Figure 3. Schematic diagram illustrating the shift in the Fermi level (E_f) and corresponding increase in C 1s binding energy (BE) due to charge transfer doping of C_{60} by Cs.

is well-documented.[15] Although it will be important to confirm the Fermi level shifts in alkali-metal-doped C_{60}, our results clearly support the idea that these films exhibit delocalized energy bands that can be doped.[7a]

Lastly, it is also interesting to compare the relative C 1s binding energy shifts at saturation coverage for Cs-doped C_{60} and graphite. In the $Cs_{7.2}C_{60}$ film there is a 1.1-eV shift while at a similar Cs

concentration the shift for Cs-GIC is 0.6 eV. Within the context of the simple charge-transfer doping model discussed above, the greater shift in C_{60} indicates that the density of electronic states near the Fermi level may be significantly lower in C_{60} than in graphite.

Conclusions

In summary, we have used XPS to characterize in situ the changes in C 1s binding energy of C_{60} films upon Cs doping. We showed that increasing Cs coverage results in an increase in the C 1s binding energy and that subsequent oxidation yields a binding energy characteristic of undoped C_{60} films. Similar studies carried out on Cs-intercalated graphite, which also show an increase in C 1s binding energy, demonstrate that Cs doping causes strikingly similar changes in these two carbon-based materials. The C 1s binding energy shifts are consistent with Cs charge donation to a C_{60} (or graphite) energy band that results in an increase in the Fermi level position. Hence, our results further confirm the idea that thin-film C_{60} has the well-developed energy bands characteristic of a delocalized solid.

(15) Dresselhaus, M. S.; Dresselhaus, G. *Adv. Phys.* **1981**, *30*, 139.

Solvent Effects on the Adiabatic Free Energy Difference between the Ground and Excited States of Methylindole in Water

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Molecular dynamics simulations have been used to compute the adiabatic free energy difference between the electronic ground and ^1L_a excited states of 3-methylindole in water. Partial atomic charges for the two electronic states were derived from fits to the (gas phase) quantum mechanical electrostatic potentials produced by semiempirical INDO/S wave functions. The computed solvent reorganization energy ($\sim$3 kcal/mol) is smaller than values deduced from experimental spectroscopic data for various indole derivatives in polar solvents (4-12 kcal/mol). The solvent reorganization energy computed from the simulations is close to the value estimated from the Onsager dipole cavity reaction field model when a previously suggested, but ad hoc, molecular volume parameter is used with the model. However, this model is shown to generally not approximate reaction field energies well for a large planar molecule like indole, since it does not distinguish among different charge distributions which produce the same change in the magnitude of the chromophore dipole moment but very different reaction fields. Additional free energy simulations are carried out to demonstrate this point. In contrast, a recently proposed molecular dielectric model, which explicitly incorporates the effects of the solute structure and charge on the solvent dielectric response, is found to agree with the simulated free energy changes to within a few percent.

Analysis of medium effects on optical absorption and emission bands of indole and its derivatives continues to receive considerable attention.[1-8] Reasons for this interest include the following: indole is the chromophore of the amino acid tryptophan and is of basic importance for optical studies of proteins; the near-ultraviolet absorption and emission spectra of indole are extremely sensitive to solvent interactions and the solvent-induced Stokes shifts provide

information about the excited-state energetics and charge-transfer dynamics; indole is used as a model system for studying electronic structure aspects of two energetically proximal, low-lying (π, π^*) excited states (^1L_a, ^1L_b). The ^1L_a state has a considerably larger dipole moment than the ^1L_b state and is the lower excited state in polar solvent.[3,4] From a theoretical perspective, the development of models for interpreting optical experiments on indoles in solution has two principal components: (1) modeling the ground- and excited-state charge distributions of the chromophore, and (2) modeling the solvent reaction fields induced by these charge distributions. The Onsager dipole cavity reaction field model has often been used to estimate the energetic effects of solvation, including the analysis of optical spectra.[9-11] This is a continuum solvent model. While recent molecular dynamics free energy

(1) Beecham, J. R.; Brand, L. *Annu. Rev. Biochem.* **1985**, *54*, 43.
(2) Eftink, M. R.; Selvidge, L. A.; Callis, P. R.; Rehms, A. A. *J. Phys. Chem.* **1990**, *94*, 3469.
(3) Rehms, A. A.; Callis, P. R. *Chem. Phys. Lett.* **1987**, *140*, 83.
(4) Lami, H.; Glasser, N. *J. Chem. Phys.* **1986**, *84*, 597.
(5) Lakowicz, J. R.; Szmacinski, H.; Gryczynski, I. *Photochem. Photobiol.* **1988**, *47*, 31.
(6) Ilich, P.; Haydock, C.; Prendergast, F. G. *Chem. Phys. Lett.* **1989**, *158*, 129.
(7) Ludescher, R.; Johnson, I.; Volwerk, J.; deHaas, G.; Jost, P.; Hudson, B. *Biochemistry* **1988**, *27*, 6618.
(8) Petrich, J. W.; Longworth, J. W.; Fleming, G. R. *Biochemistry* **1987**, *26*, 2711.

(9) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
(10) McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562.
(11) Birks, J. B. *Photophysics of Aromatic Molecules*; John Wiley: New York, 1970.
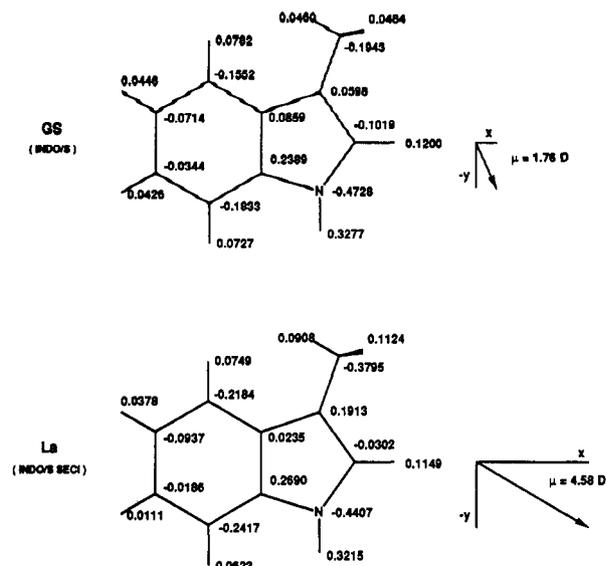
Figure 1. Partial atomic charges for the 3-methylindole electronic ground (GS) and excited (^1L_a) states used in the simulations. The classical charges were fit to quantum mechanical electrostatic potentials generated from INDO/S wave functions (Hartree–Fock for GS, full singly excited configuration interaction for ^1L_a) with the ESPPAC program.[33] Dipole moment magnitudes and directions are shown for each state.

simulations with explicit molecular solvent have verified the accuracy of the formula for small spherical solutes with an embedded point dipole,[12] the formula is often applied to interpret the spectra of large, planar organic molecules like indole where its validity is more problematic. We have used simulations to further explore this problem.

The adiabatic free energy difference between the ground and ^1L_a excited states of indole in water includes the reorganization energy of the solvent following the optical excitation. The solvent contribution to the adiabatic free energy change can be approximated experimentally as the difference between absorption and fluorescence Stokes shifts in nonpolar solvents versus water.[11] In this Letter we report the results of molecular dynamics simulations of the adiabatic free energy difference between the ground and ^1L_a excited states of 3-methylindole in water. Although a few reports of molecular dynamics simulations of optical transitions of chromophores in solution have appeared,[13–15] most studies have made use of idealized solutes (e.g., one or two point charges embedded in a sphere).[16–19] The present work applies free energy simulation methods to the problem of solvent effects on the electronic excitation of a large, planar chromophore in a liquid. We compare the adiabatic free energy change calculated from the free energy simulations of indole in water with experiment and with the predictions of two dielectric models for the solvent response: (1) the classic dipole cavity reaction field model, and (2) a newly proposed molecular dielectric function model.[20]

