

Vibronic structure in the spectra of two-photon absorption of organic dye solutions

T. N. Smirnova, E. A. Tikhonov, and M. T. Shpak

Institute of Physics, Ukrainian Academy of Sciences

(Submitted March 2, 1979)

Pis'ma Zh. Eksp. Teor. Fiz. **29**, No. 8, 453–457 (20 April 1979)

The vibronic structure was recorded for the first time in the two-photon absorption (TPA) spectra of molecular solutions of organic dyes at room temperature. We conclude that the appearance of structure in the TPA spectra and the absence of such structure in the one-photon absorption spectra is attributable to preferential excitation of certain asymmetric molecular vibrations due to two-photon absorption.

PACS numbers: 33.10.Lb, 33.80.Kn

Most of the two-photon absorption (TPA) spectra investigated until now differ substantially from the corresponding one-photon absorption (OPA) spectra for centrally symmetrical and noncentrally symmetrical molecules.^{1,2}

The difference between the TPA and OPA spectra for organic dye molecules was reported by us earlier.³ A further increase of the resolution of the measurements made it possible to observe the structure of a number of well-known xanthene, coumarin, and polymethine dyes in the TPA spectra at 300 K. To obtain the TPA spectra, we used a "Colorit" dye laser tunable in the 710 to 1100-nm range (developed by the Institute of Physics, Ukrainian Academy of Sciences) and excited by an OGM-20 ruby laser. The laser beam was linearly polarized and the width of the generation line was <0.5 nm. The two-photon absorption was measured by recording the fluorescence intensity in the 400-cm^{-1} -wide spectral band by a high-speed photomultiplier and an oscillograph with a total resolution of 5 nsec. Figures 1a, 1b, and 1c show the TPA and OPA spectra of the standard solutions of rhodamine 110 (R110), rhodamine 6G (R6G), and coumarin 47.

We note the similarity between the TPA spectra of the R110 and R6G rhodamines, which have a slightly different molecular structure. We can assume from this that the observed TPA structure is due to the electron-vibrational transitions characteristic of the given molecules.

The lowest-frequency peak in the spectra coincides in frequency with the pure electronic transition, which is determined from the known OPA and fluorescence spectra. The following peaks are shifted to the frequencies 330, 630, and 1400 cm^{-1} for R110 and to 400 and 1400 cm^{-1} ($\pm 25\text{ cm}^{-1}$) for R6G.

The higher-frequency peaks in the TPA spectra are treated as progression terms $1400 + \nu_{01}, \nu_{02}$, and $2 \times 1400 + \nu_{01}, \nu_{02}$ (the oscillation frequencies determined in this manner are shown by identical arrows in Figs. 1a and 1b. It can be seen that they are in good agreement with the observed peaks in the TPA spectrum).

