# Inverse electronic relaxation in the case of multiphoton excitation of molecules by infrared laser radiation

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The first systematic account is presented of the current status of the problem of inverse electronic relaxation under the conditions of multiphoton excitation with infrared laser radiation, which converts a strong vibrational excitation of a molecule into an electronic excitation and gives rise to ultraviolet or visible radiation. This review deals with the fundamental principles of the appearance of inverse electronic relaxation in isolated molecules. An analysis is made of the characteristics of visible radiation generated by this relaxation process. Current ideas are used in a detailed investigation of those characteristics of infrared multiphoton excitation which determine inverse electronic relaxation. An account is given of the recently developed experimental methods for attribution of the observed radiation to a specific particle (molecular fragment). These methods include time-of-flight spectroscopy and separation of successive stages of the emission process in accordance with the laser radiation energy density. A critical analysis is made of the numerous experimental observations of collisionless visible radiation resulting from multiphoton excitation by infrared laser radiation. Some of the most thoroughly investigated molecules are used to consider the cases of inverse electronic relaxation resulting from multiphoton excitation of specific molecules and radicals, particularly  $SO_2$  and  $OsO_4$ . Apart from inverse electronic relaxation, attention is given to another nonadiabatic process occurring in the case of infrared multiphoton excitation, which is the detachment of electrons from molecular ions induced by  $CO_2$  laser radiation. The review covers the work published up to September 1986.

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### **1. INTRODUCTION**

The present review deals with a recently discovered process which occurs in isolated polyatomic molecules and is due to the coupling between the electronic and nuclear motion: this process is collisionless relaxation of the vibrational energy into electronic energy and its consequences. It has become possible to investigate this process because of the appearance and development of a universal method for the preparation of isolated vibrationally excited molecules in the ground electronic state, which is multiphonon excitation (MPE) by infrared laser radiation<sup>1-3</sup> (for reviews see Refs. 4)</sup>

and 6 and a monograph on the subject<sup>7</sup>).

It is well known that the nonadiabatic or spin-orbit coupling between different electronic terms gives rise to nonradiative conversion of electronic into vibrational excitations in isolated molecules.<sup>8,9</sup> When an ultraviolet  $\hbar\omega_{UV}$  or visible radiation photon is absorbed, a molecule is raised to an excited electronic state S<sub>1</sub>, which can decay either by a spontaneous transition to the ground electronic state S<sub>0</sub> accompanied by the emission of a luminescence photon  $\hbar\omega_{lum}$  or by *direct* relaxation of the electronic energy into the vibrational energy of the ground electronic term S<sub>0</sub><sup>\*</sup>:

$$\begin{array}{c|c} & \hbar\omega_{\rm UV} & | & ---- & S_0^*, \\ S_0 & \longrightarrow & S_1 & \\ & & | & --- & S_0 + \hbar\omega_{\rm lum} \end{array}$$
(1.1)

The result of this transfer of the electronic excitation energy to the relative motion of atoms is a strong vibrational excitation of the molecule in its ground electronic state  $S_0^*$  and reduction of the quantum efficiency of the appearance of an additional nonradiative decay channel.

It has been clear for some time that under certain conditions the coupling between the electronic and nuclear motion should result in the inverse process of transformation of the vibrational into the electronic energy (see, for example, Ref. 10). However, a universal method for the preparation of isolated vibrationally highly excited molecules has become available only recently. Infrared MPE makes it possible to prepare molecules with practically any average vibrational energy which, depending on the size of the molecule, is limited to a variable extent by its dissociation decay channel.<sup>6,7</sup> Consequently, a new opportunity has become available for the investigation of the effects of the nonadiabatic (or spin-orbit) interaction in an isolated molecule which is in a strongly excited vibrational state. The observable physical consequence of such molecular excitation is the luminescence emitted in the visible or ultraviolet parts of the spectrum, i.e., visualization of infrared (IR) laser radiation is achieved:

$$S_0 \xrightarrow{\hbar i \Omega I \mathbf{K}} S_0^* \xrightarrow{} S_0 \xrightarrow{} S_0 + \hbar \omega_{\text{lum}} . \tag{1.2}$$

In both cases described by Eqs. (1.1) and (1.2) the straight lines correspond to radiative transitions and the wavy lines represent nonradiative transitions.

The most frequently used name for the process of transformation of the vibrational into the electronic excitation as a result of infrared MPE is *inverse electronic relaxation* (IER).<sup>1)</sup>

We must mention at the outset that the present review will not deal with the rapidly growing subject of chemiluminescence and collisional vibrational-electronic (V-E) energy transfer when collisions are a necessary stage in the preparation of excited particles and in the initiation of transitions (see, for example, the review in Ref. 12).

The first investigations of inverse electronic relaxation involved the search for the relaxation of excited molecules themselves.<sup>13-15</sup> However, later investigations have shown that the main difficulty is interpretation of the observed visible radiation. This is because a sufficiently strong infrared laser field dissociates a molecule into fragments and many of these may be excited by the same laser radiation pulse and they can also luminesce. More recent experimental methods can be used to identify that a particular luminescence belongs to the molecule or its fragments. The result has been to show that a sufficiently strong infrared laser field can induce during one infrared radiation pulse a whole chain of the processes creating luminescence: IER-multiphoton dissociation of the molecule itself, IER-multiphoton dissociation of the primary fragment, etc. In the case of some molecules a particular luminescence stage may be missing. It should also be mentioned that IER (after infrared MPE) may excite electronic states direct one-photon transitions into which are strongly forbidden.

The problems of theoretical interpretation of the main experimental results on IER are discussed quite thoroughly in the present review. We have developed simple models by means of which we can calculate the dependences of the intensity of the observed luminescence on the main parameters of laser radiation.

Another nonadiabatic process discussed in the present review, which can now also be investigated as a result of infrared MPE, is the detachment of an electron from a negative molecular ion. Dissociation of many such ions requires a higher energy than that needed to detach an electron. In such cases it is found, by analogy with IER, that the detachment of an electron requires the lowest vibrational activation of an anion by infrared laser radiation and if the electronic and nuclear motions are coupled, this occurs before multiphoton dissociation.

The multiphoton infrared excitation is at present the only method which can be used to "prepare" isolated highly excited molecules for the investigation of IER. It should be mentioned in this connection that there is also an inverse relationship between IER and MPE. In particular, it is the observation of visible radiation after infrared excitation that provided the first proof of the existence of collisionless MPE.<sup>1</sup> Moreover, studies of the luminescence properties provide a useful instrument for the determination of various characteristics of MPE itself. For example, the excitation spectrum of visible luminescence is related directly to the spectral parameters of infrared excitation.

Such close and fairly general relationship between MPE and IER has been largely responsible for the organization of the present review. We shall present the experimental methods and theoretical models relating directly to intramolecular relaxation and luminescence and to the characteristics of infrared MPE governing the observed characteristics of IER.

In our opinion, not all the opportunities for investigating IER after MPE have yet been utilized experimentally. This applies to other molecules for which IER may be observed and also to extracting detailed information on the intramolecular interactions from the dependences that are investigated. In this review we would like to give a comprehensive account of the available experimental results, methods, and the available theory in order to draw attention to new vistas in the traditional field of the physics of intramolecular relaxation.

### 2. DIRECT RELAXATION OF ELECTRONIC ENERGY INTO VIBRATIONAL ENERGY OF AN ISOLATED MOLECULE

Before we turn directly to the proper subject of our review, we must recall some of the fundamentals of the theory of nonradiative transitions in polyatomic molecules.<sup>8,9</sup> For the sake of clarity, we shall confine ourselves to the simplest model case.

We shall assume that an isolated vibrational level of an excited electronic state  $|s\rangle$  is coupled by the electronic-vibrational nonadiabatic interaction  $v_{sl}$  to high-lying vibrational states  $|l\rangle$  of the ground electronic term. The wave functions  $|j\rangle$  (eigenstates of the complete molecular Hamiltonian) can be written in the form

$$|j\rangle = a_{sj} |s\rangle + \sum_{l} a_{lj} |l\rangle.$$
(2.1)

Selection of a special basis  $\{|s\rangle, |l\rangle\}$  for expansion is convenient because the initial nonstationary state  $|\psi(t=0)\rangle = |s\rangle$  can be created by optical excitation. At any moment in time, we have

$$|\psi(t)\rangle = \sum_{j} a_{js} e^{-iE_{j}t/\hbar} |j\rangle, \qquad (2.2)$$

and the probability  $P_s(t)$  of finding a molecule in a state  $|s\rangle$  at a time t > 0 is

$$P_{s}(t) = \left| \sum_{j} |a_{sj}|^{2} e^{-iE_{j}t/\hbar} \right|^{2}.$$
 (2.3)

The problem of the nature of the initial state and the ways of exciting it are discussed in greater discussed in greater detail in Ref. 8.

Depending on the ratio of the parameters (which are the average matrix element  $\overline{v}_{sl}$  and the density of levels  $\rho_l$ ), we can have qualitatively different time dependences  $P_s(t)$ . For example, if  $\overline{v}_{sl}\rho_l \gtrsim 1$ , the initial exponential decay of  $P_s(t)$  with a characteristic time  $\tau_n$  changes to recovery after a long time T (Refs. 8 and 9). The recovery time is governed by the density of levels  $\rho_l$  of the ground state  $|l\rangle$ :

$$T \geqslant 2\pi\hbar\rho_l. \tag{2.4}$$

The expression for  $\tau_n$  in terms of the parameters of the investigated molecular system can be found using a specific model. In particular, one of the simplest Bixon-Jortner models<sup>17</sup> gives

$$\tau_n = \frac{\hbar}{2\pi v^2 \rho_l} , \qquad (2.5)$$

and the inequality (2.4) is transformed into the exact equality. In this model it is assumed that the matrix elements  $v_{s'}$  of the interaction are identical and equal to v.

We can speak of relaxation of the initially prepared states  $|s\rangle$  only if the process is irreversible, i.e., if there is no return of the excitation to  $|s\rangle$ .<sup>8</sup> Such irreversibility appears,

for example, when the level  $|s\rangle$  is coupled to the continuum of states  $|l\rangle$  ( $T = \infty$ ). However, if in reality the time for the observation of a molecular system  $\tau_{max}$  is for some reason limited and we have

$$\tau_{\max} \ll T, \tag{2.6}$$

the escape of excitation from the  $|s\rangle$  level is also perceived by the observer as an irreversible process. In the latter case it is usual to speak of *practical irreversibility*. Therefore, a direct or inverse relaxation process can occur if two conditions are satisfied: 1) the initially prepared state should be *nonstationary*; 2) the *irreversibility* of the transition should be ensured.

### 3. INVERSE ELECTRONIC RELAXATION

We shall now assume that the group of high-lying vibrational levels of the ground electronic state  $|l\rangle$  is excited by multiphoton infrared laser radiation. We can easily see that the main conditions for relaxation of the vibrational excitation are now satisfied: 1) MPE prepares states which are known to be nonstationary (infrared transitions are possible between vibrational levels of the same term, which after allowance for the nonadiabatic interaction are not eigenstates of the molecular Hamiltonian); 2) irreversibility of the process may be ensured by the loss of vibrational excitation because of electronic relaxation, i.e., because of the emission of a visible photon from a state  $|s\rangle$ .

Depending on the formulation of the problem, we can select (as in the direct relaxation case) one of the equivalent methods of describing IER: in terms of the Born-Oppenheimer states or using the language of the exact molecular states. Figure 1 shows the schemes of energy levels which appear when one of the bases is selected initially (see also Ref. 11). Here, the states  $\{|j\rangle\}$  are the eigenstates of the molecular Hamiltonian  $H_{\rm M} = H_{\rm BO} + V$ , where V is the interaction operator;  $\{|G\alpha\rangle\}$  and  $\{|S\beta\rangle\}$  are the eigenstates of the Born-Oppenheimer Hamiltonian  $H_{BO}$  corresponding to the ground  $|G\rangle$  and excited  $|S\rangle$  electronic states. The lower molecular states  $|j\rangle$  ( $E_i < E_0$ ) are nearly identical with the Born-Oppenheimer states  $\{|G\alpha\rangle\}$ . These states can be excited by infrared laser radiation, but spontaneous decay to the ground state  $|G0\rangle$  accompanied by the emission of one photon is forbidden, i.e., the rate of such a transition is  $\gamma_i = 0$ . Beginning from the energy  $E_0$  corresponding to the limit of the upper electronic term, the molecular states represent linear combinations of  $\{|S\beta\rangle\}$  and  $\{|G\alpha\rangle\}$ . The nature of an admixture of the states  $\{|S\beta\rangle\}$  to  $\{|G\alpha\rangle\}$  is governed by the



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FIG. 1. Explanation of inverse electronic relaxation in terms of molecular and Born-Oppenheimer (BO) states.

magnitude of the matrix element of the interaction operator V. In the simplest case when only one state, for example  $|S0\rangle$ , is mixed with the vibrational quasicontinuum  $\{|G\alpha\rangle\}$ , the distribution of the admixture  $|S0\rangle$  is Lorentzian with its center at  $E_0$  and a half-width at midamplitude  $\Delta$  (Ref. 11). In view of the fact that the molecular states are mixed in the range  $E \ge E_0$ , a spontaneous one-photon transition from these states to the ground state  $|G0\rangle$  is possible at a finite rate  $\gamma_j > 0$ . In terms of the Born-Oppenheimer states, the situation can be described as follows: electronic-vibrational levels of the excited state  $\{|S\beta\rangle\}$  may decay radiatively to the ground state  $|G0\rangle$  at a rate  $\Gamma_s$ , but the interaction V between the terms alters this decay rate so that it becomes  $\gamma_i < \Gamma_s$ .

