LA-UR- 93 - 4143

Approved for public release;
distribution is unlimited.

Title: EXCITATIONS AND OPTICAL PROPERTIES OF
PHENYLENE BASED POLYMERS

Author(s): N. Kirova*
S. Brazovskii* & **
A. R. Bishop
D. McBranch
V. Klimove

Submitted to: Invited presentation at "International Conference Synthetic Metal:
Montpellier, France, July 1998 to appear in "Synthetic Metals"

RECEIVED
AUG 18 1999
OSTI

Los Alamos

NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RECEIVED
AUG 18 1999
OST

Excitations and optical properties of phenylene based polymers.

N. Kirova^{1,2}, S. Brazovskii^{1,2,3}, A.R. Bishop¹, D. McBranch¹, V. Klimov¹

¹ Los Alamos National Laboratory, Los Alamos, NM 87544, USA.

² Brookhaven National Laboratory, Upton, NY 11973-500, USA.

³ Landau Institute, 2, Kosygina St., 117940 Moscow, Russia.

Abstract

A complex picture of phenylene-based polymers is developed which unifies features of band and molecular exciton models. It incorporates major experimental finding in direct, and photoinduced optical absorption, stimulated photoemission and photoconductivity. We give new assignments for the most disputed features and identify new ones as edge states. We confirm a low binding energy for the principle emitting exciton and show that it dominates also in the fundamental absorption. Contradictions in the current modeling state-of-art are displayed and discussed.

Keywords: Optical absorption and emission spectroscopy. Photoinduced absorption spectroscopy

1. Introduction

The physics of luminescent conjugated polymers and oligomers based on phenylenes [1] is extremely rich, as they lie at the boundary between small conjugated molecules and extended one-dimensional semiconductors, exhibiting important properties from each class. Surprisingly there is no agreement yet on basic issues after a nearly decade of diverse studies. Assignment of several features, their origin and scaling remain in dispute. Even a quantitative diversity sometimes is also too strong to be tolerated without impact on observations and in guiding strategy for applications: especially concerning the binding energy of the light emitting exciton for which estimates range over nearly an order of magnitude. Among theories, computational studies [3, 4] derive essential optical features from the size quantization for oligomers. Analytical studies invoke the coexistence of localized and delocalized states, which is a special feature of phenyl based polymers. They branch between the picture of excitons exploiting the language of molecular spectroscopy derived from the isolated phenyl ring [5, 6], and the band picture of delocalized electronic states exploiting a solid state physics language relevant to polymers with dominating delocalization of electrons [7].

For these multi-electronic systems any quantitative method is expected to give a noticeable inaccuracy. The numeric methods do not help much: the first principle quantum chemistry [3] does not go beyond one molecule and already for oligomers truncated methods are exploited [3, 4] which have been known [8] to give inconsistent results even for the single ring. While one cannot rely upon a good quantitative agreement among various approaches, a qualitative

similarity might be expected. Instead several existing pictures [3, 4, 5, 6] remain incompatible. Here we argue for the necessity of new assignments for the most disputed features and find quite transparent ones extending those in [7, 17].

2. Experimental.

The linear optical absorption spectrum of a solution of MEH-DSB in *p*-xylenes is shown in Fig. 1. [10] together

Figure 1: Ground- (solid line) and excited-state (dashed line) optical transitions in MEH-DSB. The position of PA_2 is indicated as observed in [9]

with the transient photoinduced absorption (PA) spectrum taken at a relative delay time of 2 ps, from 1.1 eV to 2.6 eV. Detailed studies [10] of the spectral dependence and the intensity-dependent dynamics of the PA in MEH-DSB have shown that the primary photoinduced features [i.e. the PA band at 1.4 eV (PA_1) and the stimulated photoemission band at 2.3 eV (SE)] arise from intrachain emissive excitons as the sole excited-state species at low excitation densities [10, 11]. Previous studies of several other PPV derivatives have shown similar bands for both PA and SE at similar energies. [9, 12, 13] In addition, a low energy band at approximately 0.8 eV has been identified, which is also due to an excited-state transition of the intrachain excitons [9, 13]. Hence, the ground-state optical transitions to be assigned are $A_1 = 2.9$ eV, $A_2 = 3.6$ eV, $A_3 = 4.5$ eV, $A_4 = 6.0$ eV, while the excited-state transitions from the primary exciton are $PA_2 = 0.8$ eV, $PA_1 = 1.4$ eV, and $SE = 2.3$ eV. We also observe the shoulder near $A_0 = 5.2$ eV which has not been observed in polymers. Details may be found in [10].

