

## SELECTIVITY OF CHEMICAL REACTIONS STIMULATED BY INFRA-RED LASER RADIATION IN MOLECULAR GAS MIXTURES

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### Summary

Binary mixtures of molecules with identical physical and chemical properties are considered. Infra-red laser radiation is assumed to excite vibrations of the chosen molecular component. Various possibilities for stimulation of selective chemical reactions are discussed. Appropriate estimations and numerical calculations of selectivity are presented.

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### Introduction

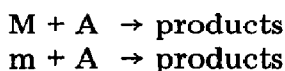
The problem of vibrational excitation is important for initiation of chemical reactions with laser radiation. The infra-red photochemical effect was demonstrated as early as 1963 [1]. But the progress was achieved only after high-power infra-red gas lasers had been created. There are three main questions which have been raised in a number of experimental and theoretical works.

(1). *The role of vibrationally excited molecules in chemical transformations.* The problem of the contribution made by various molecular degrees of freedom to the value of the chemical reaction rate constant is fundamental to the chemical physics. At present it is known that the vibrational energy is more essential for the thermal dissociation process [2] and for some chemical reactions [3 - 6] than the translational one. The work of Odiorne *et al.* [6] especially should be noted. In this work, the vibrational excitation of HCl molecules was carried out by HCl laser radiation and an anomalous increase of the rate of the reaction  $\text{HCl} + \text{K} \rightarrow \text{KCl} + \text{H}$  was detected for HCl molecules with the vibrational quantum number,  $v = 1$ .

(2). *The possibility of primary vibrational excitation by resonance laser radiation.* This is important for the interpretation of recently obtained laser chemical reactions with their activation energies,  $E_a \gg \hbar\omega$  [7 - 9], and the experiments on dissociation of molecules stimulated by infra-red laser radiation [10 - 12]. Resonance interaction between molecular vibrations and infra-red laser radiation was considered theoretically [13 - 18] and exper-

imentally [19, 20]. The conclusion can be drawn that primary heating of a selected molecular vibrational mode is possible if the reverse time  $\tau_0^{-1}$  of its vibrational energy transformation in other degrees of freedom is smaller compared to the rates of laser pumping and  $V-V$  exchange process.

(3). *The possibility of selective chemical reaction of certain molecules mixed with chemically identical molecules.* The essence of the problem was discussed by Letokhov [21]. It is of great interest for the laser-chemical isotope separation by infra-red laser radiation. The first experiment was described by Mayer *et al.* [22]. In the present work this third problem is considered theoretically. Let us suppose that the reactions:



both occur under usual thermal heating of the M,m and A molecular mixture, and their rate constant values are similar. Is it possible to initiate chiefly the first reaction, if irradiating the mixture by a laser radiation which is absorbed by the molecules M on the  $0 \rightarrow 1$  transition and is not absorbed by the molecules m (for example due to isotope level shift)? In order to answer this problem it is necessary to take into account the primary resonance  $V-V'$  processes of exchange between the vibrational mode  $\nu_j^M$  of the molecules M, interacting with a radiation, and the appropriate vibrational mode  $\nu_j^m$  of the molecules m. Any selectivity with respect to molecules M laser chemical reaction is possible if there is a primary excitation of the vibrational mode  $\nu_j^M$  in comparison with that of  $\nu_j^m$  up to reactive levels.

In the case  $E_a \sim \hbar\omega$  a molecule is capable of reacting after having absorbed nothing but a laser radiation quantum. In this case a high selectivity may be achieved when the reaction rate value exceeds that of a  $V-V'$  exchange process. It is possible also to obtain a high reaction selectivity if diluting the mixture with a buffer gas we increase the deactivation rate of vibrationally excited molecules m.

When  $E_a \sim \hbar\omega$  the situation can be easily given by the model of two-level systems. The formula for the utmost reaction selectivity is deduced in the next section without thermal selectivity losses being taken into account. Thermal heating of the molecular mixture is particularly considerable under continuous irradiation. But this effect limits first-level reaction selectivity in the case of laser pulse action also. Thermal excitation of levels is taken into consideration as well. The estimations here show that one can always determine the buffer gas pressure in the mixture at which the thermal process of selectivity losses would be depressed. Beside reactions with low-energy activation the two-level system model is applicable completely to describe the two-step photodissociation process [23 - 25] and may be useful for selective chemical reactions, stimulated by laser action, when one of the agents is under electron excitation.

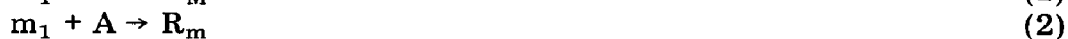
In the case  $E_a \gg \hbar\omega$  it is necessary to excite high vibrational energy levels. Being close to the resonance the rate of the vibrational-vibrational

exchange between the modes  $\nu_j^M$  and  $\nu_j^m$  considerably exceeds that of energy transfer to other degrees of freedom. Thus, when the pulse duration is smaller than the time of vibration deactivation, we can separate the vibrational temperatures of  $\nu_j^M$  and  $\nu_j^m$  modes from those of other degrees of freedom. As far as the difference between the temperatures of  $\nu_j^M$  and  $\nu_j^m$  vibrational modes is concerned, then it consists of two components. This has been confirmed by the calculations made later for the harmonic oscillator model. The first component  $(T_M - T_m)_1 > 0$  depends on excitation. It increases with an increase in the ratio between  $V-V$  and  $V-V'$  exchange rates and decreases as the vibrational temperature rises. The second one  $(T_M - T_m)_2$  is related to the energy difference between vibrational quanta of the two modes and does not depend on either of two molecular kinds interacting with the radiation\*. Its value is of the same sign as the difference  $E_m - E_M$  and, in principle, describes the equilibrium of the two molecular vibrations modulated by harmonic oscillators, with the relaxation processes of the vibrational energy to other degrees of molecular freedom to be neglected [26, 27].

