MULTIPHOTON EXCITATION OF ORGANIC MOLECULES

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structural formulas I-VI

Figure 1: structural formulas I-VI

Abstract

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MULTIPHOTON EXCITATION OF ORGANIC MOLECULES

Modern lasers make it possible to obtain radiation densities at which higher-order radiation effects, involving several photons in the elementary act, become observable. The range of phenomena caused by multiphoton excitation of particles is very broad. Of particular interest are processes produced by the action of laser radiation on organic compounds. In the present work, multiphoton excitation of complex organic molecules has been investigated, followed by radiative (luminescence) and nonradiative (decay) deactivation of the excited state.

Luminescence was observed for a number of organic compounds when they were excited by the light of a ruby Q-switch laser. The laser operated in a modulated-Q mode and had a peak power of 40 MW. The duration of the generation pulse was 40 μsec. All measurements connected with recording the luminescence were carried out according to the method of ([1]). In this case the maximum radiation density of the Q-switch laser reached $\sim 7.5 \cdot 10^7$ W/cm^2 (the corresponding photon flux intensity $\sim 2.6 \cdot 10^{26}$ cm^{-2}sec^{-1}). Polycrystalline samples of the compounds studied were placed in evacuated-to-10^{-5} mm Hg and sealed quartz capillaries. The capillaries could be placed in a special cryostat with liquid nitrogen.

For the experiments, compounds were chosen which, when excited by ultraviolet light with $\lambda = 365$ mμ, had different luminescent properties. Thus, the benzquinone, naphthoquinone, and anthraquinone that we took only phosphoresce at 77° K; compounds I-VI at 77 and 300° K only fluoresce; N-ethylacridone at 77° K phosphoresces and fluoresces.

When these compounds were excited by the light of a ruby laser, fluorescence bands were detected with maxima at: 460 mμ for N-ethylacridone and 520, 435, 485, 500, 525, 550 mμ for compounds I-VI, respectively; phosphorescence of benzquinone, naphthoquinone, anthraquinone, and N-ethylacridone was not observed. This result can apparently be explained by the weak intensity of

Figure 1 graph: dependence of fluorescence intensity maxima on laser intensity

Figure 2: Figure 1 graph: dependence of fluorescence intensity maxima on laser intensity

phosphorescence under this method of excitation. During the duration of the laser pulse, $\tau \sim 10^{-8}$ sec, a relatively small number of particles reaches the metastable level T, which then emit light over the course of $0.01 \div 1$ sec. If τ is large in comparison with the lifetime of the system in the S^*-state, but small in comparison with the lifetime of the system in the T-state, then the phosphorescence intensities

or phosphorescence I_{phosph} and fluorescence I_{fl} are related by the ratio

$$I_{\text{phosph}}/I_{\text{fl}} = W_{21}\omega_{32}\tau/W_{31}, \tag{2}$$

where W_{21} and W_{31} are the probabilities of the transitions $T \to S$ and $S^* \to S$, respectively; ω_{32} is the probability of the nonradiative transition $S^* \rightsquigarrow T$. For example, for N-ethylacridone $W_{31} \sim 10^8$ sec^{-1}, $W_{21} \sim 1$ sec^{-1}, $\omega_{32} \sim 10^9$ sec^{-1}, and at $\tau \sim 10^{-8}$ sec,

$$I_{\text{phosph}}/I_{\text{fl}} \sim 10^{-7}. \tag{3}$$

At continuous excitation with ultraviolet light of the corresponding compounds, however, their phosphorescence is readily observed, since in this case $I_{\text{phosph}}/I_{\text{fl}} = \omega_{32}/W_{31}$. For example, for N-ethylacridone $I_{\text{phosph}}/I_{\text{fl}} \sim 10$.

Fig. 1. Dependence of the intensities of the maxima of fluorescence bands I_{fl} of polycrystals of compound VII (*a*), N-ethylacridone (*b*), compound II (*v*), and triphenylmethane (*g*) at 77°K on the excitation intensity of the ruby laser I_{las} (on a logarithmic scale).

