SPECTROSCOPY AND NONLINEAR PROPERTIES OF CHARGE TRANSFER ORGANIC CRYSTALS

J. Ehooman, M. Pierre, Patrice L. Baldeck, D. Block

► To cite this version:

J. Ehooman, M. Pierre, Patrice L. Baldeck, D. Block. SPECTROSCOPY AND NONLINEAR PROPERTIES OF CHARGE TRANSFER ORGANIC CRYSTALS. Journal de Physique IV Proceedings, 1991, 01 (C7), pp.C7-541-C7-545. 10.1051/jp4:19917142 . jpa-00250816

HAL Id: jpa-00250816

<https://hal.science/jpa-00250816>

Submitted on 1 Jan 1991

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

SPECTROSCOPY AND NONLINEAR PROPERTIES OF CHARGE TRANSFER ORGANIC CRYSTALS

J.B. EHOOMAN, M. PIERRE, P.L. BALDECK and D. BLOCK

Laboratoire de Spectrométrie Physique, Associé au C.N.R.S., Université Joseph Fourier, Grenoble I, BP. 87, F-38402 St. Martin d'Hères cedex, France

Abstract

Conventional spectroscopy is used to characterize the parameters of the intense electronic transition of internal charge transfer character of a series of D-A paradisubstituted benzenes in the monocrystal. The implications of new transitions and the influence of intermolecular interactions on non-linear properties are discussed.

Internal Charge Transfer and Non Linearities.

A-D paradisubstituted benzenes are a textbook model for non-linear optics. These molecules exhibit a strong asymmetric repartition of charge in the ground and excited state, often imaged as a typical electronic push-pull model (fig.1) [1-3].

The excited state has generally a larger dipole moment so that the transition is accompanied by an Internal Charge Transfer (ICT). This intense transition, with a dipole moment along the long molecular axis Z, is responsive for the large anharmonicities observed. The exceptional non-linear properties, which appear in the visible and near infrared have found applications in second harmonic generation and parametric amplification [3,4,5]. Some of these organic crystals are commercially available (POM: 3-methyl-4-nitropyridine oxide).

In order to characterize the cause of nonlinearities, considerable interest has centered recently around the spectral properties of these molecules in the condensed phase.

Simple model showing how the presence of a donor and acceptor push-pull pair can affect the delocalized oscillating π electron. The anharmonicity of the system gives rise to high non-linearities.

L and NL molecular properties in the monocrystal

The ICT state represents the main contribution to the molecular second order polarizability β in the visible and near infrared. Its expression as function of the frequency Ω of the incident light is [6,7]

$$\beta \approx \frac{\text{Cste } \Omega_0 f \Delta \mu}{(\Omega_0^2 - \Omega^2)(\Omega_0^2 - 4\Omega^2)}$$

Ω_0 is the frequency maximum of the CT transition, f is the oscillator strength of the CT transition, proportional to the square of the CT transition dipole moment,

$\Delta \mu$ is the change of static dipole moment between the ground state and the excited CT state.

These parameters are usually measured from absorption spectra in solution. The purpose of this work is the identification of the electronic transitions in crystals of this class of molecules in the monocrystal (fig.2).

Because of the high absorptivity of the crystals, reflection spectroscopy and Kramers-Kronig transformation was used to obtain the linear susceptibilities [8].

Comparison between solution spectra and crystal spectra at RT for NPO (4-nitropyridine oxide) and (ABN) (4-aminobenzonitrile). The transition in the crystal is red shifted by respect to the solution. This is due to molecular interactions. The polarization ratios do not follow the oriented molecular gas. On the red side of the main transition of ABN appears in polarization //c a weaker transition with a dipole moment along the molecular short axis Y.

The main results of this study are:

* the resonant frequency Ω_0 is red shifted in the crystal. This shift, strongly dependent on the polarization can be attributed to coulombic interactions between molecules as in NPO or to intermolecular hydrogen bonds as in ABN (4-aminobenzonitrile).

* the oscillator strength f is larger in the crystal. However it is strongly dependent on the evaluation of the local field.

* low temperature crystal spectra show well resolved structures not visible on solution spectra. In particular, all molecules with the substituent NO_2 as acceptor become opaque in the blue region (400 - 450 nm). This effects are attributed to $n \rightarrow \pi^*$ transitions.

