



ELSEVIER

4 February 2000

Chemical Physics Letters 317 (2000) 444–450

**CHEMICAL
PHYSICS
LETTERS**

www.elsevier.nl/locate/cplett

Occupied and unoccupied electronic levels in organic π -conjugated molecules: comparison between experiment and theory

I.G. Hill^a, A. Kahn^{a,*}, J. Cornil^b, D.A. dos Santos^b, J.L. Brédas^{b,c}

^a Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA

^b Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium

^c Department of Chemistry, University of Arizona, 1306 E. University Blvd., Tucson, AZ 85721-0041, USA

Received 10 September 1999; in final form 18 November 1999

Abstract

Occupied and unoccupied densities of states of π -conjugated molecules measured via ultraviolet photoemission spectroscopy and inverse photoemission spectroscopy, respectively, are compared with corresponding densities of states calculated using the semi-empirical Hartree–Fock intermediate neglect of differential overlap (INDO) method. Excellent agreement is obtained for both occupied and unoccupied levels for PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride), α -NPD (N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1' biphenyl-4,4' diamine), and Alq₃ (tris(8-hydroxy-quinoline)aluminum). The results provide a full description of the electronic structure of these molecules and demonstrate that semi-empirical techniques can be successfully applied to describe the unoccupied levels of these molecules. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Over the past decade, the development of electronic and photonic devices made of organic π -conjugated molecular semiconductors has spurred an increased effort to investigate the electronic structure of these molecular materials. Improving the performance of organic-based devices by designing new structures and molecules demands a detailed understanding of transport and optical processes that take place in these devices, which can ultimately be

achieved only through a fundamental understanding of the electronic structure of the constituent molecules and the molecular thin films.

A great deal of insight into the electronic structure of solids is obtained from comparing measured and calculated densities of states. Ultraviolet photoemission spectroscopy (PES) has been extensively used to collect experimental densities of occupied states from numerous organic solids. Theory, however, has been somewhat hampered by fundamental difficulties. Molecular solids are collections of weakly interacting, van der Waals-bonded closed-shell molecular moieties. In these materials, intermolecular energy bands are very narrow, electrons and holes are local-

* Corresponding author. Fax: +1-609-258-6279; e-mail: kahn@ee.princeton.edu

ized, and conduction occurs via tunneling and hopping between molecular sites. The one-electron approximation, which is at the core of band-structure calculations in periodic delocalized inorganic solids, cannot provide a full description of the electronic structure of molecular solids. The molecules are relatively small electron systems in which the excitation and addition or removal of charge carriers by optical transitions or transport processes causes a significant rearrangement of electronic structure and atomic configuration. Final state effects, in particular in photoemission spectroscopy, are generally important. Also, the typical size of the molecules of interest is such that various alternative routes to *ab initio* Hartree–Fock calculations of electronic structures were developed over the years, including the non-empirical Valence Effective Hamiltonian method [1,2], and techniques based on semi-empirical Hartree–Fock Hamiltonians [3,4] and those derived from the density functional theory (DFT) [5,6]. Recently, the intermediate neglect of differential overlap (INDO) method based on a semiempirical Hartree–Fock Hamiltonian approach was used to reproduce UPS valence spectra of a number of π -conjugated molecules [7]. Excellent agreement was obtained with the measured densities of states, providing confidence that a good understanding of the electronic structure of occupied states of these molecules can be achieved with semi-empirical quantum-chemical methods. To date, however, a similar comparison has yet to be achieved for unoccupied states, in spite of their obvious importance in optical and transport processes. One of the reasons is the paucity of spectroscopic data on unoccupied states. In this paper, we present an analysis of data obtained with both UPS and inverse photoemission spectroscopy (IPES) on three molecules: 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), tris(8-hydroxy-quinoline)aluminum (Alq_3) and *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1' biphenyl-4,4' diamine (α -NPD). The chemical structure of each molecule is given in Fig. 1. Because of its remarkable growth and anisotropic transport properties, PTCDA has served as a model system for a number of fundamental studies over the past decade. Alq_3 and α -NPD are extensively used as electron and hole transport materials in modern organic light-emitting diodes [8]. We demonstrate that the

