RELAXATION PROCESSES FROM HIGHLY-EXCITED VIBRATIONAL LEVELS
OF FLUORENONE MOLECULES

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Until recently only a limited number of spectroscopic methods useful for studying the relaxation processes in the quasi-continuum of vibrational levels have been known. Those methods, which are based on studying nonstationary IR absorption or IR luminescence during a multiphoton excitation (MPE) of the ground-state molecules by CO_2 lasers, exhibit an insufficient temporal resolution and sensitivity in order to expand into the area of low vapor pressures [1]. This hinders studies of various fast relaxation processes, including intramolecular, which play an important role during the excitation to high vibrational levels.

The MPE method was proposed and utilized previously in studying a number of triplet molecules excited by a CO_2 laser [2-5]. The method can be used for studying the relaxation processes in the vibrational quasi-continuum of the triplet state by means of the IR-activated delayed luminescence (DL) either in the visible or the UV region. This method broadens the scope of photochemical studies by the IR of such complex multiatom molecules like anthracene, anthraquinone, and benzophenone which represent the most complex objects studied by methods of the IR laser photochemistry [2-5]. In the present work the vibrational MPE of triplet molecules has been utilized for studying photophysical processes undergoing in fluorenone ($C_{13}H_8O$) vapors during high vibrational excitation in the triplet state.

Fluorenone exhibits a delayed emission in the gas phase [6]. According to [6], the emission consists of two bands in a narrow temperature interval (500-530) K. This emission has been interpreted in [6] as consisting of the phosphorescence band ($\nu_{max} = 17,000$ cm^{-1}) and thermally-activated delayed fluorescence (DF) ($\nu_{max} = 21,000$ cm^{-1}), in spite of the sufficiently high singlet–triplet splitting ($\Delta E_{ST} \cong 7000$ cm^{-1}) between the lowest singlet S_1 and triplet T_1 levels. If the temperature is further increased, the fluorenone luminescence consists mainly of the DF, which gives a dominant contribution to the total emission. The phosphorescence intensity diminishes quickly and can be observed as the low-frequency tail. It should be noted that the basic characteristics of the first singlet S_1 and the first triplet T_1 states in the gas phase are reported only in [6] and until now have not been studied in detail. In solutions the delayed emission of fluorenone has been interpreted as DF due to annihilation [7]. It is known that in the gas phase the nature of delayed emission depends not only on ΔE_{ST} but also on an average amount of vibrational energy of triplet molecules. At the initial temperature of the experiment T = 438 K this amount is $\bar{E} = 3000$ cm^{-1}. The functions of molecular distribution over the vibrational levels of the triplet state, calculated by us with an assumption of identical vibrational frequencies in the electronic ground and the triplet states, demonstrate that the $T_1 \rightsquigarrow \rightarrow S_1$ transition is energetically accessible for a fraction of triplet molecules only at T > 500 K. Since the half-widths of the distribution functions at these temperatures already exceed 3000 cm^{-1}, a certain fraction of molecules from the distribution "tail" will occupy vibrational levels of the triplet state located above S_1. The vibrational levels (IR and RS) of fluorenone, even in the ground electronic state, have not been studied in detail in the entire spectral range, which makes it difficult to determine the complete set of vibrational frequencies reliably. Fluorenone exhibits several IR absorption bands in the radiation range of a CO_2 laser at $\nu_{max} = 915$, 960, and 975 cm^{-1}. The absorption bands of the vapor were studied in a multipath heated cuvette ($\ell = 100$ cm) with NaCl windows at T = 458 K and the vapor pressure of 8.64×10^2 Pa. The IR pulse was generated by a CO_2 laser with transverse discharge. The pulse width at half-height was 90 nsec and the energy was 5 J. IR excitation of triplet molecules was accomplished by line 20P (944 cm^{-1}) of the CO_2 laser. The absorption cross section at the laser frequency was $\sigma = 1.4 \times 10^{-19}$ cm^2.

Delayed luminescence (DL) of fluorenone was studied in a heated quartz cuvette with NaCl windows. The temperature of its optical part determined the initial temperature of the vapor. The studied substance was placed in the cuvette extrusion. The vapor pressure of fluorenone was determined by the temperature of the extrusion kept below the temperature of the active part of the cuvette at least by 15°C. Additional gases were allowed into the cuvette from the vacuum system through a dry shutter. In order to carry out the experiment, process obtained data, and store and output results, a specially designed detection and computational system, based on a DZ-28 electronics and digital S9-8 oscilloscope, was used. This system led to a significant increase in the precision of measurements and analysis of the luminescence kinetics due to extensive averaging and background subtraction. In the course of experiment acquired results were displayed on a graphic screen.