The absence of absorption in all the compounds investigated at the laser radiation frequency (14 400 cm^{-1}) and the proportionality of the fluorescence intensity to the square of the laser-light intensity indicate a two-photon mechanism of excitation of these compounds. The dependence of the fluorescence intensity on the laser-radiation intensity for a number of substances is given in Fig. 1. The slopes of the straight lines a, b, and v correspond to two-photon excitation, while the slope of straight line g corresponds to three-photon excitation.

In certain azomethines containing an intramolecular hydrogen bond, a proton transfer (tunneling) is observed from one atom to another, as a result of which two forms of the substance arise (^{4}). This transition is associated with a change in the electronic configuration of the whole molecule and occurs during the lifetime of the system in the excited electronic state. The two forms of the substance have their own bands in the fluorescence spectrum. Experiments show

Fig. 2. Fluorescence spectra of polycrystals of compound VII at 77° (1) and 300°K (2), excited by UV light with $\lambda = 365$ mμ (a) and by a ruby laser (b)

Figure 3: Fig. 2. Fluorescence spectra of polycrystals of compound VII at 77° (1) and 300°K (2), excited by UV light with $\lambda = 365$ mμ (a) and by a ruby laser (b)

(see Fig. 2) that, both upon excitation with ultraviolet light with $\lambda = 365$ mμ and upon laser excitation, for azomethines of the type shown in scheme VII, a considerable change is observed in the fluorescence spectra on going from 300 to 77°K. For the samples studied, the intensity of the 565 mμ band sharply decreases, while the intensity of the 525 mμ band increases, which is associated with proton transfer from the nitrogen atom to the oxygen atom.

$$\text{VII} \qquad \lambda_{\text{fl}} \approx 565\,\text{m}\mu \quad \underset{\text{heat}}{\overset{h\nu}{\rightleftharpoons}} \quad \lambda_{\text{fl}} \approx 525\,\text{m}\mu$$

The possibility of such a transition was pointed out by E. A. Smirnov and L. N. Kirichenko. The quadratic dependence of the fluorescence intensity on the intensity of the laser radiation (see Fig. 1, line *a*) and the absence of absorp-

in azomethines at the frequency 14 400 cm^{-1} make it possible to regard the formation of the second form of the substance as induced by two-photon excitation.

As objects for the study of photolysis processes under the action of a laser, the following compounds were taken: toluene, diphenylmethane, triphenylmethane, fluorene, β-methylnaphthalene, nitromethane, nitrobenzene, α-nitronaphthalene, n-nitrotoluene, and trinitrotoluene. All nitro compounds and triphenylmethane were irradiated at 77°K with dysprosium ($\lambda = 2.36$ μ, $P = 80$ W/cm^2 in continuous mode) and ruby ($\lambda = 0.69$ μ, $P = 8 \cdot 10^7$ W/cm^2 at $\tau \simeq 40$ nsec) lasers and yielded radicals, recorded by an EPR spectrometer with a sensitivity of $5 \cdot 10^{11}$ spins/G. The remaining substances were irradiated at 77°K only with the light of the ruby laser and also yielded radicals. In this case the duration of irradiation with the dysprosium laser was ~ 1 min, and the number of ruby-laser pulses was about 10.

Fig. 2. Fluorescence spectra of polycrystals of compound VII at 77° (1) and 300°K (2), excited by UV light with $\lambda = 365$ mμ (a) and by a ruby laser (b)

The most detailed studies were made of triphenylmethane (TPM) $(C_6H_5)_3 \equiv$ C—H and α-nitronaphthalene $C_{10}H_7NO_2$. A TPM molecule, upon successive absorption of two quanta $h\nu_1$ and $h\nu_2$ with total energy

$$\simeq 5.5\ \text{eV}: \quad S \xrightarrow{h\nu_1} S^* \rightsquigarrow T \xrightarrow{h\nu_2} T^*$$

dissociates with formation of the triphenylmethyl radical (TPMR) $(C_6H_5)_3\dot{C}$ and a hydrogen atom $^{(5)}$. It should be noted that this process proceeds through the excited electronic state of the molecule: the energy obtained (5.5 eV) is redistributed over many degrees of freedom, and only part of it ($\simeq$ 2 eV) goes into the formation of TPMR.

When TPM was irradiated with ruby-laser light, a broad luminescence band was observed (410-580 mμ) with a principal maximum at 515 mμ, characteristic of TPMR. The formation of TPMR is also confirmed by luminescence spectra (under UV excitation with $\lambda = 365$ mμ) and EPR of TPM samples after their irradiation with a ruby laser. Luminescence in the region of 515 mμ and EPR signals having the form of a singlet line ($g \simeq 2.0$; $\Delta H \simeq 12.6$ G) were observed. The cubic dependence of the TPMR luminescence intensity on the intensity of the laser radiation (see Fig. 1, straight line g) indicates a three-photon excitation mechanism. Indeed, the tripled quantum energy of the ruby-laser radiation (5.4 eV) agrees well with the above excitation energy of 5.5 eV. In the case considered, a two-step excitation mechanism is also probable:

$$S \xrightarrow{2h\nu} S^* \rightsquigarrow T \xrightarrow{h\nu} T^*.$$

Such an excitation process may, generally speaking, include several acts of multiphoton absorption, for example,

$$S \xrightarrow{2h\nu_1} S^* \rightsquigarrow T \xrightarrow{2h\nu_2} T^*.$$

However, under the conditions of our experiment such a process is impossible.

Irradiation of TPM with the dysprosium laser did not lead to noticeable formation of radicals. Therefore it may be considered that the decomposition of the TPM molecule upon irradiation with a ruby laser occurs through an electronically excited state. It should be noted that TPM almost does not absorb in the region of 2.36 μ.

When α-nitronaphthalene was irradiated with both ruby and dysprosium lasers, no luminescence was recorded. In the EPR spectra there is a poorly resolved triplet, which can be explained by the interaction of the spin of the unpaired electron with the nucleus of the nitrogen atom ($I_{N^{14}} = 1$). A study of the mass spectra of the photolysis products showed that in the mixture of gases formed—

···formed in the decomposition of α-nitronaphthalene contain particles with a mass of 30 units. This value may be assigned to the mass of the paramagnetic particle NO $\cdot$. Mass-spectrometric studies of nitrobenzene (^{6}) and α-nitronaphthalene also show that the decomposition of these compounds proceeds with the formation of NO $\cdot$, while the energy of rupture of the C—NO$_2$ bond is, respectively, 32.2 and 26 kcal/mol. Since the quantum energy of the dysprosium laser is 0.5 eV, it may be assumed that in this case the observed photolysis processes occur through stepwise absorption of 2-3 quanta upon excitation of the corresponding vibrational sublevels of the ground electronic state.

In contrast to TMP, α-nitronaphthalene has strong absorption in the region of 2.36 μ. When the samples were irradiated with the dysprosium laser, their temperature was measured with a thermocouple. Since the samples were in liquid nitrogen, during irradiation a steady thermal regime was established in which the temperature inside the sample did not exceed several tens of degrees; thus, for α-nitronaphthalene it was 20° C. In a control experiment with thermal heating of α-nitronaphthalene samples, EPR signals appeared only at temperatures above 100° C.

Qualitative experiments on the photolysis of nitro derivatives of benzene and naphthalene under the action of radiation from a ruby laser show that their decomposition in this case proceeds many times more intensely than under irradiation with a dysprosium laser and, apparently, occurs through an electronically excited state. The formation of $NO\cdot$ radicals is also observed upon irradiation of the indicated compounds with ultraviolet light with $\lambda \leq 365$ mμ.

Thus, excitation of vibrational degrees of freedom can occur both directly and through electronic excitation of the molecule followed by redistribution of energy over the vibrational degrees of freedom (including to the given bond), and in the former case the presence of absorption at the wavelength of the exciting radiation corresponds to "resonance." It is known (7) that the probability of dissociation of polar molecules in this case exceeds by several orders of magnitude the probability of dissociation in the absence of "resonance."

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Note: Figure translations are in progress. See original paper for figures.