Within the molecular mechanics framework used in simulations, the crucial quantity which induces the solvent reaction field is the distribution of partial atomic charges on the chromophore. We have derived partial atomic charges for the ground and ^1L_a states
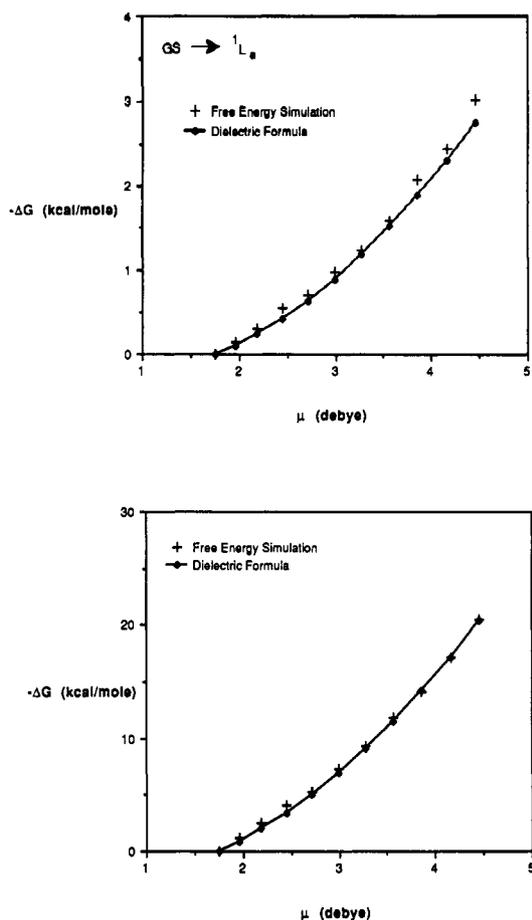

Figure 2. All simulations were performed with the IMPACT program package[34] at constant temperature and pressure (298 K and 1 atm) with periodic boundary conditions. The simulations included 1 solute molecule (3-methylindole) and 394 SPC[36] water molecules. The free energy simulations were performed using 10 windows (2-ps simulation in each window) to scale the partial charges on the chromophore from the initial to the final states. Starting from the ground-state charge distribution of 3-methylindole (see Figure 1, top), the charges were scaled linearly in each window. In Figure 2, top, the final state corresponds to the charge distribution of the ^1L_a excited state (see Figure 1, bottom). In Figure 2, bottom, the final state is obtained by linearly scaling up the ground-state charges until the dipole moment magnitude $\mu = 4.58$ D is reached. In Figure 2, top and bottom, (+) corresponds to the free energy perturbation result. The results of the free energy simulations are compared with the molecular dielectric formula (– ● –; see text, eq 2). The parameters for the molecular dielectric function formula ($\bar{V}_i$, and $\langle \Delta V_i \Delta V_j \rangle$), were calculated from a 30-ps simulation of 3-methylindole (ground-state charge distribution) in water.

of 3-methylindole using classical electrostatic potential fits to the quantum mechanical electrostatic potential given by the semi-empirical INDO/S procedure.[21] A detailed analysis of the electrostatic potentials and partial charges for 3-methylindole using various electronic structure methods and correlated wave functions will be presented elsewhere.[22] The INDO/S partial charges and dipole moments are presented in Figure 1. The computed dipole moment increases from 1.76 D (ground state) to 4.58 D (^1L_a state), in general agreement with experimental estimates.[23] The changes in the partial charges are delocalized over the chromophore; the largest changes occur at and around the methyl group, leading to a rotation of the direction of the excited-state dipole moment relative to the ground state. The solvent reorganization energy associated with the charge rearrangement on methylindole can

(12) Alper, H. A.; Levy, R. M. *J. Phys. Chem.* **1990**, *94*, 8401.
(13) Ohmine, I. *J. Chem. Phys.* **1986**, *85*, 3342.
(14) (a) Blair, J. T.; Krogh-Jespersen, K.; Levy, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 6948. (b) Levy, R. M.; Kitchen, D. B.; Blair, J. T.; Krogh-Jespersen, K. *J. Phys. Chem.* **1990**, *94*, 4470. (c) Belhadj, M.; Kitchen, D. B.; Krogh-Jespersen, K.; Levy, R. M. *J. Phys. Chem.* **1991**, *95*, 1082.
(15) DeBolt, S.; Kollman, P. *J. Am. Chem. Soc.* **1990**, *112*, 7515.
(16) Herman, M.; Berne, B. *J. Chem. Phys.* **1983**, *73*, 4103.
(17) Karim, O.; Haymet, A. D.; Banet, M. J.; Simon, J. D. *J. Phys. Chem.* **1988**, *92*, 3391.
(18) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 5044.
(19) Carter, E. A.; Hynes, J. T. Solvation Dynamics for an Ion Pair in a Polar Solvent: Time Dependent Fluorescence and Photochemical Charge Transfer. *J. Chem. Phys.*, in press.
(20) Levy, R. M.; Belhadj, M.; Kitchen, D. B. Gaussian Fluctuation Formula for Electrostatic Free Energy Changes in Solution. *J. Chem. Phys.*, in press.