So in contrast to low-energy reactions ( $E_a \sim \hbar\omega$ ) the selectivity of high-energy reactions ( $E_a \gg \hbar\omega$ ) is limited by the values of the molecular parameters and rate constants of elementary processes. The equation for the reaction's selectivity is deduced below for the case  $E_a \gg \hbar\omega$ . A contribution to the selectivity value made by the two components is estimated also.

#### The selectivity of photochemical reaction in the case $E_a \sim \hbar\omega$

Let us consider the gas mixture of molecules M and m taken as two-level systems  $M_i$  and  $m_i$  ( $i = 0, 1$ ). The elementary processes which are of particular importance are shown schematically in Fig. 1. Induced by radiation transitions between the ground energy level  $M_0$  of the system M and the excited one  $M_1$  are supposed to occur with the probability  $W$ . Excited molecules react with the molecules A giving the products  $R_M$  and  $R_m$ :



For one gas-kinetic collision the probabilities of eqns. (1) and (2) are expressed as  $K_1$  and  $K_2$ .

Of all the non-elastic impact processes the excitation exchange and the excited state deactivation are taken into consideration.  $Q_1$  and  $Q_2$  are the probabilities of the excitation exchange processes:



where  $\Delta E$  is the excitation energies difference, and  $Q_1 = Q_2 \exp(-\Delta E/kT)$ .

\*The importance of this effect is pointed out by Belenov *et al.* [28].

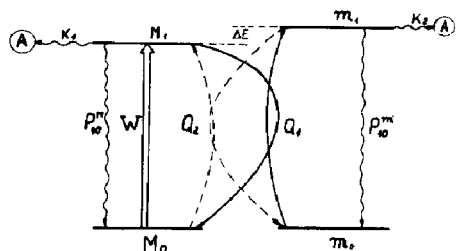


Fig. 1. The diagram of levels and the processes taken into consideration for reactions with  $E_a \sim \hbar\nu_0$ .

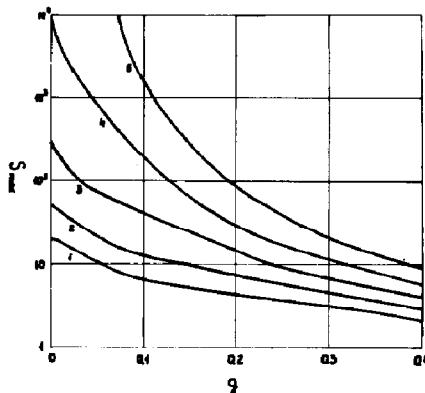


Fig. 2. The dependence of maximum selectivity  $S_{\max}$  on the parameter  $g$  for various values of  $\theta_0$ : 1, 0.25; 2, 0.2; 3, 0.15; 4, 0.1; 5, 0.05.

$P_{10}^M$  and  $P_{10}^m$  are the deactivation probabilities of  $M_1$  and  $m_1$  respectively. Both  $Q_{1,2}$  and  $P_{10}^{M,m}$  are taken into account for a gas-kinetic collision.

It is reasonable to make some assumptions about the corresponding elementary process rates: (a)  $K_1 \simeq K_2$ , i.e., the molecules  $M$  and  $m$  are chemically identical with respect to the molecules  $A$ ; (b)  $Q_1 \simeq Q_2 = Z_{VV}^{-1}$ , i.e., the vibrational quantum value of  $m$  is sufficiently close to that of  $M$  and we neglect the factor  $\exp(-\Delta E/kT)$ ; and (c)  $P_{10}^M \simeq P_{10}^m = Z_{VT}^{-1}$ . It is also reasonable to take the molecules  $A$  in excess with respect to  $M$  and  $m$  in order to provide greater reaction and deactivation rates. So the concentration of molecules  $aA$  may be considered constant during the reaction: (d)  $[A] \simeq \text{constant}$ .

With regard to (a)–(d) the set of kinetic equations giving the populations  $N_i = [M_i]$ ,  $n_i = [m_i]$  takes the form:

$$\begin{aligned} \frac{dN_0}{dt} &= -W(N_0 - N_1) + \frac{Z}{Z_{VV}D}(N_1n_0 - N_0n_1) + \frac{Z}{Z_{VT}}N_1 \\ \frac{dN_1}{dt} &= W(N_0 - N_1) - \frac{Z}{Z_{VV}D}(N_1n_0 - N_0n_1) - \frac{Z}{Z_{VT}}N_1 - \kappa N_1 \\ \frac{dn_0}{dt} &= -\frac{Z}{Z_{VV}D}(N_1n_0 - N_0n_1) + \frac{Z}{Z_{VT}}n_1 \\ \frac{dn_1}{dt} &= \frac{Z}{Z_{VV}D}(N_1n_0 - N_0n_1) - \frac{Z}{Z_{VT}}n_1 - \kappa n_1 \end{aligned} \quad (5)$$

Here  $Z$  is gas-kinetic collision frequency, expressed in  $s^{-1}$ ;  $D$  is the total concentration of molecules in the mixtures;  $Z_{VV}$ ,  $Z_{VT}$  correspond to efficient

collisional numbers required for excitation exchange and excitation deactivation;  $K = K_1 Z[A]/D$  is the reaction rate expressed in  $s^{-1}$ . In such a form equations (5) are convenient to give the two-step photodissociation. In this case  $K$  is the photodissociation rate from the excited state, and ultra-violet photons play a role in the molecules  $A$ .