The obtained structure of the TPA spectra is in qualitative agreement with the

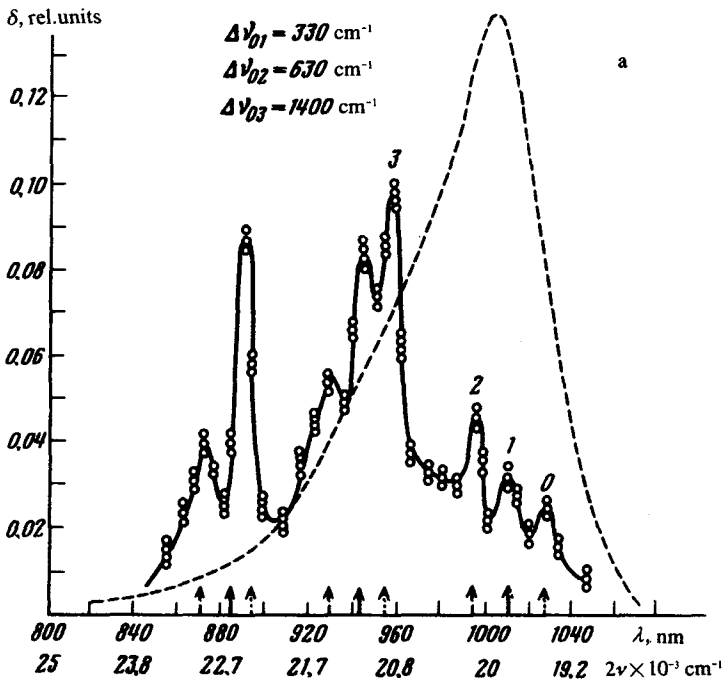
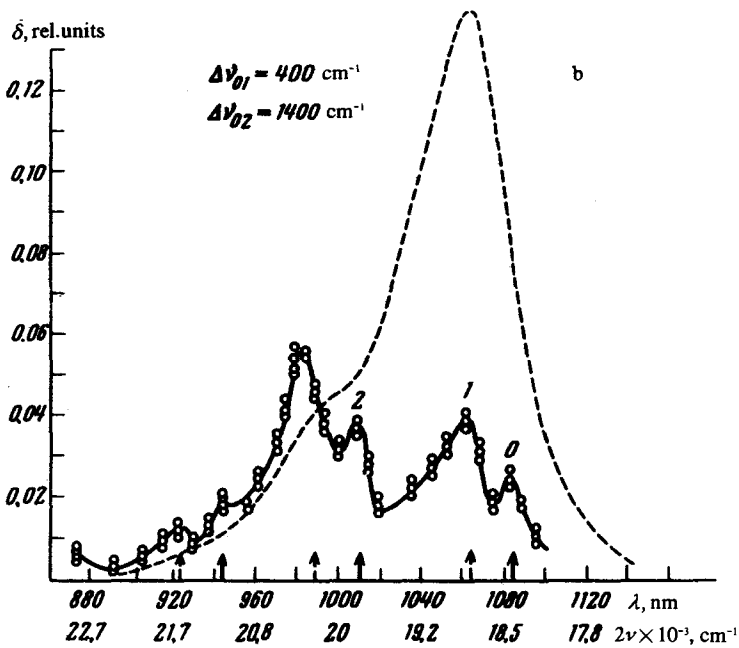
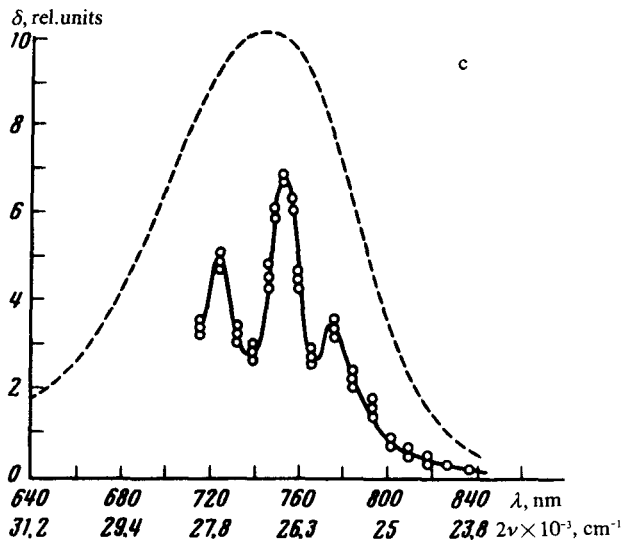


FIG. 1.





theoretically predicted structure for the forbidden two-photon transitions in the centrally symmetrical molecules.^[4]

The symmetry of the investigated molecules of the R6G and R110 dyes is described by the C_{2v} group ($mm2$). The electronic states are related to the following types of symmetry— S_0 to A_1 , S_1 to B_2 , and S_2 tentatively to A_1 , since the molecule is planar and the probability of the symmetry transition $A_1 \rightarrow B_1$ is low and $A_1 \rightarrow A_2$ is forbidden.

The group-theoretical analysis of the two-quantum transitions carried out by McClain^[5] showed that for monochromatic radiation the $A_1 \rightarrow A_1$ transitions are allowed in the C_{2v} symmetry molecules, whereas the other transitions, particularly the $A_1 \rightarrow B_2$, are forbidden. This conclusion is in good agreement with the earlier observed^[3] large increase of the cross section of two-photon absorption in the $S_0 \rightarrow S_2$ band in contrast to the $S_0 \rightarrow S_1$ band. Therefore, the two-photon electronic transition $S_0 \rightarrow S_1$, which is forbidden, can be an allowed transition only as a result of interaction with the asymmetric oscillations, which change the symmetry of the initial or the final state.