* the ICT intense transition remains broad even at low temperatures. This indicates a strong damping due to the deactivation to lower energy states as $n \rightarrow \pi^*$ states. However in ABN, an additional weaker transition ($f=0.04$) with a transition dipole moment along the molecular short axis is clearly visible on the red side of the CT transition, in the polarization //b, already observed for most substituted benzenes [9,10]. This transition exists in NPO and POM, but is probably surimposed with the main CT transition [11]. It should contribute significantly to the relaxation of the CT exciton.

Concerning the variation $\Delta \mu$ of the static dipole moment between the ground and the excited state, no precise experimental values are available. This value is generally obtained from theoretical MO calculations [4] and is often overestimated [11].

Crystal CT states & new trends

NPO	c/a	b/c
theoretical	1.29	0
experimental	1.93	0.15

ABN	c/a	b/c
theoretical	260	0.35
experimental	-	0.17

In order to derive the crystalline susceptibilities from the local molecular parameters, the model of the oriented gas is generally used. This model takes into account the relative orientations of the molecules in the monocrystal. Comparison between the theoretical and experimental values of the polarization ratios in the absorption spectrum shows a noticeable discrepancy in NPO and ABN. (Tab.1).

Such a difference in polarization ratios, uncommon for intense transitions is related to molecular interactions in the excited state.

In NPO, intermolecular charge transfer is induced by coulombic interactions between acceptor and donor substituents belonging to neighbouring molecules [12,13].

In ABN, intermolecular hydrogen bonds are shorter in the excited state and enhance the charge transfer [14].

Crystallographic structure of NPO. All molecules are in the (a,c) plane. Intermolecular coulombic interactions take place between $-N \rightarrow O$ and $-NO_2$ substituent belonging to adjacent molecules (distance $3.2 \text{ \AA}$).

Crystallographic structure of ABN. Molecules are arranged in chains, linked by hydrogen bonds between $-NH_2$ and $-CN$ substituents. In the CT excited state, this hydrogen bond is stronger, and reciprocally, the CT is enhanced.

All these molecular interactions depend on the molecular packing in the crystal. They can lead to collective excitations, or excitons playing a fundamental role in the third order susceptibility. In NPO, POM or ABN, due to the presence of other molecular transitions, a rapid decay takes place and localizes the exciton (ref.). In ABN and PNA (4-nitroaniline), the intermolecular hydrogen bonds should favorize the formation of a "dressed exciton", propagating along chains with a local hydrogen bond deformation.

References

- 1 M.D.Gordon Tetrahedron 36,(1980),2113-2118.
- 2 J.F.Nicoud, R.J.Twieg, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol.1, Ed. D.S.Chemla, J.Zyss (Academic Press, NY 1987) chap. II-3.
- 3 B.F.Levine, Chem. Phys. Lett. 37,(1976), 516-520.
- 4 J.Zyss, D.S.Chemla, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol.1, Ed. D.S.Chemla, J.Zyss (Academic Press, NY 1987) chap. II-1.
- 5 J.Zyss, D.S.Chemla, J.F.Nicoud, J.Chem.Phys. 74,(1981),4800.
- 6 D.Pugh, J.O.Morley, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol.1, Ed. D.S.Chemla, J.Zyss (Academic Press, NY 1987) chap. II-2.
- 7 P.N.Prasad, D.J.Williams, in *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, (J.Wiley & Sons, NY 1991).
- 8 M.Pierre, P.L.Baldeck, D.Block, R.Georges, H.P.Trommsdorff and J.Zyss, Chem.Phys. 155,(1991), in press.
- 9 J.Petruska, J.Chem.Phys. 34,(1961),1120-1136.
- 10 T.P.Carsey, G.L.Findley, S.P.McGlynn, J.Am.Chem.Soc.,101,(1979),4502-4517.
- 11 R.M.Hochstrasser, D.A.Wiersma, J.Chem.Phys. 55,(1971),5339-5343
- 12 Y.Wang, R.H.Blessing, F.K.Ross, P.Coppens, Acta Cryst. B32,(1976),572.
- 13 M.Joyeux, N.Q.Dao, J. of Raman Spect.19,(1988),441.
- 14 S.Merlino, F.Sartori, Acta Cryst. B38,(1982),1476-1480.