ROLE OF HIGHLY EFFICIENT COLLISIONS IN COLLISIONAL TRANSFER OF VIBRATIONAL ENERGY IN BENZOPHENONE-FOREIGN GAS MIXTURES


Collisional losses of vibrational energy in mixtures of benzophenone excited by nitrogen laser radiation ($\lambda = 337$ nm) and foreign gases (Ar, Kr, SF$_6$, C$_3$H$_2$) were studied by time-resolved delayed luminescence. It is established that the intensities and rates of decay of the fast and slow components of delayed luminescence can be used to evaluate the characteristics of $V-V$- and $V-T$-transfer of vibrational energy. For the $V-V$-process, the efficiencies and mean energies transferred in a collision are determined. It is shown that in the mixture with multiatomic gases, vibrational equilibrium is reached after a few collisions, the number of which decreases as the molecule of the foreign gas becomes more complicated. The $V-V$-process is characterized by high efficiencies of collisions typical for "supercollisions". The experimental characteristics of $V-V$-transfer correlate well with ergodic transfer of vibrational energy predicted by statistical theories.

Key words: collisional transfer of vibrational delayed luminescence, ergodic theory, "supercollisions".

Introduction. Collisional deactivation of vibration-excited molecules is an important competitive process for many photochemical and photophysical reactions. The rate of collisional transfer (CT) of vibrational energy (VE) is determined by the efficiency of the collisions. In recent decades it has been shown that the efficiency of collisions in collisional transfer of VE can vary within wide limits [1]. At present there are active debates concerning the dependence of the efficiency on the internal energy of an excited molecule, the nature of the collision partners, and the variety of the vibrational relaxation process: $V-V$ or $V-T$ ($V-V$ is the intermolecular vibrational relaxation leading to vibrational equilibrium, $V-T$ is the vibrational-to-translational energy conversion). Of great interest are the experimentally revealed highly efficient collisions, the so-called "supercollisions", where large amounts of VE are transferred. The "supercollisions" exert the most pronounced influence on deactivation of vibration-excited molecules [2]. The nature of such strong collisions is still unknown. The goal of the present work is to study the dependence of the VE CT and mean energies $\langle \Delta E \rangle$ transferred in a collision on the nature of vibrational relaxation for mixtures of benzophenone with various foreign gases (FG).

Among the direct experimental methods used for quantitative VE CT studies, the luminescence methods are most sensitive and allow comprehensive information to be obtained on collisional processes [3]. In the present work, we studied vibrational relaxation in long-lived triplet state $T_1$ with respect to the delayed luminescence (DL) of benzophenone vapors (BV), which occurs after molecule excitation to the first singlet state $S_1$ by nitrogen laser radiation ($\lambda = 337$ nm). The delayed luminescence of BV is caused by fast singlet-triplet intercombination conversion $S_1 \rightarrow T_1$ to state $T_1$. The characteristics of the DL of rarefied BV initiated by laser excitation of molecules to $S_1$, unlike heat-stimulated DL, are sensitive to the pressure of the BV and FG. At FG pressures of $P_{FG} < 10$ Torr which are of interest for us, the singlet molecules, whose lifetime in $S_1$ does not exceed several tens of picoseconds, do not experience collisions. In the absence of collisional transfer of VE to the $S_1$-state, the process of fast interconversion at rate $K_{ST} = 5 \times 10^{10}$ sec$^{-1}$ allows triplet molecules to accumulate a certain amount of VE.
equal to $h\nu - E_T$, where $h\nu$ and $E_T$ are the energies of the exciting quantum and triplet level.

Results and Discussion. Measurements were made on a pulsed laser fluorimeter in a time interval of up to 200 $\mu$s from the moment of action of the exciting pulse. Excitation was conducted by a Lambda-Physics laser with a pulse width at a halfwidth of 2.5 $\mu$s. The analyzed wavelength range was filtered by an interference filter at $\lambda = 480$ nm with a halfwidth of 1.5 nm. Similarly, results were obtained for $\lambda_{\text{obs}}$ in the 400-500 nm range. The signal was recorded by a photomultiplier and a digital oscillograph constituting an IBM PC-based measuring unit. Data were accumulated and processed by a computer. To improve the signal, the data were subjected to mathematical processing using the following algorithm: oscillograms differing from mean statistical analogs by more than 10% were excluded; from the remaining oscillograms we excluded the signals caused by low-frequency noise and background illumination; finally, the selected ~150 oscillograms processed by the mentioned method were subjected to mathematical averaging. The recording system provided time resolution of $10^{-8}$ sec. In the measurements, we used a heated quartz cuvette which was connected to the vacuum system via a dry gate. The vapor temperature was kept constant (433 K) with the upper furnace, and the required concentration of vapors was specified by the temperature of their saturation. In the mixtures with FG, the BV pressure was maintained constant (0.41 Torr). As a FG, use was made both of monoatomic (He, Ar, Xe) and polyatomic neutral gases (SF$_6$, C$_5$H$_{12}$) which were admitted from the vacuum system via the dry gate.

In rarefied BV, decay is a nonexponential process (Fig. 1). Under collision-free conditions, the characteristic decay times of the first two components are highly different and equal to 10 and 200 $\mu$s which agrees well with the data reported previously in [4, 5]. Figure 2 shows the decay rates of the fast DL component of BV as a function of the pressure of some of the foreign gases. For the same FG, Fig. 3 demonstrates the variation of the time-integrated intensity of the fast component $I_{21}$ with increasing $P_{FG}$. The change in the ratio of the time-integrated intensities of the slow $I_2$ and fast $I_1$ components is represented in Fig. 4. The components $I_1$ and $I_2$ were evaluated as a product of the corresponding characteristic decay time by the intensities of the components at moment $t = 0$. It is pertinent to note that the kinetics of decay, as is known, are independent of $\lambda_{\text{obs}}$. The shape of the time-resolved DL spectra does not change with $P_{FG}$, which allows measurements to be made at one $\lambda_{\text{obs}}$.

All of the reported results show that the decay rates and intensities of DL depend on the FG pressure in the following way: