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INVERSE ELECTRONIC RELAXATION AT IR MULTIPLE-PHOTON EXCITATION OF MOLECULES

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The radiationless transitions of electronic energy to vibrational one in isolated molecules are well known at present and under intense study[1,2]. These transitions result in a decrease in visible luminescence quantum yield and are often used as a method of preparing vibrationally excited molecules[3-5]. The process in which, on the contrary, the strong vibrational excitation of a molecule transfers to its electronic excitation that, in its turn, may induce light in the visible or UV has become the subject of investigation rather recently[6-10]. Such a process was called inverse electronic relaxation (IER)[6,7]. The discovery and development of IR multiple-photon excitation (MPE), a universal method for preparation of vibrationally excited molecules, stimulated a search for this process and its investigation. MPE allows preparing molecules almost with any desired average vibrational energy, which, depending on the molecular size, is limited only by the channel of its dissociative decay[11]. At sufficiently high levels of vibrational excitation MPE results in IR multiple-photon dissociation (MPD) of molecule via the ground electronic state. It should be noted that the process of MPD itself was experimentally disclosed in 1971 by observing the visible luminescence induced by IR laser radiation[12]. Since then a great number of molecules has been found whose MPE is

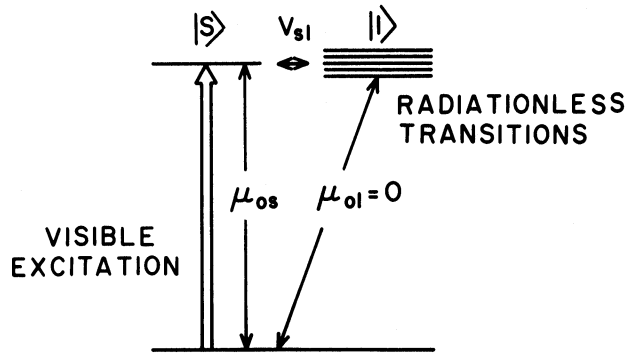

FIGURE 1a To the explanation of direct electronic relaxation.

followed by visible or UV emission[13]. But in most cases the nature of visible luminescence remains to be cleared up. This is mainly caused by the fact that it is difficult to identify the luminescent species. It is this problem that explains the basic difficulties in search of IER and its investigation.

1. DIRECT ELECTRONIC RELAXATION

Before discussing the process of inverse electronic relaxation we must consider briefly the basic conditions under which direct relaxation of electronic energy to vibrational one occurs in isolated molecule. In more detail this point is discussed in[1,2].

Let a vibrational level of the excited electronic state $|s\rangle$ be coupled, for example by the nonadiabatic interaction v_{sl}, with a certain group of isoenergetic high-lying vibrational levels $|l\rangle$ of the ground electronic state (Figure 1a) so that the full wave function of the molecular state $|j\rangle$ is

$$|j\rangle = a_{sj}|s\rangle + \sum_{l} a_{lj}|l\rangle \qquad (1)$$

Let the molecule at the time t = 0 be in the $|s\rangle$ state. It is essential that the $|s\rangle$ state is nonstationary and hence the probability of the molecule being found in this state will be varied in

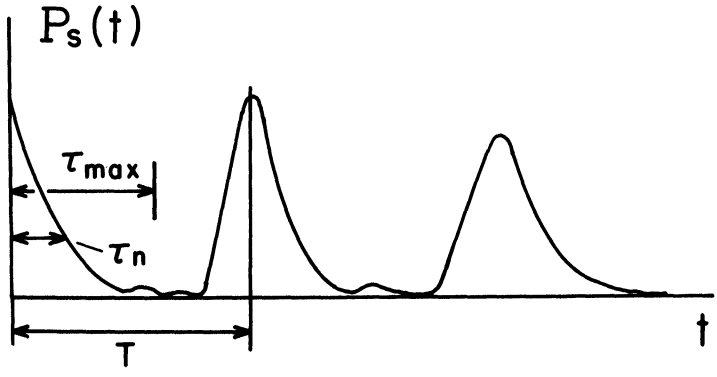

FIGURE 1b The qualitative time behaviour of the P_s probability to find the molecule in the initial state $|s\rangle$.

time. The probability of the molecule being found in the $|s\rangle$ state P_s at the time $t > 0$ is

$$P_s(t) = |\sum_j |a_{sj}|^2 \exp(-iE_j t/\hbar)|^2 \qquad (2)$$

The qualitative character of the time behaviour of $P_s(t)$ is given in Figure 1b. It can be seen that the drastic fall of probability with a characteristic time τ_n is followed again by successive recurrences of P_s with a certain recurrency time T. This means that the molecule will be found again in the initial state $|s\rangle$ in the time T. The recurrency time T is apparently defined by the level density ρ_1 of the $|1\rangle$ state[1]

$$T = 2\pi\hbar\rho_1 \qquad (3)$$

The value τ_n can be expressed through the parameters of the molecule system within a specific model. For example, one of the simplest model of Bixon and Jortner gives

$$\tau_n = \hbar/2\pi v^2 \rho_1 \qquad (4)$$

where the matrix elements v_{sl} are assumed to be the same and equal to v.