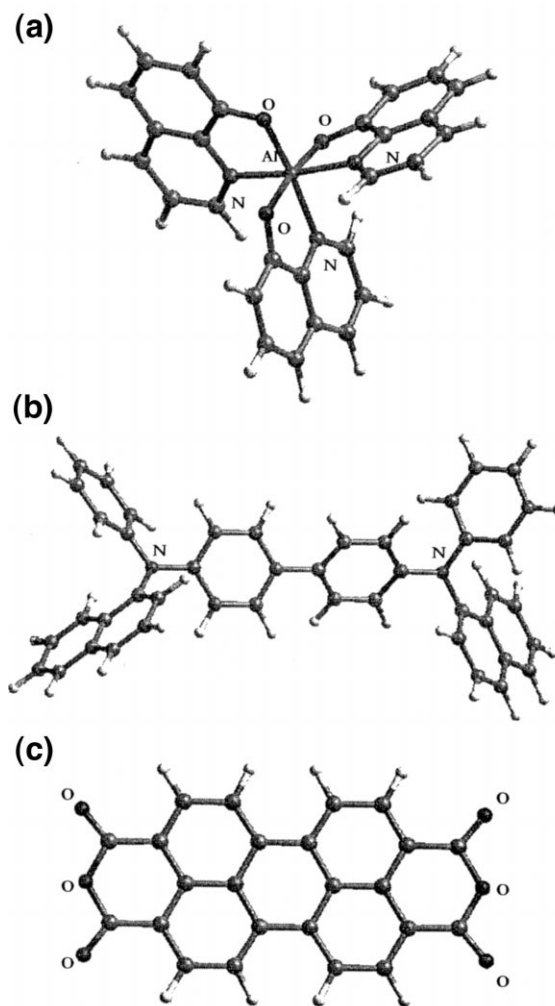


Fig. 1. Chemical structure of the molecules investigated in this work: (a) tris(8-hydroxy-quinoline)aluminum (Alq_3), (b) *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1' biphenyl-4,4' diamine (α -NPD), and (c) 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA).

density of states calculated using the semiempirical Hartree–Fock INDO method shows excellent agreement with both UPS and IPES measured spectra, thus paving the way for a complete description of the electronic structure of these molecules.

2. Experimental aspects

The deposition of the organic films and the PES and IPES measurements were performed in two in-

terconnected ultra-high vacuum systems, allowing measurements on unexposed pristine surfaces. The spectroscopy chamber (base pressure = 5×10^{-11} Torr) was equipped with a helium discharge lamp and a double-pass cylindrical mirror analyzer for UPS, and a low energy electron gun and an isochromat band-pass photon detector for IPES. The details of the system and the IPES set-up have been published elsewhere [9]. The resolution of the UPS and IPES measurements were 0.15 and 0.5 eV, respectively. The energy scales of the UPS and IPES systems were aligned by matching the Fermi energies obtained by measuring the position of the Fermi edge on freshly evaporated Au surfaces.

The films were prepared by evaporating organic molecules in vacuum (10^{-9} Torr) on highly conducting Si(100) wafers coated with ~ 200 Å Cr and 1000 Å Au. PTCDA and Alq₃ were purchased commercially while α -NPD was provided by the group of M.E. Thompson (University of Southern California). All three compounds were purified via three consecutive cycles of gradient sublimation, and placed in vacuum in evaporation cells where they were extensively degassed. The thickness of the organic films was 50–100 Å, which is sufficient to eliminate the substrate signal in PES and IPES while avoiding charging during spectroscopy. Each organic film was first studied with UPS (He I and He II) to measure the density of occupied states. The same film was then studied using IPES to measure the density of unoccupied states. IPES spectra were collected using several incident electron currents in the range of 10^{-3} – 1 μ A, allowing inspection of the data for evidence of rigid energy shifts due to charging. Additionally, higher current densities were found to damage the surface of some organic films. Decreasing the current, at the expense of the count rate, was generally found to result in spectra of superior quality.

3. Theoretical details

We simulate the PES spectra according to the systematic procedure detailed in Ref. [7]. The energy scale associated to the raw results provided by the

INDO Hamiltonian (spectroscopic version developed by Zerner and co-workers [10]) is first compressed by a factor of 1.2–1.3, in order to compensate for the electron correlation effects neglected in Koopmans' approximation. The calculated spectrum is then rigidly shifted to lower binding energies to account for the impact of solid-state polarization effects. Finally, all spectra are convolved with Gaussian functions with the full-width at half-maximum (FWHM) adapted to the experimental linewidths (no photoionization cross-sections are included in the calculations). The inverse photoemission spectra are obtained by shifting the raw results to higher binding energies in order to match the energy of the lowest peak in the experimental spectrum and are also convolved with Gaussian functions. However, a compression of the energy scale is found not to be required to achieve a good match between the experimental and theoretical lineshapes. Though the origin of this difference is not easily understood, it is consistent with the fact that the INDO parameterization systematically gives the total width of the valence band larger than the width of the band built from the unoccupied levels. On the basis of the INDO results, the LCAO (linear combination of atomic orbitals) patterns of the HOMO and LUMO levels of the three compounds have been plotted with the graphical interface InsightII of Molecular Simulations [11].

The INDO simulations of the PES and IPES spectra of Alq₃ are based on the geometric structure of the meridional isomer, obtained using the local spin density approximation (LSDA) level of DFT and the Vosko–Wilk–Nusair (VWN) exchange-correlation potential, with a DNP (double numerical + polarization) basis set (see Ref. [6]); the three ligands of Alq₃ are hereafter labelled L1, L2 and L3 as in Ref. [5] and can be distinguished from the relative locations of the oxygen and nitrogen atoms along the vertices forming the distorted octahedron around the central aluminum atom [5]. The geometries of PTCDA and α -NPD are optimized with the semiempirical Hartree–Fock Austin Model 1 (AM1) method that has a good track record for reproducing the ground-state geometry of organic molecules [12]; note that the AM1 method has been shown to provide less reliable geometries in the case of organometallic compounds such as Alq₃ [5].

4. Results and discussion

The UPS and IPES spectra of the Alq₃ thin films are presented in Fig. 2 together with the corresponding INDO simulated spectra convolved with Gaussian functions; the LCAO pattern of the HOMO and LUMO levels are sketched in Fig. 5. A background based on the high kinetic energy part of the smooth secondary electron peak was removed from the UPS data, but similar treatment of the IPES data was not performed, given our lack of understanding of the overall shape of the IPES background. Nevertheless, the correspondence in the number and energy of individual measured and calculated features is excellent.

The gas phase ionization potential of the investigated organic compounds can be estimated within Koopmans' approximation as the absolute value of

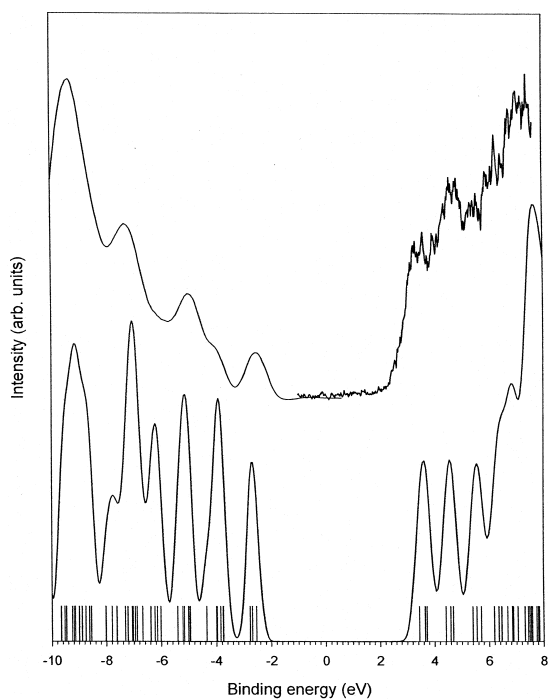


Fig. 2. Comparison between UPS and IPES spectra measured from an Alq₃ thin film (top) and INDO-simulated UPS and IPES spectra (bottom). The energy scale is referenced to the Fermi level. A compression factor of 1.2 is used to simulate the UPS spectrum and the FWHM is set to 0.5 eV prior to compression. The vertical bars at the bottom of the graph refer to the calculated energies of the molecular orbitals.