As a result we are interested in the concentration values of the reaction products  $R_M$  and  $R_m$ . The relations:

$$\frac{d[R_m]}{dt} = KN_1 \text{ and } \frac{d[R_M]}{dt} = Kn_1 \quad (6)$$

are obvious.  $[R_M]$  and  $[R_m]$  may be found if relations (6) are integrated together with (5). It is reasonable to give the result in terms of selectivity value,  $S$ :

$$S = \frac{b}{B} \frac{[R_M]}{[R_m]} \quad (7)$$

Here  $B$  and  $b$  are the initial concentrations of molecules  $M$  and  $m$  correspondingly. One can see from the definition (7) that the value of  $S$  shows how many times the ratio  $[R_M]/[R_m]$  is greater than the "usual" concentration ratio,  $B/b$ .

The system (5) may be solved for the case when the induced transition probability  $W$  is much greater than those of other processes considered. The selectivity value,  $S$  corresponding to the reaction end is given by:

$$S = \left\{ 1 - F \left[ 1, 2 \left( 1 + \frac{Z}{KZ_{vt}} \right), - \frac{2Z}{KZ_{vv'}} \frac{B}{D} \right] \right\}^{-1} \quad (8)$$

Here  $F$  is the degenerated hypergeometric function defined usually as a series:

$$F(\alpha, \gamma, y) = 1 + \sum_{k=1}^{\infty} \frac{\alpha(\alpha+1) \dots (\alpha+k-1)}{\gamma(\gamma+1) \dots (\gamma+k-1)} \cdot \frac{y^k}{k!} \quad (9)$$

High selectivity values might be obtained if only the second expansion term of  $F$  is smaller compared with unity. It results in the requirement:

$$\frac{Z}{Z_{VV'}} \frac{B}{D} \left( K + \frac{Z}{Z_{VT}} \right)^{-1} \ll 1 \quad (10)$$

and for this case eqn. (8) takes the form:

$$S \approx \frac{Z_{VV'}}{Z} \frac{D}{B} \left[ K + \frac{Z}{Z_{VT}} \right] \quad (11)$$

Hence there are two possibilities to produce a high selectivity. The first one is realized if  $K(Z_{VV'}D)/(ZB) \gg 1$ , *i.e.* when the reaction rate is much greater than that of the exchange transfer. The second one is realized if  $Z_{VV'}D/Z_{VT}B \gg 1$ , *i.e.* when the population of  $m_1$  is small because the deactivation rate is much greater than that of the exchange transfer. However,

the selectivity value is fundamentally limited [23] by the equilibrium population of  $m_1$ . Even in the absence of laser radiation the concentration of the reaction products  $R_m$  is really:

$$[R_m] \approx b [1 - \exp(-K t^* e^{-E_\alpha/kT})] \approx b [1 - \exp(-K t^* e^{-h\omega/kT})] \quad (12)$$

Here  $T$  is the gas temperature,  $t^*$  is a time interval embracing the interaction between the molecules  $m$  and  $A$ , *i.e.* the mixture existence time. If  $R_M$  arises mainly during a laser pulse, the reaction selectivity is limited by the condition:

$$S < \frac{1 - \exp(-K t_p/2)}{1 - \exp(-K t^* e^{-h\omega/kT})}, \quad (13)$$

where  $t_p$  is the laser pulse duration. Thus high selectivity values are possible if only

$$t^* e^{-h\omega/kT} \ll K^{-1} \lesssim t_p \quad (14)$$

When  $t^*$  is the time of "usual" gas mixing and separation then

$$t^* \gg t_p, K^{-1} \quad (15)$$

and requirement (14) is practicable with high-energy states being excited directly or with the gas mixture being cooled. The qualitatively different situation may be realized when

$$t^* \sim t_p \sim K^{-1} \quad (16)$$

It is possible for: (a) a two-step photodissociation process; (b) reactions in crossing molecular beams; (c) reactions with short-lived intermediate products of a secondary reaction such as  $A$  to take place.

The upper selectivity limitation (13) may become stronger if the deactivation rate of excited states is much greater than that of the reaction. In this case a considerable gas temperature increase may occur during the reaction.

The calculations dealing with the thermal selectivity limitation effect are given below for the two cases (15) and (16).

*The case  $t^* \sim t_p \sim K^{-1}$*

In this case the highest selectivity  $S_{\max}$  depends on the relation between  $\theta_0 = kT_0/h\omega$  ( $T_0$  is the initial gas temperature) and the parameter  $g$ :

$$g = \frac{B}{2cD} \frac{Z}{KZ_{VT}} \quad (17)$$

where  $c$  is the specific heat of the mixture. The condition:

$$g \ll \theta_0^2 \quad (18)$$

serves as a criterion for the heating to be negligible. This condition may be obtained through a proper buffer gas-diluted mixture.

Appropriate calculations were made for the laser pulse duration  $t_p = (2/K)\ln 2$ , *i.e.* when half of the molecules  $M$  react during a laser pulse. The dependence  $S_{\max}$  on the parameter  $g$  is given in Fig. 2 for the various values of  $\theta_0$ .

*The case  $t^* \gg t_p, K^{-1}$*

In this case the temperature variation after a laser pulse action is of importance. The mixture cooling is caused by heat conduction. The typical time of this process is

$$\tau_T \simeq (\chi \pi^2 l^2)^{-1} \quad (19)$$

Here  $\chi$  is the coefficient of temperature conductivity and  $l$  is the typical transversal dimension of the excited gas volume. Practically, it can be considered that:

$$t^* \gtrsim \tau_T \gg t_p \quad (20)$$

If requirement (14) is valid for  $t^* \gg K^{-1}$  then it corresponds to very small values of  $\exp(-\hbar\omega/kT_0)$ . Through the sharp exponential dependence either requirement (14) is broken or it is valid with a considerable excess. So requirement (14) is equivalent to  $\theta_0 = 0$  and in view of (20) the thermal reaction during the time interval  $\tau_T$  should be treated as the main cause of selectivity losses.

