Kinetics of excitation of molecular gases by laser radiation

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An analytic solution is obtained for the set of kinetic equations for the vibrational state population of molecules in the field of resonant radiation. The solution is obtained in the harmonic approximation at arbitrary relations between the characteristic times (the pulse duration, the vibration-vibrational and vibration-translational relaxation times, and the stimulated radiative transition time), under the assumption that rotational relaxation occurs. The time dependence of vibrational energies and vibrational level populations in a mixture of two gases is derived in the case when the natural oscillation frequencies of the molecules are close to each other. Optimization of the parameters of the problem is discussed in connection with chemical reactions of two types.

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1. INTRODUCTION

The possibility of using laser to stimulate chemical reactions has been widely discussed in the literature in recent years.[1-7] A number of experimental investigations of chemical reactions in a field of a resonant infrared-radiation source has confirmed this possibility.[8-11] The resonant action of laser radiation of frequency ω not only can greatly accelerate the chemical reactions, but can also initiate reactions that do not occur in thermal excitation of molecules.

For adiabatically slow collisions of excited and unexcited molecules it can be assumed that the activation energy ϵ_0 is determined only by the electronic wave functions. In this case the height of the barrier ϵ_0 does not depend on $\hbar\omega$. If the molecules are excited in the first vibrational state with the aid of the induced transition $0 \rightarrow 1$, then the vibrational energy can go over during the collision process, with a probability P_{10}, into translational energy. Thus, an additional fraction of the molecules, whose kinetic energy prior to the collision was smaller than ϵ_0 by an amount $\hbar\omega$, can enter in the reaction. The relative change of the reaction yield, upon excitation of the vibrational level, is then given by an expression of the type

$$\delta=1+\rho P_{10}(e^{\hbar\omega/kT}-1), \tag{1.1}$$

where ρ is the fraction of the excited molecules. It is assumed that the excitation of the upper vibrational states as a result of the collisions is insignificant. This mechanism can lead to an increase of the reaction rate by several times (if $\hbar\omega \ll \epsilon_0$). If $\hbar\omega \lesssim \omega_0$, as is the case, e.g., under experimental conditions,[10] then the increase of the reaction rate can be much larger.[3]

Another catalysis mechanism consists of rapid heating of a selected vibrational degree of freedom of the molecule up to its dissociation. The produced free radicals become capable of actively entering in the reaction. As they interact with one another, the molecules become successively excited to a dissociation energy ϵ comparable with the reaction barrier. Thus, the reaction time is determined to a considerable degree by the time required for the molecule to acquire an energy $\sim\epsilon$. The vibrational temperature begins to differ appreciably from the translational one, and the rates of the reactions initiated by laser radiation can exceed the rate of the vibration-translational relaxation. This makes it possible to realize intense special-purpose chemical reactions.[1,2] Selective excitations of the molecules of one of the isotopes by laser radiation makes possible photochemical separation of the isotopes in the infrared band, a fact already demonstrated experimentally.[10,12]

The kinetics of the excitation of molecular systems in the field of resonant infrared radiation, with account taken of the relaxation in the collisions, have been considered in a number of papers[1,2,4-8,13,14]. Thus, the kinetics of oscillatory systems was studied in[13], in the diffusion approximation, in the case when the relaxation of the rotational degrees of freedom has no time to take place because of the large probabilities W of the induced radiative transitions, such that $W\tau_{\text{rot}} \gg 1$, where τ_{rot} is the rotational-relaxation time. This is accompanied by the so-called "bottleneck" effect, which limits the rate of excitation of the molecules in the system. In[2] is considered the kinetics of oscillatory molecular systems. Here, too, a diffusion approximation is used and presupposes a continuous distribution of the population of the vibrational levels; this is valid, of course, only in the case of sufficiently small $\hbar\omega$. Cases when $\hbar\omega$ is not small in comparison with ω_0 are far from rare, so that an exact solution of the initial kinetic equations is in general essential. Artamonova, Platonenko, and Khokhlov[1] discuss the continuous irradiation regime, and also a pulsed regime with very short pulses of duration $t_0 \ll \tau_0$, where τ_0 is the time of the vibration-vibrational relaxation. A number of papers[4,5,14] deal with the kinetics in the so-called cutoff oscillator model, according to which the molecule is described by a harmonic oscillator with a finite number of levels, and the rate of decay of the upper vibrational level determines the molecule dissociation rate. A solution of this problem has been obtained, however, only in the case of stationary and quasistationary excitation of the molecules. Of very great interest are the results of an investigation of the distribution function for the vibrational-level population and dissociation rate in a more realistic model that takes the anharmonicity of the molecule into account.[4,5] The solution of the stationary and quasistationary problems has shown in this case that allowance for the anharmonicity greatly influences the vibrational temperature and leads to a noticeable deviation from a Boltzmann distribution function. We note that in spite of the large number of recent papers devoted to the kinetics of molecular gases in laser-radiation fields, the nonstationary problem has not yet been solved even in the simplest harmonic-oscillator model.

This paper is an attempt at an analytic solution of the system of kinetic equations in the harmonic approximation for an arbitrary ratio of the characteristic times t_0, τ_0, $1/W$, and τ_1. Here τ_1 is the vibration-translational relaxation time. It is assumed that rotation relaxation does take place in the system, so that

$$W\tau_{\text{rot}} \ll 1. \tag{1.2}$$

We consider here two cases: the case when cascade excitation of the molecules takes place, which obtains at small anharmonicity, and the case when only the first vibrational state of the molecule is resonantly excited by the radiation (the 0 → 1 transition). The upper excited levels are then populated only by collisions. The second case occurs at large anharmonicity. Thus, the two models describe the real situation from two aspects. Actually there exist conditions when laser radiation can be used to excite several vibrational levels in succession. The cascade-excitation model is therefore optimistic in the case of the mechanism of reactions with dissociation, while the model of the one-step excitation is, to the contrary, pessimistic. We consider the kinetics of the excitation in both a single-component gas and in a mixture of different gases. The mathematically simpler case of cascade excitation will be treated quite briefly, and only the results necessary for a comparison of the cascade and one-step excitation of molecular systems will be presented.

2. CASCADE EXCITATION IN A ONE-COMPONENT SYSTEM

If we neglect the change of the population balance of the vibrational levels on account of the reaction, then the system of kinetic equations for n_k can be represented in the form

$$\begin{gathered} dn_k/dt=(k+1)W_{10}n_{k+1}+kW_{01}n_{k-1}-n_k[(k+1)W_{01}+kW_{10}] \\ +\tau_0^{-1}\{(k+1)[(1+\alpha)n_{k+1}-\alpha n_k]-k[(1+\alpha)n_k-\alpha n_{k-1}]\} \\ +\tau_1^{-1}\{(k+1)(n_{k+1}-e^{-\Theta}n_k)-k(n_k-e^{-\Theta}n_{k-1})\}. \end{gathered} \tag{2.1}$$

It is assumed here that the relaxation times τ_0 and τ_1, and also $\Theta = \hbar\omega/T$, do not depend on the temperature and that the radiative relaxation is small. The probabilities of the radiative transitions 0 → 1 and 1 → 0 are designated W_{01} and W_{10}.

It is easily seen that the "reserve" of the vibrational energy

$$\alpha=\sum_{k=0}^{\infty} kn_k$$

depends on the time in the following manner: in the time of action of a rectangular pulse t_0 we have

$$\alpha(t)=W\tau_1(1-e^{-t/\tau_1}), \tag{2.2}$$

and after the pulse is switched off, α relaxes in accord with the law

$$\alpha(t)=\alpha(t_0)\exp[-(t-t_0)/\tau_1]. \tag{2.3}$$

We have accordingly for the populations of the vibrational levels

$$\begin{gathered} n_0=[1+W\tau_1(1-e^{-t/\tau_1})]^{-1} \quad \text{if} \quad t\leqslant t_0, \\ n_0=[1+W\tau_1(e^{-(t-t_0)/\tau_1}-e^{-t/\tau_1})]^{-1} \quad \text{if} \quad t>t_0. \end{gathered} \tag{2.4}$$

We note that the function $n_k(t)$ is determined only by the cross-relaxation time τ_1 and by the intensity of the source W. In the case of a short pulse, such that $t_0 \ll \tau_1$, we have

$$n_0\approx(1+Wt_0)^{-1}, \quad n_1\approx Wt_0(1+Wt_0)^{-2}.$$

If the intensity is such that $Wt_0 \gg 1$, then

$$n_1\approx n_0\approx 1/Wt_0,$$

i.e., at high intensities we have n_0, $n_1 \ll 1$ and the upper excited states are strongly populated. This is bad in the case of the first mechanism for the stimulation of chemical reaction, but is suitable in the case of the second mechanism. At low intensities $Wt_0 \ll 1$ we have

$$n_0\approx 1-Wt_0, \quad n_1\approx Wt_0(1-2Wt_0).$$

Therefore this case is bad from the point of view of both reaction-stimulation mechanism. If the pulse duration is large, so that $t_0 \gg \tau_1$, then $\alpha_\infty = W\tau_1$,

$$n_0=(1+W\tau_0)^{-1}, \quad n_{k>1}=\frac{1}{1+W\tau_1}\left(\frac{W\tau_1}{1+W\tau_1}\right)^k. \tag{2.5}$$

In this case the vibrational temperature is

$$T_{\text{rib}}=\hbar\omega/\ln\frac{1+W\tau_1}{W\tau_1}. \tag{2.6}$$

At high intensities, such that $W\tau_1 \gg 1$, we can formally obtain a very high vibrational energy α, and correspondingly $T_{\text{vib}} = \hbar\omega W\tau_1$. It must be remembered, however, that the inequality $W\tau_1 \gg 1$ can contradict the condition (1.2), the satisfaction of which is necessary for the foregoing calculation. We note that the population of the first excited state cannot exceed 1/4 (in which case $n_0 = 1/2$, a value attained at intensities corresponding to the condition $W\tau_1 = 1$). In light of the mechanisms that proceed from the first excited state this is the optimal case in the continuous irradiation regime.

3. CASCADE EXCITATION IN A TWO-COMPONENT SYSTEM

Let the system constitute a mixture of two molecular gases A and B. In analogy with (2.1) we can write down systems of kinetic equations for the populations n_k^A and n_k^B, assuming, for example, that the gas A is at resonance with the laser radiation, and that the molecules of the gas B can be excited via collisions. We then have for the gas A

$$\begin{gathered} \frac{dn_k^A}{dt}=(k+1)W_{10}n_{k+1}^A+kW_{01}n_{k-1}^A-n_k^A[(k+1)W_{01}+kW_{10}]+Z_{11}^A\{(k+1)n_{k+1}^A \\ -[(k+1)\exp(-\Theta_A)+k]n_k^A+k\exp(-\Theta_A)n_{k-1}^A\}+Z_{12}^A\{(k+1)(\alpha+\rho_A)n_{k+1}^A \\ -[(k+1)\alpha+k(\alpha+\rho_A)]n_k^A+k\alpha n_{k-1}^A\}+Z_{13}^A\{(k+1)(\beta+\rho_B)n_{k+1}^A \\ -[(k+1)\beta\exp(\Theta_B-\Theta_A)+k(\beta+\rho_B)]n_k^A+k\beta\exp(\Theta_B-\Theta_A)n_{k-1}^A\}. \end{gathered} \tag{3.1}$$

Here

$$Z_{11}^A=Z_{AA}P_{10}^{AA}\rho_A+Z_{AB}P_{10}^{AB}\rho_B, \quad Z_{12}^A=Z_{AA}Q_{10}^{AA}, \quad Z_{13}^A=Z_{AB}Q_{10}^{AB};$$

Z_{AA} and Z_{BB} denote the frequencies of the molecule collisions A → A and A → B, respectively, P_{10}^{AA} is the probability of the transition from vibrational to translational energy, Q_{10}^{AA} is the probability of the transfer of vibrational excitation in molecule collisions, ρ_A and ρ_B are the fractions of gases A and B in the mixture:

$$\rho_A=\sum_{k=0}^{\infty} n_k^A; \quad \rho_B=\sum_{k=0}^{\infty} n_k^B,$$

and β is the dimensionless vibrational energy for the gas B.

The system of kinetic equations for n_k^B, in contrast to (3.1), does not contain radiative terms. Multiplying (3.1) by the corresponding system of equations for n_k^B by k and summing from 0 to ∞, we obtain equations for α and β:

$$\frac{d\alpha}{dt}=-Z_{11}{}^A[1-\exp(-\Theta_A)]\left[\alpha-\frac{\rho_A\exp(-\Theta_A)}{1-\exp(-\Theta_A)}\right]$$
$$+Z_{13}[\beta\exp(\Theta_B-\Theta_A)(\alpha+\rho_A)-\alpha(\beta+\rho_B)]+\alpha(W_{01}-W_{10})+W_{01}\rho_A, \tag{3.2}$$

$$\frac{d\beta}{dt}=-Z_{11}{}^B[1-\exp(-\Theta_B)]\left[\beta-\frac{\rho_B\exp(-\Theta_B)}{1-\exp(-\Theta_B)}\right]$$
$$+Z_{13}{}^B[\alpha\exp(\Theta_A-\Theta_B)(\beta+\rho_B)-\beta(\alpha+\rho_A)]. \tag{3.3}$$

We consider the case when the frequencies of the molecules A and B are close, as, e.g., in the case of an isotope mixture. The system (3.2) and (3.3) is then linearized. Assume that the rates of the vibration-translational and vibration-vibrational relaxations in gases A and B and in the mixture are the same. This assumption slightly overestimates the rate of energy transfer from the molecules of gas A to the molecules of gas B and vice versa, for in the real case it is necessary to take into account the resonance defect, which is equal to the isotopic shift. At such small resonance defects, however, the cross sections for excitation transfer are only insignificantly decreased (see, e.g.,[15]). Taking these remarks into account, we obtain at $t \leq t_0$

$$\alpha(t)=\alpha_\infty-\varepsilon_1\exp(-t/\tau_1)-\varepsilon_2\exp[-(1/\tau_0+1/\tau_1)t],$$
$$\beta(t)=\beta_\infty-\frac{\rho_B}{\rho_A}\varepsilon_1\exp\left(-\frac{t}{\tau_1}\right)+\varepsilon_2\exp\left[-\left(\frac{1}{\tau_0}+\frac{1}{\tau_1}\right)t\right] \tag{3.4}$$

where

$$\alpha_\infty=\rho_A\frac{W\tau_1(\rho_A+\tau_0/\tau_1)}{1+\tau_0/\tau_1},\quad \beta_\infty=\rho_A\rho_B\frac{W\tau_1}{1+\tau_0/\tau_1},$$
$$\varepsilon_1=\rho_A{}^2W\tau_1,\quad \varepsilon_2=\rho_A\rho_B\frac{W\tau_1}{1+\tau_0/\tau_1}\frac{\tau_0}{\tau_1}.$$

We introduce the function

$$\varphi(t)=\beta(t)/\alpha(t). \tag{3.5}$$

It is interesting that $\varphi(t)$ does not depend on the intensity of the source. This function is plotted in Fig. 1 for different ρ_A and τ_0/τ_1. At $t \geq \tau_1$, the function $\varphi(t)$ tends to a limiting value $\varphi_\infty = \rho_B/(\rho_A + \tau_0/\tau_1)$. At small ρ_A, when the content of one of the isotopes in the mixture is small, we have $\beta_\infty \gg \alpha_\infty$ if, furthermore, $\tau_0/\tau_1 \ll 1$. This is inconvenient in the case of isotope separation under continuous irradiation, because of the small yield of the required isotope. At small ρ_A it is convenient to have $\tau_0/\tau_1 \lesssim 1$. Since as a rule in real gases we have $\tau_0/\tau_1 \ll 1$, we can decrease τ_1 by adding a buffer gas that does not resonate with the main mixture. This role can be played by the reagent itself in the case of chemical reactions. We note that $\alpha = \beta$ at $t \approx 2\tau_0$. We can therefore work effectively in the pulsed regime, by limiting the time t_0 of the pulse to certain values τ_0 (depending on the ratios ρ_A/ρ_B and τ_0/τ_1, see Fig. 1). It is convenient to deal with the relations between α and β in the case of isotope separation in chemical reactions of the second type. When seeking for the optimal variant for isotope separation in reactions of the first type, it is necessary to know the behavior of the function

$$Q(t)=n_1{}^B(t)/n_1{}^A(t).$$

It is necessary, in addition, to indicate the conditions under which the population of the first excited state of the molecule of the required isotope is appreciable while A(t) is small.

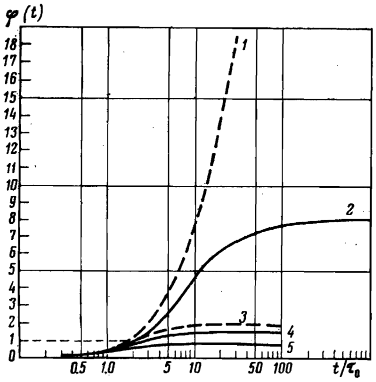

FIG. 1. The function $\varphi(t)$ for different system parameters in the case of cascade excitation: curve 1–$\rho_A = 0.01$, $\tau_0/\tau_1 = 10^{-2}$; 2–$\rho_A = 0.1$, $\tau_0/\tau_1 = 10^{-2}$; 3–$\rho_A = 0.01$, $\tau_0/\tau_1 = 0.5$; 4–$\rho_A = 0.1$, $\tau_0/\tau_1 = 0.5$; 5–$\rho_A = 0.1$, $\tau_0/\tau_1 = 1$.

To ascertain these conditions it is necessary to have expressions for $n_k^A(t)$ and $n_k^B(t)$; these are easily obtained by the method of generating functions. We present here only the final result. For $k \geq 1$ we have

$$n^A_{k\geq1}=n_0{}^A\left(1-\frac{n_0{}^A}{\rho_A}\right)^k,\quad n^B_{k\geq1}=n_0{}^B\left(1-\frac{n_0{}^B}{\rho_B}\right)^k, \tag{3.6}$$

and for n_0^A and n_0^B we obtain the expressions (at $t \leq t_0$)

$$n_0{}^A(t)=\rho_A(1+\tau_0/\tau_1)[1+\tau_0/\tau_1+W\tau_1(\rho_A+\tau_0/\tau_1)$$
$$-\rho_AW\tau_0(1+\tau_0/\tau_1)e^{-t/\tau_1}-W\tau_0\rho_B\exp\{-(1/\tau_0+1/\tau_1)t\}]^{-1},$$
$$n_0{}^B(t)=\rho_B(1+\tau_0/\tau_1)[1+\tau_0/\tau_1+W\tau_1\rho_A-\rho_AW\tau_0(1+\tau_0/\tau_1)e^{-t/\tau_1}$$
$$+W\tau_0\rho_A\exp\{-(1/\tau_0+1/\tau_1)t\}]^{-1}. \tag{3.7}$$

Figure 2 shows plots of Q(t) for various values of ρ_A, $y = \tau_0/\tau_1$, and $x = W\tau_0$.

The function Q(t) increases monotonically with time. At low initial concentrations of one of the isotopes ($\rho_A \sim 10^{-2}$) and small y we have $Q < 1$ at very short pulse durations $t_0 \lesssim 0.1\tau_0$. At small ρ_A and $\tau_0/\tau_1 \lesssim 1$, we get $Q < 1$ already for $t_0 \lesssim \tau_0$, and the largest value of Q does not exceed 3. The function Q(t) assumes its asymptotic value faster the larger $W\tau_0$. In the case $\rho_A = 0.5$ and small y, the function Q(t) is small up to $t_0 \approx 0.5\tau_0$. On the other hand if $\tau_0/\tau_1 \lesssim 1$ and $W\tau_0 \lesssim 1$ we have $Q(t) < 1$ for any pulse duration. In this case Q assumes its asymptotic value at t_0 amounting to several

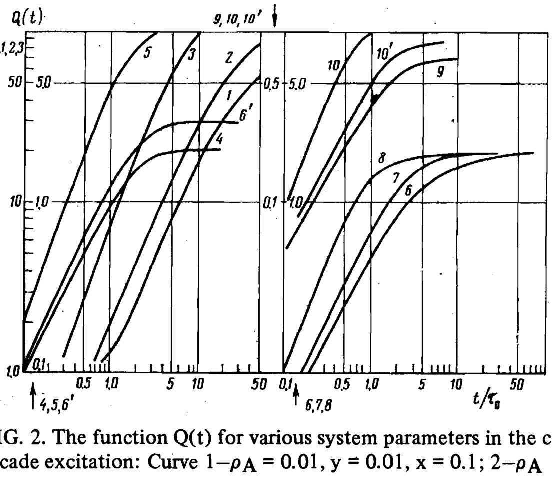

FIG. 2. The function Q(t) for various system parameters in the case of cascade excitation: Curve 1–$\rho_A = 0.01$, y = 0.01, x = 0.1; 2–$\rho_A = 0.01$, y = 0.01, x = 1.0; 3–$\rho_A = 0.01$, y = 0.01, x = 10; 4–$\rho_A = 0.01$, y = 1.0, x = 0.1; 5–$\rho_A = 0.01$, y = 1.0, x = 10; 6–$\rho_A = 0.5$, y = 0.01, x = 0.1; 7–$\rho_A = 0.5$, y = 0.01, x = 1.0; 8–$\rho_A = 0.5$, y = 0.01, x = 10; 9–$\rho_A = 0.5$, y = 1.0, x = 0.1; 10–$\rho_A = 0.5$, y = 1.0, x = 10; 6'–$\rho_A = 0.01$, y = 1.0, x = 1.0; 10'–$\rho_A = 0.5$, y = 1.0, x = 1.0.

times τ_0. Depending on the values of the parameters considered above, one can organize isotope separation in chemical reactions of the first type in such a way that the molecules of the unneeded isotope B enter in the compound. It is necessary then to have $Q > 1$, which is attained at relatively large pulse durations. To the contrary, if the excited isotope A is separated in a new chemical compound, then the values of the function Q should be small. It must be remembered here that at small Q the population n_1^A should be appreciable to obtain noticeable amounts of matter of the required isotopic composition.

4. ONE-STEP EXCITATION IN A ONE-COMPONENT SYSTEM

Let the frequency of the laser radiation be resonant with the transition $0 \to 1$. In this case the system (2.1) remains in force only for k = 0 and k = 1. At $k \geq 2$, there are no radiative terms and the relaxation of the excited states is determined by the collisions. If we introduce for the generating function

$$\Phi = \sum_{k=0}^{\infty} n_k x^k$$

the expansion

$$\Phi(x, t) = \sum_{k=0}^{\infty} \gamma_k (x-1)^k,$$

then all the required properties of the system are determined via γ_k. Indeed,

$$n_p = \sum_{\kappa=p}^{\infty} C_k{}^p \gamma_k (-1)^{k-p}, \quad \gamma_0 = 1, \quad \alpha = \gamma_1.$$

It is easily found that the γ_k satisfy the equations ($k > 1$)

$$\frac{d\gamma_k}{dt} = k\frac{\alpha}{\tau_0}\gamma_{k-1} - k\left(\frac{1}{\tau_0} + \frac{1}{\tau_1}\right)\gamma_k, \quad \frac{d\gamma_1}{dt} = W(n_0 - n_1) - \frac{\gamma_1}{\tau_1}. \qquad (4.1)$$

Consequently γ_k can be represented in the form

$$\gamma_k = \frac{k(k-1)}{\tau_0 f^2(t)} \int_0^t dt_1\, \alpha^2(t_1) f^2(t_1) [q(t, t_1)]^{k-2}, \qquad (4.2)$$

where

$$q = -\frac{1}{\tau_0 f(t)} \int_{t_1}^{t} \alpha f\, dt, \quad f(t) = \exp\left[\left(\frac{1}{\tau_0} + \frac{1}{\tau_1}\right) t\right].$$

Substituting (4.2) in the equation for $\alpha = \gamma_1$

$$\frac{d\alpha}{dt} = W(n_0 - n_1) - \frac{\alpha}{\tau_1},$$

we obtain

$$\frac{d\alpha}{dt} = -\frac{\alpha}{\tau_1} + W\left[-\frac{\tau_0}{\tau_1} + \frac{1+\tau_0/\tau_1}{[1+q(t,0)]^2} - 2\int_0^t \frac{dt_1}{[1+q(t,t_1)]^3} \frac{d\alpha(t_1)}{dt_1} \frac{f(t_1)}{f(t)}\right]. \qquad (4.3)$$

An analogous equation for α was presented without proof in[14].

We proceed to investigate this equation in various time intervals. We consider first the case of high intensities, such that $W^{-1} \ll \tau_0 \ll \tau_1$. It then follows from (4.3) that at $t \gg \tau_0$

$$\int_{\tilde{\alpha}}^{\alpha} d\alpha(\alpha+2)\left[\frac{\alpha(1+\alpha)^2}{W\tau_1} + \frac{\tau_0}{\tau_1}(1+\alpha)^2 - 1\right]^{-1} \approx \frac{t - \tilde{t}}{\tau_0},$$

$$\tilde{\alpha} \sim 1, \quad \tilde{t} \sim \tau_0.$$

If $W\tau_0 > (\tau_1/\tau_0)^{1/2}$, then

$$\alpha(t) \approx \left(\frac{\tau_1}{\tau_0}\right)^{1/2} [1 - e^{-2t/\tau_1}].$$

Consequently in the continuous regime ($t \gg \tau_1$) and at $\tau_1/\tau_0 \gg 1$ the vibrational temperature is

$$T_{\text{vib}} \approx \hbar\omega(\tau_1/\tau_0)^{1/2}.$$

This result agrees with the conclusions of[1,2]. However at source intensities that satisfy the inequality

$$(W\tau_1)^{-1/3}\left(\frac{\tau_1}{\tau_0}\right)^{1/2} > 1,$$

$\alpha(t)$ takes the form

$$\alpha(t) \approx (W\tau_1)^{1/3}\left\{1 - \exp\left[-\frac{3t}{\tau_0}(W\tau_1)^{-2/3}\right]\right\}.$$

For $W\tau_1 \gg 1$, the vibrational temperature is asymptotically proportional to $I^{1/3}$, where I is the source intensity. At low intensities, such that $W\tau_0 \ll 1$, the asymptotic behavior of $\alpha(t)$ is different:

$$\alpha(t) \approx \frac{W\tau_1}{1+2W\tau_1}\left\{1 - \exp\left[-t\left(\frac{1}{\tau_1} + 2W\right)\right]\right\}. \qquad (4.3')$$

If $W\tau_1 \ll 1$, then expression (4.3′) holds true in the entire region $t \gg \tau_0$, but if $W\tau_1 \gtrsim 1$, then the validity range is

$$\tau_0 \ll t \ll 1/2W.$$

At $t \gtrsim 1/2W$ we obtain

$$\alpha(t) \approx (W\tau_1)^{1/3}\left\{1 - \exp\left[-\frac{3(t-\tilde{t})}{\tau_1}\right]\right\}, \quad \tilde{t} \sim \frac{1}{2W}.$$

We note that the vibrational temperature depends here on the source intensity logarithmically.

Let $W^{-1} \ll \tau_0 \ll \tau_1$. Then at $t \ll \tau_0$ we have

$$\alpha(t) \approx {}^1/_2(1 - e^{-2Wt}).$$

In the region $\tau_0 \ll t \ll \tau_1$, the value of α increases with the time more weakly than $(t/\tau_0)^{1/3}$:

$$\alpha(t) \approx \left[\frac{t-\tilde{t}}{\tau_0} + (1-\xi_0)^3\right]^{1/3} + \frac{1}{3}\left[\frac{t-\tilde{t}}{\tau_0} + (1-\xi_0)^3\right]^{-2/3},$$

where $\xi_0 \approx 1/2$ and $\tilde{t} \sim 1/2W$.

At low source intensities ($W\tau_0 \ll 1$) we have $\alpha \approx Wt$ at $t \ll \tau_0$.

In the region $\tau_0 \ll t \ll \tau_1$ it turns out that

$$\alpha(t) \approx (C + 3Wt)^{1/3} - 1,$$

where $C \sim 1$.

