

Effect of powerful resonant radiation field on degenerate vibrations in polyatomic molecules

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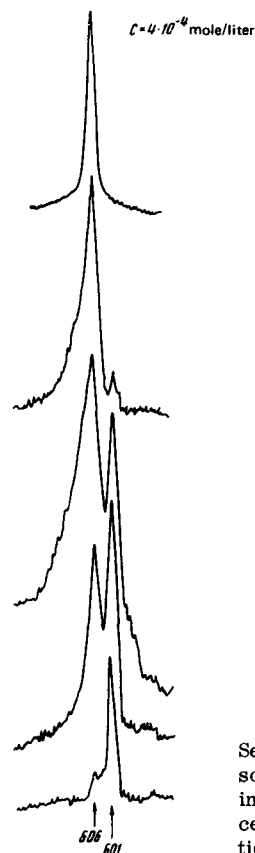
We investigate jointly the spectra of resonant spontaneous Raman scattering and resonant simulated Raman scattering of tricyanide and of a number of other polymethine dyes. "Extra" lines were observed in the substance at low frequencies. A hypothesis that these lines belong to components of the field-lifted degeneracy is advanced and justified.

In the study of secondary emission excited in rigid matrices of a number of polymethine dyes in vitrifying and crystallizing solvents, by sharply focusing on the sample a beam from a Q-switched ruby laser, we have observed new phenomena, the description and interpretation of which is the subject of this article. The secondary emission spectra consist of continuous and discrete parts, and the latter contains as many as 17 emission and absorption lines. The absorption lines are as a rule located in the neighborhood of the emission lines (always on the short-wave side).^[1] Both types of line follow exactly the frequency of the exciting line, which we were able to vary within a range of 10 cm^{-1} by cooling the ruby rod with nitrogen vapor. In our opinion, these results, together with the sharpness and large intensity of the spectrum, prove that all the lines belong to resonant stimulated Raman scattering (RSRS).

What is essentially new is the behavior of the section of the spectrum at $\sim 600 \text{ cm}^{-1}$ as a function of the dye concentration in the matrix. We demonstrate this using as an example tricyanine vitrified in ethyl alcohol (see the figure). Complete data on the RSRS spectra and on the spectrum of the resonant spontaneous Raman scattering, together with the structure formula of the tricyanine, are given in the table. The resonant spontaneous Raman scattering spectra were obtained in liquid solutions and in the crystalline state of the material, by using the method of pelleting in KBr. The excitation was produced by radiation from helium-neon, argon, and cadmium lasers.

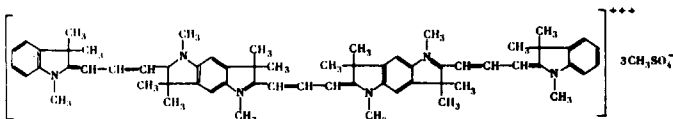
We see that only the 606 cm^{-1} line is excited at $C = 4 \times 10^{-4}$ mole/liter. In the spectra of the dilute solutions, a 601 cm^{-1} line appears and becomes systematically stronger. At the maximum dilution obtainable in the ex-

periment, the 606 cm^{-1} line practically vanishes. At the same time, resonant spontaneous Raman scattering spectrum of the same substance, particularly when compressed with KBr, contains in this region a single



Section of RSRS spectrum of tricyanine solution in ethyl alcohol, frozen to 77°K , in the region $\sim 600 \text{ cm}^{-1}$ at different concentration of the medium. The concentration decrease in the downward direction.

Resonant simulated and spontaneous Raman spectra of tricyanine at 77 °K.



RSRS: 483, 524, 591, 596, 601, 606, 628 (abs.), 630, 650, 680 (abs.), 682, 753 (abs.), 758, 887, 938, 968 (abs.), 972

RSpRS: 556, (w), 580 (w), 604 (v. int), 630 (w), 648 (w), 693 (w), 755 (w), 796 (w), 828 (w), 888 (med), 930 (w), 970 (w), 990 (int)

Note. The numbers designate the frequencies in cm^{-1} . The parenthesis contain estimates of the intensity: *w*—weak, *m*—medium, *int*—intense, *v. int*—very intense. For resonant spontaneous Raman scattering RSpRS we cite only the lines that fall in the spectral region that is common with the RSRS. The resonant spontaneous Raman scattering was obtained for tricyanine pelleted with kBr .

line without noticeable traces of fine structure, even at the temperature of liquid nitrogen.