We shall now consider the connections between these two quantities. When the interaction of each individual vibrational level of an excited electronic state (for example,  $|S0\rangle$ ) with a vibrational quasicontinuum of the ground electronic state  $\{|G\alpha\rangle\}$  can be regarded in isolation, an allowance for the interaction V creates instead of  $|S0\rangle$  a broadened certain Lorentzian profile of width  $\Delta = 2\pi \langle S0 | V | G\alpha \rangle^2 \rho_{\rm G}$ , where  $\rho_{\rm G}$  is the density of the vibrational levels of the ground electronic state<sup>11</sup> (see Fig. 1). Such broadening redistributes the oscillator strength of the investigated transition, corresponding to the radiative rate  $\Gamma_s$  of decay of the state, between all the states in the Lorentzian profile and this reduces the radiative decay rate by the same factor. The number of such states N in a Lorentzian profile can be estimated by replacing this profile with a rectangle of width  $\Delta$  equal to the width of the profile. We then have

$$N = 2\pi \langle \mathrm{SO} | V | \mathrm{Ga} \rangle^2 \rho_{\mathrm{G}}^2. \tag{3.1}$$

This is known as the *dilution factor*. Consequently, the observed rate of radiative decay is now

$$\gamma_j \approx \frac{\Gamma_S}{N}.\tag{3.2}$$

This estimate is valid if in the region of interaction between the ground and excited electronic states the density of levels of an excited electronic state is sufficiently low so that  $\rho_S \Delta < 1$ .

In the opposite case when  $\rho_s \Delta \ge 1$ , we have to consider the interaction of two vibrational quasicontinua corresponding to the ground and excited electronic states. In this case the dilution factor is governed by the statistical ratio of the densities of vibrational levels of the relevant electronic states:

$$N = \frac{\rho_{\rm S} + \rho_{\rm G}}{\rho_{\rm S}} \approx \frac{\rho_{\rm G}}{\rho_{\rm S}} , \qquad (3.3)$$

since we usually have  $\rho_G \gg \rho_S$ . A redistribution of the strength of an electron transition due to mixing of the Born-Oppenheimer states belonging to different terms alters the luminescence time. The rate of spontaneous radiative transitions of an exact state is approximately N times less than the rate of decay of an electronically excited Born-Oppenheimer state. The resultant increase in the duration of the luminescence is one of the main criteria of IER in the case of collisionless MPE. The luminescence time itself can be compared with: 1) characteristic times of electronic transitions in moelcules without mixing of the terms; 2) a time which is expected on the basis of the integrated absorption intensity

in an electronic band of the molecule itself. In the case of IER the duration of luminescence may be many orders of magnitude longer than either of these two times, which are typically  $\sim 10$  ns (Table I).

Experimental investigations are concerned not only with the duration of the luminescence but usually also with various dependences of the peak intensity of the observed luminescence, i.e., of the amplitude of the peak of the luminescence pulse, on various parameters. The peak intensity of the luminescence  $I_L$  is governed not only by the radiative rate of the transition, but obviously also by the populations of the relevant vibrational sublevels. For example, if  $\rho_s \Delta > 1$ , then

$$I_{\rm L} = n\Gamma_{\rm S} \int_{E_0}^{\infty} \frac{\rho_{\rm S} (E - E_0)}{\rho_{\rm G} (E)} f_{\rm G} (E) \, \mathrm{d}E, \qquad (3.4)$$

where *n* is the total number of molecules excited vibrationally by an infrared laser field;  $E_0$  is the energy separating the ground and excited electronic states;  $f_G(E)$  is the function representing the vibrational distribution of molecules after the action of an infrared laser pulse.

It follows directly from Eq. (3.4) that in order to observe visible luminescence as a result of IER, we have to select the molecules so that the factor  $\rho_S / \rho_G$  is not too small. These molecules include primarily those with few (between three and five) atoms.

### 4. PREPARATION OF VIBRONICALLY HIGHLY EXCITED MOLECULES BY MULTIPHOTON EXCITATION WITH INFRARED LASER RADIATION

In Sec. 4 we shall consider those aspects of MPE of molecules by infrared laser radiation which are essential for the understanding and theoretical interpretation of the observed characterisitcs of ultraviolet or visible luminescence which appears as a result of IER. They include primarily the following:

1) universality of the vibrational activation of isolated molecules as a result of MPE, based on the general property of higher vibrational states of molecules (formation of a vibrational quasicontinuum);

2) ability to describe MPE theoretically and to predict on its basis the resultant distribution of molecules between the vibrational states;

3) the degree of maximum possible excitation of molecules, limiting the energy range in which electronically excited terms needed in IER may be observed;

4) the influence of monomolecular decay of a molecule (multiphoton dissociation) as a result of IER.

Since typical frequencies of vibrational and electronic transitions obey the familiar relationship  $\omega_{vib} \ll \omega_{el}$ , the necessary condition for the observation of IER  $(E_{vib} \sim \hbar \omega_{el})$  can be satisfied only as a result of absorption of a large number of infrared photons  $N_{IR} \gg 1$  ( $N_{IR} \omega_{vib} \sim \omega_{el}$ ). In the case of molecules for which the experimental data on IER are described below the value of  $N_{IR}$  was 20–40.

We shall now consider the characteristics of the states excited as a result of MPE and the nature of the vibrational distribution function  $f_G(E)$  of Eq. (3.4) which is then obtained.

### 4.1. Vibrational Hamiltonian and properties of eigenstates

High values of N make it possible to divide vibrational states or molecules into several specific regions (Fig. 2). The lowest levels are those employed in infrared spectroscopy and they are characterized by specific occupation numbers of the individual modes. We shall now write down the Hamiltonian of a molecule which interacts with an external infrared field of amplitude  $\mathscr{C}$ :

$$H = H_{\rm vib} - \mu \mathscr{E} \cos \Omega t; \tag{4.1}$$

here,

$$H_{\rm vib} = H_0 + V_{\rm anh} = \sum_{i=1}^{N} \hbar \omega_i \left( a_i^* a_i + \frac{1}{2} \right) + V_{\rm anh}, \quad (4.2)$$

where  $\omega_i$  are the frequencies of normal vibrations;  $a_i^+$  and  $a_i$  are the photon creation and annihilation operators for the *i*th mode;  $V_{anh}$  is the anharmonic term of the vibrational Hamiltonian. In the dipole approximation the interaction with the field is ensured by the operator  $\mu = \mu_{01}(a_1 + a_1^+)$  and we shall assume specifically that the first mode is infrared-active.

The ability to represent the zeroth-order approximation Hamiltonian of a molecule by a set of harmonic oscillators depends on the smallness of the anharmonic interaction  $V_{anh}$  in Eq. (4.2):

$$V_{anh} = \frac{1}{3!} \sum V_{ijh}^{(3)} (a_i + a_i^{\dagger}) (a_j + a_j^{\dagger}) (a_h + a_h^{\dagger}) + \frac{1}{4!} \sum V_{ijhl}^{(4)} (a_i + a_i^{\dagger}) (a_j + a_j^{\dagger}) (a_h + a_h^{\dagger}) (a_l + a_l^{\dagger}) + \dots$$

(4.3)

Here, the *n*th order anharmonicity constants  $V_{ij}^{(n)} \dots$  decrease on increase in *n* approximately in a geometric progression, the denominator of which can be regarded (to the nearest order of magnitude) as the Born-Oppenheimer parameter.

The lower vibrational states ( $N_{IR} \leq 3-5$  for molecules with five to seven atoms) are usually described satisfactorily by the harmonic approximation. Each vibrational state is characterized by a specific set of vibrational quantum numbers  $\{v_i\}$ . In most cases the anharmonicity is a small perturbation, since typical frequencies of vibrations are  $\langle \omega \rangle \sim 100-1000 \text{ cm}^{-1}$  and the main anharmonic third-order constants are  $\langle V^{(3)} \rangle \sim 1-10 \text{ cm}^{-1}$ . As usual, such a perturbation shifts the vibrational levels and gives rise to small corrections to the harmonic wave functions. These corrections are responsible for the familiar appearance of weak overtone and combination vibration bands in the infrared spectra.

Even in the case of the lower vibrational levels this analysis is not always correct. If there is a Fermi resonance (for example,  $v_1 \approx 2v_2$  in the CO<sub>2</sub> molecule), perturbation theory does not work and the interacting levels are pushed apart by an amount  $2V_{ahn}$  and the corresponding wave functions represent linear combinations of the harmonic functions with approximately the same coefficients, which corresponds to complete mixing. The condition of such mixing is  $|V_{anh}| \gtrsim |\Delta_F|$ , where  $\Delta_F$  is the detuning from the Fermi resonance. However, in the case of the lower levels the Fermi resonance is quite rare and in most cases the anharmonicity is simply a small correction.

The increase in the vibrational energy  $E_{vib}$  has two effects: on the one hand, it increases the density of the vibrational states with the effect that for each level there are many





other levels with a similar energy and, on the other, it increases  $V_{anh}$ . Consequently, the mixing condition is readily satisfied by many levels. The Fermi resonances cease to be accidental and they in fact form true molecular states  $|E\rangle$ , so that these states include comparable contributions of many harmonic states with energies close to  $|E\rangle$ :

$$|E\rangle = \sum_{v} \langle v | E \rangle | v \rangle. \tag{4.4}$$

Mode "mixing" takes place. The range of energies where this happens is called the vibrational quasicontinuum.<sup>18,19</sup> Mode mixing should be described in terms of decay of a mode pumped by infrared excitation: a vibration may decay into two or more other vibrations, each of which is linked to the next modes and then each of these decays in turn and so on.

## 4.2. Vibrational intramolecular relaxation and the condition of validity of a statistical description

The magnitude of the perturbing anharmonic interaction is much less than the eigenfrequencies of the Hamiltonian  $H_0$ . Therefore, the evolution of the non-equilibrium parameters of the system (such as the energy carried by a given mode) can be described conveniently as a relatively slow process against the background of fast motion characterized by  $\sim \omega^{-1}$ . Under mixing conditions (Sec. 4.1) this process is called intramolecular vibrational relaxation, implying the feasibility of a thought experiment in which a certain superposition of the  $|E\rangle$  states, for example a harmonic state  $|v\rangle$ , is excited initially. The evolution of this state [or, in an equivalent approach,<sup>18</sup> the properties of the eigenstates of Eq. (4.4)] can be described completely analogously to nonradiative conversion of the electronic to the vibrational energy [see Eqs. (2.1)-(2.3)]. The only difference is in respect of the interaction causing the mixing. In the case of electronicvibrational nonradiative transitions the Born-Oppenheimer adiabatic approximation breaks down because of the nonadiabatic component  $V_{\text{nad}}$ , whereas in the case of intramolecular vibrational relaxation the harmonic approximation of independent modes is invalid because of the anharmonic intermode interaction  $V_{anh}$ . Continuing this analogy, we readily conclude that the condition for going over to a statistical description of intramolecular vibration relaxation is an excess of the anharmonic interaction over the intermode resonance defect. In the theory of nonradiative transitions (see, for example, §9 in Ref. 8) this criterion is formulated for the effective states (in the case of intramolecular vibration relaxation the corresponding states are coupled by an intermode resonance). When the above condition is satisfied, i.e., if

$$\langle V_{anh} \rangle > \langle \Delta \omega \rangle,$$
 (4.5)

evolution of the observed quantitites obeys the Markov relaxation equations.<sup>20</sup> For example, in the case when a specific oscillator of the *i*th mode is coupled to the remaining vibrational degrees of freedom, which act as a reservoir linear in respect of the *i*th coordinate of the molecule, we find that relaxation of the energy  $\varepsilon_i$  to its equilibrium value  $\langle \varepsilon_i \rangle$  is described by<sup>21</sup>

$$\frac{\mathrm{d}\varepsilon_i}{\mathrm{d}t} = -\frac{1}{2\gamma_i} \left(\varepsilon_i - \langle \varepsilon_i \rangle\right). \tag{4.6}$$

The expression for the relaxation constant  $\gamma_i$  is in the form of the Fermi golden rule. At high energies the order of magnitude of this constant is given by

$$\gamma_i = \frac{\pi}{\hbar^2} \sum_m \overline{V^{(m)2}n^{m-2}} \rho_{\text{res}}^{(m)}(\omega_i), \qquad (4.7)$$

where  $\overline{V^{(m)2}}$  is the mean-square value for the *m*th order interaction and  $\overline{n}$  is the average occupancy number of vibrational modes. By analogy with the rate of nonradiative transitions proportional to the density of the effective states,<sup>8</sup> Eq. (4.7) contains the density of intermode resonances which include the mode  $\omega_i$ . The quantity  $\rho_{\rm res}^{(m)}$  is readily calculated either by a simple sampling of the frequencies for a specific molecule or with the aid of expressions that allow for the "accidental nature" of the frequency distribution.<sup>21</sup> An important feature of Eq. (4.7) is that the value of  $\rho_{res}^{(m)}$  is finite for any energy, whereas the density of the vibrational states can reach very high values. For example, in the case of the  $CF_3I$  molecule ( $\omega_1$  mode) the density of the resonances is  $\rho_{\rm res}^{(3)} \sim 2 \times 10^{-2} \, 1/{\rm cm}^{-1} \text{ and } \rho_{\rm res}^{(4)} \sim 5 \times 10^{-2} \, 1/{\rm cm}^{-1}, \text{ where-}$ as the density of the vibrational levels is  $\rho(E) \sim 3 \times 10^5$  1/  $cm^{-1}$  for  $E \sim 20 \times 10^3 cm^{-1}$ .