the INDO-calculated HOMO level energy; in the case of the 4,4'-bis-(*m*-tolylphenylamino)biphenyl (TPD) molecule, the INDO-calculated value (6.74 eV) is found to be in remarkable agreement with the experimental estimate (6.69 eV) [7]. The comparison with thin-film samples is more complicated, since the molecular levels are broadened by solid-state effects and disorder in the generally amorphous films. For the purpose of this comparison, we define the ionization energy of the thin-film samples as the energy difference between the vacuum level and the peak of the UPS HOMO, which corresponds to the average HOMO binding energy in the film. Additionally, the three highest occupied levels of Alq₃ (HOMO, HOMO-1, HOMO-2) are too closely spaced to be resolved in UPS, and result in a further broadened feature. We have therefore chosen to compare the mean position of these three levels in the calculated gas phase spectrum with the UPS peak position. Within this definition, the gas phase ionization potential of Alq₃ is estimated from the INDO levels to be 7.15 eV while accurate experimental measurements in the solid solid-state give values between 6.3 eV [4,13] and 6.5 eV [14]; the stabilization of the HOMO level induced by the solid-state polarization effects is thus estimated to be on the order of 0.8 eV, which is in the typical range of the polarization energies reported for organic solids [15].

The lowest binding energy peak in the INDO-simulated UPS spectrum of Alq₃ originates from the highest three molecular levels. These levels are non-degenerate and mostly localized on the phenoxide moiety of the ligands L3, L2 and L1, respectively, in order of decreasing energy. The lowest three bands in the calculated IPES spectrum find a one-to-one correspondence with clearly resolved features in the experimental spectrum; each of them originate from a triplet of π^* -molecular levels localized on a single ligand (L1, L2 and L3 in order of ascending energy). The wavefunction of the lowest three unoccupied levels is mainly distributed over the pyridyl moiety of the 8-quinolinolate ligand. The levels contributing to the highest three PES bands and the lowest four IPES bands possess vanishingly small weight on the central aluminum atom; the latter is thus expected to play a minor role in the transport and optical processes associated with Alq₃ layers. Noteworthy, the analysis of the one-electron structure of Alq₃ carried

out with the PM3 (Parameterized Method 3) Hamiltonian reveals a significant weight on the aluminum atom in the lowest three unoccupied levels [4]; this discrepancy can be attributed to the low reliability of the optimized geometry obtained for Alq₃ at the PM3 level [5].

The main characteristics of the one-electron structure of Alq₃ inferred from the INDO calculations are fully consistent with those derived from gradient-corrected density functional calculations (see Refs. [5] and [16] where a detailed description of the one-electron properties of Alq₃ are reported). However, we stress that it is of great interest to validate here the use of the INDO Hamiltonian, since optical properties can also be derived with this approach through coupling to a configuration interaction scheme; in contrast, DFT techniques still have limited access to the description of excited states in organic molecules.

We display in Fig. 3 the experimental and theoretical PES and IPES spectra obtained for α -NPD. The

