

Direct determination of the difference in the nature of the band broadening in relaxational and configurational continuous vibron spectra of complex molecules by four-photon spectroscopy

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Four-photon spectroscopy has been used to study the broadening of hidden electronic-vibrational subbands in the continuous vibron spectra of triphenylmethane dyes of various degrees of complexity. The results show that the relaxation vibron spectra are broadened uniformly, in contrast with the nonuniformly broadened configurational spectra.

The relaxational continuous vibron spectra of molecules which were discovered in Ref. 1 (the term "relaxational" stems from Ref. 2) of those members of homologous series of fluorescing organic compounds which are the most complex (especially in terms of the symmetry of the nuclear framework) have been interpreted as a consequence of an extreme instability, i.e., of the short duration of Franck-Condon states reached in the course of optical transitions and the large uncertainty in their energy. Experiments have shown that the width of all of the relaxational spectra (the absorption and fluorescence in various solutions and in vapor) is determined by a single dependence on exclusively the average size of the quanta which participate in the transitions associated with the given band.^{3,4} This circumstance evidently rules out the use of a Born-Oppenheimer separation of the electronic and vibrational energies to relaxational spectra. This separation procedure has been used to determine the width and shape of the ordinary ("configurational" in the terminology of Ref. 2) continuous vibron spectra of several less complex molecules, which are controlled by the values of the Franck-Condon factors.

According to the interpretation which we will discuss here, the continuous relaxational vibron spectra of complex molecules should be homogeneously broadened, while the configurational continuous spectra should be inhomogeneously broadened, having an internal structure determined by a set of overlapping subbands associated with various electronic-vibrational transitions. In the present letter we are reporting a test of this difference.

The test was carried out by the method of four-photon spectroscopy in the three-wave-mixing version which was proposed in Ref. 5. The method can be summarized as follows: During biharmonic pumping of a sample by waves $J_1(\nu_1)$ and $J_2(\nu_2)$ one studies the dependence of the intensity $J_c(\nu_c)$, i.e., the intensity of the coherently scattered wave $\nu_c = \nu_1 + \Delta\nu$, on the frequency deviation $\Delta\nu = \nu_1 - \nu_2$. This intensity is proportional to the square modulus of the cubic nonlinearity of the susceptibility, $|\chi^{(3)}|^2$. If the frequencies ν_1 and ν_2 lie within the width $\delta\nu$ of a homogeneously

broadened element of the continuous spectrum, i.e., if the relation $\Delta\nu < \delta\nu$ holds, then we have

$$\log|\chi^{(3)}| \sim -\log(\Delta\nu) \quad (1)$$

If, on the other hand, the relation $\Delta\nu > \delta\nu$ holds, i.e., if one of the pump waves lies outside element $\delta\nu$, then we have

$$\log|\chi^{(3)}| \sim -2\log(\Delta\nu) \quad (2)$$

We evidently have $\delta\nu = (\Delta\nu_c)$, where $(\Delta\nu_c)$ is the frequency deviation at which relation (1) becomes the same as relation (2). Expressions (1) and (2) were derived in Ref. 5 for a group of overlapping Lorentzian resonances corresponding to two-level systems. A non-Markovian theory was derived in Ref. 6 for a more appropriate model of a complex molecule. That theory makes it possible to work from experimental data to find the value of the decay parameter of the correlation function of a vibrational perturbation of an electronic transition and, in particular, the parameter q' , which characterizes the decay of the low-frequency contribution to this function.

As in Ref. 7, the surface of the biharmonic excitation was made up of two tunable dye lasers (the width of the output spectrum was $\sim 0.3 \text{ cm}^{-1}$) which were pumped by the second harmonic from a Nd:YAG laser system. The frequency of the first dye laser (ν_1) was held constant, and that of the second (ν_2) was tuned. The thickness of the cell holding the solution was $\sim 0.1 \text{ mm}$; the transmission for light at frequency ν_1 was $T \approx 15\%$. The angle between the ν_1 and ν_2 beams was $\sim 1^\circ$; the power density of the beams did not exceed 10 MW/cm^2 .

As samples we selected solutions of triphenylmethane dyes: malachite green (I), whose spectra were classified as configurational in Ref. 2; brilliant green (II), an analog of malachite green in terms of molecular structure and spectra; midnight blue (III) whose spectra were classified as relaxational in Ref. 2; and its analog methyl blue (IV). Figure 1 shows the structural formulas of the molecules and their vibron spectra (the results for molecule III were taken from Ref. 8) along with the positions of the excitation frequency ν_1 (the vertical arrows) and the regions over which the frequency ν_2 was tuned (the horizontal arrows).

The results of the measurements—curves of $\log|\chi^{(3)}| = f[\log(\Delta\nu)]$ —are shown in Fig. 2. We would like to point out that the structure seen on the curves of $\log|\chi^{(3)}|$ in the frequency region of the natural vibrations of the molecules is associated with anti-Stokes Raman spectra was eliminated through a graphical interpolation. The results nevertheless lead to unambiguous conclusions regarding the question of interest.

