in the majority of cases the onset of a laser-chemical reaction actually calls for satisfaction of the condition $\varepsilon\gtrsim1$.[1)] In that case, however, the general meaning of ε should be taken in accord with Eq. (1). Expression (2) and the estimate $\varepsilon=0.01$, as will be shown below, are valid only for low-lying levels, where the vibrational quantum number is $n=1$ or 2. In the region $n\geqslant3$, Eq. (2) is not valid. We shall show that in the region $n\geqslant5$–7, under the conditions indicated above, the parameter ε can readily reach unity or more. The main cause[2)] of the increase of ε is the abrupt increase of the level density in the upper quasi-continuous section of the energy spectrum of a polyatomic molecule (see Sec. 3 below).

The kinetic mechanism of laser-chemical reactions can be, in our opinion, of the following form. Let the parameter $\varepsilon<1$ if the energy E of the excited mode is less than the critical energy E_{qc}, and let $\varepsilon>1$ if $E>E_{qc}$. Laser excitation results in resonant molecules with $E<E_{qc}$. In this case, however, $\varepsilon<1$; the result is mainly heating of the gas. In addition, the laser radiation interacts with a small number of strongly excited resonant molecules, whose number at the initial instant of time is determined by the Gibbs distribution. For these molecules $E>E_{qc}$ and $\varepsilon>1$; as a result, they are excited even more strongly and acquire an activation energy sufficient to enter into the reaction. This process violates the Gibbs distribution, and the population of the levels with $E\gtrsim E_{qc}$ decreases while that of the levels with $E\gg E_{qc}$ increases. The resultant shortage of molecules in the region $E\gtrsim E_{qc}$ is offset all the time by pumping of molecules from the region $E<E_{qc}$. This pumping is due to the collisions that restore the Gibbs distribution.

0038-5646/80/070019-04$02.40

The calculations that follow show that the proposed mechanism is realistic. The possibility of its experimental verification is considered.

2. THERMALIZATION OF STRONGLY EXCITED MOLECULES

There are no experimental data on the thermalization of vibrational mode of polyatomic molecules excited to $n=3$ and above, and an exact theory is extremely difficult to construct.[3] We are forced therefore to confine ourselves here to qualitative arguments and order-of-magnitude estimates.

According to the Landau–Zener theory the time τ_{VT} for the transfer of an energy E' from the vibrational into the translational degrees of freedom is equal to

$$\tau_{VT}=\tau_{el}\exp\,(E'/E_a)^{1/2}, \tag{3}$$

where τ_{el} is the elastic-collision time, and the energy E_a of most pairs of colliding molecules is of the order of 2.5×10^{-3} eV $=30$ K.[4] In thermalization of the low-lying levels, when the level density is still not too high, the energy E' cannot differ noticeably from the energy $\hbar\omega_l$ of the vibrational quantum. In this case the thermalization power is equal to

$$P_{th}=\hbar\omega_l\tau_{el}^{-1}\exp\,\{-(\hbar\omega_l/E_a)^{1/2}\}.$$

Putting $\tau_{el}=10^{-8}$ sec we obtain the already cited value 1.2×10^4 eV/sec.

In the case of low-lying levels, the energy E' can be much less than $\hbar\omega_l$, owing to the high level density and to the fact that with increasing n the anharmonicity of the oscillations makes possible transitions between different vibrational modes. Since the energy E' decreases, the time τ_{VT} also decreases rapidly with increasing n. However, τ_{VT} ceases decrease when the characteristic spacing of the levels between which a transition is possible decreases to the characteristic energy of the translational motion, i.e., to the gas temperature T. In this situation, not only the energy transfer $V\to T$ is possible, but also the transfer $T\to V$. Let $g(E)$ be the level density in the energy region E. A simple calculation yields in the case $g(E)T\gg1$ the following expression for the thermalization power:

$$P_{th}=\tau_{el}^{-1}E_a^2/T. \tag{4}$$

Hence $P_{th}=7.8\times10^3$ eV/sec, which is even somewhat less than the value 1.2×10^4 eV typical of lower levels.

The foregoing considerations and estimates make it possible to suggest that the thermalization power reaches its maximum value $P_{th\,\max}$ in the energy region where $g(E)T\sim1$. We then have in order of magnitude

$$P_{th\,max}=\tau_{el}^{-1}\int_0^\infty dE'\exp[-(E'/E_a)^{1/2}]=2E_a\tau_{el}^{-1} \tag{5}$$

or $P_{th\,max}=5\cdot10^5$ eV/sec.

3. ABSORPTION OF RADIATION BY STRONGLY EXCITED MOLECULES

The dipole absorption cross section, as is well known, is equal to

$$\sigma_0=\frac{4\pi^2}{3}\frac{|d|^2\omega_l}{\hbar c\Delta\omega_l}K=4.18\cdot10^{-19}|d|^2\frac{\omega_l}{\Delta\omega_l}K\ \mathrm{cm}^2, \tag{6}$$

where K is the number of final states; $\Delta\omega_l$ is the width of the spectrum of the incident radiation and is assumed to be larger than the emission line width; d is the dipole moment of the transition, expressed in units of $1\ \mathrm{D}=10^{-18}$ cgs. Substituting in (6) the typical value $=0.1$ D for the vibrational-translational transition, $\omega_l/\Delta\omega_l=10^5$, and $K=1$, we obtain $\sigma_0=4\times10^{-16}$ cm^2. It is known at the same time that for polyatomic molecules the experimental cross sections for the excitation of the vibrational transitions $0\to1$ lie in the range $\sigma=10^{-7}-10^{-20}$ cm^2. The cause of the discrepancy is the following. The molecule energy-spectrum sections that correspond to a definite vibrational state consist of a large number of levels because of rotation and other reasons. In the vibrational transition $0\to1$, the level density is not yet very large, and the resonance relation

$$|E_m-E_n-\hbar\omega_l|\leqslant\hbar\Delta\omega_l$$

is satisfied for only a small fraction of the levels. In addition, not all pairs of resonant levels have nonzero transition dipole moments. For these reasons, the fraction q of the molecules participating in the radiation absorption is of the order of $q=10^{-2}-10^{-4}$. It can be stated that q is the probability that radiation absorption is possible from a given level. Since $\sigma=\sigma_0q$, the observed is much less than σ_0.

Assume that the radiation is absorbed by a highly excited molecule. In the upper section of the spectrum the absorption cross section is influenced by the following factors. 1) Owing to the high state density, the number of levels at resonance increases. 2) Owing to the vibration anharmonicity, which increases with n, the modes become intermixed in the sense that each stationary state of the molecule corresponds not to some particular mode, but contains an admixture of other modes. As a result, the number of level pairs having a nonzero dipole moment d_{mn} increases. 3) By virtue of factors 1) and 2), a transition to a larger number of final levels is possible from a given initial level. 4) The dipole moment d_{mn}, depending on the concrete properties of the molecule, can either increase (we recall that in the case of a linear oscillator we have $d_{n+1\,n}=n^{1/2}d_{10}$), or decrease if the degree of mode mixing is small.

Factors 1) and 2) lead to an increase of the probability q, which in principle can become of the order of unity. Factor 3) increases the cross section σ_0 because of the increase in the number K of final states. This number is equal to

$$K=g(E)\hbar\Delta\omega_l$$

and can be quite large. For example,[12] for the SF_6 molecule the density is $g(E)=1.2\times10^6$ eV^{-1} at $E=0.48$

eV ($n=4$) and $g(E)=9.3\cdot 10^7$ eV^{-1} at $E=0.84$ eV ($n=7$). In the case $\hbar\Delta\omega_l=10^{-2}$ cm$^{-1}=1.2\times 10^{-6}$ eV we obtain $K=1.4$ at $n=4$ and $K=100$ at $n=7$. As to the factor 4), it is very difficult to estimate its influence. We assume that d_{mn} does not decrease too strongly, if at all, inasmuch as at large n the modes should be strongly intermixed.

According to the data on multiphoton collisionless dissociation in a field with $I=10^8$ W/cm^2, for molecules with four and more atoms, the increase in the level density exerts a decisive influence on the dynamics of the excitation, starting with $n=2$ or 3. In fields with $I=1-100$ W/cm^2 the value of n can increase to 5–7. Taking all the foregoing into account, we assume $q=0.1$, $K=100$, and $d=0.01$ D. Then $\sigma=q\sigma_0=4\cdot 10^{-17}$ cm^2 and the excitation power is $P_{exc}=5\times 10^3$ eV/sec. In the region where $g(E)T\gg 1$ this value yields $\varepsilon=0.5$. At the highest levels one can expect as before $d=0.01$ D, but $q=1$ and $K=10^3$ or more. Then $\sigma=4\times 10^{-15}$ cm^2 and $P_{exc}=5\times 10^5$ eV/sec, which coincides with the maximum value of P_{th}. At a very high level density, the restriction imposed by the sum rule may become significant. In our case this rule takes the form

$$\sum_m |d_{mn}|^2=\langle n|d^2|n\rangle=d_{nn}{}^2.$$

It is obvious that in any case we should have

$$Kd^2<\sum_m |d_{mn}|^2.$$

Let us estimate the right-hand side. We have $d_{nn}^2=e^{*2}r_{nn}^2$, where e^* is a certain effective charge. In heteropolar-mode excitation, e^* can reach the value of the elementary charge e. At high levels $r_{nn}^2\approx 10^{-16}$ cm^2. This yields $d_{nn}^2\approx 20$ D^2. In the calculations above the value of Kd^2 did not exceed 0.1 D^2, which is still fully compatible with the sum rule. We note that in our model the cross section $\sigma=q\sigma_0$ increases not only because of increase of Kd^2 and σ_0, but principally because of the increase of q, i.e., because of the increase of the fraction of molecules participating in absorption of the radiation. The same factors increase the parameter ε, which can reach values of unity and more for strongly excited molecules.

4. DISCUSSION

An increase of the level density affects differently the excitation by radiation and thermalization; it increases strongly the rate of excitation and not very strongly the rate of thermalization. The difference is due to the fact that thermalization takes place in collisions, i.e., under the influence of short-range intermolecular forces. When a molecule is excited by radiation, the characteristic interaction length should probably be taken to be the coherence length $2\pi c/\Delta\omega_l=100$ cm, which is a tremendous amount on a molecular scale. We assume therefore that at high levels the absorption cross section increases by a factor 10^2–10^5 and reaches values of the order of

$$\sigma\simeq 10^{-16}-10^{-14}\ \text{cm}^2 \qquad (7)$$

and more. This assumption is basic in the present paper.

At first glance the assumption (7) contradicts directly numerous experimental papers (see, e.g., Refs. 13–16), in which measurement of σ is reported for strongly excited polyatomic molecules, with $\sigma=10^{-18}$–10^{-20} cm^2. In all papers of this type, however, the quantity of interest to us—the cross section of single-photon absorption at intensity $I=1-100$ W/cm^2 and pressure 100–500 Torr for strongly excited polyatomic molecules—was not measured directly. In some studies the measurements were made at $I\geqslant 10^5$ W/cm^2, which leads to a bleaching of the gas and to a decrease of the effective cross section. In other studies the intensity had the required values $I=1-100$ W/cm^2, but the gas temperature was 1000–1500 K, insufficient to excite levels with $n=5-7$, or else the pressure was too low, of the order of 0.1–1 Torr. Yet it is known that for polyatomic molecules with a dense spectrum, increasing the concentration of the gas increases not only in the absorption coefficient, which is proportional to the concentration, but also the absorption cross section (see, e.g., Ref. 17). The increase of the cross section is due, in particular, to the fact that the resonant frequency ω_l is blanketed by a large number of wings of impact-broadened lines, and the absorption in such a wing increases with concentration. Therefore, when the pressure is increased to 100–500 Torr, the cross section σ should increase strongly, especially at high levels.