3. Band structure, excitons and optical features.

The PPV chain consists of phenyl rings and dimers of carbon atoms providing the vinyne linkage. Fig. 1. The energy bands may be viewed as originating from the intra-ring π -electronic levels at $\pm T$ and $\pm 2T$, as well as from vinyl dimer π -levels at $\pm \tilde{T}$. We use standard values and for hopping integrals between adjacent atoms within the ring $T = 2.4$ eV, within the dimer $\tilde{T} = 2.6$ eV and between them $t = 2.1$ eV. The ring states are classified in terms of their parity (g, g^*) and (u, u^*) with respect to the chain axis. The u, u^* states have zero amplitude at the connection to the vinyl group and hence they *do not hybridize with the dimer*; the levels do not acquire a band dispersion. We have found the analytical solution providing the dispersion equation for free electrons and transition intensities [7]. The Coulomb corrections are included by the rigid displacements of all π, π^* bands by ± 0.6 eV correspondingly. The resulting band structure is presented in Fig. 2.

The bands L_1, L_1^* are flat, originating from the u, u^* states of the phenyl ring, while the dispersion of bands D_1, D_1^* is remarkably high ($\sim 0.7T \approx 1.7$ eV). To quantitatively estimate the degree of electronic delocalization, we have calculated the Participation Ratios (PRs) of the electronic wave functions on the ring (PR_R) and on the dimer (PR_D) as a function of the quasi-momentum. Fig. 2 (top) shows results for the HOMO - LUMO bands D_1, D_1^* . The especially strong hybridization in PPV is an apparent consequence of the resonance between $\pm T$ levels of the ring and $\pm \tilde{T}$ levels of the dimer. The small variations of the PRs justify the application of a uniform Coulomb correction for the whole band. For a finite system we have found also the "edge states" localized near the chain ends. Their energies are located in the gaps between D_1, D_2 and D_1^*, D_2^* , that is around ± 3.1 eV. This band picture naturally allows for three different excitons (EX) confined by long range Coulomb interactions. We introduce "excitons" in the sense of solid state physics, only as *bound states of excited electron-hole pairs*.

EX_1 is a *weakly bound state of delocalized electron*

Figure 2: Band structure of electronic states for the PPV chain. Optical transitions are shown for the electrons only. Top: Participation ratio of ring states (solid line) and dimer states (dashed line) for the lowest $D_1 D_1^*$ band.

and hole from D_1^*, D_1 bands, which is adequately described within the effective mass approximation. The series of binding energies E_{b_n} and of localization radii R_n can be written as [14]: $E_{b_n} = \hbar^2/2m^* R_n^2$, $R_n = (\hbar^2 \epsilon / m^* e^2) (n / \ln R_n / a_\perp)$ with $n = 1$ attributed to the primary 1B_u exciton. Here $m^* \approx 0.067m_e$ is derived from the D, D^* dispersion, $a_\perp \sim 2\text{\AA}$ is the chain width. Importantly, $\epsilon = \epsilon_\perp$ is the susceptibility in a perpendicular direction with respect to the chain axis, that is the one of the solvent $\epsilon \approx 2$ in our solution experiments. We see that E_b is not intrinsic and in this way we explain variations of E_b between films, solutions and various side group substitutions. The large $R_1 \sim 30\text{\AA}$ validates our approximation. The resulting binding energy is rather small ($E_{b1} \sim 0.1 - 0.2$ eV), corresponding well to the values deduced from measurements of charge transport and injection [2, 15, 16].