It is very difficult to provide a satisfactory description of the region of transition from the lower near-harmonic levels to a vibrational quasicontinuum. The self-consistent solution for  $\gamma_i$  given in Ref. 19 represents a phase transition: we have  $\gamma_i = 0$  for  $E \leq E_{vqc}$ ,  $\gamma_i \propto (E - E_{vqc})^{1/2}$  for  $E \approx E_{vqc}$ , and finally for  $E \gg E_{vqc}$  the energy dependence of  $\gamma_i$  is given by Eq. (4.7).

An experimental proof of the existence of intramolecular vibrational relaxation and, consequently, of mode mixing in a molecule was provided by the observation of collisionless conversion of energy from one mode to other vibrations under MPE conditions (see Ref. 22). For some molecules with between five and seven atoms the vibrational quasicontinuum limit is  $E_{\rm vac} \sim (4-8) \times 10^3$  cm<sup>-1</sup>.

### 4.3. Infrared spectra of absorption from excited states

Resonance excitation of high vibrational levels by an infrared laser field is possible if the intermode interaction  $V_{ahn}$  ensures such a modification of the infrared absorption spectrum which compensates the anharmonic shift. A complete transformation of the spectrum of the excited molecule can occur at such high energies that  $\langle V^{(3)} \rangle \sim \langle \omega \rangle$ . In this hypothetical case the vibrational spectra lose completely the individual modes observed for unexcited molecules. In reality, a resonance of MPE can be ensured by a much weaker condition, which disturbs the approximation of independent oscillators  $\langle V^{(m)}(E) \rangle \sim \langle \Delta \omega^{(m)} \rangle$ , where  $\langle \Delta \omega^{(m)} \rangle$  is the average defect of an *n*th order resonance.

If one of the modes  $\omega_1$  is active in the infrared range, it follows from the expansion represented by Eq. (4.4) that an oscillator strength is either concentrated at one  $|n_1,\tilde{n}\rangle \rightarrow |n_1 + 1,\tilde{n}\rangle$  transition below  $E_{vqc}$  or it is redistributed between many  $|E\rangle \rightarrow |E'\rangle$  transitions, where  $|E'\rangle$  is a set of states with an energy close to  $E + \hbar\omega_1 + \Delta E_{anh}$ , and  $\Delta E_{anh}$ is the average anharmonic shift of a band described by the constants  $X_{1\ell}$  of intramode and intermode anharmonicity. Such a redistribution of the strength of the transition, i.e., broadening of the spectrum, can be called *homogeneous* bearing in mind that for each separate eigenstate  $|E\rangle$  we can have many transitions within the limits of the absorption band in the vibrational quasicontinuum.

The experimental confirmation of the qualitative transformation of the spectrum at high energies was obtained already in the first investigations of MPE. This was contained in the following estimate. If we assume that the anharmonic shift in a mode is  $\Delta \sim 3 \text{ cm}^{-1}$ , we find that the condition for effective excitation of an anharmonic oscillator is that the defect  $\Delta$  should be exceeded by the field broadening:  $\Omega_{\rm R} = \mu_{01} \mathscr{C}/2\hbar \gtrsim \Delta$ . For typical values of  $\mu_{01} \sim 0.1$  D we obtain the required intensity  $I \gtrsim 10$  GW/cm<sup>2</sup>. On the other hand, MPE is observed already in the range  $I \lesssim 1$  MW/cm<sup>2</sup>. This is an indirect confirmation that the spectra of the transitions are transformed when the rate of excitation is sufficiently high.

At low energies, i.e., when the values of  $\langle V_{ahn} \rangle$  are also low, allowance for the interaction of Eq. (4.3) results in a small shift of levels and the appearance of weak satellities in the absorption spectrum (combination bands). The intensity of the satellites is much less than that of the main peak (Fig. 2). This limitation on the relaxation constant  $(\gamma_i \ll \omega_i)$  yields also a similar relationship between the width of the absorption spectrum and the frequency of the infrared-active vibration. When the frequency shift of the maximum of the cross section representing a transition from a given state depends only on the total energy in the system formed by a mode and the reservoir of the remaining vibrations, the absorption spectrum is Lorentzian and the absorption cross section (corresponding to up transitions) is given by

$$\sigma^{a}\left(E\right) = \frac{S_{bi}}{\pi} \left(\overline{n}_{i}\left(E\right) + 1\right) \frac{\gamma_{i}\left(E\right)}{\delta_{i}^{2}\left(E\right) + \gamma_{i}^{2}\left(E\right)} , \qquad (4.8)$$

where  $S_{0i}$  is the total absorption cross section which is independent of E (after allowance for the up and down transitions) and  $\delta_i(E)$  is the detuning from the center of the *i*th band. At high energies the shift  $\delta_i(E)$  rises linearly with the energy. However, the energy dependence of the width of the spectrum  $\gamma_i(E)$  is governed by the order m of intermode resonances [Eq. (4.7)]:

$$\gamma \propto E^{m-2}.\tag{4.9}$$

## 4.4. Multiphoton excitation in the region of the quasicontinuum

It follows from the values of  $E_{vqc}$  given above that the range of resonant nonadiabatic mixing of the ground and excited electronic terms of polyatomic molecules is located as a rule already in the vibrational quasicontinuum states of the ground term.

The fact that the eigenstates of a molecule are anharmonic is insufficient to determine the nature of states excited as a result of MPE. If the excitation rate is sufficiently high, then intramolecular vibrational relaxation is not completed during a pulse. The exact criterion of statistical equilibrium excitation of the eigenstates  $|E\rangle$  is the condition

$$\Omega_{\rm R} \ll \gamma_{\rm vgc}, \qquad (4.10)$$

where  $\Omega_R$  is the field broadening and  $\gamma_{vqc}$  is the characteristic broadening in the vibrational quasicontinuum.

Excitation in the vibrational quasicontinuum region for any intensity of an external field limited only by the condition  $\Omega_{\mathbf{R}} \ll \omega_i$  is described by the generalized Bloch equations.<sup>20</sup> If the condition of Eq. (4.10) is satisfied, these equations are transformed into rate equations for the populations  $z_n$  in narrow bands of vibrational states near the energy  $n\hbar\Delta$ (Refs. 23 and 24):

$$\frac{\mathrm{d}z_n}{\mathrm{d}t} = L\left\{z\right\} = -\left(\sigma_n^a + \sigma_n^e\right) Iz_n + \sigma_{n-1}^a Iz_{n-1} + \sigma_{n+1}^e Iz_{n+1},$$
(4.11)

where I is the infrared radiation intensity (photons  $\cdot$  cm<sup>-1</sup>  $\cdot$  s<sup>-1</sup>) and  $\sigma$  represents the stimulated absorption and emission cross sections related by

$$\frac{\sigma_{n+1}^e}{\sigma_n^a} = \frac{\rho_n}{\rho_{n+1}}, \qquad (4.12)$$

where  $\rho_n$  are the density of vibrational states with the energy  $n\hbar\Omega$ . Breakdown of the condition (4.10) clearly occurs only in a few cases<sup>25,26</sup> when picosecond lasers are used for MPE. In the majority of cases the vibrational distribution function in the quasicontinuum  $[f_G(E_n) \approx z_n/\hbar\Omega]$  can be found from the condition of balance of the populations described by Eq. (4.11).

At energies above the 0–0 transition in the lower excited electronic state the distribution  $f_G(E)$  determines the observed IER characteristics [Eq. (3.4)]. The existence of the IER channel at a sufficiently high vibrational energy of the ground term does not alter the qualitative nature of MPE, because decay via IER and subsequent emission of visible or ultraviolet photons is a process which is slow compared with the duration of infrared radiation pulses.

The system of equations (4.11) has been solved numerically for various types of cross sections<sup>24,27–30</sup> and analytic solutions have been obtained in some cases. In particular, it has been shown that a good approximation to  $f_G(E)$  is provided by the Poisson distribution.<sup>30</sup> Naturally, in each specific case a rigorous calculation is needed for a detailed comparison with the experimental results. An example of such a calculation for the OsO<sub>4</sub> molecule will be given in Sec. 7.3.

#### 4.5. Overexcitation above the dissociation limit

The system of equations (4.11) ignores the decay process which can occur above the dissociation limit. Monomolecular decay quenches the luminescence and can alter qualitatively the nature of the dependence  $I_{\rm L}(\Phi)$ , where  $\Phi$  is the infrared radiation energy flux. A special feature of pulsed excitation of a molecule is the possibility of overexcitation above the dissociation limit *D*. Such an overexcitation is readily estimated. The hypothesis of the existence of a vibrational quasicontinuum is an essential part of all the statistical theories of decay. In one of the theoretical variants (RRKM) the dissociation rate  $k_n$  ( $z_n = L\{z\} - k_n z_n$ ) is defined as follows<sup>31</sup>:

$$k_n = \mathcal{L} \frac{Q_{\rm R}^*}{Q_{\rm R}} \frac{N^* (E_n)}{h\rho (E_n)} , \qquad (4.13)$$

where  $\mathscr{L}$  is a symmetry factor;  $Q_R^+/Q_R$  is the ratio of the rotational partition functions of an activated complex and an excited molecule;  $N^+(E_n)$  is the number of states in an activated complex up to the energy  $E_n - D$ . Monomolecular dissociation in the case of a statistical distribution of the energy between the molecular modes is a consequence of fluctuations in which energy is accumulated at the weakest bond. Therefore, the larger the molecule, the longer the lifetime for a given degree of overexcitation above D, because the probability of a decay configuration of the vibrating nuclei is lower. This is clearly supported also by an estimate of the rate described by Eq. (4.13) if we use the classical expression for the density of states:

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$$k(E) = A\left(\frac{E-D}{E}\right)^{s-1}, \qquad (4.14)$$

where A is a constant of the order of the characteristic vibration frequency and s is the number of vibrational degrees of freedom. The dependence of the overexcitation  $E - D = \Delta E$ on the size of the molecule has also been confirmed experimentally. For example, the value  $\Delta E \approx (2-4) \times 10^3$  cm<sup>-1</sup> is reported in Ref. 32 for a series of pentatomic molecules and under approximately the same excitation conditions it has been found<sup>33</sup> that  $\Delta E \sim 20 \times 10^3$  cm<sup>-1</sup>  $\sim D$  for the (CF<sub>3</sub>)<sub>3</sub>CI molecule.

Another factor which governs the degree of overexcitation  $\Delta E$  is the radiation intensity *I*, because  $\Delta E$  can be estimated from the condition of equality of the excitation and decay rates:

$$\sigma (D + \Delta E) I \approx k (D + \Delta E).$$
(4.15)

Therefore, at a high infrared field intensity and particularly in the case of large molecules we can expect IER resulting from MPE to occur also in electronic states above the dissociation limit of the ground term.

The above discussion of the vibrational activation of isolated molecules by infrared laser radiation shows that the range of vibrational energies ( $E > E_{vqc}$ ), most important from the point of view of IER, can be described satisfactorily by the existing theory. A theoretical model of the process of MPE in a range of low-lying levels ( $E < E_{vqc}$ ) requires solution of the Schrödinger equation [Eq. (4.1)], i.e., as a minimum it requires the knowledge of the full set of actual spectroscopic constants of a molecule governing  $H_{mol}$ . Such modeling attempts have been made only for a few molecules.<sup>34,35</sup>

### 5. SEARCH FOR AND EXPERIMENTAL INVESTIGATIONS OF INVERSE ELECTRONIC RELAXATION

The universality of MPE of molecules by infrared laser radiation, the relative simplicity and availability of sources of such radiation (in the form of pulsed  $CO_2$  lasers)<sup>2)</sup> have all been responsible for the rapid development of this method and accumulation of experimental data on vibrational excitation of molecules in the ground electronic state. In the last decade the interest in this subject has been maintained mainly by two circumstances: 1) the absence of full understanding of the MPE mechanism; 2) the feasibility of practical utilization of MPE in the separation of isotopes of various elements.<sup>36,37</sup> As a result, several hundred polyatomic molecules have by now been investigated in considerable detail by the MPE method.<sup>5–7</sup> In about one-tenth of the investigated compounds the process of MPE is accompanied by visible luminescence.<sup>16</sup>

What is the nature of this luminescence and how can one identify those cases when the visible luminescence is due to IER? Before considering the specific luminescence, we shall formulate several general requirements that must be satisfied by the luminescence associated with IER.

The first condition is that the process should be monomolecular. In other words, the appearance of the luminescence must be related to a single molecule. This monomolecular nature is readily checked experimentally on the basis of the linearity of the dependence of the luminescence intensity on the gas pressure, which makes it possible to exclude collisional chemiluminescence.

The second condition is related to the dilution (discussed in Sec. 3) of vibrational states of an electronically excited term because of the interaction with high-lying vibrational levels of the ground electronic state. It follows from Eqs. (3.2)-(3.3) that such dilution should considerably lengthen the radiative luminescence time. Therefore, from the point of view of search for IER one should concentrate first on the luminescence characterized by a relatively long radiative lifetime.