The calculations were made for the chemical reaction selectivity value. The following parameter values were taken:

$$\frac{Z_{VT}}{Z_{VV}} = 10^3; \quad 2 \frac{Z_{\tau T}}{Z_{VV}} = 10^9; \quad c = 1.5; \quad \frac{Z}{KZ_{VT}} = 10^2 - 10^4; \quad \frac{b}{B} = 10^{-2} - 10^4$$

Besides  $S$  the value  $\theta_p = kT_p/\hbar\omega$  ( $T_p$  is the gas temperature at the end of the laser pulse) was calculated for two various cases of laser stimulation:  $t_p \gg K^{-1}$  and  $t_p = (2/K)\ln 2$ . The calculations show that a certain typical dilution value  $(D/B)^*$  corresponds to a fixed set of parameters. If  $(D/B) > (D/B)^*$  then the heating is of no importance and the formula (11) may be used for the selectivity value calculation. If  $(D/B) < (D/B)^*$  then the reaction selectivity decreases sharply as a function of  $(D/B)$ , *i.e.* the thermal reaction predominates. Typical values of  $\theta_p$  corresponding to  $(D/B)^*$  are approximately equal to 0.04 - 0.06. The dependence of  $S$  and  $\theta_p$  on  $(D/B)$  is illustrated by the curves represented in Fig. 3. The dependence of  $(D/B)^*$  on the isotopic composition  $(b/B)$  is shown in Fig. 4.

The main conclusions are correct if only the value of  $\theta_0$  is considerably less than that of  $\theta_p$  corresponding to  $(D/B)^*$ . The vibrational quantum values are usually not more than 0.1 - 0.5 eV. It corresponds to  $\theta_0 \sim 0.05 - 0.25$  for the room temperature. Thus in the case of "usual" gas mixing the selective chemical reactions from the first vibrationally excited level may be realized if the gas mixture is cooled to a temperature considerably less than ambient.

Solid curves:  $t_p \gg K^{-1}$

Dotted curves:  $t_p = (2/K)\ln 2$

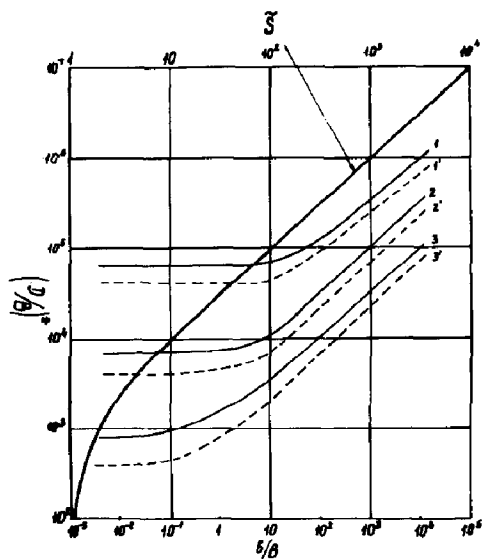
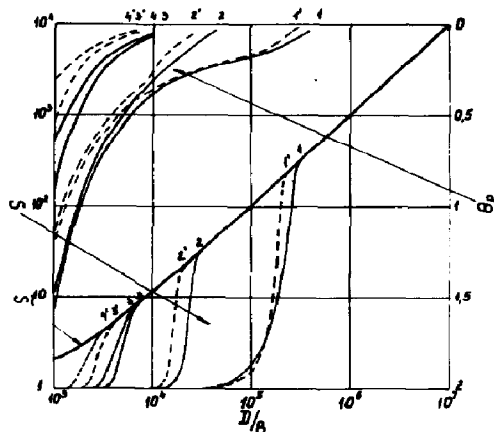


Fig. 3. The dependence of  $S$  and  $\theta_p$  on the value of dilution ( $D/B$ ) in the case  $t_p \gg K^{-1}$  and in the case  $t_p = (2/K)\ln 2$  for the following values of parameters:  $Z_{VT}/Z_{VV'} = 10^3$ ; 2,  $(Z_{VT}/Z_{VV'}) = 10^9$ ;  $Z/KZ_{VT} = 10^3$ ;  $c = 1, 5$ ; 1, 1',  $b/B = 10^4$ ; 2, 2',  $b/B = 10^2$ ; 3, 3',  $b/B = 1$ ; 4, 4',  $b/B = 10^{-2}$ . The  $S$  curve corresponds to the values of selectivity calculated without heating and the thermal reaction being taken into account.

Fig. 4. The dependence of  $(D/B)^*$  on isotopic composition ( $b/B$ ) in the case  $t_p \gg K^{-1}$  and in the case  $t_p = (2/K)\ln 2$  for the following values of parameters:  $Z_{VT}/Z_{VV'} = 10^3$ ; 2  $(Z_{VT}/Z_{VV'}) = 10^9$ ;  $c = 1, 5$ ; 1, 1',  $Z/KZ_{VT} = 10^4$ ; 2, 2'  $Z/KZ_{VT} = 10^3$ ; 3, 3'  $Z/KZ_{VT} = 10^2$ . The  $S$  dependence on  $(D/B)^*$  corresponds to the values of selectivity calculated without heating and the thermal reaction being taken into account.

The limitations are not so essential if a vibrational overtone is excited directly, and completely disappear if the laser quantum energy corresponds to that of a molecular electron transition. The developed theory is entirely applicable for these cases.

