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CONTROL OF CHEMICAL REACTIONS BY RESONANCE PHOTOACTIVATION OF MOLECULES

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The possibility of producing chemical reactions with the aid of resonance interaction between a particular vibrational degree of freedom of a molecular system and infrared laser radiation is discussed. This interaction leads to a weakening of the chosen bond and to a rapid increase in the rate of reactions involving the breaking up of this bond. It is shown that the realization of this idea in practice requires the use of radiation sources with realistic parameters.

1. One of the most interesting possibilities which can be realized since the advent of variable-frequency infrared lasers is the control of chemical reactions. This can be based on the resonance interaction between the laser radiation and a given vibrational degree of freedom of molecules, and its selective "heating." This paper is concerned with the elucidation of the conditions necessary for this phenomenon and the estimation of the corresponding radiation parameters. To be specific, consider the reaction

$$AB + C \rightarrow A + BC, \qquad (1)$$

where A, B, and C are atoms or atomic complexes. The reaction rate K in thermodynamic equilibrium is given by $K = K_0 \exp(-E_a/kT)$, where E_a is the activation energy and K_0 is a slowly varying function of temperature.

A molecular system may occupy a nonequilibrium state in which the distribution of each vibrational degree of freedom over the energy levels is close to the Boltzmann distribution, but the "temperatures" of the different degrees of freedom are different.[1]

Under these conditions the reaction rate for (1) depends on the "temperature" T_{vib} of the A-B vibrations (vibrations whose energy is largely concentrated in the A-B bond) and the temperature T associated with the translational motion.

Let us suppose that all the degrees of freedom apart from the chosen one have the same temperature T, where $T_{vib} \gg T$. We may suppose that we then have

$$K \approx K_0 \exp(-E_a / kT_{\text{vib}}).$$

Under the usual conditions $T_{vib} = T$. By using radiation of given frequency it is possible to "heat up" the chosen degree of freedom without appreciably heating the medium as a whole, so that T_{vib} is much greater than T. The reaction rate for the reaction defined by Eq. (1) will then rapidly increase, although the temperature T will remain relatively low.

Let us consider in greater detail the conditions for this resonance photoactivation of molecules. We shall have to consider the following processes: 1) absorption of resonance-frequency photons which takes the molecules from, for example, the zero vibrational level to the first level; 2) redistribution of the level population for the given vibrational degree of freedom (vibration-vibration relaxation); 3) transfer of energy to other degrees of freedom of the molecular system, either vibrational or kinetic (cross relaxation), and 4) chemical reactions.

The rate of the first of these processes depends on the intensity of the incident radiation. The other processes occur largely during collisions, so that their rates are proportional to the number of collisions of the molecules per unit time. Vibrational-vibrational relaxation is the fastest process.[1] It is determined by the effectiveness of the resonance or nonresonance interaction of the molecules, and occurs at a sufficiently high rate. For example, for CO_2 molecules the number of collisions necessary to establish an equilibrium distribution over the levels of antisymmetric vibrations is approximately 100. For a partial CO_2 pressure of 1 Torr this requires a time of 10^{-5} sec.[2] Although this time may vary substantially between different molecules, it is usually small.[1]

The cross-relaxation process involving the transfer of energy to other degrees of freedom is a deleterious process for our purposes. It proceeds relatively slowly in the absence of a resonance energy transfer between the different degrees of freedom. For example, for the CO_2 molecules the time for energy redistribution among all the degrees of freedom is higher by more than two orders of magnitude than the vibrational-vibrational relaxation time.[2,3]

2. If we neglect the loss of energy-rich molecules in the chemical processes, we can write the equations describing the change in the population n_v of vibrational levels (v is the level number) in the form

$$\begin{aligned}\frac{\partial n_v}{\partial t} &= W_{v-1,\,v}\, n_{v-1} + W_{v+1,\,v}\, n_{v+1} - (W_{v,\,v-1} + W_{v,\,v+1})\, n_v + \\ &+ \frac{1}{\tau_0}\{(v+1)[(1+\alpha)n_{v+1} - \alpha n_v] - v[(1+\alpha)n_v - \alpha n_{v-1}]\} + \\ &+ \frac{1}{\tau_1}\{(v+1)(n_{v+1} - e^{-\theta_0} n_v) - v(n_v - e^{-\theta_0} n_{v-1})\}. \qquad (2)\end{aligned}$$

In these expressions $W_{v,v\pm1}$ is the probability of the $v \pm 1 \rightarrow v$ transition induced by the radiation, $1/\tau_0$ and $1/\tau_1$ are the rates of vibrational-vibrational and cross-relaxation processes, $\alpha = \Sigma v n_v$, and $\theta_0 = h\nu/kT$. This form of the equations is valid provided the transfer of energy from the heated to the other degrees of freedom occurs sufficiently slowly, so that the energy distribution over all the degrees of freedom except one is an equilibrium distribution. The quantities τ_0 and τ_1 then depend only on the pressure and temperature of the other degrees of freedom. Since the latter varies slowly, we can solve Eq. (2) by assuming that $1/\tau_0$, $1/\tau_1$, and $e^{-\theta_0}$ are all constants (a detailed justification of equations of the type of Eq. (2) and an analysis of the conditions under which they are valid is given, for example, in[1]).

Henceforth we shall assume that the frequency of the radiation is exactly equal to the frequency of the vibrational-vibrational transition from the $v = 0$, $j = j_0$ level to the $v = 1$, $j = j_1$ level, where j is the set of quantum numbers describing the rotational state of the molecule. Under these conditions the only nonzero probabilities are (I is the intensity of the radiation)

$$W_{01} = \frac{c^2 n(j_1)}{8\pi^2 \tau\delta h\nu^3} I,$$

$$W_{10} = \frac{n(j_0) g(j_1)}{n(j_1) g(j_0)} W_{01}. \tag{3}$$

In these expressions τ is the time of spontaneous radiative transition between the corresponding levels, δ is the absorption-line half-width (we are assuming collision broadening), and n(j) and g(j) are the population and statistical weight of the j-th level, respectively. We shall confine our attention to the case where the quantities $W_{01}/n(j_1)$, $W_{10}/n(j_0)$ are much smaller than the reciprocal of the rotational relaxation time. The population n(j) is then given by

$$n(j) = g(j) \exp(-E_j / kT_0) Z_{\text{rot}}^{-1}. \tag{3$'$}$$

where E_j is the rotational level energy and Z_{rot} is the rotational partition function.

3. We shall investigate Eq. (2) in two special cases.

Suppose that the duration t_0 of the light pulse is much greater than τ_0. Equation (2) can then be solved in two stages. During the first stage we neglect all relaxation processes and find the populations n_0 and n_1 during the time t_0. With the initial conditions $n_0 \approx 1$, $n_{v\neq 0} \approx 0$, we have from Eqs. (2), (3), and (3′)

$$n_0 = \frac{a}{1+a}\left\{1 + \exp\left[-\int_0^{t_0} (W_{10} + W_{01}) dt'\right]\right\}, \tag{4}$$

$$n_1 = \frac{1}{1+a}\left\{1 - \exp\left[-\int_0^{t_0} (W_{10} + W_{01}) dt'\right]\right\};$$

when $n_{v\neq 0,1} \approx 0$

$$a = \exp\left(-\frac{E_{j_1} - E_{j_0}}{kT_0}\right).$$

Next, we can solve the homogeneous system given by Eq. (2), taking Eq. (4) as the initial conditions. The solution of this system is well known.[4] The population n_v becomes near-Boltzmann in a time somewhat greater than τ_0. Its "temperature" T_{vib} is determined by the condition

$$\Sigma v n_v(t = t_0) = (e^{h\nu/kT_{\text{vib}}} - 1)^{-1}.$$

Next, during a time of the order of τ_1 the temperature T_{vib} falls to T_0.[4] In this case, $\Sigma v n_v(t = t_0) = n_1(t = t_0)$. The maximum temperature $T_{\text{vib max}}$ which can be obtained with the aid of a short light pulse corresponds to $n_1 = (1 + a)^{-1}$ and is given by

$$T_{\text{vib } max} \approx \frac{h\nu}{T_0} [\ln(2 + a)]^{-1}.$$

When $a \approx 1$ ($|E_{j_0} - E_{j_0}| \ll kT$), the temperature $T_{\text{vib max}}$ is close to the characteristic temperature of the vibrations, $h\nu/k$ (when ν is in cm^{-1} we have $h\nu/k \approx 1.45\,\nu$°K). If the medium is exposed to light of frequency corresponding to $0 \to v_0$ transitions we can, in principle, obtain T_{vib} of the order of $v_0 h\nu/k$. In this case, the distribution n_v at time t_0 is the solution of Eq. (4) with the subscript replacement $1 \rightleftarrows v_0$.

Let us estimate the intensity I which is necessary to ensure that we shall reach the temperature T_{vib} close to maximum, i.e., to ensure that the following condition is satisfied

$$\int_0^{t_0} (W_{10} + W_{01}) dt \gg 1.$$

For the sake of simplicity, we shall assume that the radiation pulse is rectangular. Substituting $W_{01} \approx W_{10}$, we then find from Eq. (3) that

$$I \gg \frac{4\pi^2 \tau\delta h\nu^3}{c^2 n(j_1)} \frac{1}{t_0} \gg \frac{4\pi^2 \tau\delta^0 h\nu^3}{c^2 n(j_1)} \frac{1}{\tau_0^0} p^2. \tag{5}$$

In this expression p is the gas pressure, and δ^0 and τ_0^0 are the line half-widths and time for vibrational-vibrational relaxation reduced to unit pressure, respectively, i.e., $\delta = \delta^0 p$, $1/\tau_0 = p/\tau_0^0$. The numerical value of the factor in front of p^2 on the right-hand side of Eq. (5) for CO_2 molecules ($\nu_3 = 2349$ cm^{-1}) is about 0.003 W-cm^{-2} Torr^{-2}. The value obtained for N_2O molecules ($\nu = 2223$ cm^{-1}) is roughly the same. In our estimates we used the following values of the constants. For CO_2: $\tau \approx 10^{-2}$ sec[5], $\tau_0 \approx 10^{-5}$ sec-Torr[2], $\delta = 5 \times 10^6$ sec^{-1} Torr^{-1} (calculated from the data in[5] on molecular collision cross sections). For N_2O: $\tau \approx 3 \times 10^{-3}$ sec,[6] and τ_0 and δ are assumed to be equal to their values for CO_2. The populations n(j) were assumed equal to the maximum population of the vibrational level for $T_0 = 300$°K (of the order of 0.1).

The intensity satisfying Eq. (5) at atmospheric pressure would amount to a few tens of kW/cm^2 in the case of CO_2 and N_2O.

We note that the conditions $2Wt_0 > 1$ for $t_0 \ll \tau_0$ and $W/n(j) \ll 1/\tau_{\text{rot}}$ (τ_{rot} is the rotational relaxation time) may turn out to be inconsistent because τ_{rot} and τ_0 are frequently not different enough.

4. Let us also consider the case where the length of the light pulse is much greater than the cross-relaxation time. We shall seek the stationary solution of Eq. (2), assuming that $\partial n_v/\partial t = 0$. Equation (2) are satisfied if n_v is of the form

$$n_{v\geq 1} = n_1 \exp[-(v - 1)\theta], \tag{6}$$

$$n_1 = \frac{\alpha + W_{10}\tau_0 + e^{-\theta_0}\tau_0/\tau_1}{\alpha + 1 + W_{01}\tau_0 + \tau_0/\tau_1} n_0, \tag{6$'$}$$

where

$$e^{-\theta} = \frac{\alpha + e^{-\theta_0}\tau_0/\tau_1}{1 + \alpha + \tau_0/\tau_1}. \tag{7}$$