(21) Culberson, J. C.; Zerner, M. C. *Chem. Phys. Lett.* **1985**, *122*, 436.
(22) Westbrook, J. D.; Levy, R. M.; Krogh-Jespersen, K. Electrostatic Potentials and Partial Atomic Charges from Correlated Wavefunctions. To be submitted for publication.
(23) (a) Sun, M.; Song, P. S. *Photochem. Photobiol.* **1977**, *25*, 3. (b) Meech, S. R.; Phillips, D.; Lee, A. G. *Chem. Phys.* **1983**, *80*, 317.

be extracted from free energy simulations[24] along pathways in which the Hamiltonian is perturbed from the initial ground-state model of the chromophore interacting with solvent to the final excited-state chromophore interacting with solvent.[15] The results of free energy simulations are shown in Figure 2, top (see the figure legend for details of the simulations). The solvent reorganization energy is plotted as a function of the change in the solute dipole moment. The calculated solvent reorganization energy is $\sim$3.0 kcal/mol (Figure 1). For comparison, the experimentally observed values for the solvent shifts ($\Delta\nu_{max}$(absorption) – $\Delta\nu_{max}$(fluorescence)) of indole in polar solvents relative to hexane are, e.g., 4.6 kcal/mol in acetonitrile and 5.7 kcal/mol in ethanol.[23a] Considerably larger values have been reported for the spectroscopic shifts of 3-methylindole in polar solvents relative to cyclohexane (8.5 kcal/mol in acetonitrile; 9.1 kcal/mol in butanol).[23b] Interestingly, the solvent shift of indole in water appears to be anomalously large (12.1 kcal/mol); this has been attributed to specific solute–solvent interactions, e.g., exciplex formation.[25] The quantitative discrepancy between theory and experiment suggests two problems which we are pursuing. First, we have omitted the effects of electronic polarization of the chromophore by the solvent on the charge distribution of the chromophore; our experience[14a] suggests that including this effect will lead to an even more polar excited state relative to the ground state and a larger free energy difference between the two surfaces, as suggested by the experimental spectroscopic results. Second, it will be interesting to repeat these free energy simulations in nonaqueous polar solutions in order to further address the question of the apparent "anomalous" behavior of water.

We have used the free energy simulations of methylindole in water to examine two reaction field models. The simplest model that has long been used to interpret solvent effects on absorption spectra is the Onsager dipole cavity reaction field model.[9–11] In this model, the solvent reorganization term ΔG depends on the square of the change in the dipole moment $(\Delta\mu)^2$, a molecular volume parameter a^3, and the static and optical frequency dielectric constants (ϵ, ϵ_∞):

$$\Delta G = \frac{2(\Delta\mu)^2}{a^3}\left[\frac{\epsilon - 1}{2\epsilon + 1} - \frac{\epsilon_\infty - 1}{2\epsilon_\infty + 1}\right] \qquad (1)$$

