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A simple method to obtain information on the conformation of dipole-dipole coupled dimers

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Abstract

A dimer is considered where the two monomers are coupled by dipole-dipole interactions. Upon electronic excitation the interaction leads to a drastic change of the dimer absorption spectrum compared to that of the non-interacting monomers. The method presented here uses sum rules, to obtain information on the interaction strength between the monomers and the conformation of the dimer directly from the measured spectra. Comparison with previous results [1], obtained by diagonalisation of the dimer Hamiltonian, shows remarkable agreement.

Key words: Aggregates, Dipole-dipole-interaction, Vibrational broadening, Sum rules
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In recent years there is a growing interest in dipole-dipole coupled chromophore systems [2–10] where the chromophores are organic dyes (in solution [11] or helium nanodroplets [12]), cold Rydberg atoms [13], quantum dots [14] or metallic nanoclusters [15]. The interaction between the monomers leads to entangled states and a drastic change in the absorption spectrum compared to that of the single monomer. The attention dipole-dipole coupled chromophore systems have received, stems not only from the changes in the absorption spectra (which can be used e.g. for the quantitative determination of membrane potentials [16]). Strong interactions between the monomers leads to efficient energy transport processes [17,18] and such aggregates are possible candidates for artificial light harvesting units [19]. Furthermore the occurrence of collective, entangled quantum states upon aggregation enables possible application in quantum computing [3]. In this respect it is necessary to know the magnitude of the interaction V between neighbouring monomers. Much inside into the complicated behaviour of such complex systems can be gained by studying the molecular dimer. It is investigated intensely in physics [20,15,14], chemistry [11] and biology [7,21,22]. One way to determine information of the often unknown arrangement of the monomers in the dimer is optical spectroscopy. Since the optical properties of the dimer depend strongly on the interaction V and on the geometrical arrangement of the individual chromophores effort was undertaken to obtain these parameters from the absorption spectrum of the dimer [11,7,23,24]. However disorder, internal and external vibrations complicate the interpretation of measured absorption spectra.

Before we consider the method developed in this paper, which is based on spectral moments, we explain the changes that occur upon dimerisation in a simple model, ignoring vibrations and disorder altogether. In this model, which is discussed in many textbooks (e.g. Ref. [7]) the monomers are described by purely electronic two level systems. It is assumed that there is no overlap of the wavefunctions of the two monomers which interact via Coulomb interaction $\hat{V}$. We assume further that the monomers have equal transition energies given by $\hbar\omega_{\mathrm{M}}$ and set the energy of the ground state as the zero of energy. The spectral changes upon dimerisation can be understood as follows (see Fig. 1): The energy of the dimer ground state $|\,gg\,\rangle$, where both monomers are in their electronic ground state, is reduced by $U_g = \langle\, gg\,|\hat{V}|\,gg\,\rangle$ w.r.t. the ground state of the non-interacting monomers. In the state $|\,eg\,\rangle$ monomer 1 is electronically excited and monomer 2 is in its electronic ground state. In the state $|\,ge\,\rangle$ monomer 2 is electronically excited [2]. Due to the transition dipole-dipole interaction $V = \langle\, eg\,|\hat{V}|\,ge\,\rangle = \langle\, ge\,|\hat{V}|\,eg\,\rangle$ the states $|\,eg\,\rangle$ and $|\,ge\,\rangle$ are not eigenstates of the dimer. The eigenstates of the electronically excited dimer are

$$|\,\psi_\pm\,\rangle = \frac{1}{2}(|\,eg\,\rangle \pm |\,ge\,\rangle) \qquad (1)$$

with energies

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[2] The state $|\,ee\,\rangle$ where both monomers are electronically excited will not be considered in the present work, since its transition frequency is twice that of the monomer.