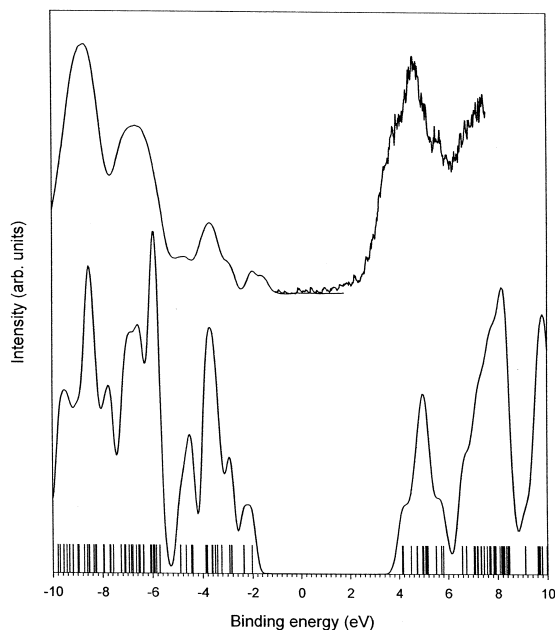


Fig. 3. Comparison between UPS and IPES spectra measured from α -NPD thin film (top) and INDO-simulated UPS and IPES spectra (bottom). The energy scale is referenced to the Fermi level. A compression factor of 1.3 is used to simulate the UPS spectrum and the FWHM is set to 0.5 eV prior to compression. The vertical bars at the bottom of the graph refer to the calculated energies of the molecular orbitals.

gas phase ionization potential calculated at the INDO level is 6.80 eV, i.e., very similar to that obtained for TPD (6.74 eV); the experimental value reported in the solid state is 5.6–5.9 eV (using the definition given above) [14,17–20], thus leading to an estimate of the solid-state polarization energy on the same order of magnitude as for Alq₃ (~ 1 eV). The theoretical results show that the HOMO level energy is not affected by the substitution of the tolyl groups by naphthyl groups when going from TPD to NPD. This can be understood by the fact that the HOMO level is mostly localized on the lone pairs of the nitrogen atoms and on the para carbon atoms of the two benzene rings in the biphenyl core (see Fig. 5); this is also supported by a PM3 study of the one-electron structure of the TPD molecule [4]. Noteworthy, the nitrogen atoms do not have a pure sp^2 character as a result of steric hindrance between the rings connecting them. The lowest binding energy peak in the UPS spectrum around ~ 2.0 eV actually originates from the highest two occupied levels; the HOMO-1 level is centered on the lone pairs of the nitrogen atoms. The following three peaks mainly result from π -molecular orbitals localized either on the naphthalene units or on the biphenyl core and the attached benzene rings. The absence of levels fully delocalized over the whole molecule is explained by the large torsion angles ($\sim 40^\circ$) calculated at the AM1 level between the planes of the conjugated moieties connected to the nitrogen atoms. The intense band with a pronounced shoulder on each side observed in the IPES spectrum is the signature of the lowest fourteen unoccupied levels of the α -NPD molecule. The shoulder on the low energy side mostly arises from the contribution of three levels; the almost degenerate LUMO and LUMO + 1 orbitals are mainly localized on the naphthalene units (Fig. 5) and the LUMO + 2 level, located 0.3 eV above, is delocalized over the biphenyl core. This contrasts with the situation in the TPD molecule whose LUMO level is mostly localized over the biphenyl, as also suggested by PM3 calculations [4].

We report in Fig. 4 the experimental PES and IPES spectra of PTCDA together with the INDO simulations. There is once again an overall good agreement between theory and experiment; however, we note that the peak calculated around -5 eV does not find any correspondence in the UPS experimen-

tal spectrum, which displays a minimum in that energy range. The HOMO level of PTCDA is well separated from the rest of the occupied molecular orbitals and is delocalized over the benzene rings and the oxygen atoms (see Fig. 5). The four levels giving rise to the second UPS band have a similar delocalization while the third broad band centered around -5 eV arises from contributions of the oxygen lone pairs; for the latter band, the lack of correspondence with the experimental spectrum might be inherent to the INDO parameterization. However, due to their very different origins, the two bands are expected to be affected to a different extent by solid-state polarization effects; as a result, another explanation to rationalize the discrepancy is that different shifts should be applied to the two bands in order to improve the matching between the experimental and theoretical lineshapes. The fourth