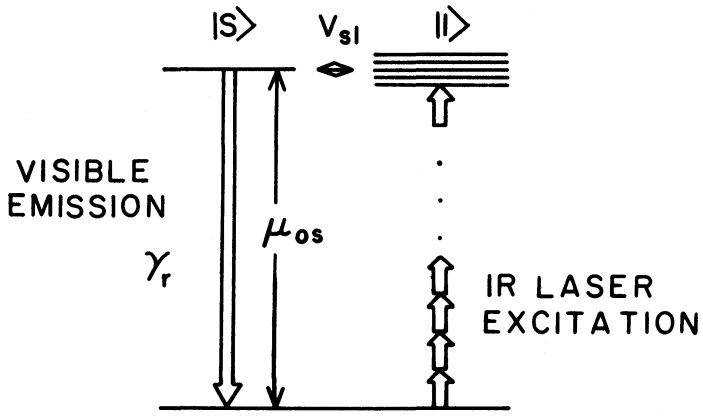

FIGURE 1c To the explanation of inverse electronic relaxation.

We can speak about the relaxation of the initial state |s> only if the process is irreversible, that is there is no recurrence in |s>. Such irreversibility will take place when, for example, the |s> level is coupled with the continuum of the |l> states ($T = \infty$). But, if the time τ_{max} during which we observe the molecule is actually limited for some reason (finite experimental time) and the relation

$$\tau_{max} \ll T \tag{5}$$

takes place, the excitation transfer from the |s> level will be considered as an irreversible too. In this case it is ussually to speak of so-called practical irreversibility. If the condition (5) is not fulfilled, the relaxational transition of electronic energy to vibrational one is impossible. In this case only quantum beats between the |s> and |l> states take place.

Formally the finite time of experiment means that the |l> levels may have the width

$$\gamma_{max} = 2\pi\hbar/\tau_{max} \tag{6}$$

so as their energy will be

$$\tilde{E}_l = E_l - i\gamma_l \qquad (7)$$

It can be seen from (2) and (7) that in this case an exponentially damping factor appears in $P_s(t)$.

Thus, before speaking about a relaxational process in isolated molecule (direct or inverse) two conditions will be fulfilled:

1) The initially prepared state must be nonstationary;

2) the irreversibility has to take place.

2. INVERSE ELECTRONIC RELAXATION

Assume that the group of high-lying vibrational levels of the ground electronic state $|l\rangle$ is excited in the process of MPE by IR laser radiation (Figure 1c). As may be seen, the basic conditions of relaxation, of the vibrational excitation to excited electronic term are fulfilled here: 1) nonstationary states are usually prepared at MPE; 2) the irreversibility is provided by a loss of vibrational excitation due to electronic relaxation, that is, because of visible emission from the $|s\rangle$ state.

There are two approaches in the theoretical description of IER in terms of Born-Oppenheimer (BO) states or in terms of the molecular states. The both approaches are fully equivalent and only give different names of the process. Figure 2 schematically shows the levels corresponding to these descriptions[7]. The $\{|j\rangle\}$ states here are eigenstates of the molecular Hamiltonian, $H_M = H_{BO} + V$ where V is the coupling operator; $\{|G\alpha\rangle\}$, $\{|S\beta\rangle\}$ are the eigenstates of the BO Hamiltonian H_{BO} for ground $|G\rangle$ and excited $|S\rangle$ electronic states, respectively. The lower molecular states $|j\rangle$ ($E < E_o$) are identical to the BO states $\{|G\alpha\rangle\}$. These levels can be excited by IR laser field but the spontaneous transition to the ground state $|G0\rangle$ with one photon emission is forbidden, that is, the rate of this transition $\gamma_j = 0$. Starting from the E_o energy

