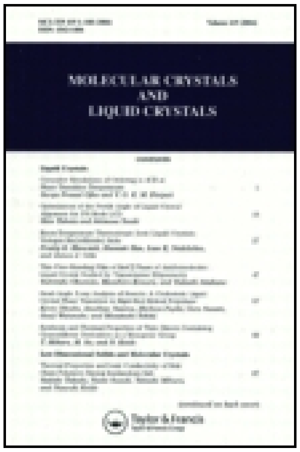

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Effect of the Coupling with Frenkel States on the Electroabsorption Signal of Charge Transfer Excitons

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The recently proposed nearest-neighbour model of the coupling between the Frenkel and charge transfer (CT) excitations of a molecular crystal, successfully applied for the calculation of the electroabsorption (EA) spectra of polyacenes and fullerene, is applied to probe the influence of different intramolecular excited states on the EA signal in the CT energy range. The study highlights the pre-eminent role of Frenkel excitons that are energetically close to the CT manifold, even if they are inactive in conventional absorption spectroscopy. The high-energy intense excitons are found to have a lesser effect. The study suggests EA spectroscopy as a potential tool to detect and locate some of the absorption-inactive intramolecular excitations.

Keywords electroabsorption, Frenkel excitons, charge transfer states, poliacenes, fullerene

INTRODUCTION

The intramolecular excitations (Frenkel excitons) appear in electroabsorption spectroscopy in several distinct capacities. Firstly, spectroscopically active Frenkel states give rise to their own EA signals, in some experimental geometries considerably strengthened by the coupling to the CT manifold[1]. Secondly, owing to the same coupling, they lend absorption intensity to the CT states, thereby affecting the EA signals of the latter[2-4]. Thirdly, spectroscopically inactive Frenkel states may exhibit non-negligible electroabsorption signals due to electric-field-induced transfer of absorption intensity from the allowed states. Finally, in view of the sensitivity of the EA spectrum to even minor shifts of the observed states, the coupling between the forbidden Frenkel states and the CT manifold may affect the EA spectra of the latter[5].

In the present paper we would like to illustrate the above effects on several examples where theoretical reproduction of the experimental electroabsorption spectra, based on a microscopic and essentially non-empirical model, has been successfully completed. This was achieved for polyacenes[6], where the theoretical model provided a good quantitative reproduction of the experimental spectra, including even the absolute intensities (normally difficult to account for), and for fullerene C60, where the theoretical description was less rigorous and the agreement with experiment was semi-quantitative[7,8]. The corresponding models are described in other papers, to which the reader is referred for details[5-8]; here we focus our attention on the physical conclusions.

LOWEST INTRAMOLECULAR EXCITATION

In polyacenes, the transition to the lowest intramolecular singlet excited state is allowed, giving rise to a well defined EA signal. This signal is amplified in the crystal[1,5,6], which can be qualitatively rationalized in terms of the coupling with the CT states which, by lending a fraction of their large dipole moment to the Frenkel excitons, increase the apparent polarizability of these latter states almost by an order of magnitude[1]. Reciprocally, this same coupling mediates the transfer of some absorption intensity from the lowest Frenkel state to the CT manifold, providing some 80% of the EA signal intensity of the CT states in tetracene and pentacene crystals; the rest of their intensity is due mostly to their inherent transition dipole moment[5]. In anthracene, this latter contribution is dominant and the admixture of the S_1 state to the eigenstates of CT parentage has a lesser effect on the EA spectrum (some 20% of the intensity[5]), which is due to the interaction with the spectroscopically mute intramolecular excitations (*vide infra*).

In fullerene, the S_0-S_1 transition (at about 1.86 eV) is dipole-forbidden[9-12]. In effect, it is not observable in electroabsorption and lends no transition dipole moment to the CT states, having practically no influence on their properties.

HIGHER INTRAMOLECULAR EXCITATIONS

In C60, the first prominent EA signal (approximately first-derivative, at about 2.5 eV[13]) is due to the HOMO-to-LUMO CT states, mostly of (1/2,1/2,0) parentage[14,15]. It is followed by an approximately second-derivative feature at about 2.75 eV, essentially of the same provenance. This shows that, owing to the relatively prominent off-diagonal interactions within the CT manifold and to the coupling with the nearby forbidden Frenkel states (*vide infra*), the splitting between different eigenstates of (1,/2,1/2,0) CT parentage is substantial. However, in spite of the common origin of the EA features at 2.5 and 2.75 eV, the source of their intensity is different: while the latter signal is due to the inherent transition dipole moment carried by the CT states, the former one is activated by intensity borrowing from high-energy Frenkel states. This effect is shown in Fig.1 where the relevant fragment of the C_{60} EA spectrum is calculated with and without inclusion of the coupling of the CT states with high-energy intramolecular excitations, which in our model are represented by one effective state at 5.2 eV, carrying the combined absorption intensity of all Frenkel states located above 4 eV. As is readily seen, the EA signal at 2.5 eV practically disappears if this state is removed from the model. Worth noting in comparison is the marginal importance of the contribution to the intensity of the CT states that is borrowed from the lowest dipole-allowed intramolecular excitation at 3.75 eV: the high intensity of the effective 5.2 eV state outweighs its larger energy gap from the CT manifold.