#### The photochemical reaction selectivity in the case $E_a \gg \hbar\omega$

A reaction of primary vibrationally excited molecules presupposes a selective vibrational heating up to the activation energy. The time of such a process must be less than that of the vibrational energy transformation in other degrees of freedom,  $\tau_0$ . It is not always possible. For example, in the case of monomolecular mixture the activation energy must comply with the requirement [14, 17]:

$$E_a < \hbar\omega \left( \frac{\tau_0}{\tau_{VV}} \right)^{1/2} \quad (21)$$

if even the  $0 \rightarrow 1$  transition is saturated. Here  $\tau_{VV}$  is the relaxation time within the absorbing vibrational mode. Requirement (21) appears to be due



to the deactivation process with the typical time,  $\tau_0$ . The analogous requirement for the considered case of a binary system must be more rigid, because the  $V-V'$  resonance exchange process takes away some vibrational energy. This requirement will be deduced below. For the present, let us suppose that the necessary vibrational temperature can be achieved despite the vibrationally excited molecular relaxation.

Thus it is reasonable to take into consideration the  $V-V$  relaxation process within the vibrational mode  $\nu_j^M$  interacting with the laser radiation, that within the appropriate vibrational mode  $\nu_j^m$  of the molecules  $m$ , and the  $V-V'$  exchange process between  $\nu_j^M$  and  $\nu_j^m$ . The relaxation processes under study are shown in Fig. 5. As before, the intensity of radiation is supposed to be sufficient to saturate  $0 \rightarrow 1$  transition of the vibrational mode  $\nu_j^M$ , i.e. the relation:

$$N_0 \approx N_1 \quad (22)$$

is valid during a laser pulse. With respect to (22) the populations  $N_v$  of vibrational levels of the molecules  $M$  and those  $n_v$  of the molecules  $m$  are given in the harmonic approximation by the following set of equations:

$$\frac{dN_1}{dt} = \frac{Z}{Z_{VV}^M} \frac{B}{D} [(1 + \alpha_M)N_2 - \alpha_M N_1] + \frac{Z}{Z_{VV'}} \frac{b}{D} [\epsilon(1 + \alpha_m)N_2 - \alpha_m N_1] \quad (23)$$

$$\begin{aligned} \frac{dN_v}{dt} = \frac{Z}{Z_{VV}^M} \frac{B}{D} \left\{ (v+1) [(1 + \alpha_M)N_{v+1} - \alpha_M N_v] - v [(1 + \alpha_M)N_v - \alpha_M N_{v-1}] \right\} + \\ + \frac{Z}{Z_{VV'}} \frac{b}{D} \left\{ (v+1) [\epsilon(1 + \alpha_m)N_{v+1} - \alpha_m N_v] - \right. \\ \left. - v [\epsilon(1 + \alpha_m)N_v - \alpha_m N_{v-1}] \right\} \quad (v \geq 2) \end{aligned} \quad (24)$$

$$\begin{aligned} \frac{dn_v}{dt} = \frac{Z}{Z_{VV}^m} \frac{b}{D} \left\{ (v+1) [(1 + \alpha_m)n_{v+1} - \alpha_m n_v] - v [(1 + \alpha_m)n_v - \alpha_m n_{v-1}] \right\} + \\ + \frac{Z}{Z_{VV'}} \frac{B}{D} \left\{ (v+1) [(1 + \alpha_M)n_{v+1} - \epsilon \alpha_M n_v] - \right. \\ \left. - v [(1 + \alpha_M)n_v - \epsilon \alpha_M n_{v-1}] \right\} \quad (v \geq 0). \end{aligned} \quad (25)$$

Here, as above,  $Z$  is the gas-kinetic collision frequency, expressed in  $s^{-1}$ ;  $D$  is the total concentration of molecules in the mixture,  $B$  is the concentration of the molecules  $M$ ;  $b$  is the concentration of the molecules  $m$ .  $\alpha_M$ ,  $\alpha_m$  are the numbers of vibrational quanta per one molecule  $M$  and one molecule  $m$  respectively:

$$\alpha_M = \frac{1}{B} \sum_{v=0}^{\infty} v N_v \quad \text{and} \quad \alpha_m = \frac{1}{b} \sum_{v=0}^{\infty} v n_v \quad (26)$$

$Z_{VV}^M$ ,  $Z_{VV}^m$ ,  $Z_{VV'}$  correspond to the efficient collisional numbers required for

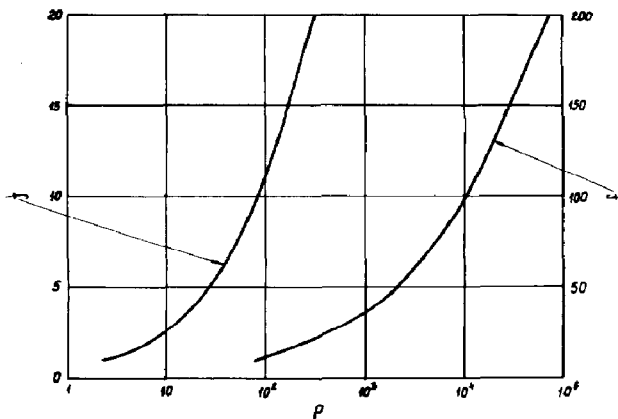
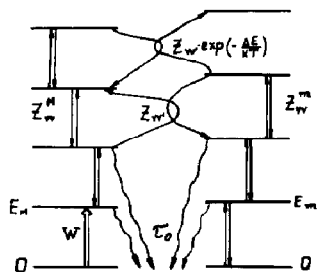


Fig. 5. The diagram of levels and the processes taken into consideration for reactions with  $E_a \gg \hbar\omega$ .

Fig. 6. The function  $f(p)$  determined by eqn. (51).

the vibrational quantum exchange in the following processes:



$\epsilon = \exp\left(-\frac{E_m - E_M}{KT}\right) = \exp\left(-\frac{\Delta E}{KT}\right)$  is the value showing the ratio of the reverse process rate to the rate of process (29).

The equations giving the change of  $\alpha_M$  and  $\alpha_m$  are also necessary. These may be deduced from eqns. (23) - (26) directly:

$$\begin{aligned} \frac{d\alpha_M}{dt} = & \left\{ \frac{Z}{Z_{VV}^M} \frac{B}{D} (1 + \alpha_M) + \frac{Z}{Z_{VV'}} \frac{b}{D} \epsilon (1 + \alpha_m) \right\} \frac{(N_1 - N_2)}{B} + \\ & + \frac{Z}{Z_{VV'}} \frac{b}{D} [\alpha_m (1 + \alpha_M) - \epsilon \alpha_M (1 + \alpha_m)] \end{aligned} \tag{30}$$

$$\frac{d\alpha_m}{dt} = \frac{Z}{Z_{VV'}} \frac{B}{D} [\epsilon \alpha_M (1 + \alpha_m) - \alpha_m (1 + \alpha_M)] \tag{31}$$

Equations (23) - (25), (30) and (31) together with the initial conditions:

$$\begin{aligned} N_0|_{t=0} = N_1|_{t=0} = \frac{B}{2}, \quad N_v|_{t=0} = 0 \quad (v \geq 2), \\ n_0|_{t=0} = b, \quad n_v|_{t=0} = 0 \quad (v \geq 1) \end{aligned} \tag{32}$$

in the harmonic approximation give the vibrational excitation kinetics with

the transformation of vibrational energy into other degrees of freedom being neglected. With a considerable stock of vibrational energy the vibrational molecular distribution approximates to the Boltzmann one, the vibrational temperature of which corresponds to the instantaneous values of  $\alpha_M$  and  $\alpha_m$ . It follows from the fact that  $(N_1 - N_2) \sim B/\alpha_M^2$  and therefore if  $\alpha_M, \alpha_m \gg 1$  one can see from eqns. (30) and (31) that the variation rate of  $\alpha_M$  and  $\alpha_m$  is less than that of the  $V-V$  relaxation. Thus a considerable vibrational heating may be given in terms of vibrational temperatures  $T_M$  and  $T_m$ :

$$T_M = -\frac{E_M}{k \ln x_M}, \quad T_m = -\frac{E_m}{k \ln x_m}, \quad (33)$$

where

$$x_M = \frac{\alpha_M}{1 + \alpha_M}, \quad x_m = \frac{\alpha_m}{1 + \alpha_m}. \quad (34)$$

We are interested in the asymptotic behaviour of  $T_M$  and  $T_m$  when  $T_M, T_m \gg \hbar\omega/k$ . If a change of variables in eqns. (30) and (31) is made in accordance with eqn. (34) and  $t$  is eliminated, then eqns. (30) and (31) take the form:

$$(1 - x_M)^2 \left\{ \left[ \frac{Z}{Z_{VV}^M} \frac{B}{D} (1 - x_m) + \frac{Z}{Z_{VV'}} \frac{b}{D} \epsilon (1 - x_M) \right] \frac{(N_1 - N_2)}{B} + \right. \\ \left. + \frac{Z}{Z_{VV'}} \frac{b}{D} (x_m - \epsilon x_M) \right\} \frac{dx_m}{dx_M} = (1 - x_M)^2 \frac{Z}{Z_{VV'}} \frac{B}{D} (\epsilon x_M - x_m) \quad (35)$$

This gives in zero-order approximation:

$$x_m \simeq \epsilon x_M \quad (36)$$

The combination of eqn. (23) with eqns. (30), (31) and (34) gives in zero-order approximation:

$$\frac{N_1 - N_2}{B} \simeq x_M (1 - x_M) \quad (37)$$

This corresponds to the relation for the Boltzmann populations  $N_1$  and  $N_2$ .

From eqns. (36) and (37) one can deduce the relation between  $x_m$  and  $x_M$  in a first approximation:

$$x_m \simeq \epsilon x_M (1 - \delta) \quad (38)$$

where

$$\delta = (1 - x_M)^4 \left[ B \frac{Z_{VV'}}{Z_{VV}^M} (1 - \epsilon x_M) + b \epsilon (1 - x_M) \right] \left[ B (1 - \epsilon x_M)^2 + b \epsilon (1 - x_M)^2 \right]^{-1}.$$

Finally, the relation between  $T_M$  and  $T_m$  may be expressed as:

$$\frac{1}{T_m} - \frac{1}{T_M} \approx \frac{k}{E_m} \left( \frac{E_M}{kT_M} \right)^4 \left[ B \frac{Z_{VV'}}{Z_{VV}^M} \left( \frac{E_M}{kT_M} + \frac{\Delta E}{kT} \right) + b \frac{E_M}{kT_M} \right] \quad (39)$$

$$\left[ B \left( \frac{E_M}{kT_M} + \frac{\Delta E}{kT} \right)^2 + b \left( \frac{E_M}{kT_M} \right)^2 \right]^{-1} + \frac{\Delta E}{E_m} \left( \frac{1}{T} - \frac{1}{T_M} \right)$$

Here only the first expansion terms are taken into account for  $\epsilon$  and  $x_M$ .

So the difference between the vibrational temperatures  $T_M$  and  $T_m$  is given by two terms. The pumping is responsible for the positive first term in the right hand side of eqn. (39). The second one corresponds to the equilibrium in the binary system of harmonic oscillators and its sign depends on that of  $\Delta E$ . If the first term is less in absolute value than the second one, then the vibrational levels of molecules with the lesser vibrational quantum energy are always more excited.

Let us estimate the selectivity of the reaction of the molecules M and m with the molecules A. In contrast to the previous section it is reasonable here to take the molecules A in deficiency with respect to M and m because a considerable dilution results in a decrease of the vibrationally excited molecules relaxation time. Thus any chemical reaction does not affect the vibrational excitation kinetics considered. Let us take the rate constants  $K_M$  and  $K_m$  of the reactions:



expressed in  $s^{-1}$  according to Arrhenius:

$$K_M = K \exp\left(-\frac{E_a}{kT_M}\right) \text{ and } K_m = K \exp\left(-\frac{E_a}{kT_m}\right) \quad (42)$$

It is reasonable to consider that activation energies and pre-exponential factors are the same for both reactions.