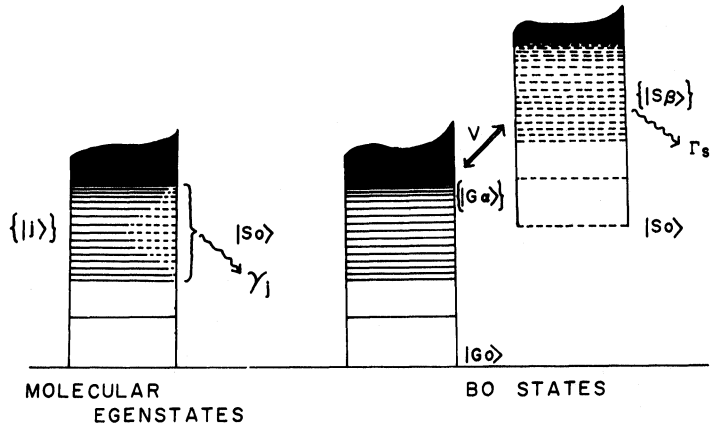

FIGURE 2 The explanation of IER in terms of molecular and Born-Oppenheimer states.

corresponding to the onset of the upper electronic term, the molecular states represent a linear combination of the state $\{|G\alpha\rangle\}$ and $\{|S\beta\rangle\}$. The character of the admixture of $\{|G\beta\rangle\}$ to $\{|G\alpha\rangle\}$ here is determined by the overlap region of these levels. In the simplest case when just one state, for example $|SO\rangle$, is mixed with the ground state vibrational quasi-continuum $\{|G\alpha\rangle\}$, a Loretzian distribution of the admixture of $|SO\rangle$ state with its centre at E_o and half-width Δ takes place[7]. Because of the molecular states with $E \geqslant E_o$ are of mixed type a spontaneous single-photon transition from these states to the ground state $|GO\rangle$ with a certain rate γ_j is possible. In the BO basis set the vibronic levels of the excited state $\{|S\beta\rangle\}$ may radiatively decay to the ground state $|GO\rangle$ with a certain rate Γ_s. But the coupling term V decreases the decay rate.

Let us consider how Γ_s changes in the presence of coupling term V. In the simplest case when the coupling of each particular vibrational level of the excited electronic state, for example

$|S0\rangle$, with the vibrational quasi-continuum of the ground electronic state $\{|G\alpha\rangle\}$ can be considered separately the introduction of the coupling V will give rise, instead of $|S0\rangle$, to a Lorentzian contour with its width $\Delta = 2\pi|\langle S\beta|V|G\alpha\rangle|^2\rho_G$, where ρ_G is the vibrational level density of the ground electronic state [6,7] (see Figure 2). As a result of such broadening the oscillator strength of the transition which corresponds to the radiative decay rate Γ_s spreads over all the states in the Lorentzian contour and this causes Γ_s to decrease. The number of such states N in the Lorentzian contour can be estimated if it is replaced by a rectangle with its width Δ being equal to that of the Lorentzian contour. In this case

$$N = 2\pi|\langle S\beta|V|G\alpha\rangle|^2\rho_G^2 \qquad (8)$$

where N is called the dilution factor. Thus, the observed radiative decay rate in our case is

$$\gamma_j \simeq \Gamma_s/N \qquad (9)$$

Such an estimation is valid in the case when the vibrational level density of the excited electronic state in the region of coupling with the ground state is sufficiently low so that $\rho_s\Delta < 1$. Otherwise, when $\rho_s\Delta \geqslant 1$, the coupling of two vibrational quasicontinua of the ground and excited electronic states should be considered. In this case the dilution factor will be determined by a statistical expression as a ratio of vibrational level densities of the corresponding electronic states

$$N = \rho_G/\rho_s \qquad (10)$$

So, when there is an upper electronic state below the dissociation limit of the ground electronic state of molecule, which is coupled by a radiative transition with the ground one, this coupling will lead to a decrease in rate of this transition according to (8) - (10). Therefore, the first indication of collisionless UV or visi-

ble luminescence in IER is its radiative lifetime, which has to be longer than, that for the dipole-allowed electronic transition in a molecule.

