Nonlinear photoprocesses in bichromophores. I. Two-photon and cooperative excitation and nonlinear quenching

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We consider nonlinear photoprocesses in a bichromophore, that is, in a molecule consisting of two chromophoric groups (monomers). The phenomena considered include stepwise excitation and collective processes (summation of the excitation energy of two monomers in one of them and nonlinear quenching), as well as energy transfer between the monomers. A system of kinetic (balance) equations describing the evolution of level populations in a bichromophore is obtained. Unlike the equations used previously, which are quadratic in the populations, the equations obtained by us are linear. Nonetheless, these equations account exactly for the correlation between level populations of two monomers in a bichromophore, which is induced by energy transfer. Stationary level populations of a chromophore have been found. It is shown that the collective phenomena always deplete population of the first singlet but can either enhance or suppress excitation of the higher (second) singlet.

(Abstract translated from Russian by V.A.Markel)

Nonlinear photoprocesses in bichromophores. I. Two-photon and cooperative excitation and nonlinear quenching

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Nonlinear photoprocesses in a bichromophore—a molecule consisting of two chromophore groups (monomers)—are examined, including stepped excitation and cooperative processes (summation of the excitation of two monomers in one bichromophore and nonlinear excitation quenching) as well as energy exchange between the monomers. A system of kinetic (balance) equations describing the evolution of the level populations of the bichromophore is obtained. This system is linear, unlike the previously used population-quadratic equations. The equation system takes exact account of the correlation between the populations of two monomers induced by energy transfer between them. The stationary level populations of the chromophores are found. It is demonstrated that the cooperative processes that always deplete the populations of the first excited states of the monomers will both enhance and attenuate excitation to the higher-order singlets.

INTRODUCTION

There is an extensive variety of optical phenomena, including nonlinear phenomena, in chromophore molecules (see, for example, Ref. 1–4), and they are of great interest. A study of these processes is also important from the applied viewpoint, since chromophores (dye molecules) are used as probes and markers,[5–7] for modifying macromolecules,[8] in active laser media,[9] etc.

This study is devoted to a theoretical description of nonlinear photoprocesses in bichromophores: molecules containing two chromophore groups. There are various such groups, henceforth called monomers, in the quantum mechanics sense (their electron shells only slightly overlap), although they can experience nonradiative electronic excitation-energy exchange in both the first and in higher excited states. Bichromophores are widely encountered objects. They include the dimers of dye molecules formed in solutions in ordinary concentrations. Such dimers limit the lasing power of dye lasers.[9] Bichromophores also occur in dye–micromolecule compounds due to the positive cooperativeness of this process.[10] Moreover, many organic molecules are bichromophores (see, for example, Refs. 11 and 12).

The nonlinear phenomena specific to bichromophores are caused by excitation-energy exchange between monomers. Specifically such exchange will cause a summation of the energies (cooperative excitation); the other aspect to this problem is nonlinear quenching—the loss of excitation energy by the monomerdonor. These processes have a substantial influence on the nonlinear excitation kinetics of the bichromophore.

This study obtains a system of kinetic balance equations describing the nonlinear excitation kinetics of a bichromophore taking into account these processes. The stationary level populations of the bichromophore are determined. It is demonstrated that cooperative processes will always cause depopulation of the lower-lying excited singlets of the monomers, although they can lead to both enhancement and suppression of stepped excitation to the higher-order singlet states. Such excitation may be accompanied by a nonradiative excitation-energy transfer to the surrounding molecules.[13,14] The latter process is of significant interest since it occurs, specifically, in high-power dye lasers (energy transfer to the dye),[15] in modification of macromolecules,[8,16] etc.

A description of the correlated fluctuations in the level populations of a bichromophore and in the flux intensity of fluorescence photons is also of significant interest; this was the subject to Ref. 17.

FORMULATION OF THE MODEL AND FUNDAMENTAL EQUATIONS

We will formulate the following bichromophore model. As we know (see, for example, Ref. 18–21) at low (hydrogen) temperatures the dephasing time in the electronic excited states is measured in picoseconds and diminishes rapidly with increasing temperature in complex molecules that are impurities in the condensed phase. Hence at room temperature the dephasing rate substantially exceeds the rates of the other relaxation processes whose characteristic times are of the order of nanoseconds or picoseconds. We can therefore conclude, taking account of the quantum mechanical distinguishability of the monomers, that the latter can be considered to be in definite (pure) states. We will find the populations of these states from the balance equations, which will be obtained below.

We will designate the electronic states of the monomers $S_i^{\mathrm{I}}, S_i^{\mathrm{II}}$, where i is the energy level number; the superscript identifies the monomer in the bichromophore. We will examine the following processes. We will take into account radiative transitions with cross sections σ_{ij} in the individual monomers

$$S_j + \hbar\omega \xrightarrow{\sigma_{ij}} S_i. \qquad (1)$$

where (1) describes radiative excitation for $i>j$, while induced emission is described when $i<j$.

We will consider the relaxation rates over the vibrational sublevels $\Gamma_i^{(v)}$ (in the electronic state S_i) to significantly exceed the relaxation rates Γ_i of the electronic-state populations in accordance with the observed values. It is therefore possible to consider the decays of the latter to occur from their ground vibrational sublevels

$$S_j \xrightarrow{\gamma_{ij}} S_i, \quad i<j, \qquad (2)$$

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where Γ_{ij} are the partial rates, $\Gamma_j = \Sigma_j \Gamma_{ij}$. Due to the condition $\Gamma_i^{(v)} \gg \Gamma_i$ the upper states will be excited through the ground vibrational sublevels of lower cascade processes of the type (1) $S_0 \to S_1 \to S_2$; two-photon (not stepped) processes have a probability that is small in the parameter $\Gamma_i / \Gamma_i^{(v)}$. Here and henceforth we assume that the photon energy is not so substantial that the upper levels are populated, bypassing the cascade, i.e., in a one-quantum process.

In complex chromophore molecules the lifetime Γ_i^{-1} of the first singlet state may reach tens of nanoseconds at the same time that the upper electronic excited states decay over times of the order of a picosecond (see, for example, Refs. 22 and 23). It is therefore possible to require that the excitation intensity I will not be so substantial that it populates the upper singlet states (and the vibrational sublevels), although it will be sufficient to populate S_1

$$\Gamma_1 \ll \Gamma_2; \quad \Gamma_1 \leqslant \sigma_{ij} I \ll \Gamma_i \, (i \geqslant 2), \quad \Gamma_k^{(v)}. \tag{3}$$

By virtue of Eq. (3) we can limit our analysis to state S_i for $i = 0$ (the ground state), 1, 2; we can ignore the population of the upper levels.

The cooperative excitation (of one of the monomers) and the nonlinear quenching (of the other monomer) are described by the rate constant β_{11} by the formula

$$\begin{aligned} S_1^{\mathrm{I}} + S_1^{\mathrm{II}} &\xrightarrow{\beta_{11}/2} S_0^{\mathrm{I}} + S_2^{\mathrm{II}}, \quad \omega_{10}^{\mathrm{I}} \geqslant \omega_{21}^{\mathrm{II}}, \\ &\xrightarrow{\beta_{11}/2} S_2^{\mathrm{I}} + S_0^{\mathrm{II}}, \quad \omega_{21}^{\mathrm{I}} \leqslant \omega_{10}^{\mathrm{II}}, \end{aligned} \tag{4}$$

which also indicates the energy conditions (for the frequencies of the 0–0 transitions ω_{ij}) insuring the processes in these directions. These same conditions forbid the processes inverse to Eq. (4). Resonance energy exchange is also possible between the monomers

$$S_i^{\mathrm{I}} + S_j^{\mathrm{II}} \underset{\beta_{ji}}{\overset{\beta_{ij}}{\rightleftarrows}} S_j^{\mathrm{I}} + S_i^{\mathrm{II}}, \quad i \neq j. \tag{5}$$

The direct and reverse exchange constants satisfy the detailed-balance equation $\beta_{ij}/B_{ji} = \exp[(\omega_{ij}^{\mathrm{I}} - \omega_{ij}^{\mathrm{II}})/T_0]$, where T_0 is temperature. If the bichromophore is asymmetric (the monomers are not identical), this relation can be other than unity. We will ignore the difference of the other rate constants (1), (2), (4) for these two monomers.

Proceeding from this model we can write out a system of kinetic (balance) equations for the lower electronic level populations (the diagonal elements of the density matrix).

A system of equations was developed previously[24,25] for describing summation of excitation in activated crystals for the average populations n_i (the states S_i) of individual chromophores. For example the equation for n_1 takes the form[25]

$$\dot{n}_1 = -\Gamma_1 n_1 + \sigma_{10} I n_0 - \beta_{11} n_1^2, \tag{6}$$

where the last population-quadratic term describes cooperative excitation (nonlinear quenching). The form of the nonlinear term in Ref. 25 is determined by the fact that the probability of two monomers being in the state S_1 simultaneously is represented as the product of the probabilities n_1 for two monomers. Such a factorization is valid, however, only when there is no correlation between the level populations, which occurs when there is a low rate of the cooperative processes, i.e., with small β_{11}. Otherwise the energy migration processes induce such a correlation which in turn influences the populations and, consequently, migration. Specifically cooperative quenching (4) will obvious reduce the joint probability of both chromophores being in S_1.

We will write a system of balance equations for a compound particle—a bichromophore—to take exact account of the correlation between the populations of both monomers. The state of the bichromophore is characterized by two indices i, j. The population n_{ij} represents the probability that the first monomer is in state S_i^{I}, while the second represents the probability that it is simultaneously in S_i^{II} (i.e., n_{ij} is the simultaneous correlator).

Based on a transition balance we obtain a linear system of kinetic equations in processes (1), (2), (4), and (5)

$$\dot{n}_{00} = -2\sigma_{10} I n_{00} + (\Gamma_1 + \sigma_{01} I)\, n_{10}^{+} + \Gamma_{02} n_{20}^{+}, \tag{7}$$

$$\dot{n}_{11} = -2\left[\Gamma_1 + (\sigma_{01} + \sigma_{21})\, I + \frac{\beta_{11}}{2}\right] n_{11} + \sigma_{10} I n_{10}^{+} + \Gamma_{12} n_{21}^{+}, \tag{8}$$

$$\dot{n}_{22} = -2\Gamma_2 n_{22} + \sigma_{21} I n_{21}^{+}, \tag{9}$$

$$\begin{aligned} \dot{n}_{01} = &-[\Gamma_1 + (\sigma_{01} + \sigma_{10} + \sigma_{21})\, I + \beta_{01}]\, n_{01} + (\Gamma_1 + \sigma_{01} I)\, n_{11} + \Gamma_{02} n_{21} \\ &+ \Gamma_{12} n_{02} + \sigma_{10} I n_{00} + \beta_{10} n_{10}, \end{aligned} \tag{10}$$

$$\begin{aligned} \dot{n}_{12} = &-[\Gamma_1 + \Gamma_2 + (\sigma_{01} + \sigma_{21})\, I + \beta_{12}]\, n_{12} \\ &+ \sigma_{21} I n_{11} + \Gamma_{12} n_{22} + \sigma_{10} I n_{02} + \beta_{21} n_{21}, \end{aligned} \tag{11}$$

$$\begin{aligned} \dot{n}_{02} = &-(\Gamma_2 + \sigma_{10} I + \beta_{02})\, n_{02} + (\Gamma_1 + \sigma_{10} I)\, n_{12} + \Gamma_{02} n_{22} + \sigma_{21} I n_{01} \\ &+ \frac{\beta_{11}}{2} n_{11} + \beta_{20} n_{20}, \end{aligned} \tag{12}$$

which employs a convention for the symmetrized populations $n_{ij}^{+} = (n_{ij} + n_{ji})/(1 + \delta_{ij})$. There are three additional equations for n_{ij}, $i \neq j$ that are required for system closure and are obtained from Eqs. (10)–(12) by the permutation of indices $i \leftrightarrow j$ on n_{ij} and β_{ij}.

The populations n_{ij} are normalized by conservation of particle number

$$\sum_{i,\, j=0}^{2} n_{ij} = 1. \tag{13}$$

The sum on the left side of Eq. (13) is the integral of system (7)–(12). The level populations of the individual monomers $n_i^{\mathrm{I}}, n_i^{\mathrm{II}}$ and the population n_i averaged over the monomers are expressed through n_{ij}, as

$$n_i^{\mathrm{I}} = \sum_{j=0}^{2} n_{ij}, \quad n_i^{\mathrm{II}} = \sum_{j=0}^{2} n_{ji}, \quad n_i = \frac{1}{2}\,(n_i^{\mathrm{I}} + n_i^{\mathrm{II}}). \tag{14}$$

System (7)–(12) is linear, unlike the approximate (ignoring correlation) equations[24,25] for the individual chromophore populations [compare to Eq. (6)]. However as will be clear from the results of the present study in the weak migration limit ($\beta_{11} \ll \Gamma_1$) cooperative effects (excitation and quenching) are small, although, since $n_1^2 \approx n_{11}$, they are correctly described within the framework of theory.[24,25]

It is possible to obtain a closed system of equations for the symmetrized populations n_{ij}^{+}. It is sufficient to sum equations pairwise for n_{ij} and n_{ji} for this purpose. The system obtained here differs from Eqs. (7)–(12) by the absence of terms proportional to the exchange probabilties (5) β_{ij}, $i \neq j$. Therefore the populations averaged over the monomers are generally independent of the latter. However exchange processes (5) are very important in either describing tran-

sient processes (evolutions with given initial conditions) or in analyzing fluctuations.[17]

EXCITATION KINETICS

Within the framework of this model system (7)–(12) exactly describes nonlinear photoprocesses in a bichromophore although it is difficult to solve analytically. However condition (3) allows elimination of the rapidly relaxing variables n_{12} and n_{2i} and it is then possible to obtain a reduced system for n_{ij} $(i,j=0,1)$ that is soluble in its displayed form.

We will consider the kinetics at times t significantly exceeding Γ_2^{-1}; we will also consider the excitation radiation to be slowly varying: $d\ln(I)/dt \ll \Gamma_2$. In this case the rapidly relaxing populations (n_{ij} for i or j equal to 2) instantaneously trace variations of $I(t)$ and the slow variables n_{ij} $(i,j=0,1)$. It is then valid to set $d/dt=0$ in Eqs. (9), (11), and (12). The solution of these algebraic equations subject to conditions (3) take the form

$$n_{22} \approx \frac{\sigma_{21} I}{\Gamma_2} n_{12}^+, \tag{15}$$

$$n_{12} \approx \frac{\Gamma_2 + 2\beta_{21}}{\Gamma_2 + \beta_{12} + \beta_{21}} \frac{\sigma_{21} I}{\Gamma_2} n_{11}, \tag{16}$$

$$n_{02} \approx \frac{\Gamma_2 + 2\beta_{20}}{\Gamma_2 + \beta_{02} + \beta_{20}} \frac{\beta_{11}}{2\Gamma_2} n_{11} + \frac{(\Gamma_2 + \beta_{20}) n_{01} + \beta_{20} n_{10}}{\Gamma_2 + \beta_{02} + \beta_{20}} \frac{\sigma_{21} I}{\Gamma_2}. \tag{17}$$

Expressions for n_{21} and n_{20} are obtained from Eqs. (16) and (17) by the substitution $i \leftrightarrow j$ in n_{ij} and β_{ij}. Although the populations of Eqs. (16) and (17) are in fact small (proportional to Γ_2^{-1}) we cannot neglect these in the fundamental equations. It is necessary to take account of these quantities in order to describe the population processes of levels S_0 and S_1 after excitation to S_2 (radiative or cooperative). This property is formally expressed as compensation of one power by substitution of solutions (16) and (17) into Eqs. (7), (8), and (10).

Carrying out this substitution we obtain the desired reduced system of equations

$$\dot{n}_{00} = -2\sigma_{10} I n_{00} + (\Gamma_1 + \bar{\sigma}_1 I) n_{10}^+ + r_0 \beta_{11} n_{11}, \tag{18}$$

$$\begin{aligned}\dot{n}_{01} = &-\left[\Gamma_1 + \left(\sigma_{10} + \bar{\sigma}_1 + r_1 \frac{\beta_{02}}{\Gamma_2 + \beta_{02} + \beta_{20}} \sigma_{21}\right) I + \beta_{01}\right] n_{01} \\ &+ \left[\Gamma_1 + \left(1 + \frac{\beta_{20} - \beta_{02}}{\Gamma_2 + \beta_{20} + \beta_{02}}\right) \frac{r_1 \beta_{11}}{2} \right. \\ &\left. + \left(\bar{\sigma}_1 + r_0 \frac{\beta_{12} - \beta_{21}}{\Gamma_2 + \beta_{12} + \beta_{21}} \sigma_{21}\right) I\right] n_{11} \\ &+ \left[\beta_{10} + r_1 \frac{\beta_{20}}{\Gamma_2 + \beta_{02} + \beta_{20}} \sigma_{21} I\right] n_{10} + \sigma_{10} I n_{00},\end{aligned} \tag{19}$$

$$\dot{n}_{11} = -2\left(\Gamma_1 + \bar{\sigma}_1 I + \frac{\beta_{11}}{2}\right) n_{11} + \sigma_{10} I n_{10}^+, \tag{20}$$

which introduces conventions for the branching ratios

$$r_0 = \Gamma_{02}/\Gamma_2, \quad r_1 = \Gamma_{12}/\Gamma_2, = r_0 + r_1 = 1 \tag{21}$$

and for the depopulation cross section of the level

$$\bar{\sigma}_1 = \sigma_{01} + r_0 \sigma_{21}. \tag{22}$$

In organic chromophores the upper singlets will experience nonradiative spontaneous decay to the first singlet (compare to, for example, Ref. 26). This means that $r_0 = 0$ in terms of branching ratios (21). However, as demonstrated in Ref. 14, nonradiative excitation-energy transfer from the upper combining singlet S_2 of the chromophore to the solvent will cause a renormalization of the relaxation constants. As a result Γ_{02} and r_0 are nonzero. In terms of its physical meaning r_0 represents the energy transfer probability from S_2 to the solvent.

As before, the deficient equation for n_{10} is obtained from Eq. (19) by permutation of indices. Summing it with Eq. (19) we obtain

$$\dot{n}_{10}^+ = -[\Gamma_1 + (\sigma_{10} + \bar{\sigma}_1) I] n_{10}^+ + 2\left(\Gamma_1 + r_1 \frac{\beta_{11}}{2} + \bar{\sigma}_1 I\right) n_{11} + 2\sigma_{10} I n_{00}. \tag{23}$$

Equation (23) in conjunction with Eqs. (18) and (20) forms a closed, reduced system of equations for the symmetrized populations n_{ij}^+ (by definition, $n_{ij}^+ = n_{ji}$). This system does not contain, as anticipated (see above), the excitation exchange probabilities (5).

We will consider the (quasi) stationary exciting radiation whose intensity $I(t)$ varies over times greater than Γ_1^{-1}. It is then possible to ignore the time derivatives in Eqs. (18), (20), and (23). The solution of these algebraic equations is expressed through the instantaneous intensity I as

$$n_{00} = \frac{1}{Z}\left[(\Gamma_1 + \bar{\sigma}_1 I)\left(\Gamma_1 + \bar{\sigma}_1 I + \frac{\beta_{11}}{2}\right) + r_0 \frac{\beta_{11}}{2} \sigma_{10} I\right], \tag{24}$$

$$n_{11} = \frac{1}{Z} (\sigma_{10} I)^2, \tag{25}$$

where

$$n_{10}^+ = \frac{1}{Z} \sigma_{10} I \left(\Gamma_1 + \bar{\sigma}_1 I + \frac{\beta_{11}}{2}\right), \tag{26}$$

$$Z = (\sigma_{10} + \bar{\sigma}_1)^2 (I^2 + 2 I_s I) + \Gamma_1 \left(\Gamma_1 + \frac{\beta_{11}}{2}\right) \tag{27}$$

with a characteristic saturating radiation intensity

$$I_s = \left\{\Gamma_1 (\sigma_{10} + \bar{\sigma}_1) + \frac{1}{4} \beta_{11} [\sigma_{10} (2 + r_0) + \bar{\sigma}_1]\right\} (\sigma_{10} + \bar{\sigma}_1)^{-2}. \tag{28}$$

Equations (24)–(26) yield the desired solution to the problem of bichromophore excitation kinetics. Hence we will find the first level population averaged over the monomers in accordance with Eq. (14)

$$n_1 = \frac{1}{Z} \sigma_{10} I \left[\Gamma_1 + (\sigma_{10} + \bar{\sigma}_1) I + \frac{\beta_{11}}{2}\right] \tag{29}$$

and the population of the second level by means of Eqs. (15)–(17)

$$n_2 = \frac{1}{Z} \frac{\sigma_{10} \sigma_{21} I^2}{\Gamma_2} \left[(\sigma_{10} + \bar{\sigma}_1) I + \Gamma_1 + \frac{\beta_{11}}{2}\left(1 + \frac{\sigma_{10}}{\sigma_{21}}\right)\right]. \tag{30}$$

It is clear from Eq. (29) that quenching of S_1 will always occur due to cooperative processes (n_1 diminishes with increasing β_{11}). A fundamentally different situation follows from Eq. (30) for S_2. Cooperative processes will suppress nonlinear excitation (will diminish n_2) at intensities $I > I_c = \Gamma_1/(\sigma_{21} - \sigma_{10} - \sigma_{01})$ if $\sigma_{21} > \sigma_{10} + \sigma_{01}$. When the last condition is not satisfied or at low intensities ($I < I_c$), n_2 increases with β_{11}.

The behavior of the level populations with random saturation levels can be observed by employing results from numerical calculations (Figs. 1–3) in which $r_0 = 0$, $\bar{\sigma}_1 = 0$. These assumptions are made only for simplicity and have no influence on the qualitative conclusions. The condition $r_0 = 0$ infers neglecting energy transfer from S_2 to the solvent [compare to the discussion following Eq. (22)]. The

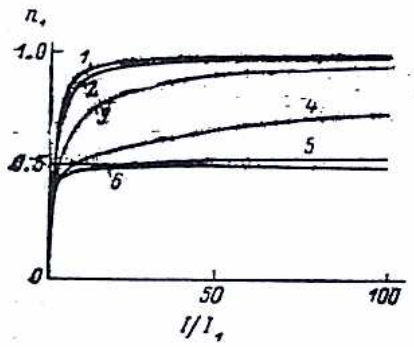

FIG. 1. First-level population n_1 plotted as a function of the relative radiation intensity I/I_1. The normalized constant $I_1 = \Gamma_1/\sigma_{10}$. The ratio $\beta_{11}/\Gamma_1 = 0$, 1, 10, 100, 1000, and 10,000 for curves *1–6*, respectively.

validity of the equality $|\bar{\sigma}_1 = 0$ also assumes smallness of σ_{01}, which is satisfied if excitation takes place outside the fluorescence band of the monomers.