Choosing $\Delta\mu \sim 3$ D, a reasonable, but ad hoc, value for the cavity radius used by others ($\sim$3.4 Å),[4,23a] and dielectric parameters appropriate to the SPC water model[26] used in the simulations ($\epsilon = 70$, $\epsilon_\infty = 1$),[27] eq 1 predicts a solvent shift for indoles of about 3.3 kcal/mol, which is close to the simulation results. Since eq 1 is often used to extract excited-state dipole moments from optical experiments, we were particularly interested in whether the changes in reaction field energies of large planar molecules like indoles scale with changes in the magnitude of the dipole moment in the simple way suggested by eq 1. Therefore, to further test the model we have carried out additional free energy simulations in which we linearly scaled up the charges on indole from their ground-state values until we reached a state with the same dipole moment magnitude as the true excited state (4.6 D) but with a significantly different detailed charge distribution. The results are shown in Figure 2, bottom. The calculated adiabatic free energy gap for this hypothetical process is more than 20 kcal/mol;

i.e., the solvent reorganization energy is much larger than that induced by the "true" charge redistribution estimated by using the excited-state INDO/S partial charges ($\sim$3 kcal/mol). More importantly, the reaction field energies are clearly not well approximated by a dipole cavity formula (eq 1), since the two charging processes have the same initial and final dipole moment magnitudes but very different changes in the reaction field energy. The solvent is apparently sensitive to the higher order multipoles generated by the indole ground- and excited-state charge distributions which do not enter in the dipole cavity model. These results also imply that incorporating solvent effects directly within electronic structure codes by adding a dipole cavity term to the Hamiltonian may not be a good procedure to follow for large planar molecules.[28] It may be possible to model solvent effects on optical spectra of chromophores like indole by solving the Poisson equation numerically using a detailed charge distribution for the chromophore—this kind of continuum solvent modeling is currently being extensively applied to analyze ground state properties.[29–32] An alternative approach which treats the solvent as explicitly molecular is described below.

We have constructed a molecular dielectric function for the combined chromophore–solvent system based on linear response theory, which can be used to model solvent effects on spectra.[20] The solvent contribution to the adiabatic free energy change ΔG between the ground and excited states of a chromophore is given by the following dielectric formula:

$$\Delta G = \sum_i \bar{V}_i \Delta q_i - \frac{\beta}{2}\sum_{i,j}\langle \Delta V_i \Delta V_j \rangle \Delta q_i \Delta q_j \qquad (2)$$

The partial charges of the chromophore at the ith atom in the ground (q^g_i) and excited (q^e_i) states are included ($\Delta q_i = q^e_i - q^g_i$), and $\beta = 1/k_BT$. The formula also contains the average electrostatic potential from the solvent at the atomic centers of the chromophore $\bar{V}_i$ as well as the correlation functions for the joint fluctuations in the solvent electrostatic potential at chromophore sites i and j, $\langle \Delta V_i \Delta V_j \rangle$. These averages can be extracted from simulations of a reference system, for example, simulations of ground-state methylindole in water. In Figure 2 (top and bottom) we compare the predictions of the molecular dielectric formula (eq 2) with the results of explicit free energy simulations. The predicted changes in the solvent polarization energy obtained by the two methods—molecular dielectric function versus explicit charging of the chromophore—agree to within a few percent. Given the accuracy of the molecular dielectric formula for predicting solvent reorganization energies, we expect that it will prove very useful in relating the detailed changes in the charge distributions which occur upon excitation of a chromophore to solvent effects on spectra, and more generally to charge-transfer processes in solution.

(24) (a) Beveridge, D. L.; DiCapua, F. M. *Annu. Rev. Biophys. Biophys. Chem.* **1989**, *18*, 431. (b) Jorgensen, W. L. *Acc. Chem. Res.* **1989**, *22*, 184.
(25) Walker, M. S. T.; Bednar, T. W.; Lumry, R. W. *J. Chem. Phys.* **1967**, *47*, 1020.
(26) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; Hermans, J. In *Intermolecular Forces*; Pullman, B., Ed.; Reidel: Dordrecht, Holland, 1981; p 331.
(27) Alper, H. A.; Levy, R. M. *J. Chem. Phys.* **1989**, *91*, 1242.

(28) Karelson, M.; Tamm, T.; Katritzky, A.; Szafran, M.; Zerner, M. *Int. J. Quantum Chem.* **1990**, *37*, 1.
(29) Gilson, M. K.; Honig, B. H. *Nature* **1987**, *330*, 84.
(30) Rashin, A.; Namboodiri, K. *J. Phys. Chem.* **1987**, *91*, 6003.
(31) Bonaccorsi, R.; Cimiraglia, R.; Tomasi, J. *J. Comput. Chem.* **1983**, *4*, 567.
(32) Grant, J. A.; