PARTIAL POPULATION INVERSION IN ELECTRON LEVELS OF
DIATOMIC MOLECULES UPON RESONANT ACTION OF IR
RADIATION

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A simple method is found for determining the numerical population inversion in electron levels of diatomic molecules for resonant action of IR radiation upon oscillatory transitions.

Producing a population inversion in electron levels of molecules is the central problem in generation of radiation in the visible wavelength range in gases. As a rule inversion is achieved by an electrical discharge. The possibility of producing it in the process of chemical reaction has been considered in many studies (for example, [1-3]). Chemical reactions have been analyzed which have as products the electron-excited molecules BaO, MgO, HF, IF.

The existence of a partial population inversion is determined by the evolution of the molecule distribution functions over oscillatory levels of the upper and lower electron states. The dynamics of change in these distribution functions depends on the rates of V-V and V-T relaxation processes, radiation decay of the upper electron state, formation of electron-excited molecules, and their distributions over oscillatory levels in the elementary act of the excitation process, for example in the elementary act of chemical reaction.

We will consider the reaction $Ba + N_2O \gtrless BaO + N_2$ in argon, which is considered a promising one to produce generation in the visible spectrum. The distribution function of the BaO molecules over oscillatory levels of the electron states $A^1\Sigma$ and $X^1\Sigma$ were found by spectral flame studies in [4]. Analysis of the results of [5] showed that in the elementary reaction act about 20% of the molecules are formed in the state $A^1\Sigma$. Then about 35% of those molecules located in the upper electron state are at the oscillatory level $v' = 1$. At low argon pressure (below 4666 Pa) maxima in the distribution function are found at the levels $v' = 1, 3, 7$. This fact has been treated as the result of oscillatory exchange between closely located oscillatory levels of the electron states $A^1\Sigma$ and $a^3\Pi$ and relaxation of the oscillatory energy of these states. With increase in argon pressure the distribution function approaches equilibrium with the oscillatory temperature ~ 900 K. The values of the Franck-Condon factors and r-centroid [6] permit calculation of the radiation lifetime of the $A^1\Sigma$ state and the probability of transitions between individual oscillatory levels. These probabilities have their highest values for the following oscillatory levels among those for which one may expect the existence of population inversion: $v' = 1 \to v'' = 6, 7, 8$, $v' = 3 \to v'' = 11, 12$, $v' = 7 \to v'' = 19$, $v' = 8 \to v'' = 20$. Radiation lifetimes of upper electron state oscillatory levels are $\sim 10^{-7}$ sec. The characteristic times of V-V and V-T relaxation processes are such that the time of existence of the partial inversion is insignificant. This does not allow increasing the pressure of the active medium to obtain a usable amplification coefficient.

For resonant action of IR radiation on the oscillatory levels of the upper electron state a process develops which can compete successfully with oscillatory relaxation processes. The characteristic radiation kinetic time of this process for a molecule with dipole moment d in a field of intensity ε is defined by the expression $\tau = \hbar/d\varepsilon$. For a BaO molecule in a field with intensity of 10^4 V/m it is equal to $\sim 10^{-8}$ sec. Such a process has a significant effect on the molecular distribution function over oscillatory levels. An analysis of the process was performed in [7], where it was shown that the radiation population of several lower oscillatory levels leads to population of the upper ones due to the oscillatory relaxation process, which preserves the store of oscillatory quanta in the system unchanged. Moreover, the intense IR radiation field will, by broadening lines, also act

upon the oscillatory levels of the long-lived electron state $a^3\Pi$, which leads to population of its upper oscillatory levels and energy transfer to the levels of the state $A^1\Sigma$. Thus, it becomes possible to increase the time of existence of population inversions for levels with oscillatory quantum numbers $v' = 7 \rightarrow v'' = 19$ and $v' = 8 \rightarrow v'' = 20$, where oscillatory relaxation leads to disappearance of the inversion for levels $v' = 1 \rightarrow v'' = 6$, 7, 8 and $v' = 3 \rightarrow v'' = 11$, 12.

We will now attempt to find a means of approximately estimating the partial population inversion in electron levels of biatomic molecules under conditions of resonant IR radiation action. We will consider a system of diatomic molecules modeled by an anharmonic oscillator, interacting with the IR radiation field. We assume that this system has a nonequilibrium distribution over electron states, two of which are optically coupled to each other by electrodipole transitions. The radiation acts in resonant fashion on the populations of the oscillatory levels of only the upper electron state. However during the process of radiation interaction the distribution over electron states cannot change significantly. We will attempt to find possible ways to estimate the partial population inversion between oscillatory levels of the optically coupled electron states.

To do this we will make use of the method developed in [8]. The equation for balance of populations N_V of oscillatory levels v of the upper electron state has the form

$$\frac{dN_v}{dt} = \frac{1}{N} \sum_m \left(Q_{v+1,v}^{m,m+1} N_m N_{v+1} - Q_{v,v+1}^{m+1,m} N_{m+1} N_v \right) -$$
$$- \frac{1}{N} \sum_m \left(Q_{v,v-1} N_m N_v - Q_{v-1,v}^{m+1,m} N_{m+1} N_{v-1} \right) +$$
$$+ \left(P_{v+1,v} N_{v+1} - P_{v,v+1} N_v \right) - \left(P_{v,v-1} N_v - P_{v-1,v} N_{v-1} \right) +$$
$$+ I_{v-1,v} \left(N_{v-1} - N_v \right) - I_{v,v+1} \left(N_v - N_{v+1} \right) + A_{v+1,v} N_{v+1} - A_{v,v-1} N_v,$$

where N is the molecular density, $Q_{i,j}^{p,q}$ is the probability of oscillatory—oscillatory exchange, when due to collision of moelcules located at the levels p and i, a transition occurs to the levels q and j: $P_{i,j}$ and $A_{i,j}$ are the probabilities of collision and spontaneous radiation transitions $i \rightarrow j$; $I_{i,j}$ is the probability of the induced radiation transition $i \rightarrow j$.

Summing the left and right sides over v from 0 to i, we obtain

$$\sum_{v=0}^{i} \frac{dN_v}{dt} = \frac{1}{N} \left(Q_{i+1,i}^{m,m+1} N_m N_{i+1} - Q_{i,i+1}^{m+1,m} N_{m+1} N_i \right) + \tag{1}$$
$$+ P_{i+1,i} N_{i+1} - P_{i,i+1} N_i - I_{i,i+1} \left(N_i - N_{i+1} \right) + A_{i+1,i} N_{i+1}.$$

The probabilities of forward and reverse transitions are related by the expressions

$$Q_{i,i+1}^{m+1,m} = Q_{i+1,i}^{m,m+1} \exp\{- 2\Delta E (m - i)/T\}, \quad P_{i,i+1} =$$
$$= P_{i+1,i} \exp\{- (E_1 - 2\Delta E_i)/T\}, \quad I_{i,i+1} = I_{i+1,i}.$$

Here T is the gas temperature, E_1 and ΔE are the energy of the lower oscillatory quantum of the upper electron state and its anharmonicity. Below, as in [8], we will assume that $T \ll E_1$, $E_1 - 2\Delta E_i \gg T$, $2\Delta E |m - i| \ll T$. Then, if the population changes slowly as a function of level number, the term $P_{i,i+1} N_i$ in Eq. (1) may be neglected.

We now turn to the diffusion approximation, introducing the continuous oscillatory distribution function f(i) such that $N_i = Nf(i)$, $N_{i+1} = Nf(i)[1 + d \ln f(i)/di]$. Replacing summation by integration and considering the quasisteady regime ($dN_V/dt = 0$), we have

$$\int Q_{i+1,i}^{m,m+1} f(m) \left[\frac{d \ln f(i)}{di} - \frac{d \ln f(m)}{dm} - \frac{2\Delta E}{T} (m - i) \right] dm + P_{i+1,i} + \tag{2}$$
$$+ A_{i+1,i} + I_{i,i+1} \frac{d \ln f(i)}{di} = 0.$$

We make use of the relationships

$$Q_{i+1,i}^{m,m+1} \approx Q_{10}(i+1)(m+1)e^{-\delta_{VV}(i-m)}(3/2 - (1/2)e^{-\delta_{VV}(i-m)}),$$

$$P_{i+1,i} \approx P_{1,0}(i+1)e^{\delta_{VT}i}, \quad A_{i+1,i} \approx A_{1,0}(i+1), \quad \delta_{VV} = (0{,}427/\alpha)\sqrt{\mu/T}\,\Delta E,$$

where μ is the reduced mass of the colliding particles, α is the constant in the exponential molecular interaction potential. Moreover, we will assume that for highly excited molecules the major ones of the V–V processes are collisions with molecules in lower oscillatory levels of the upper electron state [8]. The major contribution to the integral of Eq. (2) will then be produced by terms with small m. Therefore, in place of f(m) we may substitute the Trinorov distribution function

$$f_{\mathrm{Tr}} = f_0 \exp\{-i(E_1/T_1 - \Delta E(i-1)/T)\}, \quad T_1 = E_1/\ln(f_0/f_1). \tag{3}$$

Then after substitution of Eq. (3) and approximate integral Eq. (2) takes on the form

$$\frac{1}{f}\frac{df}{di}\left(-Q_{1,0}e^{-\delta_{VV}i}\frac{3}{2}f_0\frac{1}{\left(\dfrac{E_1}{T_1}-\delta_{VV}\right)^2} - \frac{I_{i,i+1}}{(i+1)}\right) \approx \tag{4}$$

$$\approx Q_{1,0}e^{-\delta_{VV}i}\frac{3}{2}f_0\frac{1}{\left(\dfrac{E_1}{T_1}-\delta_{VV}\right)^2}\left(\frac{E_1}{T_1} - \frac{2\Delta E_i}{T} + \frac{\Delta E}{T}\right) + P_{1,0}e^{\delta_{VT}i} + A_{1,0}.$$

We will consider the case wherein the first term on the left side of Eq. (4) may be neglected in comparison to the second, and the form of the spectral line of the acting radiation is such that

$$I_{i,i+1} = y_1(i+1)e^{-y_2 i} \tag{5}$$

(y_1, y_2 are parameters). Then Eq. (4) has the solution

$$f(i) = f_0\exp\left\{\frac{3}{2}\frac{(E_1-\Delta E)}{y_1 T}Q_{1,0}\frac{f_0}{\left(\dfrac{E_1}{T_1}-\delta_{VV}\right)^2}\left[\frac{\left(e^{(y_2-\delta_{VV})i}-1\right)}{y_2-\delta_{VV}}\frac{E_1-\Delta E}{T} + \right.\right. \tag{6}$$

$$\left. + \frac{2\Delta E}{T}\frac{\left(e^{(y_2-\delta_{VV})i}-1\right)}{(y_2-\delta_{VV})^2}\left((y_2-\delta_{VV})i-1\right)\right] -$$

$$\left. - \frac{P_{1,0}\left(e^{(y_2+\delta_{VT})i}-1\right)}{y_1(y_2+\delta_{VT})} - \frac{A_{1,0}\left(e^{y_2 i}-1\right)}{y_1 y_2}\right\}.$$

Equation (6) is valid when the rate of V–V exchange is low in comparison to the rate of induced transitions.

In the case where in Eq. (1) one can neglect terms containing Q, i.e., neglect V–V exchange processes in comparison to collision-type relaxation processes and spontaneous radiation, Eq. (2) takes on the form

$$0 = P_{1,0}(i+1)e^{\delta_{VT}i} + A_{1,0}(i+1) + I_{i,i+1}\frac{d\ln f(i)}{di}.$$

Considering Eq. (5), we obtain

$$\frac{1}{f}\frac{df(i)}{di} = -\frac{P_{1,0}}{y_1}e^{(\delta_{VT}+y_2)i} - \frac{A_{1,0}}{y_1}e^{y_2 i}.$$

Hence

$$f(i) = f_0\exp\left[-\frac{P_{1,0}\left(e^{(\delta_{VT}+y_2)i}-1\right)}{y_1(\delta_{VV}+y_2)} - \frac{A_{1,0}}{y_1 y_2}\left(e^{y_2 i}-1\right)\right].$$

We find the same solution from Eq. (6), if we take $Q_{1,0} = 0$.

To determine the populations of oscillatory levels of the lower electron state we may use the solution of [8]. Knowledge of the molecular distribution functions over oscillatory levels of the upper and lower electron states and the probabilities of molecule formation in these states in the elementary excitation act permits estimation of the partial population inversion in these electron states. Determination of the change over time of the partial population inversion requires detailed analysis of the kinetic levels off the entire set of physical processes.

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