To determine n_1, n_0, α, and θ we can use Eqs. (6′) and (7) and the following two equations which ensue from Eq. (6):

$$\Sigma n_v \equiv 1 = n_0 + n_1(1 - e^{-\theta})^{-1}, \tag{7$'$}$$

$$\alpha \equiv \Sigma v n_v = n_1(1-e^{-\theta})^{-2}. \qquad (7'')$$

It is also convenient to replace Eq. (6′) by an equation which follows from Eq. (2) if it is multiplied by v and summed over v:

$$\alpha - \alpha_0 = \frac{\tau_1}{1-e^{-\theta_0}}(W_{01}n_0 - W_{10}n_1) = \frac{\tau_1 W_{10}(a n_0 - n_1)}{1-e^{-\theta_0}}, \qquad (7''')$$

$$\alpha_0 = \frac{e^{-\theta_0}}{1-e^{-\theta_0}}.$$

The appropriate transformation of Eqs. (7)–(7‴) leads to (we are assuming that $e^{-\theta_0} \ll 1$)

$$W_{10} = \frac{1}{\tau_1}\left(\frac{e^{-\theta}}{1-e^{-\theta}} - \frac{e^{-\theta_0}}{1-e^{-\theta_0}}\right) \qquad (8)$$

$$\times\left[(1-e^{-\theta})(1-ae^{-\theta}) - \tau_0\tau_1^{-1}(e^{-\theta}-e^{-\theta_0})(2-e^{-\theta})\right]^{-1}.$$

This result gives in explicit form the probability W and, consequently, the intensity I necessary to obtain n_v with given θ. The quantities n_0, n_1, and α are uniquely determined by θ. We note that although the ratio n_1/n_0 is basically different from $e^{-\theta}$, this difference is always small. It follows that n_0, n_1, and α are practically equal to the corresponding quantities in the case of the Boltzmann distribution $n_v = n_0 e^{-v\theta}$. Next, the quantity $h\nu/k\theta$ is regarded as the temperature of the vibrations.

In principle, we can use Eq. (8) to find the function $\theta(W)$ but, in general, this function is unwieldy and inconvenient for analysis. At low radiation intensities ($W_{10} \ll 1/\tau_1$) it is clear that $e^{-\theta} - e^{-\theta_0} \approx W_{10}\tau_1$. At very high intensities $e^{-\theta}$ tends to a maximum value $e^{-\theta_m}$, which is obtained by equating to zero the denominator in Eq. (8). Apart from small factors of the order of $(\tau_0/\tau_1)^2$ we have

$$e^{-\theta_m} \approx \frac{1+a}{2a} - \sqrt{\left(\frac{1-a}{2a}\right)^2 + \frac{\tau_0}{\tau_1}}. \qquad (9)$$

When $a \leq 1$ (R and Q branches in the absorption band), the temperatures T_{vib} corresponding to Eq. (9) can hardly be reached in practice. They may exceed by an order of magnitude or more the characteristic temperature $h\nu/k$ of the vibrations. In this temperature region Eqs. (2) are not valid and anharmonic effects must be taken into account. It is readily seen that for $a > 1$ (P branch)

$$T_{\text{vib}} < \frac{h\nu}{k}\ln a = \frac{h\nu}{E_{j_0} - E_{j_1}} T_0. \qquad (10)$$

When $W_{10} \gg 1/\tau_1$ the dependence of T_{vib} on W is very weak. Therefore, if the intensity of the radiation is high enough (so that $W \gg 1/\tau_1$) we can fix the temperature T_{vib} by specifying T_0 or $E_{j_0} - E_j$ (by suitable choice of radiation frequency).

In most cases, we can neglect the term proportional to τ_0/τ_1 in the denominator of Eq. (6). If, at the same time, the condition $e^{-\theta_0}/\tau_1 \ll W$ is satisfied, Eq. (8) will transform so that

$$W = \frac{1}{\tau_1}\frac{e^{-\theta}}{(1-e^{-\theta})^2(1-ae^{-\theta})}. \qquad (8')$$

It is interesting to estimate the intensity which is necessary to obtain $W_{10} \approx 1/\tau_1$ (this corresponds to $T_{vib} \approx 0.8h\nu/k$ if $a \approx 1$).