Fluorenone was excited in the first singlet state S_1 by the second harmonic of a ruby laser. Its triplet state T_1 was populated as a result of fast $T_1 \rightsquigarrow \to S_1$ intersystem crossing. The delay between pulses from the ruby and CO_2 lasers was varied between 10 to 30 μsec, which was sufficient to establish vibrational equilibrium in T_1.

In all cases the absorption of IR photons by the triplet molecules led to the appearance of delayed emission pulses. A higher density of CO_2 laser radiation was needed for IR activation of fluorenone DL than for molecules with a small ΔE_{ST} splitting. Therefore, thorough analysis of its spectral and kinetic characteristics was conducted, which demonstrated a lack of emission of products of multiphoton dissociation at the energy density of 3-9 J/cm^2. This is attributed to the ability of multiatom molecules, like fluorenone, to undergo overexcitation well above the dissociation level. The emission was not detected unless the triplet state had been initially populated and its intensity increased with the intensity of the initial luminescence, i.e. with the concentration of the triplet molecules. The transient spectrum of the CO_2-laser activated luminescence is compared in Fig. 1 with fluorenone luminescence spectrum generated by steady-state excitation in the electronic absorption band. At $E_{CO_2} = 6.4$ J/cm^2 the spectrum of the activated emission coincides with the fluorescence spectrum. There is no emission in other spectral regions. These findings indicate that the DL is emitted by the molecules which have undergone an isoenergetic transition from high vibrational levels of T_1 to S_1 and not by products of decomposition. The contribution of DF to the overall emission intensity increases strongly when high vibrational levels of the triplet state above S_1 are populated [5]. Therefore, the emission following a nonequilibrium excitation of triplet fluorenone contains mainly the DF.

In studying the photophysical processes in fluorenone vapors the measurements were conducted starting at the pressure of 0.133 Pa, at which the time between collisions reaches several microseconds. Therefore, the exchange of vibrational energy between fluorenone molecules in the ground and triplet states does not take place during the laser pulse duration, i.e. it has no effect on populating the high vibrational levels of the triplet state. This simplifies the interpretation of the observed emission, which is induced by multiphoton excitation of the triplet state above S_1. It was assumed that intramolecular redistribution of the vibrational energy, gained during vibrational excitation, took place during the laser pulse duration.

The decay of the IR-activated fluorescence of fluorenone, as well as of earlier studied [2-5] molecules, is nonexponential. The longer component of several microseconds is weakly dependent on E_{CO_2}, since its duration is determined by the decay of thermally equilibrated triplet molecules. The dependences considered below are related to the fast decay components. They are identical for all λ of observation within the luminescence band. Figure 2 shows changes in rates K_3 and intensities integrated over the pulse with E_{CO_2}. The rates K_3 increase but slower than for molecules with low ΔE_{ST}. The time-integrated, i.e. proportional to the quantum yield, luminescence intensity increases up to 7 J/cm^2 and then drops.

With increasing vapor pressure of fluorenone the rates of the fast decay component increase linearly. The K_3 vs. E_{CO_2} dependence in the studied pressure range of 13.3-39.9 Pa is substantially different for different P and is pressure independent for P ∿ 0.266-9.21 Pa. The efficiencies of collisional exchange of the vibrational energy, presented in Table 1, were estimated from the linear dependences of K_3 vs. P for different E_{CO_2}. They were obtained from the ratio of the collisional deactivation rate constant C, calculated from $K_3 = C \cdot P$, and the gas kinetics value. Collisional diameters were assumed constant and taken as 0.8 nm.
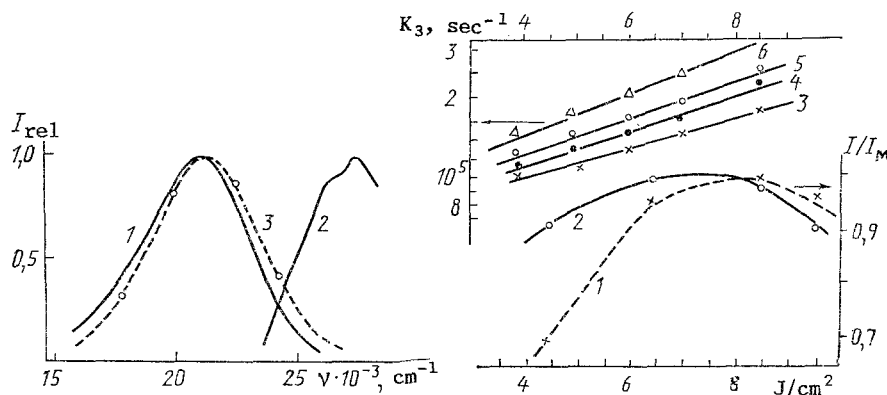
Fig. 1   Fig. 2

Fig. 1. (1) DL spectra of fluorenone vapor during steady-state excitation at T = 636 K; (3) 2 μsec after vibrational excitation of triplet molecules by CO_2 laser at $E_{CO_2} = 6.4$ J/cm^2 and P = 15.3 Pa; (2) absorption spectrum.