In the case of configurational spectra I and II, and for a position of ν_1 near the maximum of the absorption spectrum, i.e., slightly above the frequency of the 0–0 transition, the $\log|\chi^{(3)}|$ curves have a slope change at about $\Delta\nu \approx 270 \text{ cm}^{-1}$ and $\Delta\nu \approx 290 \text{ cm}^{-1}$, from a slope of $\tan \varphi \approx -1$ to $\tan \varphi \approx -2$. In the theory of Ref. 5, this result means that the width of a resonance of the purely electronic transition $v \rightarrow v^* = 0 \rightarrow 0$ is $\delta\nu \approx 270 \text{ cm}^{-1}$ for molecule I and $\delta\nu \approx 290 \text{ cm}^{-1}$ for molecule 2 in this case. A calculation by the theory of Ref. 6 leads to the values $q' \approx 100 \text{ cm}^{-1}$ and $q' \approx 180 \text{ cm}^{-1}$ for the decay parameters of molecules I and II, respectively.⁷ For molecule I we also measured a curve of $\log|\chi^{(3)}|$ at the frequency ν_1 corresponding to the

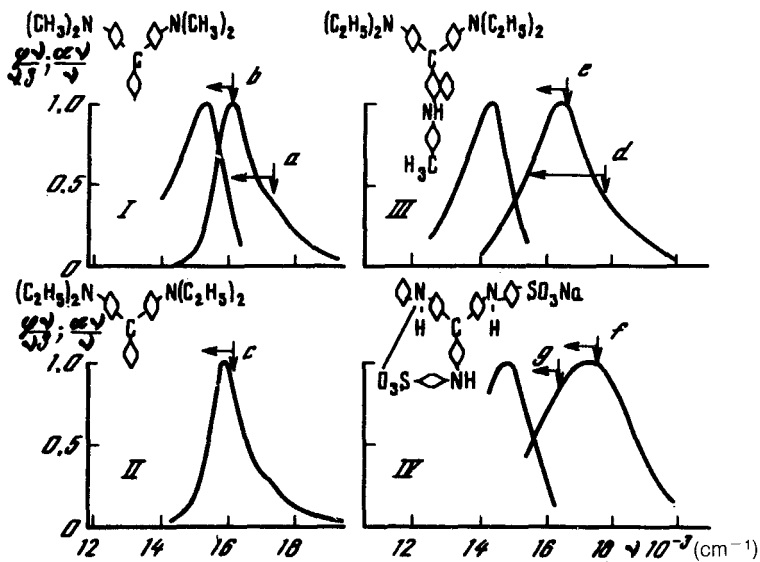


FIG. 1. Structural formulas, vibron spectra, and positions of frequencies ν_1 and ν_2 for the solutions of I, II, III, and IV studied.

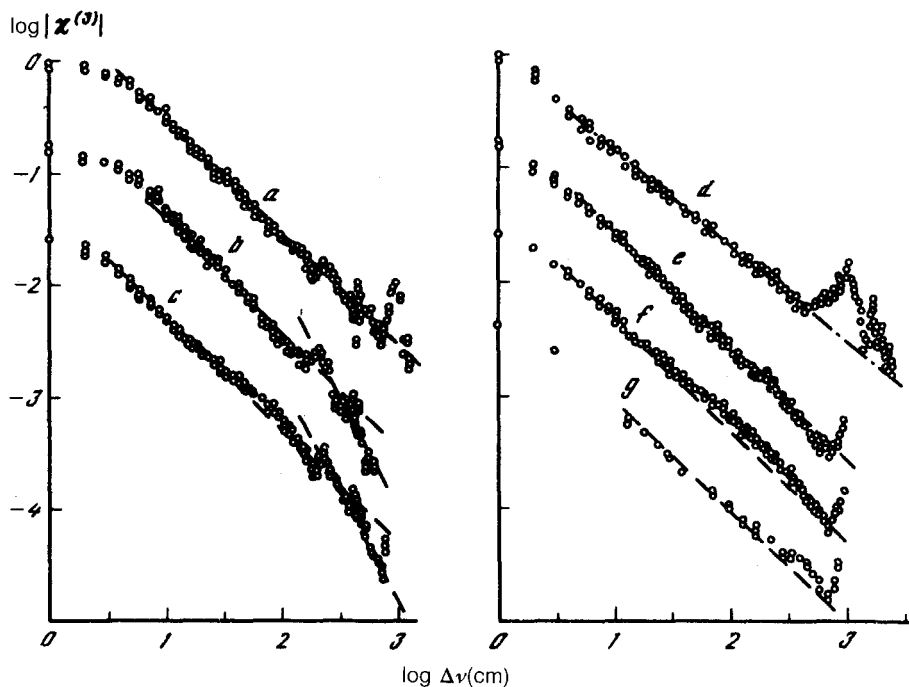


FIG. 2. Relative values of $|\chi^{(3)}|$ versus the frequency deviation $\Delta\nu$ for systems a-f in Fig. 1. Circles—Experimental data; Dashed and dot-dashed lines—interpolating straight lines.

transition $\nu \rightarrow \nu^* = 0 \rightarrow 1$. Up to values $\Delta\nu = 1000 \text{ cm}^{-1}$ the interpolating straight line has no slope change; i.e., in this case we have $\delta\nu \gtrsim 1000 \text{ cm}^{-1}$, in agreement with the present understanding of the broadening of bands corresponding to the $\nu \rightarrow \nu^* = 0 \rightarrow n$ transitions with increasing n^* (Ref. 1, for example).

For molecules III and IV, characterized by relaxational spectra, the results are totally different. Regardless of the position of exciting frequency ν_1 —near the maximum of the absorption band or at its edges—constant slope $\tan \varphi \sim -1$ up to the highest values reached, $\Delta\nu \approx 2500 \text{ cm}^{-1}$, close to the total width of the vibron band. These results are evidence that, in complete agreement with Refs. 1 and 2, the relaxational spectra of molecules III and IV are homogeneously broadened.

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