To achieve this, we can use the right-hand side of Eq. (5) by substituting $2\tau_1^0$ instead of τ_0^0 in the numerator and replacing the sign $\gg$ in (5) with an equality [the inequality (5) is obtained from the condition $W_{01} + W_{10} \gg 1/\tau_0$]. Using the above estimates, and assuming that $\tau_1^0/\tau_0^0 \sim 100$, we find that the corresponding intensity for CO_2 and N_2O is $I = I_0 p^2$, $I_0 \approx 3 \times 10^{-3}$ W-cm^{-2} Torr^{-2}. An analogous estimate for CO(ν = 2144 cm^{-1}) yields $I_0 < 2 \times 10^{-4}$ W-cm^{-2} Torr^{-2} (we have used $\tau_1 = 10^{-1}$ sec-Torr, measured in[6] with T_0 = 2200°K, i.e, a highly underestimated result).

At pressures of the order of 100 Torr the intensities for which $W_{01}\tau_1 = 1$ amount to about 30 W/cm^2 for CO_2 and N_2O, and about 2 W/cm^2 for CO. Such intensities are quite practicable. The corresponding temperatures T_{vib} for $a \approx 1$ are approximately 2500–2700°K for all three gases.

5. Let us now consider a chemical reaction taking place under the conditions of resonance heating, for example, the N_2O + NO reaction in a mixture of N_2O and NO. The change in the partial pressure of NO in the case of thermodynamic equilibrium is described by

$$\frac{1}{p_{NO}}\frac{\partial p_{NO}}{\partial t} = K_0 e^{-E_a/kT_0}. \qquad (11)$$

We are assuming that the rate of the reverse reaction is small. It is natural to assume that the rate of the above reaction is largely determined by the temperature of N_2O vibrations with frequency $\nu_3 \approx 2223$ cm^{-1}, i.e., we can replace T_0 by T_{vib} in Eq. (11).

We shall suppose that $p_{NO} \ll p_{N_2O}$. The cross-relaxation time for the ν_3 vibrations of NO are then determined exclusively by the pressure of this gas: $1/\tau_1 \approx p_{N_2O}/\tau_1^0$, and chemical processes have a slight effect on the population of the upper vibrational states. The temperature T_{vib} will therefore be given by Eq. (8), as before.

Let us estimate, for example, the temperature T_{vib}^0 at which $p_{NO}^{-1}\partial P_{NO}/\partial t$ becomes greater than $1/\tau_1$. Replacing T_0 by T_{vib} in Eq. (11), we find that under these conditions

$$T_{\text{vib}}^0 \approx E_a/R\ln K_0\tau_1{}^0.$$

For the given reaction $K_0 = 10^{14.4}$ sec^{-1}mol-cm^{-3}, $E_a \approx 50$ kcal.[7] For T_0 = 300°K we have $K_0 = 2 \times 10^7$ sec^{-1} Torr.

Finally, T_{vib}^0 = 2500°K. It follows from the estimates made earlier that such high temperatures can be achieved with the use of realistic radiation intensities. Since the reactions then occur in time intervals shorter than the cross-relaxation time, the kinetic temperature T_0 will remain almost constant during the reaction. The radiation will affect the reaction in a directional fashion, accelerating only those processes whose probability is very dependent on the temperature of the chosen degree of freedom.

6. Thus, resonance photoexcitation by coherent radiation can be used to "heat up" a particular vibrational degree of freedom to high temperatures. At such temperatures the breaking of the bond weakened by the vibrations will occur quite readily, and the corresponding chemical reactions will proceed at a substantially higher rate. Moreover, the molecular ensemble assumes completely new properties and, in particular, the chemical equilibrium during the course of the reaction will be considerably shifted toward the reaction products.

The above estimates show that effective control of a molecular system by pulsed or continuous coherent radiation can be achieved with radiation sources having realistic parameters.

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