It should also be mentioned that the simplest way of searching for IER involves detection and investigation of the visible luminescence of the molecules themselves under the action of infrared laser radiation. In fact, in the case of the majority of molecules the process of IER resulting in the appearance of the visible luminescence can only be associated with electronically excited terms located below the dissociation limit of the ground electronic state. Consequently, IER in the molecule itself is the process requiring the minimum vibrational activation by infrared laser radiation, i.e., it precedes monomolecular decay of a molecule into fragments. In spite of this, low-lying electronic terms of molecules have been investigated much more thoroughly than those of radicals, which makes it easier to identify the specific electronically excited states coupled with the ground electronic term and leading to luminescence. For these reasons the authors of the first investigations of IER searched for the luminescence of the molecules themselves. Methods for identifying luminescing particles were developed later and this has made it possible to study the process of IER also in the case of fragments formed in the course of successive breakup of molecules during a laser pulse.

Table I lists a number of coupounds which, when excited with CO<sub>2</sub> laser radiation, emit luminescence in the visible ultraviolet parts of the spectrum. In fact, there is a much larger number of such molecules which emit visible luminescence as a result of infrared MPE.<sup>16</sup> This table lists only those cases which satisfy the two conditions formulated above. In all cases the luminescence process is monomolecular. The radiative luminescence time  $\tau_{rad}$  is in the range 5– 1500  $\mu$ s, which is considerably longer than  $\tau_{rad}$  for dipoleallowed electronic transitions characterized by  $10^{-3}$ – $10^{-2}$  $\mu$ s.

The simplest case from the point of view of identification of the luminescence is the triatomic molecule SO<sub>2</sub>. However, in the case of triatomic molecules there is a difficulty associated with the preparation of vibrationally highly excited molecules in the course of MPE. The density of the vibrational states  $\rho(E)$  of such molecules is relatively low even at high vibrational energies E. For example, in the case of the SO<sub>2</sub> molecule we have  $\rho \sim 1 \ 1/\text{cm}^{-1}$  for  $E \approx 3 \times 10^4 \ \text{cm}^{-1}$ . Therefore, the vibrational quasicontinuum ensuring resonant excitation of molecules at relatively large values of E is absent. As a consequence it is necessary to use extremely high infrared laser radiation intensities to excite triatomic molecules. In the case of the SO<sub>2</sub> molecule this difficulty has been overcome successfully by MPE with the aid of short CO<sub>2</sub> laser pulses of duration amounting to 0.5 ns (the duration of the peak of the usual  $CO_2$  laser pulse is ~ 100 ns at midamplitude). Later visible radiation of SO<sub>2</sub> was induced also employing longer pulses emitted by multifrequency infrared lasers.40

#### 5.1. Inverse electronic relaxation in the SO<sub>2</sub> molecule

The ground electronic state  ${}^{1}A_{1}$  of the SO<sub>2</sub> molecule is characterized by a fairly high dissociation limit  $D = 4.5 \times 10^{4}$  cm<sup>-1</sup>. Below this limit there is a series of singlet  ${}^{1}A_{2}$ ,  ${}^{1}B_{1}$ , and  ${}^{1}B_{2}$  and triplet  ${}^{3}B_{1}$ ,  ${}^{3}A_{2}$  electronic terms.<sup>38</sup> The terms of this molecule of greatest interest in the case of IER are the lowest electronically excited terms  ${}^{1}A_{2}$  and  ${}^{1}B_{1}$ with the vibrational levels coupled by the nonadiabatic interaction to high vibrational states of the ground electronic term. Such coupling is manifested by a strong perturbation of the luminescence spectrum induced by ultraviolet radiation and by the nature of radiative luminescence times.<sup>56</sup> Estimates indicate that in this case the magnitude of the matrix element of the interaction may reach 10 cm<sup>-1</sup> (Ref. 38).

The ultraviolet luminescence induced by CO<sub>2</sub> laser radiation in the SO<sub>2</sub> molecule was first observed under collisional conditions.<sup>38</sup> The  $v_1$  mode of this molecule was excited by a CO<sub>2</sub> laser radiation pulse of 100 ns duration. This excited luminescence in the ultraviolet part of the spectrum and the main characteristics of this luminescence are listed in Table I. A detailed analysis of the process of MPE of this molecule demonstrated<sup>38</sup>: 1) luminescence appeared at laser radiation energy densities at which there was no dissociation of the molecule in the channel characterized by the lowest energy  $(SO_2 \rightarrow SO + O)$ , i.e., the appearance of this ultraviolet luminescence was preceded by decay (breakup) of the molecule and required the minimum vibrational activation of the  $SO_2$  molecule; 2) luminescence with similar spectral and time characteristics was induced also by ultraviolet laser radiation. For example, the luminescence spectrum induced by laser radiation with a wavelength  $\lambda = 282$  nm was found to be similar to the luminescence spectrum excited by CO<sub>2</sub> laser radiation.<sup>38</sup> These two circumstances led the authors of Ref. 38 to the conclusion that the appearance of the visible luminescence as a result of infrared MPE of the SO<sub>2</sub> molecule was due to IER. Collisions mainly facilitated the process of MPE itself, although to some extent they could induce collisional mixing of vibrational states of the ground  ${}^{1}A_{1}$  and excited  $({}^{1}A_{2}, {}^{1}B_{1})$  electronic terms in the range  $E \gtrsim 3 \times 10^4$  cm<sup>-1</sup> and thus ensure IER.

TABLE I.

|  | Char  | acteristics of  | umines   | cence  | Experime   | ental conditions   | 1  |
|--|---|---|--|--|--|--|--|
| }  | time  |   | spectral   |  |  |  |  |
| Molecule   | $	au_{ m rad},\ \mu s$  | k <sub>q</sub> , μs <sup>-1</sup><br>·Torr <sup>-1</sup>                  | $\lambda_{\max},$ nm   | Δ <i>ì</i> , nm  | laser radi-<br>ation ener-<br>gy densi-<br>ty <sup>a,</sup> , J/cm <sup>2</sup>  | pressure range,<br>Torr  | Ref.   |
| $\begin{array}{c} SO_{2} \\ F_{2}CO \\ OSO_{4} \\ CrO_{2}Cl_{2} \\ VOCl_{3} \\ SiH_{2}Cl_{2} \\ C_{2}\Pi_{3}CN \\ S_{2}C_{2}F_{4} \end{array}$ | $\begin{array}{c} \sim 200 \\ 9,1 \\ 1500 \\ 160 \\ 29 \\ 4,5 \\ 18 \pm 2 \\ - \end{array}$ | $2 \\ 5,6\pm0,8 \\ 10,5\pm0,5 \\ 6,5 \\ 4,3 \\ 2,6 \\ 4,5\pm0,5 \\ 4\pm1$ | $\begin{array}{c} \sim 320 \\ \sim 290 \\ \sim 500 \\ \sim 670 \\ 460 \\ 330 \\ 390 \\ > 900 \\ 500 \end{array}$ | $\begin{array}{c} 270-470\\ 240-460\\ 340-700\\ 500-800\\ 350-700\\ 250-470\\ 300-550\\ 550-900\\ 300-800 \end{array}$ | $ \begin{array}{c} \geqslant 20^{\ 6}) \\ \sim 50 \\ 0,1-2^{\ 8}) \\ \sim 4^{\ r}) \\ > 10 \\ > 50 \\ 30-150 \\ 1-10 \end{array} $ | $\begin{array}{c} (8-80)\cdot10^{-3} & {}^{5)}\\ 10^{-2}-7, 5\cdot10^{-1}\\ 10^{-4}-2\cdot10^{-1}\\ < 0,1\\ 10^{-2}-10^{-1}\\ 2\cdot10^{-2}-10^{-1}\\ 10^{-5}-10^{-1}\\ 10^{-3}-1 \end{array}$ | 38-40<br>15<br>13, 28, 41-45<br>14, 40-49<br>50<br>51<br>52-54<br>55 |

<sup>a</sup> The excitation was provided by the usual CO<sub>2</sub> laser pulses:  $\tau_{\text{peak}} \approx 100 \text{ ns at midamplitude.}$ 

<sup>b</sup> These results are given for the excitation by a 0.5-ns pulse of a  $CO_2$  laser.<sup>39</sup>

<sup>c</sup> Two new types of luminescence were observed<sup>45</sup> at laser radiation energy densities in the ranges ~ 8-50 and 50-1000 J/cm<sup>2</sup>.

<sup>d</sup> Luminescence of a different type was observed at higher laser radiation energy densities.<sup>48,49</sup>

A later investigation of MPE of the SO<sub>2</sub> molecule duration 0.5 ns (Ref. 39). This resulted in MPE under collisionless conditions and proved unambiguously that in the case of infrared MPE the energy of the vibrational excitation of the SO<sub>2</sub> molecule was converted into the electronic excitation because of IER. Figure 3 shows the dependence of the fraction of the luminescing molecules on the laser radiation intensity.<sup>39</sup> The luminescence appeared only above a certain threshold. The required laser radiation intensity was found to be very high:  $I \gtrsim 30 \text{ GW/cm}^2$ .

The use of two-frequency infrared laser radiation made it possible to reduce by about two orders of magnitude the threshold intensity of laser radiation and to observe IER under collisionless conditions when the  $SO_2$  molecule was excited by  $CO_2$  laser pulses.<sup>40</sup>

### 5.2. Visible luminescence emitted as a result of infrared multiphoton excitation of isolated molecules

Further investigations of the cases of emission of visible luminescence (Table I) showed that as the molecule became more complex, the main problem in the investigation of IER was identification of the visible radiation.

**F<sub>2</sub>CO.** The luminescence emitted by this molecule was identified by comparing the luminescence spectrum induced by CO<sub>2</sub> laser radiation with the chemiluminescence spectrum due to the reaction  $O_2({}^{1}\Delta) + C_2F_4 \rightarrow F_2CO(S_1) + F_2CO(S_0)$  (Ref. 15). It was concluded there that the luminescence appeared as a result of IER. An estimate of the luminescence intensity indicated that only  $\approx 10^{-7}$  molecules of their total number in the irradiated volume participated in the process ( $\Phi \approx 50 \text{ J/cm}^2$ ,  $\tau_p \approx 250 \text{ ns}$ ). A detailed investigation of the IER process in this molecule has not yet been carried out.

**OsO**<sub>4</sub>. The most detailed experimental investigation of the visible luminescence as a result of MPE was carried out on the OsO<sub>4</sub> molecule excited using single-frequency and two-frequency infrared laser radiation of energy density below 2 J/cm<sup>2</sup> (Refs. 13, 28, and 41–44). A theoretical model describing the experimental results<sup>28</sup> satisfactorily was developed on the assumption of MPE and of IER in the OsO<sub>4</sub>



FIG. 3. Dependence of the fraction of luminescing  $SO_2$  molecules on the intensity of  $CO_2$  laser radiation.<sup>39</sup> The parameters of laser radiation were as follows: pulse duration 0.5 ns, frequency  $1080 \text{ cm}^{-1}$ . The  $SO_2$  gas pressure in the cell was 40 mTorr.

molecule itself. An investigation carried out in a wide range of laser radiation energy densities  $(2 < \Phi < 1000 \text{ J/cm}^2)$ showed that the luminescence emitted by the OsO<sub>4</sub> molecule was generated in three stages.<sup>45</sup> Each stage was characterized by its own appearance threshold in terms of the laser radiation energy density and was applicable to the OsO<sub>4</sub> molecule itself or to its fragments formed as a result of MPE (see Sec. 7).