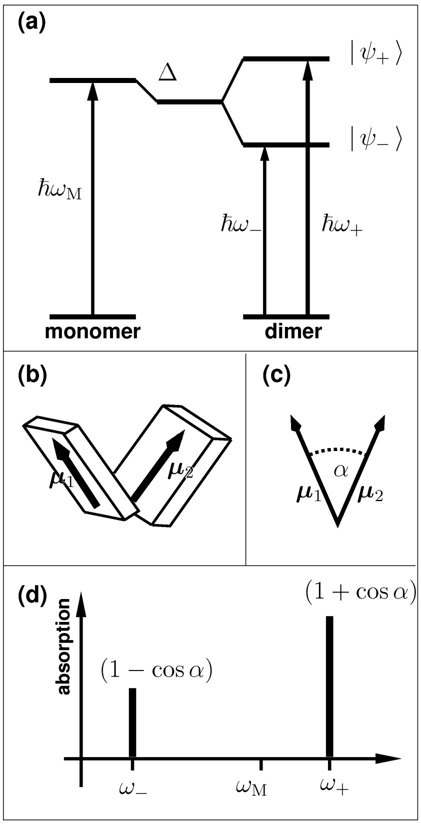

Fig. 1. (a) Sketch of the energy levels of a molecular dimer composed of identical monomers. The dipole-dipole coupling V is choosen to be positive. (b) The arrangement of the monomers. (c) Definition of the angle α. (d) Sketch of the absorption spectrum for $\alpha = 70^\circ$.

$$E_\pm = \hbar\omega_\mathrm{M} - U_e \pm V \tag{2}$$

where $U_e = \langle\, eg\,|\hat{V}|\,eg\,\rangle = \langle\, ge\,|\hat{V}|\,ge\,\rangle$. The transition dipole vector of the dimer is given by $\boldsymbol{\mu} = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2$, where $\boldsymbol{\mu}_i$ is the transition dipole for a transition from the electronic ground state to the electronic excited state of monomer i. Denoting the angle between $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ by α with $\alpha \in [0^\circ, 180^\circ]$ (see Fig. 1b) one finds for the isotropic absorption cross-section of a dimer composed of identical monomers in dipole approximation [1,7,25]

$$\sigma_\mathrm{D}(\omega) \propto \omega\Big((1+\cos\alpha)\delta(\omega-\omega_+) + (1-\cos\alpha)\delta(\omega-\omega_-)\Big) \tag{3}$$

with

$$\hbar\omega_\pm = (\hbar\omega_\mathrm{M} - \Delta) \pm V \tag{4}$$

and $\Delta \equiv U_e - U_g$. From Eq. (3) one sees that the absorption spectra of the purely electronic dimer consists of two absorption peaks at energies $\hbar\omega_\pm$. The magnitude of the two peaks depends on the geometrical arrangement, i.e. the angle α (see Fig. 1d). Although Eq. (3) relates the dimer absorption spectrum in a direct manner to the parameters α, V and Δ, it is of little practical use, since usually the monomer (and dimer) spectrum does not show the simple behaviour of the purely electronic model considered above. Due to strong coupling to vibrational modes the monomer spectrum shows usually a vibrational progression which is broadened by low-energy vibrations and fluctuations in the environment. A typical example is shown in Fig. 2 where a measured visible absorption spectra of a monomeric organic dye (solid line) is shown together with the absorption spectrum of a dimer composed of these dye molecules (dashed curve). Both spectra are measured in aqueous solution at room temperature [23]. The monomer shows a (Poissonian) vibrational progression with its maximum at $19300\ \mathrm{cm}^{-1}$ and a vibrational energy quantum of about $1250\ \mathrm{cm}^{-1}$ which is broadened by the same order of magnitude. The maximum of the dimer spectrum is shifted to higher energies and the whole spectrum has considerably changed its shape w.r.t. that of the monomer.

