

# ELECTRON-VIBRATIONAL SPECTRUM OF DIMERS IN THE CASE OF STRONG COUPLING

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It was shown in [1, 2] that electron-vibrational coupling in a dimer can lead to different spectral effects. In particular, in the case of strong coupling, when  $\epsilon$  (the energy of interaction of the monomers and the dimer  $V$ ) divided by the energy of the vibrational quanta  $\hbar\Omega$  is much larger than the electron-vibrational interaction, the theory [1, 2] predicts a decrease of the ratio of the intensity of the peak of the single-photon transition to the intensity of the phononless peak  $W_{01}/W_{00}$ , by exactly a factor of 2 upon dimerization.

We have investigated this question experimentally using as an example bicyanine molecules [3], which can be regarded as intramolecular dimers [4, 5]. We investigated the spectra of absorption, luminescence, and also the spectra of the excitation and polarization of luminescence of these molecules (see the figure). It was established as a result that the distribution of the intensity in both (+) and (-) electron-vibrational absorption bands of the investigated dimers are described by the well-known formula (see, e.g., [6]):

$$W_{0v}^{\pm} / W_{00}^{\pm} = \gamma_{\pm}^{2v} / v!, \quad (1)$$

where  $v$  is the vibrational quantum number of the excited electronic state

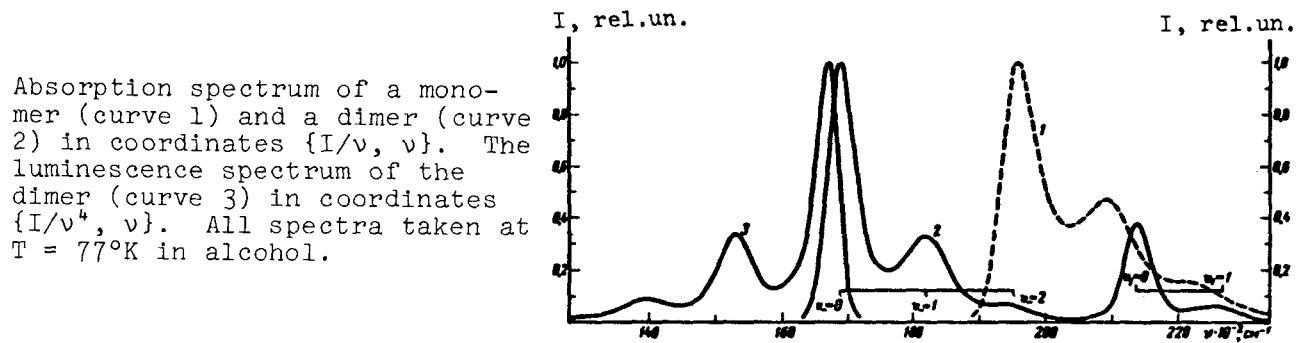
$$\gamma = (M\Omega/2\hbar)^{1/2} \Delta d,$$

$M$  and  $\Omega$  are the reduced mass and the frequency of the "rigid" oscillation [7], and  $\Delta d$  is the change of the equilibrium value of the normal coordinate upon excitation.

The table lists the values of  $\gamma_+$  and  $\gamma_-$  calculated from the spectra, pertaining to the short-wave and long-wave bands of the dimer, respectively. The last column of the table gives the values of  $|\epsilon/\gamma|$ . According to the numerical calculations of [2], in the entire range of the values  $|\epsilon/\gamma|$  obtained by us

$$\gamma_{\pm} = \gamma / \sqrt{2}. \quad (2)$$

In the experiments, however, relation (2) is satisfied only for the molecule with minimal  $|\epsilon/\gamma|$ . In the remaining cases this formula is not satisfied.



	$y_+$	$y_-$	$y/\sqrt{2}$	$\frac{y_+ + y_-}{2}$	$ \epsilon/y $
Dimer 1	$0.45 \pm 0.01$	$0.44 \pm 0.01$	$0.44 \pm 0.01$	$0.44 \pm 0.02$	$1.51 \pm 0.02$
Dimer 2	$0.35 \pm 0.02$	$0.52 \pm 0.01$	$0.44 \pm 0.01$	$0.44 \pm 0.02$	$2.15 \pm 0.02$
Dimer 3	$0.40 \pm 0.02$	$0.49 \pm 0.01$	$0.44 \pm 0.01$	$0.44 \pm 0.02$	$2.22 \pm 0.02$
Dimer 4	$0.42 \pm 0.02$	$0.58 \pm 0.01$	$0.50 \pm 0.02$	$0.50 \pm 0.02$	$2.35 \pm 0.02$
Dimer 5	$0.34 \pm 0.03$	$0.52 \pm 0.01$	$0.44 \pm 0.01$	$0.43 \pm 0.02$	$2.48 \pm 0.02$

The discrepancy between theory and experiment is connected with the fact that in [1, 2], as in all other investigations devoted to this question, the calculations of the matrix elements were carried out within the framework of a crude adiabatic approximation, i.e., without allowance for the dependence of the electronic wave functions on the nuclear coordinates. Allowance for this dependence leads to the appearance in formula (2) of an additional term:

$$y_{\pm} = \frac{y}{\sqrt{2}} - \delta y_{\pm}. \quad (3)$$

An estimate of the additional term shows that

$$\left| \frac{\delta y_{\pm}}{y} \right| \sim \kappa \left| \frac{\epsilon}{y} \right|, \quad (4)$$

where  $\kappa = (m/M)^{1/4}$  is the Born-Oppenheimer parameter. Thus, with increasing  $|\epsilon/y|$ , the additional term in formula (3) should become more and more appreciable. Then the values of  $y_+$  and  $y_-$  become unequal to each other and different from  $y/\sqrt{2}$ .

In many cases, for example, for sufficiently symmetrical splitting of the absorption band upon dimerization,  $\delta y_+ = -\delta y_-$ . Then, obviously, the following simple relation must be satisfied:

$$\frac{y_+ + y_-}{2} = \frac{y}{\sqrt{2}}. \quad (5)$$

As seen from the results in the table, this relation is well satisfied in the experiment.

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