Besides the luminescence lifetime, different dependences of the peak luminescence intensity, that is dependences of the luminescence pulse peak, are usually studied in experiments. The peak luminescence intensity I, apart from the radiative transition rate, will be defined by the population of the corresponding vibrational sublevels as well. For example, when $\rho_s \Delta \geqslant 1$,

$$I = n\Gamma_s \int_o^\infty [\rho_s(E-E_o)/\rho_G(E)] \cdot f_G(E)dE \qquad (11)$$

where n is the total number of vibrationally excited molecules, E_o is the energy gap between the ground and excited electronic states, $f_G(E)$ is the vibrational distribution function of molecules after the IR laser pulse excitation. In the case of Boltzman distribution of vibrational energy with a corresponding vibrational temperature T the peak luminescence intensity is expressed as

$$I = n\Gamma_s(Q_s/Q_G)\exp(-E_o/kT) \qquad (12)$$

where Q_G, Q_s are the vibrational partition functions of the ground and excited electronic states respectively. From (11) it follows that in order to observe the visible luminescence arising in IER one must choose such a molecule that the ρ_s/ρ_G factor is not too small. Among them there are, first of all, small molecules consisting of three to five atoms.

Let's consider now the energy position of the $|s\rangle$ state. Generally speaking, this state must lie below the dissociation limit D of the ground electronic term. Otherwise, a competitive process, unimolecular dissociation, with its rate[14]

$$W(E) \simeq A(\Delta E/E)^{s-1} \qquad (13)$$

may occur, where A is the constant, E is the total vibrational

energy of molecule, ΔE is the excess of vibrational energy over the dissociation limit, s is the number of vibrational degrees of freedom. For intermediate size molecules ($s \simeq 10$) the unimolecular decay does not allow the molecule to be overexcited considerably and hence it cannot reach the high-lying electronic states $|s\rangle$. Besides, in the accessible energy range ΔE over the dissociation limit such decay effectively competes with IER. Molecules with a large number of vibrational degrees of freedom, however, can be greatly excited over the dissociation limit. For such molecules a range ΔE with a small value of W(E) can be chosen. In this case the $|s\rangle$ state may lie over the dissociation limit within ΔE.

3. SEARCH FOR AND EXPERIMENTAL INVESTIGATION OF IER

Collisionless visible luminescence with its radiative lifetime required by the process of IER (see (8) - (10)) is revealed at present for a large number of molecules excited by IR laser radiation, for example: SO_2 [15-17]; F_2CO [10]; OsO_4 [8,18-22]; CrO_2Cl_2 [9,23-26]; $VOCl_3$ [27]; C_2H_3CN [28-30]; $S_2C_2F_4$ [31], etc. Nevertheless, in most cases it is still impossible to attribute the luminescence to any definite species (the molecule itself or its fragment).

SO_2. Below the dissociation limit D of the ground electronic term $|G\alpha\rangle$ ($^1A_1$) ($D \simeq 45 \cdot 10^3$ cm^{-1}) in the energy region $E \simeq 30 \cdot 10^3$ cm^{-1} there are several triplet and singlet electronic terms $|S\beta\rangle$ ($^3B_1$, $^3A_2$, $^1A_2$, $^1B_1$). In [15] an attempt was made to observe the visible luminescence in SO_2 arising due to IER at IR multiple-photon excitation of the ν_1 mode. The spectroscopic and kinetic characteristics of the luminescence observed coincided with those of UV induced SO_2 luminescence from the $^1B_1$ state. These experiments, however, were performed at comparatively high pressures of SO_2 gas in the cell ($P \sim 1$ Torr), where the gas was excited by usual CO_2 laser pulse ($\tau_p \simeq 100$ ns). Therefore, both the MPE and IER were realized under collisional conditions. Later, in [16], the authors

managed to excite the SO_2 molecule by a short CO_2 laser pulse (the threshold energy fluence $\Phi \simeq 15$ J/cm^2, $\tau_p \simeq 0.5$ ns) under collisionless conditions ($P \simeq 8 \div 80$ mTorr) and observe the visible luminescence caused by IER. In [17] the SO_2 molecule was excited under collisionless conditions in a two-frequency field by usual CO_2 laser pulses ($\tau_p \simeq 100$ ns) and the process of IER was observed.

F_2CO. The identification of the CO_2 laser induced emission as belonging to the F_2CO molecule has been drawn by comparing the luminescence spectrum with that of the chemiluminescence in the reaction: $O_2(^1\Delta) + C_2F_4 \longrightarrow F_2CO(S_1) + F_2CO(S_o)$ [18]. The estimation of luminescence intensity shows that $\simeq 10^{-7}$ molecules of the total number in the irradiated volume result in the emission ($\Phi \simeq 50$ J/cm^2, $\tau_p \simeq 250$ ns). Detailed studies of the luminescence of this molecule were not carried out.

OsO_4. More detailed experimental studies were performed for the visible luminescence in the OsO_4 molecule induced by MPE both in one - frequency and two-frequency IR laser fields with $\Phi \lesssim 2$ J/cm^2 [8,18-20]. A theoretical model that described experiment well was developed within MPE and IER of the OsO_4 molecule[18]. The studies in a wider range of laser fluences (2 J/cm^2 $< \Phi <$ 1000 J/cm^2) show that the luminescence of OsO_4 has three different stages[22]. Each of them has a definite fluence threshold. A theoretical model has been developed, which explains well the three-stage luminescence of the OsO_4 molecule by the sequence of the processes taking place during an IR laser pulse: IER-MPD of the parent molecule (stage I), IER-MPD of the primary fragments (stage II), and IER-MPD of the secondary fragments (stage III). This sequence of processes is apparently rather a general mechanism of emergence of luminescence, and, according to the molecule under IR laser excitation, the molecular or any of the fragmentary emission stage may be absent.

CrO_2Cl_2. The visible luminescence arising at MPE of the CrO_2Cl_2

molecule has been the subject of intense studies, too[9,23-26]. Nevertheless, the nature of luminescence in this case is still unclear. There are indirect indications to the molecular character of luminescence at rather low laser fluences[24,25]. It has been shown that at high fluences the luminescence is caused by fragments[26].

C_2H_3CN. The nature of luminescence is still unclear at present. But the latest experiments with supersonic molecular jets have shown that only two fragments, C_2HCN or C_2CN, can be responsible for the observed luminescence[30]. The authors believe that the most probable mechanism is the sequence of the processes of fragmentation of the C_2H_3CN molecule to C_2HCN and C_2CN and their IER during a CO_2 laser pulse.

For the other molecules given above ($VOCl_3$, $S_2C_2F_4$), as well as for some other cases[13], the collisionless visible luminescence induced by MPE has not been indentified.

4. VISIBLE LUMINESCENCE OF THE OsO_4 MOLECULE

To give an idea of the character of the visible emission induced by IR laser radiation we shall consider below in more detail the case of the OsO_4 molecule[18]. Figure 3 shows a typical time evolution of visible luminescence as the OsO_4 molecule is excited by CO_2 laser pulse. If we choose proper excitation conditions, it is possible to observe easily the collisionless luminescence stage (the excitation of the far "red" wing of the P-branch of the ν_3 OsO_4 mode, the P(40) CO_2 laser line). When excitation is at the centre of the P-branch (the P(10) CO_2 laser line), collisional luminescence occurs in addition to collisionless one. This behaviour is connected with the characteristic property of the MPE which is considered comprehensively in [18,20]. Here we shall discuss in detail the nature of collisionless visible luminescence and particularly the problem of its identification. For this pur-

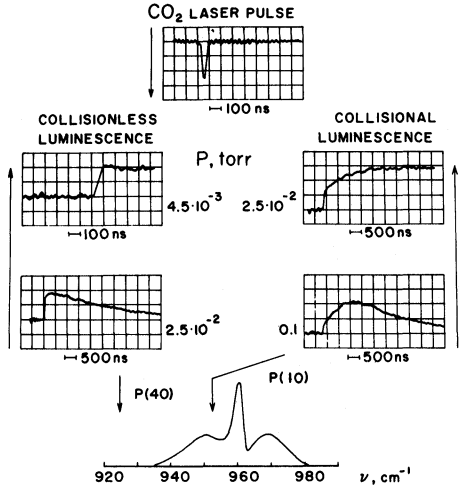

FIGURE 3 The time evolution of the visible luminescence of OsO_4 induced by CO_2 laser radiation[18]. Φ = 0.7 J/cm^2. The IR absorption spectrum of OsO_4 (ν_3 mode) and the excitation frequencies used (bottom).

pose rather a general approach was developed in[21,22]. It is based on separating all possible successive processes at MPE with respect to the energy required for their realization. Really, if IER takes place, this is a process with the lowest energy E_o. This means that, first of all, we must observe IER of the parent molecule. The next process, molecular dissociation, requires the energy D (usually $E_o < D$, see section 2). To accomplish the process of IER of the primary fragment, we must produce it and then excite to the onset of the upper electronic term E_o^f, that is, expend the energy $E \gtrsim (D + E_o^f)$, and so on for the next fragments. Thus, each of the assumed processes - IER - MPD of molecule, IER - MPD of primary fragment, IER - MPD of secondary fragment - needs a higher laser fluence for its realization. The next important factor is that in this sequence of processes MPD must always quench the luminescence

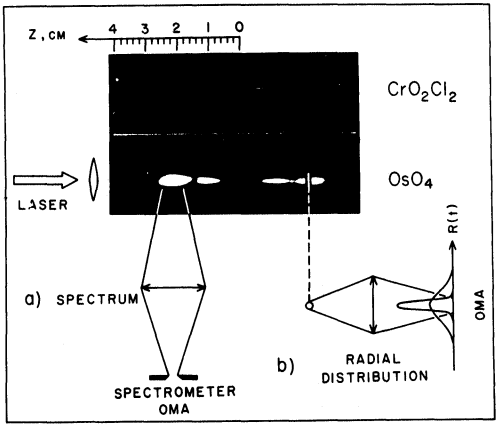

FIGURE 4 Typical photographs of the visible luminescence induced by CO_2 laser radiation focused into a cell with OsO_4 and CrO_2Cl_2 [22]. The focal length of the lens f = 10 cm, the laser pulse duration τ_p = 50 ns, the OsO_4 pressure in the cell P = 80 mTorr, CrO_2Cl_2 - P = 160 mTorr. The used methods of luminescence analysis: a) the study of spectra for each stage; b) the study of the time-of-flight distribution of luminescent species.

caused by IER. So, if this sequence is assumed to be possible for MPE, the luminescence of the parent molecule with increasing laser fluence will appear and then disappear. Then luminescence of primary fragments will take place, and this emission will be quenched again by their dissociation, and so on.

Direct analysis of the spatial distribution of the luminescence produced by focusing the CO_2 laser beam into the cell with the gas is a convenient experimental approach of obtaining such dependences over a wide range of Φ. In this case it is possible to realize laser fluence scale along the focused beam of CO_2 laser in the cell, with the maximum fluence in the focus. This longitudinal spatial luminescence distribution can be recorded with an optical multichannel analyzer (OMA) and thus the total dependence of

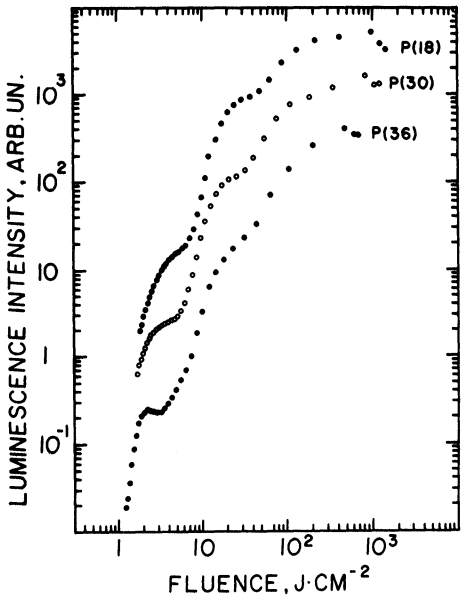

FIGURE 5 The dependence of the luminescence intensity (at the peak of emission pulse) on the laser fluence at the P(18), P(30), and P(36) CO_2 laser lines[22]. The experimental conditions: τ_p = 50 ns, P = 80 mTorr, the gate duration Δ = 400 ns.

luminescence intensity on laser fluence can be obtained after proper processing. Such measurements can be taken during a single CO_2 laser pulse. For qualitative estimation of the presence of different luminescence stages the OMA diode array can be replaced by an ordinary photographic plate. Such photos of the visible luminescence induced by CO_2 laser radiation are presented in Figure 4 for the OsO_4 and CrO_2Cl_2 molecules to explain the used experimental techniques. One can clearly see light and dark spots conditioned by the creation and further quenching of luminescence with increasing laser fluence as the focus z = 0 is approached. The light spot between two dark areas corresponds to a separate luminescence

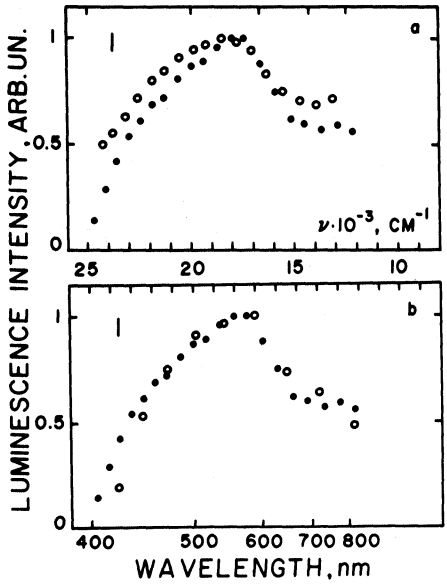

FIGURE 6 The visible luminescence spectrum of stage I obtained at Φ = 6 J/cm^2 for the emission pulse peak (dark circules), (the delay between the emission pulse peak and the gate Δt = 0) and for its "tail" (Δt = 3 μs) (open circules) - (a). The luminescence spectrum for the pulse peak (Δt = 0) with Φ = 6 J/cm^2 (dark circules) and Φ = 3.7 J/cm^2 (open circules) - (b)[22]. The OsO_4 molecule was excited at the P(14) CO_2 laser line, τ_p = 50 ns, P = 80 mTorr, Δ = 250 ns.

stage. The change of the photographic plate by a more sensitive diode array makes it possible to observe three different luminescence stages and to attain dependences of visible luminescence intensity on laser fluence. Some of such dependences obtained at different CO_2 laser lines are given in Figure 5. The luminescence spectra of each stage were obtained. The time-of-flight distribution of luminescent species were measured, to find their velocities.

Figures 6, 7, and 8 show visible luminescence spectra of OsO_4

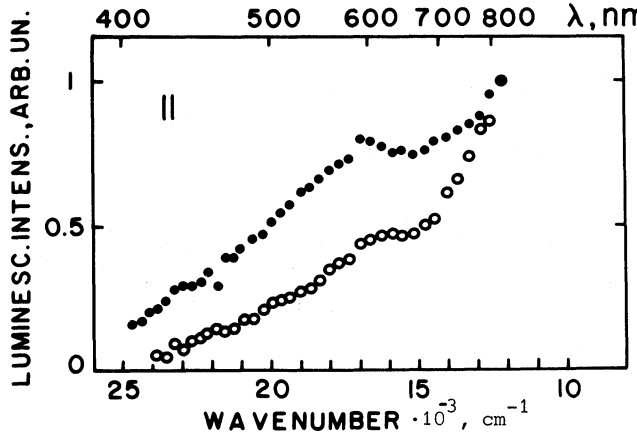

FIGURE 7 The luminescence spectrum of stage II at Φ = 23 J/cm^2 for the luminescence pulse peak (dark circules) and for its tail (Δt = 3 μs) (open circules). The conditions of experiment are similar to those in Fig. 6.

induced by CO_2 laser radiation for each of stages I, II, III (in order of their appearance with fluence increase; Figures 6, 7, and 8 respectively). Each stage in Figures 6a, 7, and 8a have two spectra characterizing the peak of the luminescence pulse (Δt = 0, dark circules) and its "tail" (Δt = 3 μs, open circules). All these spectra are mormalized to the maximum luminescence intensity in the spectral range under study (400 ÷ 800 nm).

Stage I. This stage is characterized by a wide luminescence spectrum with its maximum near $1.8 \cdot 10^4$ cm^{-1} (Φ = 6 J/cm^2). For stage I the spectrum slightly changes in time in the course of luminescence quenching (open circules, Figure 6a). The spectrum at the luminescence pulse "tail" is broadened a little. The spectrum variation with increasing laser fluence Φ within stage I is shown in Figure 6b. As Φ increases, the luminescence spectrum becomes broadened. With its further increase the luminescence spectrum changes stepwise which fully corresponds to the threshold appear-

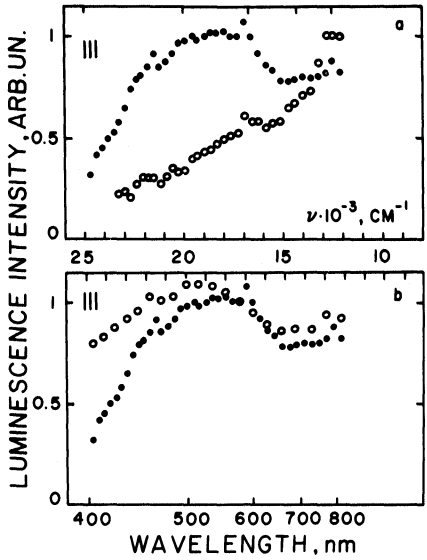

FIGURE 8 The luminescence spectrum of stage III with Φ = 250 J/cm^2 for the pulse peak (dark circules) and its "tail" (Δt = 3 μs) (open circules) - (a). The luminescence spectrum for the pulse peak with Φ = 250 J/cm^2 (dark circules) and Φ = 1000 J/cm^2 (open circules) - (b). The conditions of experiment are similar to those given in Fig. 6 [22].

ence of luminescence at stage II.