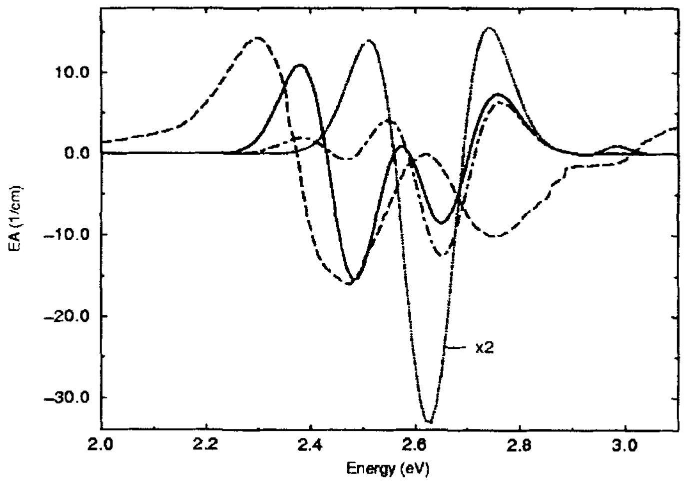

FIGURE 1. Low-energy electroabsorption spectrum of C60: dashed line experimental, solid line - calculated within complete model, dash-dot line - calculated without inclusion of the coupling with high-energy Frenkel states, dotted line - calculated without inclusion of the coupling with forbidden Frenkel states at 2.9 and 3.2 eV.

This situation contrasts with that encountered in polyacenes, where the lowest allowed state (S_1) is the main intensity lender, and the contributions from higher allowed intramolecular excitations only marginally influence the EA spectrum[5].

ABSORPTION-INACTIVE FRENKEL STATES

Most molecules have some optically inactive states. Their inactivity in absorption spectroscopy need not necessarily imply their inability to contribute to the EA spectrum. If, for instance, the interaction with the electric field couples them to allowed states, the ensuing intensity transfer should be observable in electroabsorption. Moreover, in view of the sensitivity of the EA spectrum to even minor shifts of the observed states, the coupling between the forbidden (in absorption) Frenkel states and the CT states may affect the EA spectra of the latter.

This effect is quite prominent in anthracene, endowed with two low-energy intramolecular excited states (at 3.4 and 3.65 eV) forbidden in conventional absorption spectroscopy[5,6]. Their energetic proximity to the CT manifold (starting at about 3.6 eV) considerably perturbs the latter, reducing its EA intensity and causing major changes (additional shoulder) in the shape of its EA signal. The effect partly compensates the intensity borrowing by the CT states from the S_1 Frenkel exciton, and may be thought of as indirect intensity transfer from the allowed to the forbidden Frenkel states, mediated by the intervening CT excitons. It allows one to rationalize the above-mentioned relatively weak influence of the S_1 Frenkel state on the signal attributed to charge-transfer states[5].

In fullerene, the interaction with optically inactive Frenkel states (at 2.9 and 3.2 eV) considerably increases the splitting in the HOMO-to-LUMO series of CT states (between 2.4 and 2.7 eV), producing an additional EA feature (analogous to the additional shoulder in anthracene). If this interaction were absent, the CT states of (1/2,1/2,0) parentage would give rise to one second-derivative signal, as shown in Fig.1.

CONCLUSIONS

Apart from their own signals, Frenkel states contribute to the EA spectrum also indirectly, by affecting the EA response of charge-transfer states. The main effect of allowed Frenkel states consists in lending intensity to the (otherwise weak) eigenstates of CT parentage. If in a given molecule the S_0-S_1 transition is allowed, the intensity it lends to the HOMO-to-LUMO CT manifold either is comparable to (as in anthracene) or dominates over the inherent CT contribution (as in tetracene and pentacene). If the transition to the lowest intramolecular excited singlet state is forbidden (as in C_{60}), the borrowing from high-energy Frenkel states, favoured by their large absorption intensity, may dominate over the borrowing from the *lowest allowed* Frenkel exciton, favoured by the relative proximity of that state to the HOMO-to-LUMO series of CT states.

The effect of the coupling of the CT manifold to the forbidden Frenkel states may be quite prominent if the energy gap between the two groups of states is small enough. In that case, the coupling typically affects the energetics of the CT states (which may give rise to new EA features, as in anthracene or C_{60}). In some instances (as anthracene), secondary intensity transfer may occur from the allowed to the forbidden Frenkel states via the CT manifold. Generally, the indirect influence of the forbidden Frenkel excitons on the EA signal of CT excitons may potentially become useful for studying the intramolecular excited states that are inaccessible for conventional absorption spectroscopy.

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