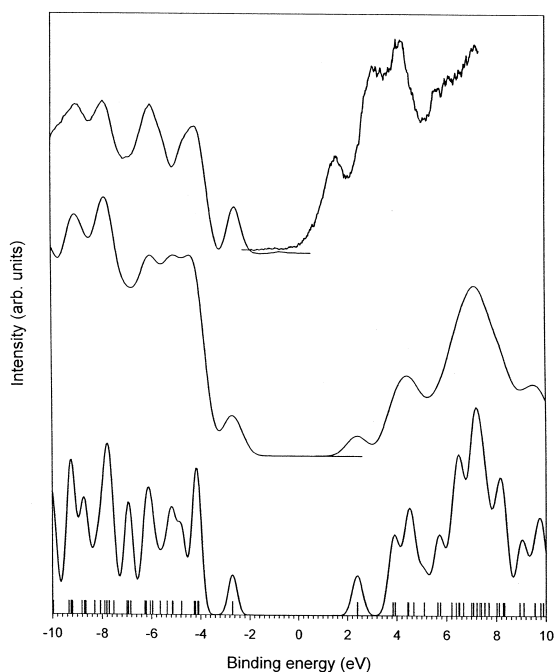


Fig. 4. Comparison between UPS and IPES spectra measured from a PTCDA thin film (top) and INDO-simulated UPS and IPES spectra (bottom). The energy scale is referenced to the Fermi level. A compression factor of 1.2 is used to simulate the UPS spectrum; the FWHM values are set to 0.5 and 1.0 eV prior to compression for the bottom and middle graphs, respectively. The vertical bars refer to the calculated energies of the molecular orbitals.

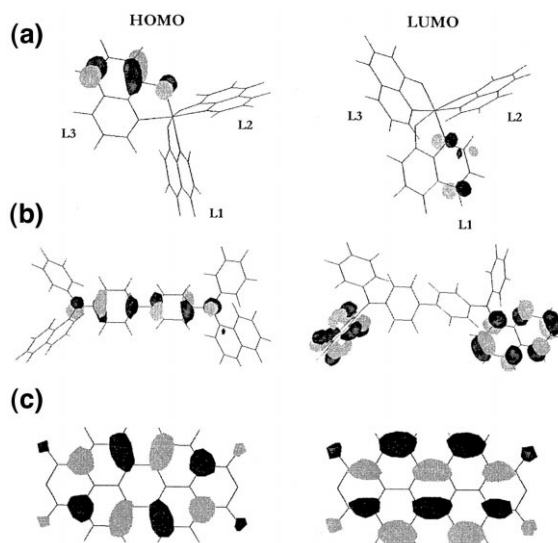


Fig. 5. LCAO patterns of the HOMO and LUMO levels, calculated at the INDO level, for Alq_3 (a), $\alpha\text{-NPD}$ (b), and PTCDA (c); the three ligands of Alq_3 have been labelled L1, L2 and L3 according to Ref. [5].

band localized around -6 eV shows the signature of the highest σ levels. Regarding the IPES spectrum, the calculations indicate that six unoccupied levels give rise to the lowest three bands that are clearly resolved in the spectrum; these levels have very different LCAO patterns but have in common a rather delocalized character, as illustrated for the LUMO level in Fig. 5. The gas phase ionization energy, estimated using the INDO-calculated HOMO energy, is 8.15 eV, while the experimental value is 7.1 eV (again, using the UPS peak position, as discussed above). The solid-state polarization energy is therefore ~ 1 eV, consistent with the other two materials, and previous studies [15].

5. Summary

We have shown that the simulated densities of occupied and, for the first time, unoccupied states of three π -conjugated molecules, obtained using the semiempirical Hartree–Fock intermediate neglect of differential overlap (INDO) method, are in excellent agreement with data obtained from thin films of

these molecules using UPS and IPES. The particularly good fit between theory and experiment in the low binding energy π and π^* parts of the spectra shows that a detailed description of the electronic structure which dominates the electronic properties of thin films of molecules can be achieved with this method.