EX_2 is a *more tightly bound state of $L_1 D_1^*, D_1 L_1^*$* . Now the dispersionless electron L_1^* or hole L_1 plays the role of an immobile Coulomb center, binding the delocalized particle of the opposite sign. With twice higher effective mass with respect to EX_1 case, the EX_2 radius is reduced to two chain units and the dispersion of ϵ will shift it to still lower values. Supposing $\epsilon^* = 1.5$ we find $R_1 \sim 10\text{\AA}$ and a binding energy $E_b \sim 0.8$ eV.

EX_3 is an *intra-ring LL^* bound state of dispersionless electron and hole* derived from u, u^* states near $\pm T$. This is a Frenkel exciton, which we assign to the absorption feature at 6.2 eV, in agreement with [4, 5]. At even higher energies we may expect ionized decoupled states where L_1 and L_1^* belong to different rings.

We can now make qualitative assignments based on the transitions in Fig. 1 and the band diagram in Fig. 2. We associate the maximum $A_1 \approx 2.9$ eV with the interband DD^* transition preceded with a hydrogen-like series of excitonic levels, beginning at about 2.7 eV (EX_1 , Fig. 2). This is followed by absorption to the EX_2 ($A_2 \approx 3.6$ eV),

split off from the peak at $A_3 = 4.5$ eV, corresponding to the unbound $D_1 L_1^* + L_1 D_1^*$ transition. Next is the sharp $L-L^*$ transition $A_4 \approx 6.2$ eV (observed at 6.0 eV for PPV[4]). The shoulder at $A_0 \approx 5$ eV, not observed in polymers, comes from the edge states.

The PA peaks $PA_1 \approx 1.4$ eV and $PA_2 \approx 0.8$ eV have been experimentally determined to arise from excited-state transitions of the emissive exciton EX_1 [13, 9, 10, 11]. For this reason, we assign PA_2 to the excitation of EX_1 to EX_2 . PA_1 is assigned to the dissociation of the EX_1 state to $D_1 L_1^* + L_1 D_1^*$ states. Finally, the SE peak at 2.34 eV corresponds well to relaxed emission from EX_1 .

We have also calculated the appropriate oscillator strengths. For the DD^* manifold we have found quite unexpected dispersion of oscillator strengths, which shifts them substantially to higher energies. As a result the band edge is not affected by the 1D square root singularity. Instead it is dominated by the weakly split exciton in spite of the fact that its position is not well distinguishable from the onset of delocalized transitions. This result readily explains experiments showing opposite shapes for PC and absorption, see Fig.3. apparently this observation is important for the optical pumping efficiency.

Figure 3: Calculated absorption (solid line) and PC (dashed line) spectra. Insert: experimental data taken from [18]

In our model the A_1 , A_4 peaks in the optical absorption should be polarized parallel to the chains and A_2 , A_3 - perpendicular. Fortunately the scheme [4] gives the opposite prediction for the polarization of A_2 in compare to both peaks, our model and that of [6]. This will allow for a complete resolution in future experiments on fully oriented samples. Notice that the partial orientation may be confusing. Thus our modeling of data from the very informative work [4] shows that the strong $\parallel$ -polarized A_1 background emulates a wrong polarization of intrinsically $\perp$ -polarized A_2 . In Fig.4 we present the calculated optical

absorption for the 80% polarized material. In spite of the perpendicular polarization of the A_2 peak, the tail from A_1 results in a seeming parallel polarization.

Figure 4: Calculated polarized absorptions ($\parallel$, $\perp$) and their difference ($\parallel - \perp$) for an 80% oriented material. Insert: experimental $\parallel - \perp$ absorption taken from [4].