Thus, even with single-quantum excitation it is possible to obtain large values of α, and consequently also a large difference between the vibrational and translational temperatures, provided the laser-radiation intensity is not too low. Particularly optimal from this point of view is a regime in which $W\tau_0 \gg 1$, but the vibrational temperature exceeds the translational one even in the case of much lower radiation intensities. At low gas pressures, $W\tau_0$ exceeds unity at very modest radiation fluxes. For example, in the case of CO_2 ($\lambda = 10.7\ \mu$) at $A = 10^2\ \text{sec}^{-1}$ we have $\sigma_{01} \sim 10^{-16}\ \text{cm}^2$. At a pressure $P \sim 1$ Torr, we have $\tau_0 \sim 10^{-5}$ sec.[1] Under these conditions $W\tau_0 \sim 10$ at $I \sim 10^2\ \text{W/cm}^2$.

Comparing the single-quantum excitation with the cascade excitation, we can see that at equal parameters of the radiation and of the medium the value of α is much larger in the cascade case, which is quite natural. Thus, for example at $t \gg \tau_1$ we have $\alpha_{\text{cas}} = W\tau_1$, while the optimal value of α in single-quantum excitation is $\sim(\tau_1/\tau_0)^{1/2}$. Therefore for stimulation of chemical reactions of the second type, the cascade regime, if realizable, offers great advantages.

In concluding this section, we write out the calculated level populations $n_k(t)$. For $n_0(t)$ and $n_1(t)$ we have

$$n_0(t)=-\frac{\tau_0}{\tau_1}+\frac{1+\tau_0/\tau_1}{1+q(t)}-\int_0^t\frac{f(t_1)}{f(t)}\frac{d\alpha(t_1)/dt_1}{[1+q(t)-q(t_1)]^2}dt_1, \qquad (4.4)$$

$$n_1(t)=\left(\frac{1}{\tau_0}+\frac{1}{\tau_1}\right)\frac{q\tau_0}{(1+q)^2}+\int_0^t\frac{f(t_1)}{f(t)}\frac{d\alpha(t_1)}{dt_1}\frac{1-q(t)+q(t_1)}{1+q(t)-q(t_1)}dt_1, \qquad (4.5)$$

which coincides with the results of[14]. For $k \gg 2$ we obtain

$$n_{k\geqslant 2}=(k+1)(k+2)\int_0^t dt_1\frac{\alpha^2(t_1)f^2(t_1)}{\tau_0 f^2(t)}\frac{[a(t,t_1)]^k}{[1+q(t)-q(t_1)]^k}$$
$$\times\left[a^2(t,t_1)-2k\frac{a(t,t_1)}{k+2}+\frac{k(k-1)}{(k+1)(k+2)}\right], \qquad (4.6)$$

where $a(t, t_1) = [q(t_1) - q(t)]/[1 + q(t) - q(t_1)]$.

5. SINGLE-QUANTUM EXCITATION IN A TWO-COMPONENT SYSTEM

In the case of a mixture of two gases A and B, when only the transition $0 \to 1$ is resonant (for the gas A), the system of equations for n_k^B is the same as in cascade excitation, and the system for n_k^A in the form (3.1) is valid for $k = 0$ and $k = 1$; for $k \geq 2$ there are no radiative terms.

The method of generating functions leads to the following equations for α and β:

$$\frac{d\alpha}{dt}=-\frac{1}{\tau_1}[1-\exp(-\Theta_A)]\left[\alpha-\frac{\rho_A\exp(-\Theta_A)}{1-\exp(-\Theta_A)}\right]$$
$$+\frac{1}{\tau_0}[\beta\exp(\Theta_B-\Theta_A)(\alpha+\rho_A)-\alpha(\beta+\rho_B)]+W_{01}n_0{}^A-W_{10}n_1{}^A; \qquad (5.1)$$

$$\frac{d\beta}{dt}=-\frac{1}{\tau_1}[1-\exp(-\Theta_B)]\left[\beta-\frac{\rho_B\exp(-\Theta_B)}{1-\exp(-\Theta_B)}\right]$$
$$+\frac{1}{\tau_0}[\alpha\exp(\Theta_A-\Theta_B)(\beta+\rho_B)-\beta(\alpha+\rho_A)]. \qquad (5.2)$$

We have neglected in these equations the dependence of the excitation-transfer cross sections on the resonance defect, i.e., we have put

$$Z_{11}=1/\tau_1, \quad Z_{12}=Z_{13}=1/\tau_0.$$

We shall henceforth assume that $W_{10} = W_{01}$, and furthermore that the natural frequencies of the molecules A and B are close enough. The procedure for eliminating n_1^A and n_0^A from Eq. (5.1) is analogous to the case of one component, which was described in the preceding section. We therefore present only the final result:

$$\frac{d\alpha}{dt}=-\left(\frac{\rho_B}{\tau_0}+\frac{1}{\tau_1}\right)\alpha+W\left\{\rho_A\right.$$
$$\left.-2\int_0^t dt_1\frac{f(t_1)}{f(t)}\frac{(1/\tau_0+1/\tau_1)\alpha+d\alpha/dt_1}{A^3}\right\}+\frac{\rho_A\beta}{\tau_0}, \qquad (5.3)$$

$$A=1+\int_{t_1}(\alpha+\beta)f(t_2)\frac{dt_2}{f(\bar{t})\tau_0};$$

$$\frac{d\beta}{dt}=\frac{\rho_B\alpha}{\tau_0}-\left(\frac{\rho_A}{\tau_0}+\frac{1}{\tau_1}\right)\beta,$$

where

$$f(t)=\exp[(1/\tau_0+1/\tau_1)t].$$

We consider first the continuous radiation regime ($t \gg \tau_1$). Since the equations for β in the case of a cascade and single-step excitation coincide, the asymptotic value of the function $\varphi = \beta/\alpha$ remains the same as before. Therefore the recommendations described in Sec. 3 and concerning the continuous regime remain in force in this case, too, but the values of α and β, at the same source and medium parameters, differ noticeably in the cascade and single-step excitation cases. At $t \gg \tau_0$ in the case $W\tau_0 \gg 1$ and $\tau_0/\tau_1 \ll 1$ it follows from (5.3) that

$$\alpha_\infty=(\rho_A+\tau_0/\tau_1)[(1+\rho_A\tau_1/\tau_0)^{1/2}-1],$$
$$\beta_\infty=\rho_B[(1+\rho_A\tau_1/\tau_0)^{1/2}-1].$$