Owing to a sharp exponential dependence of the reaction rate on the vibrational temperature, the reaction occurs practically at a certain vibrational temperature  $T^* \sim E_a/k$ . So the reaction selectivity  $S$  (7) is equal approximately to the ratio between the rate constants of the reactions (40) and (41) with  $T_M, T_m \sim T^*$ .

From eqns. (39) and (42) one can see that the selectivity value is equal to the product of the two values  $S_1$  and  $S_2$  corresponding to the two right terms in eqn. (39):

$$S_1 \approx \exp \left\{ \frac{E_a}{E_m} \left( \frac{E_M}{kT^*} \right)^4 \left[ B \frac{Z_{VV'}}{Z_{VV}^M} \left( \frac{E_M}{kT^*} + \frac{\Delta E}{kT} \right) + b \frac{E_M}{kT^*} \right] \right.$$

$$\left. \left[ B \left( \frac{E_M}{kT^*} + \frac{\Delta E}{kT} \right)^2 + b \left( \frac{E_M}{kT^*} \right)^2 \right]^{-1} \right\} \quad (43)$$

$$S_2 \simeq \exp \left[ \frac{E_a}{E_m} \frac{\Delta E}{k} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (44)$$

$$\text{if } \frac{|\Delta E|}{kT} \gg \frac{\hbar\omega}{E_a} \quad (45)$$

then  $S \simeq S_2$  and a considerable value of  $S$  can be obtained. Requirement (45) may be practically realized for the molecules which differ in the isotopic composition of light atoms. In this case a heavier component of the mixture reacts chiefly in spite of the fact that molecules absorb the radiation. The value of  $S$  does not depend on  $T^*$  since  $T^* \gg T$  and is given by:

$$S \simeq \exp \left( \frac{E_a}{\hbar\omega + \Delta E} \frac{\Delta E}{kT} \right), \text{ if } \frac{|\Delta E|}{kT} \gg \frac{\hbar\omega}{E_a} \quad (46)$$

$$\text{If } \frac{|\Delta E|}{kT} \lesssim \frac{\hbar\omega}{E_a} \quad (47)$$

then the reaction selectivity value is rather limited. In the real case when  $Z_{VV'} \sim Z_{VV'}^M$ :

$$S \simeq \exp \left[ \left( \frac{E_a}{kT^*} \right)^3 \left( \frac{\hbar\omega}{E_a} \right)^2 \right] \exp \left( \frac{E_a}{\hbar\omega} \cdot \frac{\Delta E}{kT} \right) \quad (48)$$

The use of eqn. (48) requires a more accurate determination of  $T^*$ . Besides, the activation energy  $T^*$  depends on the pre-exponential factor value. It is easy to show that the value  $T^*$  may be estimated from the following transcendental equation:

$$\left( \frac{E_a}{kT^*} \right)^3 \exp \left( \frac{E_a}{kT^*} \right) \simeq \frac{KD^2}{2ZB} \left( \frac{B}{Z_{VV'}^M} + \frac{b}{Z_{VV'}} \right)^{-1} \left( \frac{E_a}{\hbar\omega} \right)^2 \quad (49)$$

Finally, the reaction selectivity on condition (47) is defined by:

$$S \simeq \exp \left[ \left( \frac{\hbar\omega}{E_a} \right)^2 f \right] \exp \left( \frac{E_a}{\hbar\omega} \frac{\Delta E}{kT} \right) \text{ if } \frac{|\Delta E|}{kT} \lesssim \frac{\hbar\omega}{E_a} \quad (50)$$

Here  $f$  is the solution of the transcendental equation:

$$f \exp(f^{1/3}) = p \quad (51)$$

where the parameter  $p$  depends on the mixture composition, the rate constant values of elementary processes involved, and the vibrational quantum energy:

$$p = \frac{KD^2}{2ZB} \left( \frac{B}{Z_{VV'}^M} + \frac{b}{Z_{VV'}} \right)^{-1} \left( \frac{E_a}{\hbar\omega} \right)^2 \quad (52)$$

The function  $f(p)$  is presented in Fig. 6. The calculations show that in a typical case  $E_a/\hbar\omega \simeq 10$ ,  $B/b \gg 1$ ,  $2Z/KZ_{VV'}^M \simeq 1$ , i.e.  $p \simeq 10^{-2}$ , then  $f \simeq 10$  and  $S \simeq 1.1$  even if  $|\Delta E|/kT < 10^{-2}$ .

One can see from eqn. (50) that the primary reaction of a lighter component is possible only if:

$$\frac{|\Delta E|}{kT} < \left( \frac{\hbar\omega}{E_a} \right)^3 f \quad (53)$$

In the case

$$\frac{|\Delta E|}{kT} > \left( \frac{\hbar\omega}{E_a} \right)^3 f \quad (54)$$

a heavier component reacts mainly in spite of the fact that molecules interact with the laser radiation.

If the vibrational quantum energy difference is responsible for the selectivity value, the reactions with a larger activation energy are more advantageous. As noted above the activation energy is limited by vibrational energy relaxation processes. The estimation for  $E_a^{\max}$  may be received from the equation giving the relaxation kinetics of vibrational energy:

$$E_a^{\max} \sim \hbar\omega \frac{B}{D} \left[ Z\tau_0 \left( \frac{1}{Z_{VV}^M} + \frac{b\epsilon}{B Z_{VV}'} \right) \right]^{\frac{1}{2}} \quad (55)$$

If  $B/b \gg 1$  then eqn. (55) is equivalent to eqn. (21). In the case  $B/b \ll 1$   $E_a^{\max}$  is considerably less.

From eqns. (46) and (55) the value for  $S_{\max}$  may be found in the case when the difference between the vibrational quantum energies  $\Delta E$  is mainly responsible for the value of  $S$ :

$$S_{\max} \sim \exp \left\{ \frac{B}{D} \left[ Z\tau_0 \left( \frac{1}{Z_{VV}^M} + \frac{b\epsilon}{B Z_{VV}'} \right) \right]^{\frac{1}{2}} \frac{\Delta E}{kT} \right\} \quad (56)$$

In the most advantageous case when  $B/b \gg 1$  eqn. (56) gives:

$$S_{\max} \sim \exp \left[ \left( \frac{\tau_0}{\tau_{VV}} \right)^{\frac{1}{2}} \frac{\Delta E}{kT} \right] \quad (57)$$

Consider, for example, the  $\text{BCl}_3$  vibrational mode  $\nu_3$  excitation, assuming natural composition of the boron isotopes in the mixture (80% of the isotope  $^{11}\text{B}$  and 20% of the isotope  $^{10}\text{B}$ ). Absorbing bands corresponding to the  $\nu_3$  mode lie in the region  $900 - 1000 \text{ cm}^{-1}$ . The isotopic shift of these bands is approximately  $30 \text{ cm}^{-1}$ . According to Steinfeld's recent measurements [29]  $V-T$  and  $V-V$  relaxation times are approximately  $5 \mu\text{s/Torr}$  and  $0.1 \mu\text{s/Torr}$  respectively. From these data the selectivity achieved with respect to the isotope  $^{11}\text{B}$  may be estimated using the formula (56). For the temperature interval  $300 - 200 \text{ K}$  the estimation gives  $S_{\max} \sim 2.7 \div 4.5$ . In order to obtain such selectivity values the reaction with the activation energy  $E_a \sim 20 \text{ kcal/mol}$  must be chosen.

## Conclusions

The analysis shows that there is a principal possibility to conduct selective chemical reactions, stimulated by infra-red laser radiation, in mixtures of molecules with close vibrational levels and identical chemical

properties. This analysis is applicable to the problem of photochemical isotope separation under a laser radiation. Owing to isotopic shift of vibrational levels, the effect allows one of the mixture components to be excited by laser radiation. The primary reaction of a certain component is characterized by the selectivity values  $S$  (eqn. (7)).

(1). In the case when the radiation directly excites a vibrational level with its energy being close to that of activation the photochemical separation of isotopes under a laser radiation is most efficient. In this case the process of molecular activation is fully selective. The unwanted chemical reaction of the mixture component, which does not react with the radiation, is caused by three reasons. The first is conditioned by the process of vibrational excitation transmission approximating the resonance process. The second cause is related to the thermal excitation of vibrational levels arising from heating the mixture throughout a laser pulse. As noted earlier, neither excitation transmission (eqn. (11) nor heating (Fig. 3) play any part when the mixture is sufficiently diluted with a buffer gas.

The third cause is conditioned by the thermal reaction of the non-excited mixture component and, in principle, cannot be eliminated. Chemical reactions, their activation energy  $\leq 0.5$  eV, go well at room temperature. The energy of molecular vibrational quanta ranges usually between 0.1 and 0.5 eV or may be less. Therefore resonance vibrational transitions are used to conduct selective photochemical reactions in mixtures provided that: (a) the ratio between reaction rate for vibration-excited molecules with  $\nu = 1$  and reaction rate for molecules in the ground state [6, 30] is high; and (b) the duration of mixture is short (the realization of this condition is described at the end of the second section).

In this case the maximum value of  $S$  is limited only by the initial equilibrium population of the upper operating level of non-excited mixture component [condition (18), Fig. 2]. The values  $S \sim 10^3 \div 10^4$  are achieved at room temperature.

Thermal reaction, with activation energy  $\leq 1$  eV, plays no part at room temperature. Thus, a very high selectivity value can be obtained if vibrational levels with energy  $\geq 1$  eV are directly excited. Such an excitation is possible under a cascade excitation of some levels [31] as well as under a molecular overtone excitation [32].

(2). If the activation energy is much greater than that of laser radiation quantum, the molecules will be excited up to levels with energy  $\sim E_a$  in the process of the  $V-V$  relaxation. Such an excitation is possible, since the rate of the  $V-V$  relaxation for molecules exceeds considerably, as a rule, the  $V-T$  relaxation rate. Yet, as opposed to the previous case, the selectivity here can be partly lost even in the very activation process. This is caused by the  $V-V'$  relaxation which is very rapid and close to the resonance one.

Thus, with  $E_a \gg \hbar\omega$  the reaction selectivity is limited by molecular and rate constants of elementary processes. Nevertheless, we can obtain greater values of  $S$  if the components differ by the isotopic composition of light

atoms. The effect depends exponentially on the difference  $\Delta E$  of vibrational quanta energies of the two components (eqn. 46). In this case a heavier component mainly reacts, in spite of the fact that molecules interact with the radiation. The maximum achievable selectivity in this case is given by eqn. (57). The example considered at the end of the third section shows that such values as  $S \sim 10$  are also possible.

When the values of  $\Delta E$  are small the selectivity  $S$  is given by eqn. (50). In this case these are very limited. The example under consideration shows that for real values of activation energy and of pre-exponential factor the  $(S - 1)$  value does not exceed 10%.

Separation of a lighter isotope is possible only with small values of  $\Delta E$  (requirement (53)). Therefore in the reaction  $E_a \gg \hbar\omega$  it is impossible, in principle, to obtain a considerable selectivity value relative to a lighter isotope.

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