Acknowledgements

Support of the work by the MRSEC program of the National Science Foundation (DMR-9809483) is gratefully acknowledged. One of the authors (I.H.) acknowledges support from the NRSEC of Canada. The work in Mons is supported by the Belgian Federal Government (Pôle d'Attraction Interuniversitaire en Chimie Supramoléculaire et Catalyse (PAI 4/11)) and the Belgian National Fund for Scientific Research (FNRS). J.C. is an FNRS Research Fellow.

References

- [1] J.L. Brédas, R.R. Chance, R.J. Silbey, G. Nicolas, Ph. Durrant, *J. Chem. Phys.* 75 (1981) 255.
- [2] M. Fahlman, M. Lögdlund, S. Stafström, W.R. Salaneck, R.H. Friend, P.L. Burn, A.B. Holmes, K. Kaeriyama, Y. Sonoda, O. Lhost, F. Meyers, J.L. Brédas, *Macromolecules* 28 (1995) 1959.
- [3] C.B. Duke, N.O. Lipari, W.R. Salaneck, L.B. Schein, *J. Chem. Phys.* 63 (1975) 1578.
- [4] K. Sugiyama, D. Yoshimura, T. Miyamae, T. Miyazaki, H. Ishii, Y. Ouchi, K. Seki, *J. Appl. Phys.* 83 (1998) 4928.
- [5] A. Curioni, M. Boero, W. Andreoni, *Chem. Phys. Lett.* 294 (1998) 263.
- [6] N. Johansson, T. Osada, S. Stafström, W.R. Salaneck, V. Parente, D.A. dos Santos, X. Crispin, J.L. Brédas, *J. Chem. Phys.* 111 (1999) 2157.
- [7] J. Cornil, S. Vanderdonckt, R. Lazzaroni, D.A. dos Santos, G. Thys, H.J. Geise, L.M. Yu, M. Szablewski, D. Bloor, M. Lögdlund, W.R. Salaneck, N.E. Gruhn, D.L. Lichtenberger, P.A. Lee, N.R. Armstrong, J.L. Brédas, *Chem. Mater.* 11 (1999) 2436.
- [8] J.D. Anderson, E.M. McDonald, P.A. Lee, M.L. Anderson, E.L. Ritchie, H.K. Hall, T. Hopkins, E.A. Mash, J. Wang, A. Padias, S. Thayumanavan, S. Barlow, S.R. Marder, G.E. Jabbour, S. Shaleen, B. Kippelen, N. Peyghambarian, R.M. Wightman, N.R. Armstrong, *J. Am. Chem. Soc.* 120 (1995) 9646.
- [9] C.I. Wu, Y. Hirose, H. Siringhaus, A. Kahn, *Chem. Phys. Lett.* 272 (1997) 43.
- [10] M.C. Zerner, G.H. Loew, R.F. Kichner, U.T. Mueller-Westhoff, *J. Am. Chem. Soc.* 102 (1980) 589.
- [11] InsightII User Guide, Molecular Simulations, 1996.
- [12] M.J.S. Dewar, E.G. Zebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* 107 (1985) 3902.
- [13] Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, *Jpn. J. Appl. Phys.* 32 (1993) L514, Part 2.
- [14] I.G. Hill, A. Rajagopal, A. Kahn, Y. Hu, *Appl. Phys. Lett.* 73 (1998) 662.
- [15] N. Sato, K. Seki, J. Inokuchi, *J. Chem. Soc., Faraday Trans. 2* 77 (1981) 1621.
- [16] A. Curioni, W. Andreoni, R. Treusch, F.J. Himpsel, E. Haskel, P. Seidler, C. Heske, S. Kaar, T. van Buuren, L.J. Terminello, *Appl. Phys. Lett.* 72 (1998) 1575.
- [17] C. Adachi, K. Nagai, N. Tamoto, *Appl. Phys. Lett.* 66 (1995) 2679.
- [18] H. Fujikawa, S. Tokito, Y. Taga, *Synth. Met.* 91 (1997) 161.
- [19] I.G. Hill, A. Kahn, *J. Appl. Phys.* 86 (1999) 2116.
- [20] A. Rajagopal, C.I. Wu, A. Kahn, *J. Appl. Phys.* 83 (1998) 2649.