CrO<sub>2</sub>Cl<sub>2</sub>. The visible luminescence resulting from MPE of the CrO<sub>2</sub>Cl<sub>2</sub> molecule is also of major interest.<sup>14,46-49</sup> The structure of the lower electronic terms of this molecule has been investigated thoroughly.<sup>57</sup> The terms  $A_2$  and  $B_1$  are the lowest singlet electronically excited states of this molecule and are located below the dissociation limit  $(D \approx 2.3 \times 10^4)$  $cm^{-1}$ ). Their 0-0 transitions have frequencies 16 970  $cm^{-1}$ and 17 248 cm $^{-1}$ , respectively. The density of the vibrational levels of the ground electronic state  ${}^{1}A_{1}$  in the region of the 0–0 transition is  $6.5 \times 10^6$  1/cm<sup>-1</sup>. In the region of emission of a CO<sub>2</sub> laser there are two modes:  $v_1 = 995$  cm<sup>-1</sup> and  $v_6 = 1002$  cm<sup>-1</sup> (valence vibrations A<sub>1</sub> and B<sub>1</sub> of the Cr–O bonds). In the first investigations the visible luminescence was attributed to the CrO<sub>2</sub>Cl<sub>2</sub> molecule itself.<sup>14,46</sup> However, more detailed investigations showed that at laser radiation energy densities  $\Phi = 4-15 \text{ J/cm}^2$  the main luminescing object was the fragment CrO<sub>2</sub>Cl, whereas at  $\Phi \gtrsim 20$  J/cm<sup>2</sup> there was an additional luminescence due to the fragment CrO<sub>2</sub>. There was only indirect evidence that the visible radiation observed in the range  $\Phi \leq 4$  J/cm<sup>2</sup> was due to the CrO<sub>2</sub>Cl<sub>2</sub> molecule itself.<sup>48</sup>

**VOCl<sub>3</sub>.** Excitation of the V-O valence vibration of the VOCl<sub>3</sub> molecule at  $1042 \text{ cm}^{-1}$  (mode  $v_1$ ) by CO<sub>2</sub> laser radi-

ation induced visible luminescence with the main characteristics listed in Table I. A special feature of this molecule compared with the other cases discussed above is the absence of electronically excited terms located below the dissociation limit of the ground electronic state to which transitions are dipole-allowed. In fact, the dissociation limit of VOCl<sub>3</sub> is located at  $2.9 \times 10^4$  cm<sup>-1</sup>. The energy of the 0–0 transition of the longest-wavelength band ( $\lambda = 333$  nm) is also located in this region.<sup>58</sup> This makes it unlikely that IER should occur in the VOCl<sub>3</sub> molecule itself. Detachment of one Cl atom as a result of MPE of this molecule may result in the interaction of the V-O valence vibration of the VOCl<sub>2</sub> fragment with a laser pulse, which makes the process of IER very likely for this fragment. Spectral investigations made it possible to attribute the observed visible luminescence to the VOCl<sub>2</sub> fragment.50

SiH<sub>2</sub>Cl<sub>2</sub>. The longest-wavelength electronic band in the absorption spectrum of SiH<sub>2</sub>Cl<sub>2</sub> is due to transitions to Rvdberg states lying in the region of 151 nm (Ref. 59). The dissociation energy of this molecule is less than the energy of the 0-0 transition of the corresponding electronically excited term.<sup>51</sup> When the vibration  $v_2(a_1)$  of the SiH<sub>2</sub> group in the SiH<sub>2</sub>Cl<sub>2</sub> molecule is excited by CO<sub>2</sub> laser radiation, ultraviolet luminescence is observed (Table I) and it can be attributed to the  ${}^{1}B_{1} \rightarrow {}^{1}A_{1}$  transition in the SiCl<sub>2</sub> radical. This radical (fragment) does not exhibit hf vibrations that could coincide with the laser radiation frequency ( $v = 948 \text{ cm}^{-1}$ ). In fact, the frequencies of the normal vibrations have the values  $v_1 = 512.5 \text{ cm}^{-1}$ ,  $v_2 = 202.2 \text{ cm}^{-1}$ , and  $v_3 = 501.4$  $cm^{-1}$ . This led the authors of Ref. 51 to the conclusion that an electronically excited SiCl<sub>2</sub> fragment is formed directly as a result of MPE of the SiH<sub>2</sub>Cl<sub>2</sub> molecules by CO<sub>2</sub> laser radiation although the mechanism of this process is not yet clear. However, we cannot exclude the possibility of IER as a result of MPE of SiCl<sub>2</sub> in the long-wavelength wings of the bands of the  $2v_1$  and  $2v_3$  overtones.

 $C_2H_3CN$ . The reason for the appearance of the luminescence emitted by this compound is not yet clear. However, recent experiments carried out using supersonic molecular beams demonstrated that only two fragments— $C_2HCN$  and  $C_2CN$ —can be responsible for the observed luminescence.<sup>54</sup> The most probable luminescence mechanism assumed in Ref. 54 is a sequence of processes of fragmentation of the  $C_2H_3CN$  molecule by MPE producing  $C_2HCN$  or  $C_2CN$  and IER of these fragments in the course of the same  $CO_2$  laser pulse.

 $S_2C_2F_4$ . In the case of this molecule the authors of Ref. 55 proposed no mechanism to account for the visible luminescence. In our opinion one could not exclude here MPE by infrared laser radiation resulting in the formation of two SCF, fragments and subsequent IER of these fragments.

Anthracene. Excitation with  $CO_2$  laser radiation generated delayed luminescence in the  $(1.8-2.7) \times 10^4$  cm<sup>-1</sup> range.<sup>60</sup> The authors of Ref. 60 assumed that this luminescence was due to anthracene molecules in the singlet state S<sub>1</sub>. However, in the case of such large molecules the luminescence intensity should be very low [Eq. (3.3)-(3.5)].

The above analysis of the specific cases of the luminescence induced by infrared laser radiation shows that the main problem in the study of IER is identification of the luminescing object. In the case of triatomic molecules (for example,  $SO_2$ ) it is relatively easy to identify the fragments, but the task becomes gradually more difficult on increase in the size of the molecule. The luminescence spectra are wide and structure-free. In the case of many polyatomic molecules it is found that successive fragmentation occurs throughout the laser pulse and this gives rise to a large number of particles capable of emitting visible radiation. All these problems require first of all suitable experimental methods for separating the luminescing particles. Some of the principal universal luminescence identification methods will be described below.

### 6. METHODS FOR IDENTIFICATION OF VISIBLE LUMINESCENCE GENERATED BY MULTIPHOTON EXCITATION WITH INFRARED LASER RADIATION

#### 6.1. Time-of-flight spectroscopy of luminescing particles

The method which can be used to distinguish the luminescence of a molecule and its fragments is based on the difference between the energies of their translational motion.<sup>41</sup> The translational energy  $\varepsilon_0$  of a molecule is governed by the gas temperature T:

$$\mathbf{\epsilon}_{0} = \frac{1}{2} M_{0} \langle v_{0}^{2} \rangle = \frac{3}{2} kT, \qquad (6.1)$$

where  $M_0$  is the mass of the investigated molecule and  $\langle v_9^2 \rangle^{1/2}$  is the rms velocity of the molecule. On dissociation of the molecule by infrared laser radiation there is an additional contribution of an energy  $\sim \Delta E_0/s_0$  to the translational motion of the resultant fragments and the heaviest fragment with a mass  $M_1$  takes away a smaller proportion of the energy, which is given by

$$\Delta \varepsilon_1 = \frac{\Delta E_0}{s_0} \frac{M_0 - M_1}{M_0}. \tag{6.2}$$

This correction to the translational energy of a fragment of mass  $M_1$  has the effect that the rms velocity measured in the laboratory coordinate system  $\langle v_1^2 \rangle^{1/2}$  exceeds the value for the molecule itself, so that<sup>41,45</sup>

$$\frac{\langle v_1^2 \rangle}{\langle v_0^2 \rangle} = 1 + \frac{2}{3} \frac{\Delta E_0}{s_0 kT} \frac{M_0 - M_1}{M_1}.$$
 (6.3)

We shall estimate the order of magnitude of the ratio  $\langle v_1^2 \rangle / \langle v_0^2 \rangle$ , for example, in the case of MPE of a pentatomic

molecule with  $s_0 = 9$ . Let us assume that the molecule splits into two fragments with the same masses. The energy of overexcitation of the pentatomic molecule above the dissociation limit is usually equal to several CO<sub>2</sub> laser photons  $(\hbar\Omega = 1000 \text{ cm}^{-1})$ , as demonstrated by Eq. (4.25). If in these estimates we assume that  $\Delta E_0 = 3000 \text{ cm}^{-1}$ , we find from Eq. (6.3) that  $(\langle v_1^2 \rangle / \langle v_0^2 \rangle)^{1/2} \approx 1.5$ . This estimate shows that the difference between the velocities of the fragments and the molecules themselves is quite large and can be used as the basis for identifying the luminescence emitted by the investigated molecule or its fragments.

The method of determination of the velocity distribution function of the luminescing particles was developed in Ref. 41. Use was made of an experimental arrangement shown in Fig. 4. The essence of the method was the excitation of a near-point source of radiation at the center of a spherical cell and the subsequent observation of the kinetics of quenching of the luminescence at the walls. The gas enclosed in this spherical cell was excited with two-frequency infrared laser radiation (Fig. 4). This ensured smallness of the size of the luminescence zone, compared with the radius of the cell, and localization of the center of the sphere. This was due to the fact that in the case of two-frequency excitation it was possible to select the frequencies and energy densities of the laser fields so that the intensity of the luminescence in the region of intersection of the two beams exceeded considerably the intensity of the luminescence from the zone which interacted with just one of the beams.<sup>61,62</sup>

Excitation was followed by collisionless flying apart of luminescing molecules from the two-frequency excitation zone (when the pressure of the investigated gas was selected so that  $\lambda \ge R_{cell}$ , where  $\lambda$  is the mean free path and  $R_{cell}$  is the radius of the cell). An analysis of the observed visible radiation was carried out using a photomultiplier through a window of the spherical cell or, when the cell was transparent to the radiation being analyzed, directly across its wall arranged in such a way that the whole internal volume of the cell was within the field of view of the photomultiplier.

An analysis was made of the time dependence of the intensity of the visible luminescence in the course of its relaxation and quenching by the cell walls:



FIG. 4. Time-of-flight measurements of the distribution of the velocities of luminescing particles characterized by long radiative times. The infrared absorption spectrum of the OsO<sub>4</sub> molecule (showing the  $v_3$  mode) is plotted on the right and it identifies the laser radiation frequencies ( $\Omega_1$ ,  $\Omega_2$ ) optimal for the formation of a point luminescence source at the center of a spherical cell.

$$I_{\rm L}(\tau) = I_{\rm L}(0) \left(1 - \int_{0}^{\tau} f_{\rm R}^{\rm lab}(\tau) \, \mathrm{d}\tau\right) e^{-\tau/\tau_{\rm rel}}$$
$$= I_{\rm L}(0) \left(\int_{\tau}^{\infty} f_{\rm R}^{\rm lab}(\tau) \, \mathrm{d}\tau\right) e^{-\tau/\tau_{\rm rel}}; \qquad (6.4)$$

here,  $I_{\rm L}(0)$  is the intensity of the luminescence at the moment  $\tau = 0$ ;  $\tau_{\rm rel}$  is the relaxation time of the luminescence at a fixed pressure of the investigated gas inside the cell;  $f_{\rm R}^{\rm lab}(\tau)$ is the time-of-flight distribution function of the velocities of the luminescing particles, which in the specific case of the Maxwellian distribution

$$f_{\rm R}^{\rm lab}\left(|\mathbf{v}|\right) = \frac{4}{\sqrt[4]{\pi\,\bar{v}}} \left(\frac{v}{\bar{v}}\right)^2 e^{-v^2/\bar{v}^2} \tag{6.5}$$

 $[(\bar{v} = (2kT_R/m)^{1/2} \text{ is the most probable velocity of the luminescing particles}]$  is of the form

$$f_{\rm R}^{\rm lab}(\tau) = \frac{4}{\sqrt[4]{\pi\,\overline{\tau}}} \left(\frac{\overline{\tau}}{\tau}\right)^4 e^{-\overline{\tau}^2/\tau^2},\tag{6.6}$$

where  $\overline{\tau} = l/\overline{v}$  is the average time of flight,  $l = R_{cell}$  is the transit length, and

$$\int_{0}^{\omega} f_{\rm R}^{\rm lab}(\tau) \, \mathrm{d}\tau = 1.$$
 (6.7)

Figure 5 shows the dependence  $I_{\rm L}(\tau)$  plotted in accordance with Eq. (6.4) (Fig. 5a) and the experimental oscillogram  $I_{\rm L}(\tau)$  obtained for the OsO<sub>4</sub> molecule (Fig. 5b)<sup>41</sup>. In the case of sufficiently short lifetimes  $\tau \ll \overline{\tau}$ , before the luminescing particles reached the wall, the reduction in  $I_{\rm L}$  was entirely due to the relaxation term of Eq. (6.4):

$$I_{\rm L}(\tau) \approx I_{\rm L}(0) \ e^{-\tau/\tau_{\rm ref}}; \tag{6.8}$$

here,  $\tau_{rel}^{-1} = \tau_{rad}^{-1} + k_q p$ , where  $\tau_{rad}$  is the radiative time,  $k_q$  is the quenching rate constant, and p is the pressure of the investigated gas in the cell. If  $\tau \gg \overline{\tau}$ , then Eq. (6.4) becomes

$$I_{\rm L}(\tau) \approx I_{\rm L}(0) \, \frac{4}{3 \, \sqrt{\pi}} \left(\frac{\bar{\tau}}{\tau}\right)^3 \ e^{-\tau/\tau_{\rm rel}}. \tag{6.9}$$



FIG. 5. a) Time dependence of the luminescence intensity during its relaxation and quenching on the cell walls (Fig. 4).<sup>41</sup> b) Experimental oscillogram of  $I_L(t)$  obtained for the OsO<sub>4</sub> molecule at a gas pressure of  $1.2 \times 10^{-4}$  Torr in a spherical cell 75.5 mm in diameter.<sup>41</sup>

An analysis of a luminescence pulse in the interval  $\tau \ll \overline{\tau}$ makes it possible to determine  $\tau_{rel}$ . Differentiation of the function  $I_{\rm L}(\tau) \exp(\tau/\tau_{rel})$  with respect to time gives  $f_{\rm R}^{\rm lab}(\tau)$  and, consequently,  $f_{\rm R}^{\rm lab}(|\mathbf{v}|)$ , so that

$$f_{\mathrm{R}}^{\mathrm{lab}}\left(\boldsymbol{\tau}\right) d\boldsymbol{\tau} = f_{\mathrm{R}}^{\mathrm{lab}}\left(|\boldsymbol{\mathbf{v}}|\right) d\boldsymbol{\nu}. \tag{6.10}$$

The function  $f_{R}^{lab}(|\mathbf{v}|)$ , is in its turn related to the required velocity distribution function of the fragments in the center-of-mass (c.m.) system by the expression

$$f_{\mathrm{R}}^{\mathrm{lab}}(\mathbf{v}) = \int f_{\mathrm{M}}(\mathbf{v}_{0}) f_{\mathrm{R}}^{\mathrm{c.m.}}(\mathbf{v} - \mathbf{v}_{0}) d\mathbf{v}_{0} = f_{\mathrm{M}}(\mathbf{v}_{0}) * f_{\mathrm{R}}^{\mathrm{c.m.}}(\mathbf{v}),$$
(6.11)

i.e.,  $f_{R}^{lab}(\mathbf{v})$  is simply a convolution of the distributions  $f_{M}(\mathbf{v}_{0})$  and  $f^{c.m.}(\mathbf{v})$ .

It therefore follows that the experimental method described above can be used to find the distribution function of the velocities of the luminescing particles on the basis of its maximum and this involves determination of the most probable velocity of these particles and a comparison with the thermal velocity of the original molecules, so as to identify the origin of the luminescence. Two-frequency excitation is not essential in such time-of-flight experiments. It is possible to use one-frequency excitation of a gas and the usual cylindrical cell.<sup>47</sup> The main shortcoming of such a method is restriction of the luminescence duration. It is clear from Eq. (6.4) that this method can be used if the radiative luminescence time is sufficiently long, i.e., if  $\tau_{\rm rel} \gtrsim \overline{\tau}$ . For example, in the experiments on the OsO4 molecule described in Ref. 41 the cell radius was  $R_{\rm cell} = 3.8$  cm and  $\bar{\tau} \approx 250 \,\mu$ s. However, there are many molecules (see Table I) for which  $\tau_{\rm rel}$  is considerably less than this value. One can naturally reduce the size of the cell somewhat, but it is necessary to satisfy the condition of smallness of the radius of the luminescence zone  $R_{\rm L}$  compared with the cell radius:  $R_{\rm cell} \gg R_{\rm L}$ .

The method of determination of the velocities of the luminescing particles suitable for the determination of short luminescence times  $\sim 1-10 \,\mu s$  was developed in Refs. 43 and 45. The method is based on an analysis of the expansion of a luminescence zone with a diode array of an optical multichannel analyzer. Figure 6 is a simplified schematic of the experimental arrangement. Radiation from a CO<sub>2</sub> laser is focused in a cell with an excited gas and it induced visible luminescence. A small cylindrically symmetric luminescence zone is projected by a lens onto a diode array of a scanning optical multichannel analyzer. Variation of the delay between the laser pulses and a scan makes it possible to study the evolution of expansion of the luminescence zone. A typical pattern obtained by projection of this zone onto the diode array of the optical multichannel analyzer is shown in Fig. 7 for the case of MPE of the OsO<sub>4</sub> molecule by CO<sub>2</sub> laser radiation.

The distribution of the luminescing particles revealed by such an array at different moments in time is governed by two factors: 1) expansion of the luminescence zone in the cell because of flying apart of molecules or fragments; 2) projection of the luminescence zone onto the diode array. One can show that, allowing for the cylindrical symmetry, the density of the gas at a given point r at a given moment t is

$$\rho(\mathbf{r}, t) = \frac{\rho_0 R_0^2}{R_0^2 + \mathbf{v}^2 t^2} \exp\left(-\frac{r^2}{R_0^2 + \mathbf{v}^2 t^2}\right).$$
(6.12)



FIG. 6. Experimental arrangement used in determination of the velocities of luminescing particles.

It is assumed here that the initial radial distribution is Gaussian and the radius is  $R_0$ ;  $\bar{v} = (2kT/m)^{1/2}$  is the most probable velocity and  $\rho_0$  is the initial concentration of the luminescing particles. It is clear from Eq. (6.12) that at an arbitrary moment in time the radial distribution is characterized by a radius

$$R^2(t) = R_0^2 + \mathbf{v}^2 t^2 \tag{6.13}$$

when the total number of the luminescing particles in a cylindrical column of unit length is

$$N = \int_{0}^{\infty} \rho(r, t) \cdot 2\pi r \, \mathrm{d}r = \pi R_{0}^{2} \rho_{0}. \tag{6.14}$$

Projection of the radial distribution f(r) can be described by an integral

$$f(x) = 2 \int_{0}^{(r^2 - x^2)^{1/4}} f(l) \, \mathrm{d}l, \qquad (6.15)$$

where x is the horizontal coordinate on the screen of an optical multichannel analyzer (Fig. 6). In the case of a Gaussian distribution  $\rho(r, t)$  of Eqs. (6.12) and (6.15) we have

$$f(x) = \frac{\sqrt{\pi} \rho_0 R_0^2}{(R_0^2 + \mathbf{v}^2 t^2)^{1/2}} \exp\left(-\frac{x^2}{R_0^2 + \mathbf{v}^2 t^2}\right).$$
(6.16)

It therefore follows from Eq. (6.16) that if we adopt the

Gaussian approximation for the initial distribution, we find that the radius of the projection of the distribution of Eq. (6.16) determined directly is equal to the radius of the initial distribution described by Eq. (6.12). It therefore follows that if we measure R(t) at different moments in time (Fig. 7), we can use Eq. (6.16) to determine directly the velocities of the luminescing particles. A detailed analysis of this method can be found in Ref. 54.

There are also beam variants of time-of-flight methods based on different distributions of the directions of the velocity vectors of the molecules themselves and their fragments formed as a result of MPE in a molecular beam.<sup>49,54</sup>

#### 6.2. Separation of successive stages of luminescence

Time-of-flight spectroscopy of luminescing particles makes it possible to distinguish the luminescence of the molecule itself and of its fragments. However, in many cases this task is complicated by the fact that during a laser pulse there are several stages of fragmentation of a molecule and, in addition to the primary fragments, secondary fragments (radicals) may form and so on until MPE of the individual fragments by laser radiation becomes impossible. The multistage fragmentation of a molecule and the consequent feasibility of IER in the case of many fragments greatly complicates the task of identification of the luminescence and it demands a method capable of separating possible successive stages of such luminescence. A simple method for such separation is proposed in Ref. 45. In this method the likely consecutive processes in the case of MPE can be separated on the basis of the vibrational activation energy require for realization of these processes. In fact, if IER of a molecule does occur, it is characterized by the lowest vibrational energy  $E_0$ . This means that as the vibrational energy is increased, we should observe first IER of the molecule itself. The next processdissociation of the molecule—requires an energy D (it is usually found that  $E_0 < D$ , see Sec. 4). The process of IER of a primary fragment<sup>3)</sup> requires formation of the fragment and then excitation to the limit of the upper electronic term  $E_0^{f}$ , i.e., the loss of an energy  $E > (D + E_0^f)$ , and so on for IER of subsequent fragments. Therefore, each of the postulated processes (IER as a result of MPE of the molecule itself, IER as a result of MPE of a primary fragment, and IER as a

FIG. 7. Evolution of the projection of the luminous zone of  $OsO_4$  molecules onto a diode array of an optical multichannel analyzer (MCA), determined using the arrangement in Fig. 6.



result of MPE of a secondary fragment) occurs at an increasing threshold energy of laser radiation. Another important circumstance is that in this sequence of processes we can expect MPE always to quench the luminescence which results from IER. In other words, if we assume the possibility of all the consecutive processes in the case of MPE, then an increase in energy density of laser radiation can result in appearance of molecular luminescence and then in its disappearance. This should be followed by the appearance of the luminescence of the primary fragments and its quenching by dissociation, etc.

A convenient experimental method for obtaining such dependences in a wide range of energy densities  $\Phi$  is a direct analysis of the spatial distribution of the luminescence recorded by focusing CO<sub>2</sub> laser radiation in a cell containing the investigated gas. The laser beam is focused in the cell so that the CO<sub>2</sub> laser radiation energy density is spread out along the beam with its maximum at the center of the lens caustic. The resultant longitudinal spatial distribution of the luminescence can be recorded directly with an optical multichannel analyzer so that after a suitable treatment of the results (see Ref. 45), it is possible to obtain the complete dependence of the luminescence intensity on the laser radiation energy density. Such measurements can be carried out during a single CO<sub>2</sub> laser pulse. In a qualitative estimate of the existence of various stages of luminescence it is possible to replace a diode array of an optical multichannel analyzer with an ordinary photographic plate. Photographs of the visible luminescence induced by CO2 laser radiation are reproduced in Fig. 8 for the OsO<sub>4</sub> molecule. These photographs show clearly bright and dark regions representing enhancement and subsequent quenching of the luminescence as the laser radiation energy density is increased approaching the focus of the lens at z = 0. The bright spot between two dark regions represents a given luminescence stage. Replacement of a photographic plate with a more sensitive diode array has made it possible to distinguish three stages of the luminescence of the OsO4 molecule and to obtain the dependences of its intensity on the laser radiation energy density.

FIG. 8. Method for separation of successive stages of luminescence.<sup>45</sup> The photograph shows the two strongest luminescence stages (II and III) observed by fousing CO<sub>2</sub> laser radiation (f = 17.5 cm) in an OsO<sub>4</sub> cell at gas pressures (Torr): 1)  $7.5 \times 10^{-3}$ ; 2)  $2.2 \times 10^{-2}$ ; 3)  $7.5 \times 10^{-2}$ ; 4)  $1.5 \times 10^{-1}$ .

The experimental results reported in the present section could, together with the traditional spectra, be used to study effectively and identify the visible luminescence which appears as a result of multiphoton excitation of molecules by infrared laser radiation. Specific applications of this method to the visible luminescence of the  $OsO_4$  molecule will be considered below.

### 7. VISIBLE LUMINESCENCE EMITTED BY THE OsO4 MOLECULE DUE TO EXCITATION WITH CO2 LASER RADIATION AND INVERSE ELECTRONIC RELAXATION

### 7.1. Lower electronic terms of the OsO4 molecule

The OsO<sub>4</sub> molecule belongs to a large class of isoelectronic tetrahedral oxygen compounds (see Fig. 9).67 The electronic energy levels of such compounds have been calculated on many occasions by a variety of methods (see, for example, Refs. 68 and 69). The general scheme of molecular orbitals accepted at present is shown in Fig. 9. The excited electronic states with the lowest energy  ${}^{1}T_{1}$  and  ${}^{1}T_{2}$  correspond to a transition of an electron from a completely filled orbital  $t_1$ , which behaves basically as a nonbonding 2p orbital of the oxygen atom, to a partly filled orbital 2e consisting mainly of the d orbitals of the metal atom. An electronic spectrum of such oxygen complexes begins with a strong band corresponding to the dipole-allowed transition  ${}^{1}T_{2}(t_{1}^{5}2e^{1}) \leftarrow {}^{1}A_{1}(t_{1}^{6}2e^{0})$  (in the case of the OsO<sub>4</sub> molecule the energy of the 0-0 transition is  $\sim 3.1 \times 10^4$  cm<sup>-</sup>—see Refs. 68 and 70). Somewhat lower on the energy scale we have the singlet time  ${}^{1}T_{1}$  (Fig. 9) and the transition to this term from the ground electronic state <sup>1</sup>A<sub>1</sub> is forbidden.<sup>71</sup> The two-singlet terms correspond to the triplet states  ${}^{3}T_{2}$  and  ${}^{3}T_{1}$ . The singlet-triplet splitting was calculated in Ref. 69 for a range of oxygen complexes. For example, in the case of the RuO<sub>4</sub> molecule (transition  $2e \rightarrow t_1$ ) it amounts to ~0.8 eV. For OsO<sub>4</sub> the corresponding value is not known, so that the triplet terms in Fig. 9 are represented at nominal positions with an approximately the same splitting as in the case of the RuO<sub>4</sub> molecule.

The dissociation energy of the OsO4 molecule had been

FIG. 9. Molecular orbitals of tetrahedral oxygen complexes (on the right) and lower electronic terms of the  $OsO_4$  molecule (on the left). The photon energies are also shown for the most widely available ultraviolet  $N_2$ , XeCl, and KrF lasers.

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determined by a variety of methods.<sup>72-74</sup> Its most probable value  $3.8 \times 10^4$  cm<sup>-1</sup> agrees with the results of experiments involving ultraviolet excitation of OsO<sub>4</sub> by radiation from N<sub>2</sub>, XeCl, and KrF lasers (the laser radiation photon energies are given in Fig. 9).

The tetrahedral oxygen complexes have a number of shared luminescence properties. An investigation of the low-temperature luminescence of oxygen complexes  $(VO_4^{3-}, CrO_4^{2-}, MOO_4^{2-}, WO_4^{2-})^{67}$  in solid-state matrices had shown that in all cases the excitation of the strong  ${}^{1}T_2 \rightarrow {}^{1}A_1$  band results in the luminescence from the triplet levels  ${}^{3}T_2$  and  ${}^{3}T_1$ . The observed luminescence is characterized by long radiative times ( $\tau_{rad} \approx 1-10$  ms) and wide structure-free spectra shifted strongly toward the red range relative to the investigated electronic luminescence band.

# 7.2. Main characteristics of visible luminescence emitted by the $OsO_4$ molecule as a result of excitation with $CO_2$ laser radiation

Excitation of the OsO<sub>4</sub> molecule by CO<sub>2</sub> laser radiation in the infrared absorption band of the  $\nu_3(T_2) \mod^{75,76}$  gives rise to visible luminescence. Figure 10 shows typical evolution of the visible luminescence in time when the OsO<sub>4</sub> molecule is excited by CO<sub>2</sub> laser pulses of energy density  $\Phi \sim 0.7$ J/cm<sup>2</sup>. Selecting suitably the excitation conditions, we can readily separate the collisionless luminescence stage. Excitation at the center of the P branch gives rise to not only the collisionless but also to the collisional luminescence. This behavior is due to a special feature of the infrared MPE process itself, discussed in detail in Refs. 62, 77, and 78.

Luminescence with similar time and spectral characteristics (Fig. 11) can be induced by N<sub>2</sub> laser radiation  $(\lambda = 337 \text{ nm})$  under conditions such that the peak intensity of the luminescence depends linearly on the laser radiation intensity and, consequently, the processes associated with multiphoton absorption of ultraviolet radiation can be ignored.<sup>79-81</sup> The radiative luminescence lifetime in the case of ultraviolet excitation ( $\tau_{rad} \approx 1.5 \text{ ms}$ ) and the rate constant of the collisional luminescence quenching ( $k^{-1} = 95 \pm 10$ 



FIG. 10. Evolution of visible luminescence emitted by the  $OsO_4$  molecule as a result of excitation with the  $CO_2$  laser radiation.<sup>28</sup>  $\Phi = 0.7 J/cm^2$ . The infrared absorption spectrum of  $OsO_4$  ( $\nu_3$  mode) is shown below and the frequencies employed are identified.



FIG. 11. Luminescence (a) and luminescence relaxation times (b) obtained by excitation of  $OsO_4$  with  $CO_2$  laser radiation (continuous curve, symbol 1) and  $N_2$  laser radiation (dashed curve in Fig. 11a, symbol 2).<sup>28</sup>

ns. Torr) are in good agreement with the corresponding parameters of the luminescence induced by  $CO_2$  laser radiation with an energy density in the range  $\Phi \leq 2 \text{ J/cm}^2$  (Table I).<sup>28</sup> The time-of-flight measurements of the distribution of the velocities of the luminescing particles (see Sec. 5.1) demonstrate that they agree quite accurately with the Maxwellian distribution of the OsO<sub>4</sub> molecules themselves.<sup>41</sup> These experiments have led to the conclusion that the visible luminescence which appears as a result of interaction with  $CO_2$  laser radiation of low energy density ( $\Phi \leq 2 \text{ J/cm}^2$ ) is due to the osmium tetraoxide molecule itself and the most probable process which can result in the luminescence is IER.<sup>13,28,41</sup>

## 7.3. Theoretical model of multiphoton excitation and inverse electronic relaxation of the $OsO_4$ molecule

A complete theoretical description of the process of MPE of molecules is not yet possible since there is no satisfactory theory that can describe the excitation of the lower vibrational states of molecules characterized by  $E < E_{vqc}$ (see Sec. 4). However, in many cases the process of IER can be simulated in the range of vibrational energies lying above the limit of the vibrational quasicontinuum and in this range we can calculate the parameters of MPE quite readily using simple rate equations (see Sec. 4.4). Therefore, in such cases we can describe IER simply by limiting ourselves to the range  $E > E_{vqc}$  and ignore the lower vibrational states. A strong inhomogeneity of the vibrational distribution, which appears in the case of MPE of OsO<sub>4</sub>, makes it possible to separate arbitrarily the population of the lower vibrational levels from the vibrational quasicontinuum by specifying the fraction of the molecules q which are excited in this quasicontinuum.<sup>77</sup> The factor q describing the processes of interaction of infrared laser radiation with lower vibrational levels can be excluded by measuring not only  $I_{\rm L}(\Phi, \Omega)$ , but also the average energy absorbed per molecule of the excited gas  $\varepsilon(\Phi, \Omega)$  (Refs. 28 and 82). Then, in the first approximation (ignoring the gradual shift of the molecules to the vibrational quasicontinuum during a laser pulse), we have

$$I_{\rm L} = q I_{\rm L}^{\rm calc}, \quad \varepsilon = q \varepsilon^{\rm calc}, \tag{7.1}$$

where  $I_L^{calc}$  and  $\varepsilon^{calc}$  are the quantities calculated for the vibrational quasicontinuum using the rate equations (4.11). A comparison with the experimental results of a quantity representing the quantum efficiency of MPE

$$\rho = \frac{I_{\rm L}(\Phi, \Omega)}{\epsilon(\Phi, \Omega)}, \qquad (7.2)$$

makes it possible to determine the parameters of the quasi-

continuum [i.e., of the cross section in the system (4.11)] and the fraction of the excited molecules q:

$$q = \frac{\varepsilon}{\varepsilon^{\text{calc}}}.$$
(7.3)

This approach is self-consistent only if the result obtained in the form of the dependence  $q(\Phi)$  is a slow function of  $\Phi$ . In the case of OsO<sub>4</sub> this is indeed true.<sup>28</sup> There are also independent experimental methods for the determination of the fraction q of the excited molecules.<sup>77</sup>

After selection of the quantum efficiency of Eq. (7.2), which can be determined experimentally under collisionless excitation conditions and can be compared with the calculations, we still have to find the cross sections  $\sigma_n^a$  in the system of equations (4.11) in order to determine the parameters of MPE and IER. The simplest way for specifying cross sections in terms of two parameters so as to allow for the shifts and broadening of the relevant bands in the vibrational quasicontinuum is to select a Lorentzian profile of  $\sigma_n^a$ , as was done in Refs. 27 and 28 (see Sec. 4). In the case of the OsO<sub>4</sub> molecule the dependence  $\gamma(E)$  is selected to be quadratic because of the presence of good intermode fourth-order resonances of Eq. (4.9):

$$\gamma(E) = V_0 \left(\frac{E}{hv_3}\right)^2. \tag{7.4}$$

The second parameter  $X_0$  determines the linear shift of the maximum of the absorption band in the vibrational quasicontinuum:

$$\mathbf{v}\left(E\right) = \mathbf{v}_{3} - X_{0}\left(\frac{E}{h\mathbf{v}_{3}}\right). \tag{7.5}$$

The integral strength of the band is found from the known value of the dipole moment of the transition in the  $v_3$  mode:  $\mu_{01} = 0.17 \pm 0.02$  D (Ref. 76). The third independent parameter is the energy of the 0–0 transition  $E_0$  representing an electronically excited state from which transitions take place giving rise to the observed visible luminescence.

A comparison of the calculations with experimental results carried out in a wide range of  $\Phi$  and  $\Omega$  has made it possible to find the following values of the parameters of the model in the case of the OsO<sub>4</sub> molecule<sup>28</sup>

$$V_0 = 0.1 \text{ cm}^{-1}, \quad X_0 = 4.5 \text{ cm}^{-1}, \quad E_0 = 10^4 \text{ cm}^{-1}.$$
(7.6)

These parameters were obtained from the experimental results on one-frequency excitation of the molecule. They describe satisfactorily the results obtained in two-frequency excitation  $I_1$  ( $\Phi_1$ ,  $\Phi_2$ ,  $\Omega_1$ ,  $\Omega_2$ ) if the second laser field is detuned sufficiently far from the linear absorption band and does not shift new molecules to the vibrational quasicontinuum. Figure 12 shows the calculated vibrational distribution functions  $f_{\rm G}(E)$  and the relative efficiency of the luminescence of the individual levels  $\rho_{\rm S} (E - E_0) f_{\rm G} (E) / \rho_{\rm G} (E)$  $=f^{*}(E)$ . When the laser radiation energy density is increased, the distributions become broader and their maxima shift toward higher vibrational energies. The luminescence intensity increases (Fig. 13) until E < D. At high energy densities  $\Phi$  a considerable fraction of the molecules reaches the dissociation limit D and monomolecular decay of molecules,  $OsO_4 \rightarrow OsO_3 + O$ , takes place resulting in quenching of the visible luminescence (Fig. 13).



FIG. 12. Calculated distribution of the OsO<sub>4</sub> molecules between the vibrational states (curve 1) and the effective population of the luminescing levels (curve 2).<sup>28</sup> The calculation was carried out for  $\Omega_{las} = 947.7 \text{ cm}^{-1}$ and  $\Phi = 0.27 \text{ J/cm}^2$ .

# 7.4. Multistage nature of the emission of visible luminescence. Inverse electronic relaxation of the $OsO_4$ molecule and its fragments

A theoretical model of MPE and IER in the case of the OsO<sub>4</sub> molecule, based on the parameters obtained from a comparison with the experimental results at relatively low energy densities  $\Phi \leq 2 \text{ J/cm}^2$ , makes it possible to predict the behavior of the luminescence of the OsO<sub>4</sub> molecule itself in any range of  $\Phi$  (see Fig. 13) and in particular the nature of the quenching of the luminescence of the OsO4 molecule itself and the appearance of the OsO<sub>3</sub> radical fragment. The fragment OsO<sub>3</sub> contains the heavy osmium ion and naturally has an approximately the same frequency of the Os-O valence vibration as the molecule itself, so that this fragment can also absorb the radiation from the same laser pulse. The additional energy transferred to the vibrational degrees of freedom of the OsO<sub>3</sub> fragment as a result of monomolecular decay of  $OsO_4$  (see Sec. 4.5) broadens the vibrational spectrum and this improves the conditions for MPE in the case of this fragment. The characteristic structure of the electronic terms and the dissociation energy of OsO<sub>3</sub> are governed by the orbitals of the same atoms. We can therefore expect that below the dissociation limit of the fragment there are also electronically excited states which shift together with the ground electronic term. Consequently, if the laser radiation energy density is sufficiently high, we can expect a different luminescence associated with IER of the OsO<sub>3</sub> fragment. This applies equally to another fragment OsO<sub>2</sub> formed next as a result of multiphoton dissociation of OsO<sub>3</sub>.

The luminescence of  $OsO_4$  was investigated at laser radiation energies right up to  $10^3 \text{ J/cm}^2$  using a method of separation and analysis of the consecutive stages of the lumi-



FIG. 13. Calculation of the dependence of the luminescence intensity  $I_{\rm L}$  (curve 1) and of the dissociation yield  $\beta$  (curve 2) on the energy density of laser radiation  $\Phi$  interacting with the OsO<sub>4</sub> molecule.

nescence (see Sec. 6.2).45 It was found that in the case of the OsO<sub>4</sub> molecule there were three different luminescence stages, depending on the energy density of infrared laser radiation. Each of these stages has a definite threshold of the appearance depending on  $\Phi$  and the characteristic luminescence spectrum. Different stages are characterized also by different velocities of the luminescing particles. The observed luminescence stages are described by a sequence of processes occurring during one infrared laser radiation pulse: IER following multiphoton dissociation of the OsO<sub>4</sub> molecule (stage I); IER following multiphoton dissociation of the primary fragment OsO<sub>3</sub> (stage II); IER following multiphoton dissociation of the secondary fragment  $OsO_2$ (stage III). Such a chain of the processes is clearly a fairly general mechanism of the appearance of the luminescence and, depending on the actual molecule subjected to infrared laser radiation, the molecular luminescence or that emitted by one of the fragments may be absent.

Figure 14 shows typical dependences of the luminescence intensity on the laser radiation energy density obtained by the method of longitudinal focusing (see Sec. 4.2) in the excitation of the  $v_3$  molecule of OsO<sub>4</sub> at various CO<sub>2</sub> laser radiation frequencies. A characteristic feature of these curves is the presence of three clear luminescence stages. Within each stage the dependence  $I_{\rm L}(\Phi)$  is characterized by the following features: the threshold nature of the appearance of the luminescence during the initial part of each stage and the subsequent reduction in the slope of the curves on increase in  $\Phi$  until they reach saturation or even quenching. The dependences  $I_{\rm L}(\Phi)$  for the stages I and II are described in Ref. 45 by postulating and justifying a model of "similarity" of the luminescence of the molecule and its fragments from which it is found that the overall luminescence intensity is described by

$$I_{\rm L} (\Phi) = I_{\rm L}^{(m)} (\Phi) + \bigvee_{0}^{\Phi} d \left(\beta_{m} (\Phi')\right) \frac{\tau_{\rm rad}^{(m)}}{\tau_{\rm rad}^{(f)}} I_{\rm L}^{(m)} \left[ \frac{\langle \sigma^{\rm f} \rangle}{\langle \sigma^{\rm m} \rangle} (\Phi - \Phi') \right],$$
(7.7)



FIG. 14. Dependences of the intensity  $I_{\rm L}$  of the visible luminescence induced by CO<sub>2</sub> laser radiation in an OsO<sub>4</sub> gas on the laser radiation energy density, determined by the method of separation of consecutive luminescence stages.<sup>45</sup>

where the indices m and f refer to the molecule and the fragment, respectively;  $\beta$  is the dissociation efficiency;  $\langle \sigma^{m,r} \rangle$ are the characteristic absorption cross sections in the vibrational quasicontinuum. The experimental results are compared in Fig. 15 with the calculations describing two luminescence stages corresponding to MPE of OsO<sub>4</sub> and OsO<sub>3</sub>. These models cannot be used to calculate the intensity of the luminescence observed as a result of MPE of the OsO<sub>2</sub> fragment (stage III) because in the case of triatomic fragments we cannot speak of a quasicontinuum even in the range of vibrational energies close to the dissociation limit since the density of the vibrational levels is too low.