We explain the fact that there is no complete similarity between the spectra of the resonant spontaneous and stimulated Raman scattering with respect to the number of lines and their frequency (see the table), as before, within the framework of the models of scattering by vibrational levels of molecules in the normal and excited states. As to the features of the low-frequency part of the spectrum, we advance for their explanation the following new considerations.

1. Violation of the equilibrium between the monomer and aggregated molecules when the concentration of the medium is changed. This explanation, however, is contradicted by our control experiments with resonant spontaneous Raman scattering of tricyanine dissolved in dimethylsulfoxide, which hinders the dimerization of the molecules, and also by the direction of the frequency shift itself.

2. Three-photon scattering proceeding in accordance with the same scheme as on the electronic levels in alkali-metal vapors.^[2] It is assumed in this case that the exciting line is the 606 cm^{-1} RSRS line. It turns out, however, that the distance between the components does not change when the frequency of the exciting light is shifted, thereby excluding a manifestation of this scattering in our case.

3. Vibrational resonance of the Fermi type, due to induction of anharmonicity of the oscillations and to the Stark shift of the levels in the field of a high-power light wave.^[3] However, special experiments performed by us show that the position and the relative intensity of the component does not depend on the pump power, thereby eliminating also this explanation.

4. Stepwise excitation of RSRS on the transitions $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$, etc.^[4] This hypothesis, however, is difficult to reconcile with the absence of a systematic mutual approach of the components, owing to the contribution of the mechanical anharmonicity of the vibrations. In addition, it does not explain why the intensity becomes redistributed among the first two components.

We can attempt to describe qualitatively the considered phenomena with the aid of the following model.

It appears that the molecules of the polymethine dyes have no symmetry elements whatever. However, fragments of molecules, e. g., the benzene rings, do have local symmetry. It is possible to ascribe to them quasicharacteristic vibrations. In the presence of rotation axes of order higher than second, some of these vibrations can be also degenerate. It is precisely to this class of degenerate vibrations in benzene, that the 606 cm^{-1} vibration, which is little sensitive to a number of substitutes^[5] belongs. This line is preserved also in the indole spectrum.^[6]

One of the causes of the distinctive character of the vibrations is the smallness of the dynamic interaction of the atoms. One can expect such a situation to take place in the end (indol) groups of the tricyanine molecules. When the latter are electronically excited, the conditions change (the order of the bonds in the ring decreases), and this can destroy the distinctive character of the vibrations. Then their properties can no longer be regarded in the local-symmetry approximation. The degeneracy may also be lifted here.

Thus, the assumption that RSRS in tricyanine occurs on vibrational levels of excited molecules is in itself sufficient, in principle, to explain the features of the scattering in the region 600 cm^{-1} . Additional possibilities are afforded by the following. Excitation of stimulated Raman scattering is always accompanied by induced anharmonicity. This leads to a strong interaction of the vibrations, which we can no longer regard even approximately as characteristic (or normal) and still use the very concept of local symmetry. This favors the lifting of the degeneracy, especially in the case of molecules in the excited state. The latter explains also the redistribution of the intensity among the components, if it is recognized that the components of the lifted degeneracy correspond to fully-symmetrical and antisymmetrical oscillations, which in accordance with the vibronic theory of scattering should have different sensitivities to the resonance with the concentration-shifted lasing band of the dye.

We note in conclusion that a high-power high-frequency field can also cause the deformation of the nuclear core of the molecules and of their fragments, as takes place in intermolecular fields, with all the ensuing consequences with respect to the selection rules in the spectra and in the classification of the vibrations. Nor do we exclude, finally, the possibility of isomeric transformations caused by electronic excitation.

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