4. Discussion and comparison to other schemes.

The incompatibility of optical assignments between different models needs a special discussion. Limiting to only linear processes, we are able to compare to earlier analytical studies [5, 6]. There are similarities in qualitative classification of D, L states and of the corresponding excitons, quantitative differences are, however, sometimes drastic. Among these differences, the most important for laser applications is the structure of the fundamental absorption and its consequences for SE and PC. The constant oscillator strengths chosen arbitrarily in [5] results in a strong band edge absorption peak which hides the shallow exciton contrary to our conclusion above. This would imply a strong threshold for the photoconductivity (PC) response and a weak one in stimulated emission and PA in disagreement with current experiments. A principal divergence between theories concerns the most disputed A_2 peak, whose assignment is different in all suggested schemes to date. Its correct interpretation is ultimately necessary for understanding of PAs. Estimates [6] based on the Coulomb splitting for the isolated benzene ring predicted stronger shifts (~ 1 eV) between the two components $D_1 L_1^* \pm L_1 D_1^*$ of EX_2 , with inessential splitting between the exciton and the band-edge. This approach assigns A_3 to the allowed combination and A_2 to the dipole forbidden one suggesting that side groups make this transition allowed by lifting the symmetry. But the observation of the same peak [3, 4] in pristine PPV requires a mechanism independent of side-chain effects, such as that proposed in

our work. Moreover, in MEH-DSB only one ring among five is substituted, so that the intensity of the weakly-allowed combination should have been strongly reduced, which does not seem to be the case. While possible, this explanation makes difficult an observation of a weak feature on the background of a strongly allowed DD^* band. We argue that, beyond the allowance problem, the delocalization will weaken the intramolecular splitting of $DL^* \pm LD^*$ transitions below the observed 1 eV value. Our point of view is that the $A_3 \approx 4.7\text{eV}$ and $A_2 \approx 3.7\text{eV}$ features are allowed transitions to free and bound forms of the same $DL^* + LD^*$ manifold. This assignment is incorporated in the same frame as the explanation of the two PA features, thus providing a link between the linear optics at high energies and the nonlinear low energy one. The computational approaches [3, 4] assign A_2 to the $D_1D_1^*$ band. This interpretation relies upon a strongly split lowest level, which occurs only in finite oligomers. This would imply a strong size dependence which does not seem to exist experimentally.

The excitonic approach of [5] has not been extended to modern nonlinear studies. But we are obliged to compare our scheme with the extensive studies of [4]. A drastic qualitative difference is clear: the assignments for A_2 and PAs in [4, 3] are effects of the finite and fixed (3, maximum 5 rings) length which can not show up in polymers. An apparent reformulation of these statements in terms of the band theory shows that the thus constructed 3.7 eV B_{1u} and all A_g peaks will be smeared to structure-less bands. Moreover the PA intensities will vanish at large system sizes as the processes which do not conserve the quasi momenta [17]. (To compensate for an odd parity of DD^* excitation a delocalization factor of a form $\sin kx$ is necessary which requires singling out a finite momenta k .) A biexcitonic scenario for A_2 states, mentioned in [4] would require a surprisingly high ($\approx 2\text{eV}$) binding energy of two excitons and this is not acceptable to explain the PA_1 and even PA_2 peaks. Bipolaronic scenario [20] cannot work in short time resolved experiments.

Our PAs assignment may be criticized since the corresponding EX_1 - EX_2 transition is forbidden for an isolated molecule. Nevertheless there are two mechanisms to allow it: one is the same symmetry lifting, exploited by [6] for A_2 peak. Although insufficient from our point of view to describe the weakly allowed transition on the strong allowed background in direct optical absorption, this mechanism works well to allow the PA below the gap where nothing else is competing. Another and more universal mechanism for PA allowance comes from hybridization effects. All together the relative intensity is estimated very reasonably as, e.g., $PA_2/SE \sim \gamma^2 N_2$ or $\sim N_2/N_1$, where N_1, N_2 are the localization lengths for EX_1 and EX_2 and γ is the degree of parity-lifting by side groups [17].