This is also valid for molecules of polymethine dyes described by the C_{2v} and D_{2h} groups. For the coumarin dyes of the $C_s(m)$ symmetry the two-photon $A' \rightarrow A''$ transitions are forbidden if two quanta of equal energy are absorbed,^[5] so that the observed (Fig. 1c) structure apparently is also dependent upon the excitation of the vibronic states in the TPA.

We can conclude without invoking the symmetry selection rules that the TPA spectra of the investigated molecules have asymmetric oscillations that are active in the infrared spectra. The estimates show that if the electron-vibrational interaction is taken into account, the cross section for TPA between the $|1\rangle$ and $|2\rangle$ states will be determined by the terms: $\mathbf{d}_{1l} \mathbf{d}_{l2} / \omega_{1l} - \omega$, $\mathbf{d}_{1l} \vec{\lambda}_{l2} / \omega_{1l} - \omega$, and $\mathbf{d}_{l2} \mathbf{D} / \omega$, which are in-

cluded in the compound matrix element [Eqs. 4–11 (Ref. 4)]. The first term is a product of the dipole moments of the electronic transitions via the intermediate electronic $|I\rangle$ state. The second and third terms take into account the transitions with the excitation of the asymmetric oscillations. The dipole moments of the transitions in the molecules of the rhodamine dyes have the following values: $d_{S,S_1} \approx 1D$, $d_{S,S_2} \approx 0.3D$, and the dipole moment of the infrared transitions $D \leq 0.3D$. The angles between d_{S,S_1} and d_{S,S_2} is 60 to 70°. ¹⁶¹ Therefore, all three terms become commensurable as a result of absorption of two radiation quanta of plane polarization.

The occurrence of asymmetric oscillations in the TPA spectrum is also confirmed by the infrared spectra obtained in the region 400–2000 cm^{-1} . In fact, the R110 spectrum has an intensive 630 cm^{-1} line which coincides with the 630 cm^{-1} peak in the TPA spectrum. The infrared R6G spectrum has an intensive 612 cm^{-1} line in the 600–700 cm^{-1} region, which is within the limits of the broad TPA peak with the 400 cm^{-1} maximum. The infrared spectra of both rhodamines also have a number of lines in the neighborhood of the oscillation frequency of 1400 cm^{-1} . Since both rhodamines have this frequency and since the progressions based on this oscillation are in good agreement with the peaks in the TPA spectra, we can assume that it is a totally symmetric oscillation of the conjugation chain.

Thus, we can conclude on the basis of the analysis that the TPA spectra of the investigated molecules of the dyes have a vibronic structure which is dependent on the excitation of the asymmetric oscillations. It can be resolved because of the difference in the selection rules for the two-quanta and one-quanta transitions.

It should be noted that the vibronic structure could not be observed until now in the spectra of molecules of organic dyes at room temperature. Therefore, the TPA spectroscopy may be an effective method of studying the vibronic structure of large molecules.

¹S. Kimel and S. Spaicer, *Chem. Rev.* **77**, 437 (1977).

²W. Hamble, H.J. Neusser, and E.W. Schlag, *Chem. Phys. Lett.* **46**, 406 (1977).

³E.B. Aslanidi and E.A. Tikhonov, *Optika i spektroskopiya* **37**, 784 (1974) [*Optics and Spectroscopy* **37**, (1974)].

⁴V.I. Bredikhin, M.D. Galanin, and V.N. Genkin, *Usp. Fiz. Nauk* **110**, 3 (1973) [*Sov. Phys. Usp.* **16**, 299 (1973)].

⁵W.M. McClain, *J. Chem. Phys.* **55**, 2789 (1971).

⁶P.P. Feofilov, *Polyarizovannaya lyuminesentsiya atomov, molekul i kristallov* (Polarized Luminescence of Atoms, Molecules, and Crystals, GIFML, M., 1959).