### 7.5. Velocities of luminescing particles

The time-of-flight measurements (see Sec. 6.1) provide an additional illustration of the multistage nature of the observed luminescence. After multiphoton dissociation of molecules some of the overexcitation energy (in excess of the dissociation limit) is transferred to the translational degrees of freedom of the fragments. The degree of overexcitation  $\Delta E_i$  (the index i = 0, 1, and 2 applies to OsO<sub>4</sub>, OsO<sub>3</sub>, and OsO<sub>2</sub>, respectively) can be estimated from the relationship equating the decay and absorption rates [Eq. (4.20)]. In estimating the decay rate in the form of Eq. (4.19), it was found in Ref. 45 that the values of  $\Delta E_i$  are related by

$$\frac{1}{D_i} \left(\frac{\Delta E_i}{D_i}\right)^{s_i-1} = \frac{1}{D_j} \left(\frac{\Delta E_j}{D_j}\right)^{s_j-1}, \qquad (7.8)$$

where  $s_i$  is the number of the vibrational degrees of freedom of the molecules and its fragments. The translational degrees of freedom receive an energy  $\Delta E_i / s_i$  as a result of each fragmentation event and the increase in the kinetic energy  $\Delta \varepsilon_i$ for the heavier fragment is relatively small [see Eq. (6.2)]. We can use Eqs. (6.2) and (7.8) to determine the average corrections to the velocities of translational motion of the fragments as a result of multiphoton dissociation. Figure 16 shows the results of calculations of the most probable velocities of the luminescing particles expected for different degrees of overexcitation  $\Delta E_0$  above the dissociation limit of the OsO<sub>4</sub> molecules itself. The experimental values (represented by black dots in Fig. 16) were obtained by a method



FIG. 15. Comparison of the experimental and calculated dependences  $I_{\rm L}$  ( $\Phi$ ) obtained for the luminescence stages I and II in the OsO<sub>4</sub> gas.



FIG. 16. Relative changes in the velocities of luminescing particles plotted as a function of  $\Phi$  (Ref. 45). The experimental velocities (represented by black dots) are reduced to the value  $\overline{V}_0$  at  $\Phi = 5 \text{ J/cm}^2$  (stage 1). The continuous lines represent the velocities calculated for various degrees of excess of the vibrational energy in OsO<sub>4</sub> over the dissociation limit:  $\Delta E_0/\hbar\Omega_{\text{bas}} = 1, 3, 5, \text{ and } 7$ .

described in Sec. 6.2. The value of the parameter  $\Delta E_0 = 5 \times 10^3$  cm<sup>-1</sup> is in agreement with typical degrees of overexcitation in the case of MPE of pentatomic molecules.<sup>32</sup> Moreover, the dependences of the velocities of the luminescing particles on the energy density also demonstrate the threshold nature of the change in the velocity on transition to the range of energy densities  $\Phi$  corresponding to the stage II. The time-of-flight measurements therefore confirm the main assumption about the consecutive competition of the luminescence and dissociation process in the case of OsO<sub>4</sub>, OsO<sub>3</sub>, and OsO<sub>2</sub>.

The case of the  $OsO_4$  molecule demonstrates the full range of possible processes: IER after multiphoton dissociation of the  $OsO_4$  molecule itself and of its two fragments  $OsO_3$  and  $OsO_2$ . As pointed out already in Sec. 5, one of the important tasks in the study of IER is the search for specific electronic states associated with this process. In the case of the  $OsO_4$  molecule these states are most probably the lowest triplets. One should mention here also the similarity of the spectral and time characteristics of the  $OsO_4$  luminescence with those reported for other tetraoxygen complexes (see Sec. 7.1).

## 8. DETACHMENT OF AN ELECTRON INDUCED BY INFRARED LASER RADIATION

Other objects which are affected significantly by the nonadiabaticity in the interaction with infrared laser radiation are negatively charged complexes formed as a result of attachment of electrons to molecules and radicals. As a rule, the electron affinity of these complexes is less than 3 eV, whereas the binding energy of most of the compounds is 3-5 eV (Refs. 83-85). This means that the electronic terms of the neutral molecule, transition from which may result in detachment of an electron, lie below the dissociation limit of the ground electronic state of many negative ions. In fact, photodetachment of an electron by ultraviolet or visible radiation is a thoroughly investigated process.83 A new process, which has become accessible to experimental study as a result of infrared MPE, is photodetachment induced by infrared laser radiation.86 This process is closely analogous to IER described above. We are dealing here again with conversion of vibrational into electronic energy. The only difference is that the vibrational energy is transferred to the translational energy of a freely moving electron, i.e., that the photodetachment of an electron induced by infrared laser radiation is determined by the coupling of the vibrational quasicontinuum of the ground electronic state to the electronic continuum.

Experiments on detachment of an electron by infrared laser radiation have been carried out using a pulse spectrometer for investigating cyclotron resonance of ions. The required ions were generated, confined, and detected in special ion traps at pressures of  $\sim 10^{-6}$  Torr (Refs. 86–89). These ions were excited by CO<sub>2</sub> laser radiation pulses which were applied approximately 500 ms after an electron beam pulse which generated the initial anions. The photodetachment by infrared laser radiation was deduced from a change in the anion concentration due to the interaction with CO<sub>2</sub> laser pulses. A more detailed description of these experiments can be found in Refs. 86–89.

Table II lists a number of compounds for which the detachment of an electron induced by infrared laser radiation has been observed experimentally. We shall consider the acetone enolate anion by way of example.<sup>89</sup> In the case of this compound the electron-detachment and dissociation limits were  $E_1 = 1.45 \times 10^4$  cm<sup>-1</sup> and  $E_2 = (2-2.2) \times 10^4$  cm<sup>-1</sup>. When MPE was due to CO<sub>2</sub> laser radiation with an energy density ~1 J/cm<sup>2</sup>, it was found that an electron was detached preferentially, but when  $\Phi$  was increased to 2 J/cm<sup>2</sup>, both an electron was detached and the radical anion was dissociated into H-C=C-O<sup>-</sup> and CH<sub>4</sub> fragments, and the probabilities of these processes were approximately equal.

The nonadiabaticity operator resulting in the observed detachment of an electron has the familiar form (see, for example, Ref. 90):

$$V_{hn} = \sum_{i} \left[ \frac{\hbar^{2}}{2M_{i}} \langle \psi_{h} | \nabla_{Q}^{2} | \psi_{n} \rangle + \frac{\hbar^{2}}{M_{i}} \langle \psi_{h} | \nabla_{Q} | \psi_{n} \rangle \nabla_{Q} \right], \qquad (8.1)$$

where  $\psi_k(x, Q)$  are the electronic wave functions dependent on the coordinates of the electrons x and nuclei Q, and their summation over *i* extends to all the nuclei. In the case of photodetachment we have to consider electronic states of the  $A^-$  anion  $|\psi_{A^-}(x, Q)\rangle$  and the electronic states of the neutral molecule  $A^0$  together with a free electron with a wave vector **k**, which are  $|\psi_{A^0,\mathbf{k}}(x, Q)\rangle$ . Then, the probability of the photodetachment is easily estimated using the first order of perturbation theory:

$$W_{i+j} = \frac{2\pi}{\hbar} |V_{A^0, \mathbf{k}, j; \mathbf{A}^-, i}|^2 \rho_e (E_i^- - E_j^0), \qquad (8.2)$$

where  $E_i^-$  and  $E_j^0$  are the vibrational-rotational states of  $A^-$  and  $A^0$ , respectively;  $\rho_e$  is the density of the translational states of a free electron with the kinetic energy  $E = E_i^- - E_i^0$  which is of the form

$$\rho_{\rm e}(E) = \left(\frac{8m}{\hbar^2}\right)^{3/2} \frac{\pi}{4} E^{1/2}.$$
(8.3)

Since  $\rho_e(E)$  increases slowly on increase in E, the main influence on  $W_{i \rightarrow j}$  comes from the matrix element of the nonadiabatic interaction. A detailed analysis of this influence can be found in Ref. 91.

TABLE II. Anions from which an electron is detached as a result of multiphoton excitation with infrared laser radiation.

| Anion                | Chemical formula   | Electron affinity,<br>eV | Ref.               |
|----------------------|--|--------------------------|--------------------|
| Benzyl<br>Allyl      | $\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $ | 0,88<br>0,55             | 86, 87<br>87<br>87 |
| 1,3-Cycloheptadienyl |  | 0,9                      | 87                 |
| Anilide              | ——————————————————————————————————————                             | 1,15                     | 87                 |
| A cetone enolate     | O-<br>L<br>H <sub>3</sub> C CH <sub>2</sub>                        | 1,8                      | 89                 |

If should be pointed out that, even before the discovery of the feasibility of preparing vibrationally excited molecular ions by MPE by exposure to infrared laser radiation, it has been known that such anions can be generated by the processes

$$A^- + B \rightarrow [AB^-]^* \rightarrow AB + e^-, \tag{8.4}$$

$$AB + e^{-} \rightarrow [AB^{-}]^{*} \rightarrow AB + e^{-}.$$
(8.5)

In many cases it is found that decay of a vibrationally excited  $[AB^-]^*$  anion is followed by the formation of a neutral molecule and an electron. In the case described by Eq. (8.4) this process is known as associative ionization<sup>92,93</sup> and the case described by Eq. (8.5) is the familiar resonance scattering of electrons by molecules (Feshbach resonances).<sup>94</sup> During the stage of decay of a vibrationally excited complex these two processes obviously represent the photodetachment of an electron by infrared laser radiation.

#### 9. CONCLUSIONS

This review has dealt with nonradiative processes which occur in the case of collisionless MPE of the vibrational levels of the *ground electronic state* by infrared laser radiation. This excitation method and the opportunity for investigating IER and infrared photodetachment of an electron have become possible because of the discovery and the development of the method of MPE by infrared laser radiation.

However, it should be pointed out that whereas vibrational activation of the molecules in the ground electronic state has been discovered relatively recently, vibrational excitation of the upper electronic terms has been known for a long time. In fact, interaction with an ultraviolet or visible photon  $\hbar\omega$  can be used to generate a molecule in an electronically excited state with a vibrational energy reserve  $E = \hbar(\omega - \omega_e)$  ( $\omega_e$  is the frequency of the 0-0 transition). The probability of absorption of a photon of energy  $\hbar\omega$  is governed by the relevant Franck-Condon factor which limits the possible range of vibrational energies in the upper electronic state.<sup>95</sup>

In the case of excitation we find that IER has its own analog known<sup>96</sup> as "delayed fluorescence." In this case the parameters of the luminescence obtained from an electronically excited state are influenced by the adjacent electronically excited terms (for example, triplets). The additional excitation of molecules by infrared laser radiation in the *triplet* electronic states has provided a new opportunity for investigating this delayed fluorescence.<sup>97–99</sup>

An analog of infrared photodetachment in electronically excited states is vibrational autoionization of the Rydberg molecular states<sup>100,101</sup>:

$$A + hv_{UV} \rightarrow A^* \rightarrow A^+ + e^-.$$
(9.1)

This process is also being investigated extensively at present. New opportunities for a study of the nonadiabaticity using MPE by infrared laser radiation have helped to understand better also these interesting processes.

The process of IER supplements the class of the processes involving intramolecular migration of energy between the electronic and vibrational degrees of freedom. Although, as demonstrated above, there are still various unsolved problems in the interpretation of the IER experiments, studies of the characteristics of the luminescence emitted as a result of IER has become the standard *probing* method for the investigation of MPE itself.<sup>102,103</sup> This is due to the fact that, on the one hand, the observed characteristics of the visible or ultraviolet luminescence are governed by the vibrational distribution function formed as a result of infrared MPE [see, for example, Eq. (3.4)]; on the other hand, we now have sufficiently simple and sensitive methods for recording the luminescence in the relevant spectral range.

The influence of IER on luminescence observed as a result of excitation of large (with 20-50 atoms) molecules in the ultraviolet range was discussed recently in Ref. 104 in connection with astrophysical investigations and the observation of polycyclic aromatic hydrocarbons in space. Under vacuum conditions in space when the time between collisions is of the order of  $5 \times 10^5$  s, the main relaxation channel is cooling as a result of infrared luminescence  $(t_{IR}^{cool} \sim 3 s)$ . A new and unusual hierarchy of the constants makes possible the following process: after absorption of an ultraviolet photon and direct nonradiative transition a molecule may emit in the infrared and also (after inverse electronic transition) in the visible range. The effective luminescence rate is governed by the statistical ratio of the densities of states [see Eqs. (3.2) and (3.3). When the initial excitation is sufficiently strong, the visible luminescence may be emitted several times, i.e., the quantum efficiency of the luminescence may exceed 100%. The authors of Ref. 104 are of the opinion that this mechanism can account for the red luminescence observed in many regions of interstellar space.<sup>105</sup>

Further investigations of IER should develop in the direction of exact identification of the excited terms of both stable molecules and radicals responsible for the observed luminescence. It would undoubtedly be of interest to use picosecond and subpicosecond infrared excitation and to study (with the same time resolution) the dynamics of transitions between the various electronic terms of isolated molecules.

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<sup>17</sup>This term is used in the English-language literature, but the effect is also known as reverse internal conversion.

<sup>2)</sup>Typical parameters are as follows: pulse duration ~ 100 ns, energy per pulse several joules, spectral range of lasing represented by individual lines in the ranges 923-59 cm<sup>-1</sup> [P(42)-P(2)], 963-989 cm<sup>-1</sup> [R(2)-R(42)]; 1025-1062 cm<sup>-1</sup> [P(42)-P(2)], 1066-1091 cm<sup>-1</sup> [R(2)-R(42)].

<sup>3)</sup>It is specifically assumed here that only one of the two fragments formed in the course of multiphoton dissociation of a molecule can absorb infrared laser radiation and exhibit IER after such dissociation.

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