Figure 1 plots the first level populations as a function of radiation intensity. Cooperative nonlinear quenching of S_1 occurs in accordance with this discussion (n_1 diminishes with increasing β_{11} and is strongest at the final saturations). At the upper limit saturation levels $n_1 \to 1$. An intermediate asymptotic range is also visible (see curves *5* and *6*): The population $n_1 \simeq 1/2$ for $\Gamma_1 \ll \sigma_{10} I \ll \beta_{11}$, i.e., only a single monomer from the pair is excited and simultaneous excitation of both monomers is rapidly quenched. Plots of the population of the upper state S_2 as a function of the exciting radiation intensity for the case $\sigma_{10} > \sigma_{21}$ are given in Fig. 2 and for the opposite case in Fig. 3. A comparison of these figures [also compare to the discussion following Eq. (30)] clearly indicates that at low intensities cooperative processes will always enhance excitation to S_2; under saturation conditions they can both enhance n_2 (Fig. 2) and diminish it (Fig. 3).

DISCUSSION

We will briefly summarize the primary principles and results of the present study. Nonlinear (stepped) excitation and cooperative processes (summation of excitation of two monomers in one of them and the accompanying excitation damping) are examined for a chromophore dimer (a bichromophore) together with the energy exchange between monomers. With reasonable assumptions regarding the relaxation rates a system of balance equations (7)–(12) is obtained that is a linear system, unlike previous population-quadratic equations.[24,25] System (7)–(12) takes exact account of the population correlation of the two monomers, induced by the energy exchange between them and which in turn influences (in a self-consistent manner) this energy transfer.

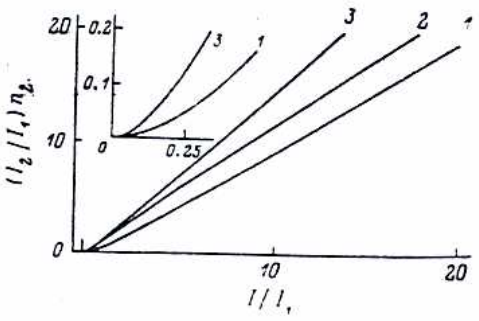

FIG. 2. The normalized second-level population $I_2 n_2/I_1$ as a function of relative intensity plotted for $\sigma_{10}/\sigma_{21} = 2.0$. The inset shows the initial curve sections. The normalized constant $I_2 = \Gamma_2/\sigma_{21}$. The ratio $\beta_{11}/\Gamma_1 = 0$, 10, 10,000 for curves *1–3*, respectively.

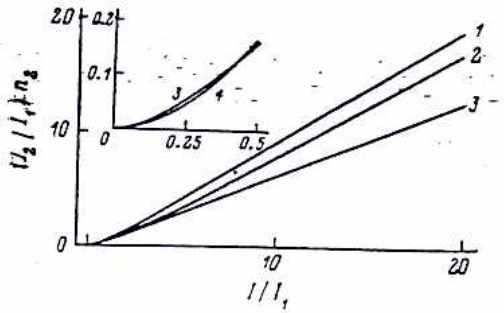

FIG. 3. Same notation as Fig. 2, but calculations employ $\sigma_{10}/\sigma_{21} = 0.3$.

Stationary populations (15)–(17), (24)–(30), see also Figs. 1–3, were obtained; these are important characteristics. Specifically the fluorescence intensity is proportional n_1 [Eq. (29)]. The photochemical transformation rates which occur from the upper-excited states (for example reactions caused by two-quantum excitation energy transfer[13,14]) are proportional to n_2 [Eq. (30)]. n_{11} [Eq. (25)] describes the simultaneous population correlation of the monomers discussed previously. These solutions are substantially dependent on the rate constant of the cooperative processes β_{11} [Eq. (4)]. Nonlinear quenching (diminishing n_1 with increasing β_{11}) is one of the dissipation channels limiting dye laser power (laser dyes in solutions are noticeably dimerized[9]).