All this allows us to regard the assumption (7) as a speculative hypothesis, but compatible with the available experimental data. In those cases when the cross section is not a suitable concept for the description of the interaction of the radiation with the molecule, the assumption made is equivalent to postulating an increase of the excitation rate and of the parameter $\varepsilon=P_{exc}/P_{th}$ on the upper levels. Generally speaking, an increase of ε to unity is obtained also when P_{th} is decreased to about 100 eV/sec; the decrease of the thermalization on the high levels, however, seems to us less probable than the increase of the excitation.

Tsay *et al.*[18] measured the absorption of CO_2 laser radiation by an SF_6 molecule as the function of the radiation frequency (radiation intensity $I\sim 10^4-10^5$ W/cm^2, pressure 0.5 Torr, temperature interval 199–500 K). It turned out that the maximum value of the absorption coefficient increases rapidly with increasing temperature.[5)] This interesting phenomenon, which, as noted in Ref. 8, has so far not been theoretically explained, becomes in principle understandable if assumption (7) is accepted. In fact, if $\varepsilon>1$ at $E>E_{qc}$, then the absorption is proportional to the population of the levels with energy $E\simeq E_{qc}$. Since $E_{qc}>T$, this population increases with temperature. A quantitative analysis of the dependence of the absorption on the temperature will be the subject of further research.

We discuss now the possibility of experimentally verifying the proposed mechanism. Assume that the reactor contains reagents A and B, one or both of which absorb the laser radiation, as well as a buffer gas C, the activation energy of the reaction $A+B \rightarrow (AB)$ being several times larger than T. We represent the expression for the reaction yield η following the laser-radiation pulse in the form

$$\eta \propto w \exp\left(-E_{qc}(I)/T\right),$$

where w is a parameter proportional to the rate of pumping of the molecules from the region $E<E_{qc}$ to the excited region $E>E_{qc}$ on account of the collisions. Since $E_{qc}(I)$ decreases with increasing I and $E_{qc}(I) \gg T$, the value of η will increase very rapidly with increasing I. This corresponds to the well known singularity of laser-chemical reactions—the presence of an intensity threshold I.[1]

Assume that the mixture $A+B$ is under moderate pressure (of the order of 100 Torr or less) and is irradiated by laser pulses of short duration (on the order of several msec). Then the bottleneck of the process is the pumping of the molecules into the excited region. We add to the mixture a heat-conducting buffer gas C (e.g., hydrogen or helium). The temperature T is then decreased, but the pumping of the molecules is increased as a result of the collisions of the reagents with the gas C, i.e., the factor w is increased. As a result, the reaction yield η can increase after the addition of C, and the threshold value of I can decrease. Of course, this occurs only if the decrease of T exerts a smaller influence on η than the increase of w. Therefore the discussed effect becomes most probable if the pressure of the buffer gas C does not exceed the pressure of the reagent mixture $A+B$.

According to Ref. 1, when the *reagent* pressure in the mixtures N_2F_4+NO and N_2F_4+CO is increased, a considerable decrease of the threshold intensity is observed. It would be of interest to observe a decrease of the threshold intensity following the addition of the *buffer* gas to the mixture. It must be emphasized that this effect is absolutely incompatible with the thermal mechanism of the reaction. It is particularly for this reason that an experimental verification of the predictions made seems to us highly desirable.

The authors thank L. V. Keldysh, M. V. Kuz'min, A. N. Oraevskii, and A. V. Pankratov for a discussion.

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[1] The feasibility of a laser-chemical reaction at $\varepsilon \ll 1$ is discussed in Ref. 9.

[2] Here and elsewhere ε is taken to have only the meaning (1).

[3] Both the theory and experimental data are available for diatomic molecules (see the review[10]).

[4] See Ref. 14 concerning the violation of relation (3) in the case of several molecule pairs.

[5] It is known that at low intensity ($I<1$ W/cm^2) the absorption decreases with increasing temperature.

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Translated by J. G. Adashko