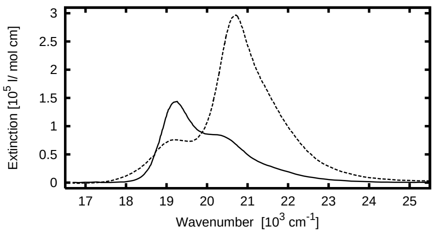

Fig. 2. The absorption spectra of 3,3'-disulfopropyl-4,5,4',5'-dibenzo--9-ethyloxa-carbocyanine measured in water by Baraldi et al.[23]. Monomer (solid line), dimer (dashed line).

It is clear from Fig. 2, for measured spectra the idealisation of the purely electronic model is an oversimplification. Therefore various approaches have been developed to describe the line-shape correctly. It was shown that the inclusion of one internal vibration leads to a more realistic theoretical model [26–28,1], which gives good agreement between theory and experiment [11,1,24] and thereby one can obtain information upon the interaction strength V, the angle α and the "dimerisation shift" Δ, which now, due to the changed interaction with the surrounding will be dependent on the solvent (for the influence of the solvent on molecules see e.g. [29–31]). However the consideration of more than one vibrational mode and methods based on density functional theory become quite demanding on computer power. Before starting such a calculation, one should at least have an idea of the geometry one expects for the dimer.

We will now show that it is possible to obtain V, α and Δ directly from the measured monomer and dimer absorption spectra. We will consider the "absorption line-shape" $A(\omega)$, a continuous function of light frequency ω, which is connected to the absorption cross-section $\sigma(\omega)$ by

$$A(\omega) = \frac{\sigma(\omega)}{\omega}. \tag{5}$$

The nth moment of $A(\omega)$ is defined as

$$\langle\, \omega^n\,\rangle = \frac{1}{\langle\, \omega^0\,\rangle}\int \omega^n A(\omega)d\omega \qquad n = 1, 2, \ldots \tag{6}$$

with

$$\langle\, \omega^0\,\rangle = \int A(\omega)d\omega \tag{7}$$

which is the area under the curve $A(\omega)$. The integration is restricted to the area of the absorption band considered.

For $n \geq 2$ it is convenient to further define the centered moments

$$z_n = \frac{1}{\langle\, \omega^0 \,\rangle} \int \left(\omega - \langle\, \omega^1 \,\rangle\right)^n A(\omega) d\omega \tag{8}$$

The quantity $\langle\, \omega^1 \,\rangle$ is the mean of the absorption line-shape $A(\omega)$, the second central moment z_2 is the variance and the third central moment z_3 is a measure of the lopsidedness (and connected to the skewness $z_3/\sqrt{z_2}^3$).

The moments of the monomer and the dimer absorption spectrum are not independent but are connected by so-called sum rules [27,32,33] which can be derived under quite general conditions (e.g. arbitrary Born Oppenheimer surfaces and uncorrelated disorder). The basic assumptions made are discussed in Ref. [33]. At the end of the paper we will consider some limitations of the method.

In the following, monomer quantities are denoted by a superscript M and dimer quantities by a superscript D. In the case of isotropically oriented dimers one obtains from the sum rules

$$\langle\, \omega^1 \,\rangle^{\mathrm{D}} = \langle\, \omega^1 \,\rangle^{\mathrm{M}} + V \cos\alpha + \Delta \tag{9}$$

$$z_2^{\mathrm{D}} = z_2^{\mathrm{M}} + V^2 \sin^2\alpha \tag{10}$$

$$z_3^{\mathrm{D}} = z_3^{\mathrm{M}} + z_2^{\mathrm{M}} V \cos\alpha \tag{11}$$

These three equations can be solved for the unknowns V, α and Δ. From Eq. (10) and Eq. (11) one finds

$$V^2 = \left(\frac{z_3^{\mathrm{D}} - z_3^{\mathrm{M}}}{2 z_2^{\mathrm{D}} - z_2^{\mathrm{M}}}\right)^2 + \left(z_2^{\mathrm{D}} - z_2^{\mathrm{M}}\right) \tag{12}$$