Fig. 2. Pulse-integrated intensity of activated DF of fluorenone (P = 15.3 Pa) and Kr (799.8 Pa) vapor mixture as a function of E_{CO_2} (1); fluorenone vapor at P = 15.3 Pa (2); decay rates of DF at 5.33-9.33 (3), 19.8 (4), 24.5 (5), and 37.85 Pa (6).

Analysis of experimental data shows that IR-activated DF of fluorenone exhibits a number of peculiarities. These include a weaker dependence of the decay rate and pulse-integrated fluorescence intensity on E_{CO_2} compared to the earlier studied molecules, as well as the excitation energy dependent increase of the decay rates with vapor pressure. We will demonstrate that these peculiarities are due to the ratio of rates for nonradiative processes, which deactivate vibrationally-excited triplet molecules with high values of E_{vibr}. Since fluorenone exhibits a large value of the singlet—triplet splitting, the transition to iso-energetic levels of S_1, necessary for observing DL, takes place from highly-excited vibrational levels of T_1. The decay time of CO_2-laser activated fluorescence is determined by $T_1 \rightsquigarrow S_0$ interconversion rates and by intermolecular vibrational relaxation of triplet molecules. As the above-presented experimental results indicate, under conditions of the experiment the photochemical and collisional deactivation have little effect.

Let us consider the peculiarities of $T_1 \rightsquigarrow S_0$ intersystem crossing on excitation of triplet molecules by CO_2-laser radiation. During intersystem crossing from T_1 to S_0 with the large energy gap, an exponential dependence of K_{TS_0} rates on the vibrational energy of triplet molecules is expected. However, for high rates of intermolecular vibrational relaxation K_V, when fluorescence decay occurs at an established vibrational temperature, this non-radiative transition exhibits activated behavior with a fast increase of the rate K_{TS_0} at low, and slower increase at high values of E_{vibr} [8]. The second case is typical for activation of DF of fluorenone by a CO_2 laser since the vibrational energy of triple molecules should exceed $\Delta E_{ST} = 7000$ cm^{-1}. The limiting vapor pressures of fluorenone were sufficiently low (0.266 Pa). Therefore, the energy dependence of rates K_{TS_0} (curve 3, Fig. 2) should be attributed to isolated molecules. It presents a great interest in analysis of various photophysical processes.

The role of collisional effects increases with increasing vapor pressure. Such experimental facts like an increase of K_3 with P and the exponential dependence of K_3 on E_{CO_2} indicate that the relational excitation and the vapor pressure are insufficient for establishing the vibrational temperature during the decay process. An interesting feature in the collisional exchange process is an increase of the rate constant C and, therefore, the efficiency of collisional exchange, with the energy density of CO_2 laser. This represents additional evidence for the dependence of the average energy $<\Delta E>$, exchanged in a single collision, on the internal energy of the molecule [9].

These studies on the DF intensity provide information supplementing that from kinetic studies. The increase of integrated intensity with E_{CO_2} is due to an increased fraction of triplet molecules occupying high vibrational levels of the triplet state and to an increase

TABLE 1. Efficiency of Vibrational Exchange as a Function of Laser Excitation Energy

E_{CO_2}, J/cm^2	$c \cdot 10^{-7}$, sec$^{-1} \cdot$ Pa^{-1}	ε
3,8	1,2	0,007
4,9	2,4	0,015
6,0	3,2	0,020
6,9	4,4	0,026
8,4	5,3	0,032

in the $K_{T_1 S_1}$ rate [4]. The increase in the intersystem crossing rate K_{TS_0} on E_{vibr}, typical for triplet molecules, is responsible for the decrease of I_{int}. Therefore, the observed weak changes of integrated intensity as well as K_3 with E_{CO_2} are the consequence of slow increase of K_{TS_0} at high E_{vibr}. The addition of other gases, which shift the distribution function of triplet molecules toward low energies, leads to slower nonradiative processes. Therefore, the enhancement of fluorescence becomes more rapid with E_{CO_2} and its attenuation becomes weaker.

The comprehensive experimental results presented in this work provide evidence about the population of high vibrational levels ($E_{vibr} \geq 7000$ cm^{-1}) of T_1 of fluorenone during MPE of triplet molecules by CO_2 laser, also under collision-free conditions. Analysis of fluorescence induced during MPE of triplet molecules provided information about processes which deactivate the vibrationally excited triplet molecules and also led to an estimate of the rate of vibrational exchange.

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