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The Vibrational Reorganization Energy in Pentacene: Molecular Influences on Charge Transport

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Oligoacenes in general and pentacene in particular (see structure in Figure 1) are currently the object of much interest following a number of recent important discoveries by Batlogg and co-workers.[1−3] In this communication, our focus is on elucidating the origins of the large intrinsic carrier mobilities found in pentacene single crystals.[1]

In π-conjugated systems, a strong coupling exists between the geometric and electronic structures which control transport properties.[4] Charge injection or electronic excitation processes lead to geometry relaxations, which in turn modify the electronic structure.[5] In a transport regime corresponding to hopping, such as that often operational around room temperature in π-conjugated systems,[6] this coupling leads to a localization of the charge carriers on individual molecules for a sufficient time so that the nuclei can relax to the optimal geometry of the charged state.[7] At the microscopic level, the charge transport mechanism can then be described as involving a self-exchange electron transfer from a charged oligomer to an adjacent neutral oligomer.

In the context of semiclassical electron transfer theory and extensions thereof,[8] there are two major parameters that determine self-exchange electron-transfer rates and ultimately charge mobility: (i) the electronic coupling (transfer integral) between adjacent molecules, which needs to be maximized (we have recently shown the electronic couplings to be large for pentacene, leading to electron and hole bandwidths on the order of 0.5 eV[9]) and (ii) the reorganization energy λ, which needs to be small for efficient transport. The reorganization energy for self-exchange essentially corresponds to the sum of geometry relaxation energies upon going from the neutral-state geometry to the charged-state geometry and vice versa. These two portions of λ are typically nearly identical to one another.[10] We note that there have been recent attempts to design functionalized pentacenes to influence the solid-state order and electronic coupling.[11,12]

Here, we discuss the reorganization energy in pentacene on the basis of a joint experimental and theoretical study of pentacene ionization. We have carried out high-resolution gas-phase photoelectron spectroscopy (PES) measurements,[13] semiempirical INDO (intermediate neglect of differential overlap) calculations, and first-principles correlated quantum-mechanical calculations[14,15] at MP2 and density functional theory levels.

The vibrational (or inner-sphere) reorganization energy λ_v of a *single* molecule (with self-exchange $\lambda \approx 2\lambda_v$) can be determined by analysis of its gas-phase photoelectron spectrum.[16] Vibrational structure present in an ionization band can be analyzed to provide values of a distortion parameter (the Huang−Rhys factor, S) that is related to λ_v by:[16]

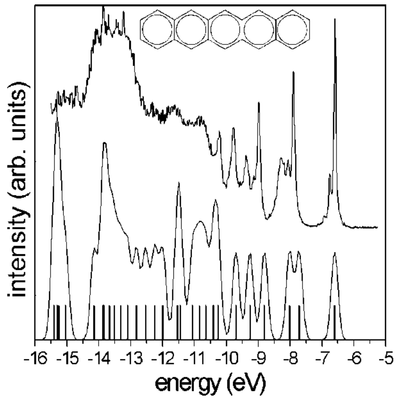

Figure 1. Gas-phase photoelectron spectrum of pentacene (top); INDO energy levels and corresponding simulated spectrum (bottom); the vertical bars refer to the calculated energies of the molecular orbitals.

$$\lambda_v = \sum_k S_k h\nu_k \tag{1}$$

where h is Planck's constant and ν_k is the vibrational frequency of the kth vibrational mode. The results of this type of analysis have recently been reported for other organic molecules[17] and for the ionization from a very localized metal−hydride σ bond.[18] λ_v can also be derived from other types of spectroscopy,[19−21] particularly resonance Raman,[22,23] or from the temperature dependence of electron-transfer rate constants.[24,25] Compared to these methods, PES has the benefit that separating λ_v from solvent reorganization energy is not necessary.

The gas-phase photoelectron spectrum of pentacene is shown in Figure 1 with the INDO simulated spectrum; the agreement between theory and experiment is remarkable; it provides for a detailed interpretation of the experimental peaks and lends support for our previous use of INDO to study oligoacenes.[9]

The first ionization corresponds to removal of an electron from the highest occupied ($3b_{2g}$) orbital. It is found to have a vertical and adiabatic ionization energy of 6.589 ± 0.001 eV and is well separated from the other ionizations of the molecule. The first ionization energy of pentacene has previously been reported as 6.64[26] and 6.74 eV.[27] Several ionizations contain partially resolved vibrational fine structure. A close-up of the first ionization that shows this structure in more detail is shown in Figure 2.

The data of Figure 2 has been deconvoluted using a series of asymmetric Gaussians[28] to allow quantitative analysis of this structure. The first ionization band clearly exhibits a high-frequency progression (ν_2) of 1347 ± 33 cm^{-1}. The frequency of ν_2 is in the

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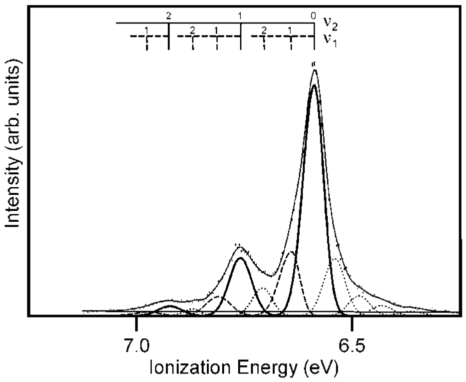

Figure 2. High-resolution close-up of the first ionization of pentacene.

region of the C−C stretching modes observed in the Raman spectrum of neutral pentacene.[29] The intensities of this progression resembles a Poisson distribution:

$$I_n = \frac{S^n}{n!}e^{-s} \tag{2}$$

where I_n is the intensity of the nth vibrational band. The best fit yields $S_2 = 0.251$. There is also contribution from one or more lower-frequency vibrations that accounts for about 30% of the integral intensity. This contribution can be modeled to fit the experimental data with a frequency progression (ν_1) of 483 ± 61 cm^{-1}. All the Gaussian peaks shown with light dotted lines in Figure 2 that are at lower ionization energy than the vertical ionization follow a Boltzmann distribution of intensities; they are attributed to hot bands resulting from the population of excited vibrational levels in the ground state of the molecule at the temperatures at which the data were collected (505 ± 5 K). The best fit to the harmonic model (eq 2) yields S_1 for ν_1 of 0.279, but the agreement is not as good as for the high-frequency progression. This value is most likely an upper limit estimate, since nonadiabatic contributions are also possible. The structure of the ionization manifold at higher energy than the vertical ionization is somewhat complicated by the fact that the vibrational progressions and hot bands of neighboring components partially overlap.

Analysis using eq 1 and the frequencies and S values listed above gives a contribution to λ_v from ν_2 of 0.042 ± 0.002 eV, and the structure modeled with ν_1 contributes 0.017 ± 0.002 eV. The total experimentally derived λ_v value for pentacene is then 0.059 ± 0.002 eV. For comparison, λ_v for other organic molecules measured in the same way[17] ranges from 0.158 ± 0.004 eV for dibenzo[a,c]-anthracene (which also contains five fused rings similar to pentacene) to 0.180 ± 0.005 eV for 1,10-phenanthroline (which contains three fused rings). The higher symmetry and resultant more delocalized nature of the orbital from which an electron is being removed from pentacene will lead to a lower λ_v.

The quantum-mechanical geometry optimizations at the B3LYP, BHandHLYP, and MP2 level (with 6-31G** or equivalent basis sets) provide consistent results. They indicate that the bond-length modifications on going from neutral to positively charged pentacene are on the order of 0.01 Å with maximum changes of at most 0.02 Å. The three methods provide λ_v energies of 0.049, 0.089, and 0.023 eV (both for relaxation of the cation state and for relaxation of the neutral state); these results bracket the experimental value, with the closest match obtained at the B3LYP level. We can compare the B3LYP reorganization energy calculated for pentacene to that calculated for an extensively exploited hole-transport material, TPD.[10] The pentacene result, $\lambda = (2 \times 0.049 =)\ 0.098$ eV, is three times as small as that for TPD, 0.29 eV.[10] Interestingly, the B3LYP λ values for the substituted pentacenes of refs 11−12 are about 50% higher than in pentacene itself.

Thus, the reorganization energy upon positive ionization of pentacene is determined both experimentally and theoretically to be remarkably low. This is an important element that, together with the large electronic couplings, allows one to rationalize the extremely high hole mobilities recently measured in pentacene.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Schön, J. H.; Berg, S.; Kloc, Ch.; Batlogg, B. *Science* **2000**, *287*, 1022.
(2) Schön, J. H.; Kloc, Ch.; Batlogg, B. *Nature* **2000**, *406*, 702.
(3) Schön, J. H. Kloc, Ch.; Dodabalapur, A.; Batlogg, B. *Science* **2000**, *289*, 599.
(4) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698; Brédas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 209.
(5) Brédas, J. L.; Cornil, J.; Beljonne, D.; dos Santos, D. A.; Shuai, Z. *Acc. Chem. Res.* **1999**, *32*, 267.
(6) Schön, J. H.; Kloc, Ch.; Batlogg, B. *Phys. Rev. Lett.* **2001**, *86*, 3843.
(7) Duke, C. B.; Schein, L. *Phys. Today* **1980**, *February*, 42.
(8) Marcus, R. A. *Rev. Mod. Phys.* **1993**, *65*, 599; Silbey, R.; Jortner, J.; Rice, S. A.; Vala, M. T. *J. Chem. Phys.* **1965**, *42*, 733.
(9) Cornil, J.; Calbert, J. Ph.; Brédas, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 1250; Brédas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J.; *Proc. Natl. Acad. Sci.* U.S.A. **2002**, *99*, 5804.
(10) Malagoli, M.; Brédas, J. L. *Chem. Phys. Lett.* **2000**, *327*, 13.
(11) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.
(12) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15.
(13) See Supporting Information for experimental details.
(14) The UPS spectrum is simulated on the basis of INDO calculations according to the procedure detailed in Cornil, J. et al. *Chem. Mater.* **1999**, *11*, 2436; the theoretical energy scale is here compressed by a factor of 1.2. To estimate the reorganization energy, we have followed the methodology of ref 10.
(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(16) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.
(17) Amashukeli, X.; Winkler, J.; Gray, H.; Gruhn, N. E.; Lichtenberger, D. L. *J. Phys. Chem. B* **2002**. In press.
(18) Lichtenberger, D. L.; Gruhn, N. E.; Rai-Chaudhuri, A.; Renshaw, S. K.; Gladysz, J. A.; Jiao, H.; Seyler, J.; Igau, A. *J. Am. Chem. Soc.* **2002**, *124*, 1417.
(19) Cornil, J.; Deljonne, D.; Heller, C. M.; Campbell, I. H.; Laurich, B. K.; Smith, D. L.; Bradler, D. D. C.; Mullen, K.; Bredas, J. L. *Chem. Phys. Lett.* **1997**, *278*, 139.
(20) Gamelin, D. R.; Randall, D. W.; Hay, M. T.; Houser, R. P.; Mulder, T. C.; Canters, G. W.; de Vries, S.; Tolman, W. B.; Lu, Y.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 5246.
(21) Nelsen, S. F.; Trieber, D. A., II; Ismagilov, R. F.; Teki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 5684.
(22) Kelley, A. M. *J. Phys. Chem. A* **1999**, *103*, 6891.
(23) Hupp, J. T.; Williams, R. D. *Acc. Chem. Res.* **2001**, *34*, 808.
(24) Di Bilio, A. J.; Hill, M. G.; Bonander, N.; Karlsson, B. G.; Villahermosa, R. M.; Malmstrom, B. G.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 9921.
(25) Kobori, Y.; Yago, T.; Akiyama, K.; Tero-Kubota, S. *J. Am. Chem. Soc.* **2001**, *123*, 9722.
(26) Clark, P. A.; Brogli, F.; Heilbronner, E. *Helv. Chim. Acta* **1972**, *55*, 1415.
(27) Boschi, R.; Murrell, J. N.; Schmidt, W. *Discuss. Faraday Soc.* **1972**, *54*.
(28) Lichtenberger, D. L.; Copenhaver, A. S. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *50*, 335.
(29) Colangi, L.; Mennella, V.; Baratta, G. A.; Bussoletti, E.; Strazzulla, G. *Astrophys. J.* **1992**, *396*, 369.

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