Stage II. This stage is characterised by a luminescence spectrum that is red-shifted and differs essentially from the analogous spectrum for stage I. For example, with Φ = 23 J/cm^2 the spectrum maximum lies beyond the spectral range under study and only its short-wave wing can be apparently observed. The time evolution of luminescence spectrum in the process of quenching is quite different for this stage, too (open circules, Figure 7). Indeed, the spectrum wing observed is red-shifted when the delay Δt between the laser pulse and the gate is increased. It is rather difficult to conclude on the character of evolution of the observ-

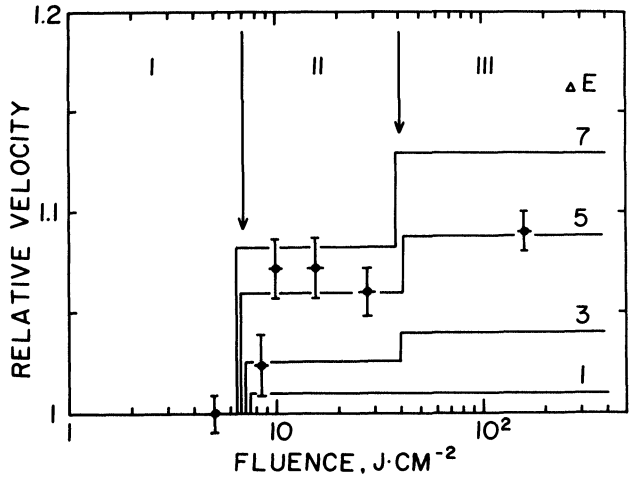

FIGURE 9 The dependence of the relative variations in velocity of luminescent species on laser fluence. All the values are normalized to the species velocity at Φ = 5 J/cm^2 (stage I). The solid straight lines denote the calculated velocities attained within the model[22] at different $\Delta E/\hbar\omega$ = 1, 3, 5, and 7 [22].

ed spectrum with fluence within stage II because there is no maximum in the studied spectral range.

Stage III. With further increase in laser fluence an absorption band appears in the region of $1.8 \cdot 10^3$ cm^{-1} (Figure 8a, dark circules) which corresponds to the luminescence of stage III (Φ = 250 J/cm^2) The luminescence quenching rate for this stage is larger than for stage II. As a result, at the "tail" the luminescence spectrum becomes similar to that of stage II (open circules, Figure 7). The spectrum evolution with increasing Φ is similar to that of stage I. As Φ increases, the luminescence spectrum of stage III is broadened, its maximum blue-shifting.

Thus, the luminescence spectra considered, along with their time evolution, quite unambiguously characterize each luminescence stage.

Analysis of the velocity of expanding of luminescence zone with the use of the same OMA diode array (Figure 4b) allowed measuring the velocities of luminescent species[22] (another method for measurement of such velocities is considered in[20]).

In Figure 9 the dots show the relative change of the luminescent species velocity as the laser fluence increases. All the measured velocities are normalized to that of the luminescent species formed at Φ = 5 J/cm^2 (stage I). When Φ corresponds to stage II, there is a stepwise increase of velocity corresponding to the threshold appearance of this stage (Figure 5). There is not any considerable increase of velocity at stage III. In more detail these results are considered in[22].

The excess of vibrational energy over the dissociation limit at MPD of the OsO_4 molecule (ΔE) is partially converted to the recoil energy of fragments thus causing their most probable velocities to be increased as compared to thermal ones. For example, according to the calculations the value $\Delta E/\hbar\omega = 5$ (where ω is laser frequency) agrees well with the observed increase of velocities[22] (Figure 9, solid lines).

Thus, the whole set of experimental data: 1) the number of potential luminescence stages, 2) the variation of luminescence intensity with Φ, 3) its spectral evolution as Φ increases within each stage and during the transition to the next stage, 4) the velocities of luminescent species at each stage — is explained by the following sequence of processes: IER — MPD of the OsO_4 molecule -- IER — MPD of the primary fragment (OsO_3) -- IER — MPD of the secondary fragment (OsO_2)[22].

In conclusion it should be noted that for a number of molecules the process of IER explains well the visible luminescence induced by IR laser radiation (SO_2, OsO_4). For other molecules it is rather difficult to use IER for interpreting the visible lumi-

nescence since the luminescent species is unknown. In the nearest future this problem seems to be solved for many other molecules as well. Another difficulty here is that the information on low-lying forbidden electronic states of molecules and particularly their fragments is practically absent. It is this information needed for detail studying the IER process itself.

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