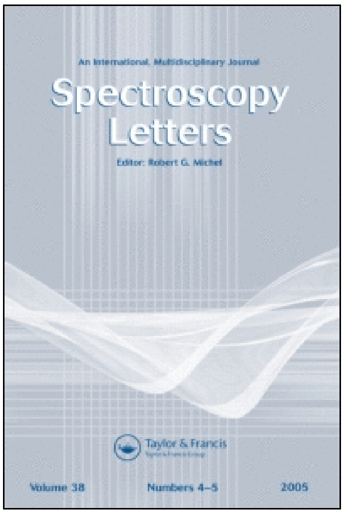

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DIRECT MEASUREMENT OF COLLISIONAL ENERGY TRANSFER BETWEEN HIGHLY VIBRATIONALLY EXCITED TRIPLET FLUORENONE AND BATH GASES

Key Words: collisional energy transfer, CO_2-laser excitation, delayed fluorescence

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ABSTRACT

Intensities and decay rates of CO_2-laser induced delayed fluorescence are used to probe collisional relaxation of vibrationally excited fluorenone diluted with bath gases: He, N_2, Kr. The average energies $\langle \Delta E \rangle$ transferred per collision are found to vary with vibrational energy, the energy dependences of the collisional efficiency eventually level off.

INTRODUCTION

The collisional transfer of vibrational energy is of primary importance for a wide range of physical and chemical phenomena. In particular, it controls any chemical and photochemical reactions which are of obvious industrial interest. Thus, a number of gas-phase reactions are of crucial importance in combustion systems, pyrolysis, free radical combinations, plasmas, discharge-pumped lasers and laser-induced chemistry.

It should be noted that today collisional energy transfer in highly excited molecules is not a well understood process [1,2]. The study of the relevant energy transfer is very urgent for polyatomic colliders which have relatively large lifetimes at vibrational energies much higher than the energy of the photochemical reactions. Several simplifying assumptions connected with characteristics of collisional energy transfer as functions of molecular species, temperature, pressure and degree of initial excitation are used, as a rule, to elucidate the mechanism of the reactions under study [1]. However, many results of direct experiments contradict these assumptions. That is why the question of collisional energy transfer from large molecules with high energies remains open.

Direct measurements of vibrational energy transfer have recently become available [1]. They are based on laser excitation methods. Most of these experiments used electronic excitation followed by rapid internal conversion [3] and direct absorption of IR photons from a CO_2 laser [1,14]. Direct monitoring of hot molecules absorption spectra [3] or detection of infrared fluorescence [4] are used to investigate the relaxation of vibrationally excited molecules.

Recently we have developed a method of direct multiphoton CO_2-laser excitation of triplet-state molecules [5,6]. Rapid disturbance of the thermal equilibrium distribution of molecules over the vibrational levels in the long-lived triplet-state initiated transient changes in delayed luminescence. In later works it was shown that delayed fluorescence induced by direct infrared multiphoton excitation of triplet-state molecules can be successfully used to control collisional deactivation of highly vibrationally excited molecules. In the present work, we have studied the collisional energy transfer between highly vibrationally excited triplet fluorenone and bath gases by using the proposed method.

The chosen molecule of fluorenone ($C_{13}H_8O$) emits long-lived luminescence in the gas phase, which exhibits a fast (10^{-9} s) and a slow component [13]. The decay time of the latter changes with increasing temperature from milliseconds to hundreds of microseconds.

The emission features are due to the high quantum yield and intersystem crossing rates from S_1 to the triplet-state T_1. Fluorenone is characterized by a large energy gap, $5400 < E_{ST} < 7000$ cm^{-1}, between the first excited singlet state S_1 and triplet T_1-state. These properties make it possible to observe thermally activated delayed fluorescence in the vapour phase at temperature lower than 500 K. Fluorescence has IR absorption bands in the CO_2-laser radiation region and can be excited by CO_2-laser radiation both in the ground electronic and the triplet-state T_1.