5. Conclusions

Conjugated polymers/oligomers represent a disputable region between domains of solid state and molecular physics. Which one is legitimate? Fortunately nature has provided us with a necessary criteria: The lowest transitions in the benzene molecule and in a polymer chain are formed with different π subshells (LD^* , DL^* and DD^* correspondingly).

Thus, observing a sequence of bands coinciding with the one for intramolecular excitations would call for approaches [4, 3, 5] while still divergent among themselves. This can happen sometimes for less important polymers with weakly bridged (e.g. orthogonally twisted like in PTP) rings and correspondingly large gaps, about 4 eV (4.7 eV is the lowest intraring transition energy). However the apparent observation of the opposite band sequence, corresponding to the intramolecular hybridization with DD^* rather than DL^* , LD^* being the lowest ones, justifies the electronic band picture as our starting point [7] with the primacy of electronic delocalization. As a proof we reach a good quantitative agreement with the minimal adjustable parameters that one can expect: only standard values for the hopping integrals and two adjustable parameters (the overall Coulomb energy shift and the dielectric susceptibility at small distances) have been exploited for the whole complex of both linear and photoinduced features. On the contrary, starting with an intramolecular scheme [5] one underestimates the hybridization qualitatively so that it is necessary to enforce it quantitatively so as to reach a correspondence with experiments. Hence the unusually large, above 3 eV in comparison with standard (2.2-2.4 eV) values of transfer integrals have to be taken as adjustable parameters.

Our approach focuses on universal properties of polymers with extrapolation to oligomers. Finite size effects have been interpreted in terms of edge states and corresponding assignment have been readily found experimentally. The basic concepts are consistent with available experimental observations in the entire phenyl-based family (see also [19]) and are suggestive for future experiments.

Acknowledgments: S.B. and N.K. acknowledge the hospitality and financial support of LANL and BNL. Work performed at BNL is supported by the US DOE under contract No DE-ACO2-98CH10886.

References

- [1] N. Sariciftci, *The Nature of the Photoexcitations in Conjugated Polymers* (World Scientific Publ., Singapore, 1997).
- [2] J. Brédas *et al.*, *Adv. Mater.* **8**, 447 (1996).
- [3] J. Cornil *et al.*, *Chem. Phys. Lett.* **247**, 425 (1995).
- [4] M. Chandross *et al.*, *Phys. Rev. B* **55**, 1486 (1997).
- [5] M. Rice and Y. Gartstein, *Phys. Rev. Lett.* **73**, 2504 (1994); Y. Gartstein *et al.*, *Phys. Rev. B* **52**, 1683 (1995).
- [6] Y. Gartstein *et al.*, *Phys. Rev. B* **51**, 5546 (1995).
- [7] S. Brazovskii *et al.*, *Optical Materials* **9**, 472 (1998); N. Kirova *et al.*, *ibid.* **9**, 465 (1998).
- [8] G. Parr, *The Quantum Theory of Molecular Electronic Structure*, W.A. Benjamin inc., NY 1963.
- [9] S. Frolov *et al.*, *Synth. Metals* **84**, 493 (1997).
- [10] V. Klimov, *et al.*, *Chem. Phys. Lett.* **277**, 109 (1997).
- [11] E. Maniloff *et al.*, *Phys. Rev. B* **56**, 1876 (1997).
- [12] J. Leng *et al.*, *Phys. Rev. Lett.* **72**, 156 (1994).
- [13] J. Hsu *et al.*, *Phys. Rev. B* **49**, 712 (1994).
- [14] R.J. Elliot and R. Loudon, *J. Phys. Chem. Sol.*, **8**, 382 (1959).
- [15] I. Campbell *et al.*, *Phys. Rev. Lett.* **76**, 1900 (1996).
- [16] Q. Pei *et al.*, *Science* **269**, 1086 (1995).
- [17] N. Kirova *et al.*, to be published.
- [18] K. Pakbaz *et al.*, *Synth. Met.*, **64**, 295 (1994).
- [19] N. Kirova *et al.*, *These Proceedings*.
- [20] C. Botta *et al.*, *Phys. Rev. B* **48**, 14809 (1994).