At $\rho_A\tau_1/\tau_0 \gg 1$ we have

$$\alpha_\infty\approx\rho_A^{3/2}(\tau_1/\tau_0)^{1/2}, \quad \beta_\infty\approx{}^1/_2\rho_A^{1/2}\rho_B(\tau_1/\tau_0)^{1/2};$$

and in the opposite limiting case

$$\alpha_\infty\approx{}^1/_2\rho_A, \quad \beta_\infty\approx{}^1/_2\rho_A\rho_B\tau_1/\tau_0,$$

so that

$$Q\approx(\tau_1/\tau_0)\rho_B.$$

At low source intensities, such that $W\tau_1 < 1$,

$$\alpha_\infty\approx(W\tau_0)^{1/3}(\rho_A\tau_1/\tau_0+1)^{1/3}$$

(if $W\tau_0 \ll (1 + \rho_A\tau_1/\tau_0)^{1/2}$).

Thus, at low source intensities I, we have $\alpha \sim I^{1/3}$. The vibrational temperature depends on I logarithmically if $\rho_A\tau_1/\tau_0 \ll 1$, and is proportional to $I^{1/3}$ if $\rho_A\tau_1/\tau_0 \gg 1$.

Let us investigate the behavior of α and β, and also of $\varphi(t)$ and $Q(t)$, in different regions of t. To find $Q(t)$ we need expressions for $n_k^{A,B}$ in terms of α and β. We present them here:

$$n_1{}^A=\int_0^t\frac{dt_1}{f(t)}\frac{d}{dt_1}[f(t_1)\alpha(t_1)]F(t,t_1), \quad n_1{}^B=\int_0^t\frac{dt_1}{f(t)}\frac{d}{dt_1}[f(t_1)\beta(t_1)]F(t,t_1), \qquad (5.4)$$

where

$$F(t,t_1)=2[1+q(t)-q(t_1)]^{-3}-[1+q(t)-q(t_1)]^{-2},$$
$$q(t)=\int_0^t(\alpha+\beta)f(t_1)dt_1/\tau_0 f(t). \qquad (5.5)$$

The general expressions for $n_{k\geq 2}^{A,B}$ take the form (4.6), except that in the case of n_k^A it is necessary to replace $\alpha^2(t_1)$ under the integral sign in (4.6) by $\alpha(t_1)[\alpha(t_1) + \beta(t_1)]$, and for n_k^B by $\beta(t_1)[\alpha(t_1) + \beta(t_1)]$, and the corresponding $q(t)$ must be used.

Let the intensity I be such that $W\tau_0 \gg 1$. We then get for α

$$\alpha(t)\approx{}^1/_2\rho_A[1-e^{-2Wt}]. \qquad (5.6)$$

Here

$$\beta(t)\approx\frac{1}{2}\rho_A\rho_B\frac{t_M}{\tau_0}\left[1-\exp\left(-\frac{t}{t_M}\right)-\frac{\exp(-t/t_M)-\exp(-2Wt)}{1-2Wt_M}\right] \qquad (5.7)$$

where

$$t_M=(\rho_A/\tau_0+1/\tau_1)^{-1}.$$

At very short times ($t \ll 1/W$), α and β are small and increase in proportion to the time (or to the pulse duration t_0):

$$\alpha\approx\rho_A Wt, \quad \beta\approx\rho_A\rho_B t/\tau_0 \quad (\tau_1/\tau_0\gg 1),$$

and $Q \approx \varphi = \rho_B(W\tau_0)^{-1} \ll 1$.

In the interval $1/W < t \ll \tau_0$ the quantity α is described by (5.6), and

$$\beta(t)\approx\frac{1}{2}\rho_A\rho_B\left\{\frac{t}{\tau_0}+\frac{1}{2W\tau_0}[1-e^{-2Wt}]\right\}.$$

The function $Q(t)$ is then much smaller than unity:

$$Q(t)\approx\varphi(t)\approx\rho_B\frac{t}{\tau_0}[1-e^{-2Wt}]^{-1}.$$

If $\rho_A\rho_B/2(\rho_A+\tau_0/\tau_1)\ll 1$, then the solutions (5.6) and (5.7) are valid for the entire range of variation of t. If the concentration of the isotope A in the initial mixture is not very small, so that $\rho_A\gg\tau_0/\tau_1$, then (5.6) and (5.7) remain in force up to the time $t\lesssim t_M$. At $t>t_M$

$$\alpha(t)\approx\rho_A^{3/2}(\tau_1/\tau_0)^{1/2}[1-e^{-2\gamma t}]^{1/2},$$
$$\beta(t)\approx\rho_B/\rho_A\alpha[1-\exp(-t/t_M)], \qquad (5.8)$$

where $\gamma=2/\rho_A\tau_1$. In the region $t_M\ll t\ll 1/\gamma$ we have

$$\alpha\approx 2^{1/2}\rho_A(t/\tau_0)^{1/2},\quad \beta\approx 2^{1/2}\rho_B(t/\tau_0)^{1/2}.$$

At $t\gtrsim t_M$ we have $\varphi(t)\to\varphi_\infty$.

In the region $t_M\ll t\ll 1/\gamma$ the populations n_1^A and n_1^B decrease with time like $(t/\tau_0)^{-1/2}$. The function Q(t) assumes its asymptotic value at times much larger than t_M. We note that at sufficiently low intensities, such that $W\tau_0\ll 1$ at τ_0/τ_1, we obtain the following: If $W\rho_A\tau_1$, then α and β are small. At $t\ll\tau_0$ we have

$$\alpha(t)\approx\frac{\rho_A Wt}{2},\quad \beta(t)\approx\frac{\rho_A W\tau_0}{2(1+\rho_A/\rho_B)}\left(\frac{t}{\tau_0}\right)^2,$$

and in the region $\tau_0\lesssim t\ll\tau_1$ we obtain

$$\alpha(t)\approx\frac{\rho_A W\tau_0}{2}[1-e^{-t/\tau_0}]+\frac{\rho_A}{2}\left(\rho_A+\frac{\tau_0}{\tau_1}\right)Wt,$$
$$\beta(t)=\frac{1}{2}\rho_A\rho_B W\tau_0\left\{\frac{t}{\tau_0}-[1-e^{-t/\tau_0}]\right\}.$$

At $t\gtrsim\tau_1$ we obtain an asymptotic solution of the type

$$\alpha(t)\approx\frac{\rho_A W\tau_1}{2}[1-e^{-t/\tau_1}],\quad \beta(t)\approx\frac{\alpha(t)\rho_B}{\rho_A+\tau_0/\tau_1}.$$

In the other limiting case when $W\rho_A\tau_1\gg 1$ but $W\rho_A\tau_0\ll 1$, the values of α and β are small up to a time $\tilde{t}$ which will be defined below.

Thus, at $t\ll\tau_0$ we get

$$\alpha\approx\rho_A Wt,\quad \beta\approx\rho_A\rho_B Wt^2/\tau_0.$$

In the region $\tau_0\lesssim t\ll 1/2W\rho_A$ we have

$$\alpha\approx\rho_A Wt+\frac{1}{2}\rho_B\frac{\tau_0}{\tau_1}(1-e^{-t/\tau_0}),\quad \beta\approx\rho_A Wt-\rho_B\frac{\tau_0}{\tau_1}(1-e^{-t/\tau_0}).$$

The quantity β is not small in comparison with unity at $t\gtrsim 1/\rho_A W>t_M$, where $t_M=(\rho_A/\tau_0+1/\tau_1)^{-1}$. At $\rho_A\tau_1/\tau_0\ll 1$ we have $\alpha_\infty\approx(\rho_A+\tau_0/\tau_1)^{1/2}\ll 1$. If the concentration of the isotope A is not too small, so that $\rho_A\tau_1/\tau_0\gg 1$, then at times $t\gtrsim\tilde{t}$ we have

$$\alpha(t)\approx\rho_A^{4/3}(W\tau_1)^{1/3}(1-e^{-3t/\tilde{t}}),\quad \beta(t)\approx\rho_B\alpha(t),$$

where the characteristic time $\tilde{t}$ depends on the source intensity:

$$\tilde{t}=\rho_A^{-1/3}(W\tau_1)^{2/3}\tau_0.$$

We note in conclusion that both in the case of stimulation of chemical reactions and in the case of isotope separation, the optimal are the laser intensities corresponding to $W\tau_0\gg 1$. However, the values of the other parameters, particularly the pulse durations, are not the same when the two types of reaction indicated above are considered.

It was assumed above that $\exp(\Theta_B-\Theta_A)\sim 1$, i.e., $\Theta_B\approx\Theta_A$. This assumption does not introduce a large error at times when the distribution of the populations $n_k^{A,B}(t)$ has not yet settled and the concept of vibrational temperature is meaningless. In this case the isotope-separation effect can be large and is characterized by the functions $\varphi(t)$ and Q(t). However, at times when a stationary distribution is established in the system, it follows from the indicated assumption that $T_{vib}^A=T_{vib}^B$. In fact, there is a difference between the vibrational temperatures, which can be determined from the solution of the stationary system of kinetic equations:

$$\xi=T\left(\frac{1}{T_{vib}^B}-\frac{1}{T_{vib}^A}\right)=\frac{T}{\hbar\omega}\ln\left(\frac{1+a}{1-b}\frac{1+c}{1+d}\right)$$

where

$$a=(\alpha+\lambda\beta)^{-1}\left[\lambda\beta\frac{\Delta\omega}{T}+\frac{\tau_0}{\tau_1}\exp(-\Theta_A)\right],$$
$$b=(\beta+\lambda\alpha)^{-1}\left[\lambda\alpha\frac{\Delta\omega}{T}-\frac{\tau_0}{\tau_1}\exp(-\Theta_B)\right],$$
$$c=(\beta+\lambda\alpha)^{-1}(\lambda\rho_A+\rho_B+\tau_0/\tau_1),\quad d=(\alpha+\lambda\beta)^{-1}(\lambda\rho_B+\rho_A+\tau_0/\tau_1).$$

$\Delta\omega=\omega_B-\omega_A$, $\lambda=\sigma(\Delta\omega)/\sigma(0)$ is the ratio of the real excitation-transfer cross section to the resonant one.[15]

In the case $\tau_0/\tau_1\ll 1$ and at $\rho_A=\rho_B$ we have

$$\xi=\frac{\Delta\omega}{\omega}\left[\frac{2\lambda}{1+\lambda}+\frac{e^{-\hbar\omega/T}}{1+\lambda}\left(\frac{2\tau_0}{\tau_1}\right)^{1/2}\right].$$

At low initial concentrations of the excited component ($\rho_A/\rho_B\ll 1$), the difference between the vibrational temperatures T_{vib}^A and T_{vib}^B is negligibly small and in the stationary case there is no hope for a noticeable isotopic effect. In the nonstationary case, however, when the pulse duration is comparable with the time of the vibrational exchange in collisions, the separation effect in selective excitation of one of the isotopic modes in chemical reactions, especially in the case of cascade excitation, can be appreciable.

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