EXPERIMENTAL RESULTS

The experimental technique used in the present work were described previously [5,6,7]. In our experiments, rapid intersystem crossing $S_1 \rightsquigarrow T_1$ of fluorenone is exploited to prepare it in the triplet-state T_1. The frequency-doubled mode-locked ruby laser is used to excite fluorenone to the S_1 singlet state. When the vibrational equilibrium was established in the T_1 state, the triplet molecules were excited by CO_2-laser radiation. The pulsed atmospheric-pressure CO_2-laser beam was focused by lenses from blenched Ge and was passed through the cell beam to beam with visible light. The samples to be irradiated were prepared in a cylindrical heated quartz cell with NaCl windows using a high vacuum line. Zone refined fluorenone was stored in a side arm of the quartz cell, which had been evacuated to less than 10^{-6} torr and was kept at a temperature of 453 K. The vapor pressure was controlled by the temperature of the thermostated side reservoir and was equal to 0.115 torr. Luminescence was observed in the direction normal to the excitation. The signal from the photomultiplier which was placed behind the monochromator slit came to the oscilloscope. The signal was averaged over several pulses by a small microcomputer.

The fluorenone vapors were diluted with a large quantity of bath gases: He, Kr, N_2 ($0 < P < 30$ torr). This permitted considering only the effects of collisional deactivation of excited molecules by the added foreign gas. The direct infrared multiphoton excitation of fluorenone triplet-state molecules induced pulses of delayed fluorescence in the spectral region coinciding with usual fluorescence (Fig. 1). As discussed in our previous papers [6,7,8] CO_2-laser-activated fluorescence exhibits the two exponentional decay behavior characterized by two distinct decay rates which are equal to $1 \cdot 10^5 - 1 \cdot 10^6$ and $1 \cdot 10^2 - 1 \cdot 10^3$ s^{-1}, respectively.

The added foreign gas causes changes in both the intensity and the decay rates of CO_2-laser activated fluorescence which can be summarized as follows.

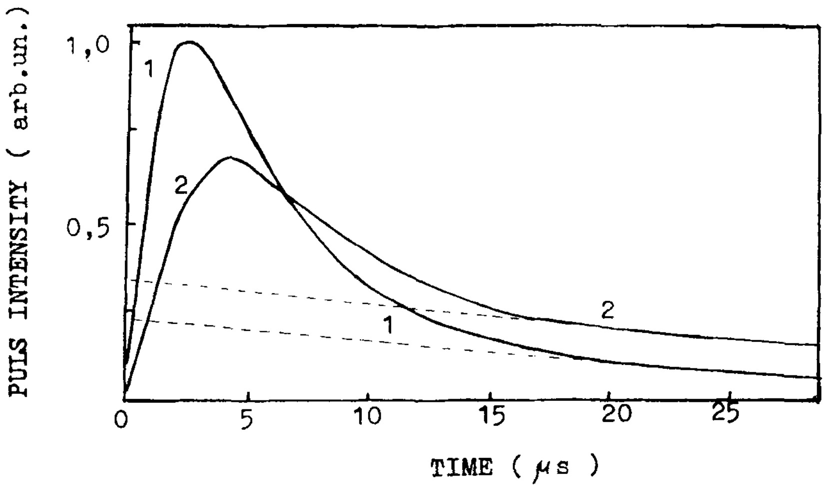

Fig. 1. Typical signal of laser-induced delayed fluorescence from mixture of fluorenone with Kr (7 torr), observed near 470 nm. Curves 1 and 2 are for E_{vib} = $= 19300\ cm^{-1}$ and $E_{vib} = 16300\ cm^{-1}$ respectively. Dashed line is contribution due to long component.

1. At a constant of CO_2-laser energy density the decay rates of the fast component of delayed fluorescence linearly increase with increasing bath gas pressure P_{bg} only in a limited range of pressures. At a higher pressure, the decay rates remain unaltered.

2. At first the decay rates of the long component decrease with the mixture pressure. Further increase in the foreign gas pressure leads to opposite changes (Fig. 2).

3. The time-resolved intensity at the maximum of induced fluorescence pulses I(t) which was measured at 453 nm is decreased with pressure.

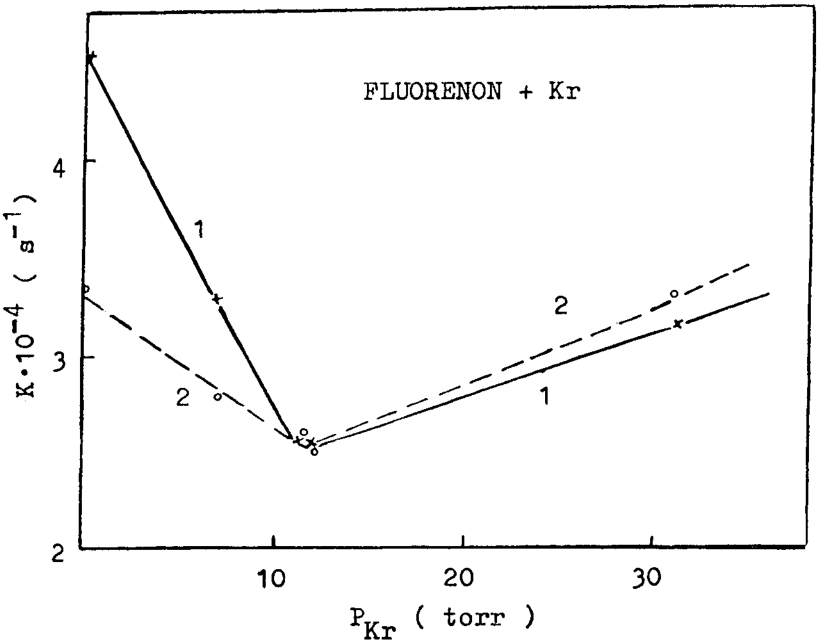

Fig. 2. Plots of the long decay rates of laser-induced fluorescence versus krypton pressures for two initial average vibrational energies: (a) 19300 cm^{-1}, (b) 16300 cm^{-1}

4. The pressure dependence of the fluorescence intensity points to a decrease in the time-integrated intensity with increasing foreign gas pressure. At high CO_2-laser energy densities the changes in the fast and the long components of the integrated intensity are different (Fig. 3).

DISCUSSION

On the whole, analysis of the spectrum and the kinetics of IR MPE-induced luminescence shows that the

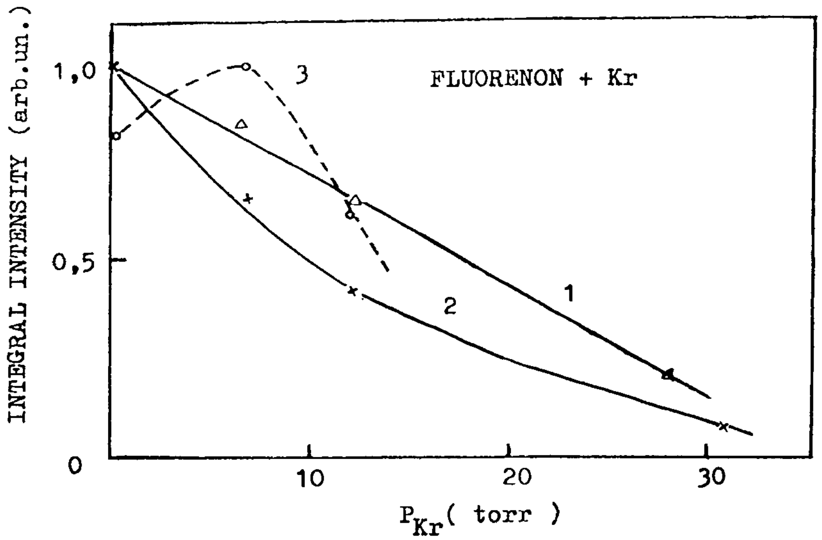

Fig. 3. The time-integrated intensity of laser-induced fluorescence versus krypton pressure at initial vibrational energy 19300 cm^{-1}. Curve 1 is for whole intensity of fluorescence signal, curve 2 and 3 are part for fast and long components

delayed fluorescence is attributed to the emission of singlet-state molecules since the triplet molecules are vibrationally excited to the energy region where the triplet-state T_1 is effectively coupled to S_1. At a given energy density luminescence did not manifest itself without preliminary excitation of vapors by ultraviolet radiation pulse. The activated emission spectrum coincides with the spectrum at single-quantum optical excitation in the electronic absorption band. The luminescence was absent in the other spectral regions. The population of high vibrational levels of the triplet-state due to the vibrational energy exchange between the vibrationally excited fluorenone molecules in the ground electronic and the triplet-state was unimportant because the fluorenone molecules were highly deluted with the bath gas. Before experimental results are described, let us consider the information on the shape of the energy distribution prepared by multiphoton infrared excitation. There have been a number of studies of the distribution function and its dependences on both the level of vibrational excitation and activated molecule complexity [9,10]. Conclusions regarding the shape of distribution are contradictory since the necessary key molecular parameters at high energy levels have not been experimentally determined. In spite of difficulties some general trends, at least, can be noticed. The molecular distribution after infrared multiphoton excitation is close to a thermal in quasicontinuum of closely spaced vibrational level. The time evolution of this distribution after the laser pulse cessation is to make in more thermal due to the effect of the up and down transmissions induced by collisions.

A important feature of multiphoton-excited (MPE) fluorenone molecules, which have 60 vibrational degrees of freedom, is the rapid collisionless redistribution of excitation energy between the vibrational modes during the IR laser pulse. Both the high density of vibrational levels in T_1 which reaches a value of $3\cdot10^5$ 1/cm^{-1} at the average vibrational energy $\bar{E}$ = = 3500 cm^{-1} (T = 453 K) and the effective anharmonic interaction of modes typical for large molecules favor a rapid flow of the vibrational energy on a picosecond time scale. Therefore, by the time of laser excitation most of the molecules are in vibrational quasicontinuum.

Experimentally, we have obtained number of evidence that Boltzmann distribution is a suitable approximation for the population distribution of IRMP excited molecules. Among them we distinguish next. 1. The time- resolved delay luminescence spectra prepared by IR laser irradiation and by thermal heating are similar during decay process. 2. The enhancement of absorption cross section at laser frequency by a bath gas is unimportant for large polyatomic molecules as fluorenone [11]. Unlike the small molecules for the large onces it isn't observed experimentally the absorption energy growth as the pressure of bath gas is increased. This phenomenon is usually treated as evidence that effect of bottlenecking is negligible.

Collisions between fluorenone and the bath gas molecules change the conditions of MPE which now depend on E_{CO_2} and P_{bg}. By varying these values which depend on the experimental conditions, we can control the conditions of establishing vibrational distribution during the laser pulse. As P_{bg} increases and E_{CO_2} decreases the population distribution over the vibrational levels in the triplet-state is shifted to the region of lower energies. This means that a smaller number of molecules can go from T_1 to the singlet-excited state S_1 due to the intersystem crossing $T_1 \rightsquigarrow S_1$.

Now we shall discuss the relaxation of the vibrational distribution following MPE of the triplet molecules. The decay of the luminescence which appears after the nonequilibrium vibrational excitation of some part of triplet molecules is due to several processes, of which those depending on the pressure are important. The intermolecular vibrational relaxation in the triplet state at the rate K_v and the collisional quenching of triplet molecules at the rate K_q can be of great significance under our experimental conditions. Analysis of the fast component decay rate alone is not enough to separate the effect of these two processes in the decrease of the fluorescence decay time with P_{bg}.

Therefore, we shall also consider the pressure dependence of the long-lived component. An example of this is shown in Fig. 3. The studies of CO_2-laser activated delayed fluorescence of many molecules have shown that the decay rates of the long component change, first of all, with the equilibrium temperature which settles upon completion of thermalization process [6]. As the bath gas pressure is increased, this temperature decreases due to the decrease in the maximum vibrational temperature reached at MPE and due to the increased mixture heat capacity. At a low gas pressure the $T_1 \rightsquigarrow S_0$ intersystem crossing whose rate K_{TS_0} is a strongly increasing function of temperature may be determining for the long component decay. First of all its decay rate decrease with the gas pressure due to the decrease in the intersystem crossing rates. Further increase of P_{bg} resulting in opposite changes points to a collisional process whose rates increase with increasing pressure can complete with the rate K_{TS_0} . The collisional quenching of the triplet molecules by a foreign gas is likely to be this same process.

For further check we have verified the pressure dependence of the time integrated fluorescence intensity I_{int}, which involves both fast I' and slow emission I" intensities, measured at the wavelength 450 nm. Since the spectrum shape of fluorenone fluorescence under study is independent of the foreign gas pressure, the time-integrated intensity was measured at the band maximum. At all excitation energies the fast fluorescence intensity and the decay time decrease with pressure.

Such dependences may be only due to a reduction of some part of triplet molecules excited above the singlet state S_1 when the vibrational relaxation in the triplet state becomes faster. It is clear that intensity of the "thermalized" fluorescence I" induced by collisions with the foreign gas can increase with P_{bg}. As shown by curve 3 of Fig. 3, at $P<7$ torr, the long-lived fluorescence intensity increases and its decay rate decreases. The foregoing shows that the collisional quenching of triplet molecules is negligible under the considered conditions. Generally, the pressure dependence of the fast component decay rate is determined by the vibrational relaxation in the triplet manifold T_1 and can be used to obtain the parameters describing the vibrational energy transfer of highly excited molecules.

The experimental information on both the intensity of fast fluorescence and its decay rates as a function of the initial vibrational energy and foreign gas pressure was used for this purpose. First of all we determined the average amount of energy transferred per collision $\langle \Delta E \rangle$. Two pieces of information are essential to carry out the analysis: the collision rate constant Z and the vibrational energy residing in the molecule after MPE as well as after the thermalization process.

The complete statistical redistribution of excitation energy into 60 vibrational modes enables us to determine the initial energy of CO_2 laser excited triplet molecules and the initial vibrational temperature in the gas mixture if these values were determined in the fluorenone vapor under the same conditions.
With this purpose the numerical results for the ratio of $I(\nu, t)/I_0(\nu, t)$ can be used. Here $I(\nu, t)$ and $I_0(\nu, t)$ are the activated fluorescence intensities at the pulse maximum measured in the gas mixture and pure fluorenone vapors, respectively. As discussed elsewhere [7, 8], at IR MPE, triplet fluorenone molecules reach energy regions where the density of vibrational levels in the singlet S_1 and the triplet T_1 state is high. Therefore, the intensities of activated fluorescence can be expressed in terms of a kinetic model [12]. To calculate the vibrational temperature by using the fluorescence intensities, we taken the fluorenone radiative decay rates $K_{T_1} = 5\ s^{-1}$, $K_{S_1} = 3 \cdot 10^6\ s^{-1}$ and the singlet-triplet energy gap $\Delta E_{ST} = 7000\ cm^{-1}$. The obtained vibrational temperature al-

lowed us to calculate both the average number of quanta per molecule $\langle n \rangle$ required to attain such T_{vib} and the corresponding vibrational energy $E_{vib} = \bar{E} + \langle n \rangle \cdot h\nu$. Here $\bar{E}$ is the average vibrational energy of molecules at equilibrium temperature T. To this end, the temperature dependence of the vibrational heat capacity of fluorenone was determined preliminary. As computations show, the experimental conditions permitted us to vary the initial E_{vib} in the gas mixture from 10000 to 28000 cm^{-1}.

The collisional process decreases the vibrational energy of CO_2 laser-excited triplet molecules. The previously studied temperature dependences of the decay rates of thermally activated delayed fluorescence were used to evaluate the temperature at the end of the thermalization process. The compared decay rates of the long component were measured at the same vapor pressure as in the temperature studies. For energy intervals which are small compared to the vibrational energy E_{vib}, the rates of energy variation are given approximately by: $dE_{vib}/dt = ZP_{bg}\langle \Delta E \rangle$ [4]. The values of $\langle \Delta E \rangle$ were obtained then on the assumption of the Lennard-Jones collision frequency. The calculated values of the gas kinetic collisional rate constant Z are 2.45; 1.27 and $2.06 \cdot 10^7$ $s^{-1}torr^{-1}$ for fluorenone vapor and its mixtures with Kr and N_2.

The thus obtained average vibrational energies transferred per collision depend on the excitation energy. The $\langle \Delta E \rangle$ values increase from 4 to 12 cm^{-1} for the fluorenone-Kr mixture in the vibrational energy interval which is equal to 7000 cm^{-1} (19300-12400 cm^{-1}). For fluorenone with a vibrational energy excess ranging from 11200 to 20900 cm^{-1} N_2 as a collider gave values $\langle \Delta E \rangle$ of 2-9 cm^{-1}.

Additional insight into the collisional dynamics can be gained by considering the collisional efficiency β . The values of β obtained by the method of [14] as $\langle \Delta E \rangle / \langle E \rangle$ for the relaxation of a number of polyatomic molecules in the Kr bath and the corresponding vibrational energies are given in the table. The vibrational energy transfer is only considered for highly excited molecules which are excited to the region of quasicontinuum states and manifest exponential decay. Pure fluorenone as well as its mixtures with Kr and N_2 as colliders, gave similar dependences of β on E_{vib} (Fig. 4). The dependences of β on E_{vib} vary with level of excitation, they are not linear. At low energies, β is found to have a stronger than linear dependence; at intermediate levels of excitation, 17000 cm^{-1}, β is proportional to E_{vib}. Linear dependences hold up to 22000 cm^{-1}. At all excitation energies the efficiency of fluorenone deactivation by fluorenone is con-

TABLE 1

Collisional Efficiencies β for Vibrational Relaxation of Polyatomic Molecules in Bath Gases

Molecule	Bath gas	E_{vib} (cm^{-1})	$\beta \cdot 10^4$	References
$C_{13}H_8O$	$C_{13}H_8O$	28300	158.0	Present study
$C_{13}H_8O$		19300	6.2	Present study
CS_2	Kr	20000	4.5	13
		36000	7.7	
SF_6	Kr	18800	4.1	14
C_7H_8		52000	25.0	3
$C_{10}H_8$		30600	63.0	4
$C_{13}H_8O$		20900	4.3	Present study
CS_2		20000	13.0	13
		36000	20.0	
C_6H_6		52400	10.9	3
C_7H_8		52000	25.0	3
$C_{10}H_8$		30600	96.0	4
C_9H_{12}		41600	48.0	3

siderable lower than it is usually supposed for the case of strong collisions [2]. For the fluorenone with Kr and N_2, the present results are close to the values 3.4×10^{-4} and $1 \cdot 10^{-4}$ that are evaluated as $\beta = K_{col}/Z$ at the conditions, when rate constant satisfied the Stern-Volmer relation.

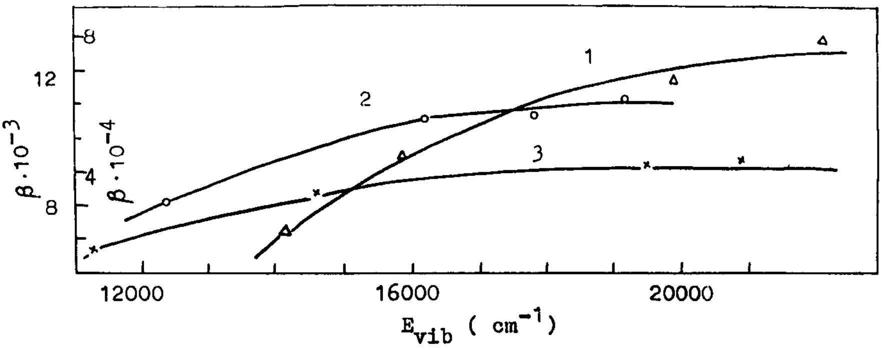

Fig.4.Relative collisional efficiencies for relaxation of vibrationally excited fluorenon molecules as a function of the initial average vibrational energy; 1,for pure fluorenone (no bath gas) (left scale); 2, for mixture with Kr; 3, for mixtures with N_2

It should be noted that the latter method of evaluating the collisional efficiency by using the constant of the Stern-Volmer relation has not provided a realistic picture for a gas mixture. At a constant laser energy density, however, it gives the value of averaged over E_{vib} due to a change in the initial vibrational energy with bath gas pressure P_{bg}.

In the case of fluorenone, the values of $\langle \Delta E \rangle$ and β are slightly lower as compared with those found for some molecules. This discrepancy may be due to several different causes. First of all, comparison of the results obtained in different ways depend upon both the experimental error bars and the uncertainties associated with the evaluation of the internal energy.

As a rule, a comparison of energy transfer quantities from different research groups calls for extra caution. Especially, its appears difficult to draw similar conclusions from experiments using different methods. At appropriate vibrational energy our results are much close to those examples of CO_2 laser excitation for which single population function characterizer overall population distribution is approximately valid. Calculations based upon two distinct ensembles with "cold" and "hot" molecules give much greater values of $\langle \Delta E \rangle$ and β , as well as numerous data obtained by internal conversion method using unrealistic assumption regarding monoenergetic distribution of vibrational energy in the ground electronic state [3].

Moreover, the tendency for increase in $\langle \Delta E \rangle$ with increasing number of vibrational degrees of freedom should be taken into account when considering the values of $\langle \Delta E \rangle$ and β for fluorenone which is one of the largest molecules tabulated in the table [14-17]. In the second place, the energy-transfer parameters depend on the nature of the relaxation process. The energy transfer between the highly vibrationally excited molecules and the surrounding bath gases can be accompanied by acceration of the vibrational-vibrational energy transfer if an energy distribution in a small subset of internally excited molecules is prepared. The studies employing such an excitation method demonstrate a higher efficiency of vibrational energy transfer. In our case, the direct absorption of IR photons from a CO_2 laser produce an ensemble of excited molecules, which become vibrationally equilibrium during the IR laser pulse. Therefore, only a less efficient process energy transfer between vibrational and translational degrees of freedom can take place.

In summary, energy transfer processes in mixtures of fluorenone and bath gases have been investigated using the new method developed at our laboratory based on direct absorption of IR photon from the CO_2 laser to excite triplet molecules up to high vibrational energy. It is shown that by studying both the intensities and decay rates of CO_2 laser induced delayed fluorescence as a function of initial excitation energy and gas pressure, we are able to reveal rates of vibrational energy transfer, collisional efficiency and average energy transferred per collision.

Specific details of energy transfer between fluorenone and Kr, N_2 as collider are similar to those obtained for large molecules which are excited in a vibrational quasicontinuum. The deactivation of vibrationally excited fluorenone by bath gas is found to be relatively slow because the collisional mechanism leading to relaxation of highly excited triplet molecules is the V-T energy transfer between vibrational and translational degree of freedom, it differs from those that favor radiationless relaxation from triplet to the ground electronic state.

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