Cooperative processes can both enhance and suppress excitation to S_2. The physical cause for the suppression is clear: Cooperative excitation, unlike radiative excitation, not only causes population of the S_2 level but also will cause depopulation of S_1 and will hence inhibit subsequent population of S_2. Summation of excitations will enhance an increase in n_2 only when the relaxation excitation channel to S_2 is not effective (with low saturation or a small radiative excitation cross section, i.e., when $\sigma_{21} < \sigma_{10} + \sigma_{01}$). We note that to the best of our knowledge cooperative suppression of nonlinear excitation has not been identified previously (compare to Refs. 24 and 25).

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Mechanism of vibrational relaxation of chlorine state in the presence of buffer gases

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Energy degradation processes have been studied upon photoexcitation of a mixture of Cl_2 with buffer gases. Anomalous vibrational excitation of the D' state of Cl_2 in the presence of argon is detected. A small quenching efficiency of the D' state as well as a dependence of the quenching rate constant on the temperature of the mixture are associated with this. The indicated experimental facts agree with the conclusions of a model for the quenching of the D state of the chlorine molecule by argon, the primary stage of which is the formation and dissociation of the ionic complex $Cl_2^- \cdots Ar^+$.

INTRODUCTION

In Ref. 1, which is devoted to the study of processes of electronic–vibrational relaxation in the Cl_2 molecule ($D \rightarrow D' \rightarrow A'$) in the presence of buffer gases (He, CF_4, Ar) a difference of the quenching efficiency for the D' state by the argon atom upon use of He and CF_4 as a buffer gas is detected. A quenching mechanism of the D' state was proposed, the primary stage of which is the formation and dissociation of the ionic complex $Ar^+ \cdots Cl_2^-$. Quenching of the D' state proceeds owing to a decrease of the probability for dissociation of the complex along the $Cl_2(D') + Ar$ channel upon decrease of the vibrational excitation energy of the complex below the dissociation threshold of $Cl_2(D')_{v=0} + Ar$. Thus the presence of a store of the vibrational excitation for the $Cl_2(D')$ molecule (in the case with He) leads to a decrease of the quenching efficiency of the D' state by argon.

In the present paper we have continued the investigation of electronic–vibrational relaxation in the Cl_2 molecule under the action of buffer gases with the goal of checking the model proposed in the preceding report.

The setup and method of the experiment were thoroughly described in Ref. 2. It should be mentioned in the present paper that the determination of the quenching efficiency of the D' state of Cl_2 by the argon atom was done in terms of the slope of the function $\Phi_{D'-A'}^{-1}(P_{Ar})$—the magnitude of the inverse quantum yield of the $D' \rightarrow A'$ luminescence as a function of the argon pressure. The luminescence spectra of Cl_2 $D' \rightarrow A'$ under various conditions of photoexcitation were recorded with a resolution of $\Delta\lambda = 2.2$ Å. The pressure of the chlorine was maintained at 0.6 Torr.

EXPERIMENTAL RESULTS AND DISCUSSION

If we assume that the vibrational relaxation of the Cl_2 molecule in the presence of a buffer gas proceeds according to a mechanism of elastic collisions, then Ar and CF_4 are similar relaxers in terms of efficiency because the masses of these particles differ from the mass of Cl_2 by factors of 1.3 (for CF_4) and 1.75 (for Ar). Then in the limits of the model proposed previously for the quenching of the D' state of a chlorine molecule, the following behavior is expected for the dependence of the magnitude of the inverse quantum yield of luminescence $D' \rightarrow A'$ ($\Phi_{D'-A'}^{-1}$) as a function of the argon pressure (upon photoexcitation of the Cl_2–Ar mixture). At small pressures of the buffer gas when the vibrational relaxation is far from completion, the quenching efficiency of the D' state is low and the quantity $\Phi_{D'-A'}^{-1}(P_{Ar}) = \text{const}$. Then in proportion to the completion of the assumed relaxation (in terms of the mechanism of elastic collisions), the rate constant of the quenching process grows and attains at completion a vibrational relaxation of the magnitude obtained earlier when a small amount of argon was added to the mixture of Cl_2–CF_4 ($P_{CF_4} = 760$ Torr). A Boltzmann distribu-

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