$$\sin^2\alpha = \frac{z_2^{\mathrm{D}} - z_2^{\mathrm{M}}}{V^2} \tag{13}$$

Since $(z_2^{\mathrm{D}} - z_2^{\mathrm{M}}) \geq 0$, see Eq. (10), there are no problems taking the roots in Eqs. (12) and (13). Thus Eqs. (12) allows the determination of V up to the sign and, from Eq. (13), the angle α. The sign of $z_3^{\mathrm{D}} - z_3^{\mathrm{M}}$ restricts possible values of V and α (which can be obtained from Eq. (11)). One finds that for $z_3^{\mathrm{D}} - z_3^{\mathrm{M}} > 0$ either $V > 0$ and $\alpha \in [0°, 90°[$ or $V < 0$ and $\alpha \in]90°, 180°]$. For $z_3^{\mathrm{D}} - z_3^{\mathrm{M}} < 0$ either $V > 0$ and $\alpha \in]90°, 180°]$ or $V < 0$ and $\alpha \in [0°, 90°[$. From Eq. (11) and Eq. (9) the energy shift Δ can be obtained from

$$\Delta = \left(\langle\, \omega^1 \,\rangle^{\mathrm{D}} - \langle\, \omega^1 \,\rangle^{\mathrm{M}}\right) - \frac{z_3^{\mathrm{D}} - z_3^{\mathrm{M}}}{2 z_2^{\mathrm{D}} - z_2^{\mathrm{M}}} \tag{14}$$

Equations (12), (13) and (14) allow in principle the calculation of the parameters V, α and Δ.

To demonstrate the applicability of the approach presented above, calculation of V, α and Δ are performed on the measured spectra shown in Fig. 2 using Eqs. (12), (13) and (14). The values obtained are compared with results from Ref.[1], where the same spectra are investigated, but the dimer Hamiltonian is diagonalised numerically including one vibrational mode per monomer. The values obtained using formulas Eqs. (12), (13) and (14) are summarised in Table 1 together with the values from Ref. [1]. The agreement between the two different approaches is remarkable. Especially the interaction strength V and the angle α are identical within the errors of the two methods. The dimerisation shift Δ is at least of the same order of magnitude. This shows that the method presented in this work can be used to extract important parameters of the dimer from the measured absorption spectra alone.

Table 1

Comparison between the results of this work with those of Ref. [1].

	this paper	Ref. [1]
V	± 950 cm^{-1}	$\pm 925 \pm 30$ cm^{-1}
α	32° (148°)	$28 \pm 5°$
Δ	-34 cm^{-1}	0 ± 20 cm^{-1}

Of course there are limitations of the applicability of the method. One of the basic assumptions used to derive the sum rules was to consider only one excited state of the monomer. Thus when interactions with higher excited states become important [7] one expects deviations from Eqs. (12), (13) and (14). Furthermore it has been assumed that the shape of the Born Oppenheimer surfaces of the monomers does not change upon dimerisation. If the broadening of the monomer spectrum is mainly due to diagonal disorder and the fluctuations of the transition energies of the two monomers are correlated the approach will probably give no good results anymore. Since the third moment depends strongly on the form of the spectrum in the wings it is important to consider the spectrum over the whole electronic transition.

Even with its limitations, the method can be used as a first estimate of the geometrical arrangement of the dimer. Especially for the analysis of complex high resolution spectra (obtained e.g. in helium nano droplets [12]) it might be helpful. Since for such spectra many individual vibrational modes are resolved, the methods used in Ref. [1] are confronted with the problem that the inclusion of several vibrational modes makes the calculation of dimer spectra very time consuming, so that a fit of the parameters V, α and Δ without any knowledge of the geometry seems a very hard task. The good results of the method presented in this work, suggest to extend it from dimers to larger aggregates. This might help to understand the geometrical arrangement and the energy transfer properties of such systems.

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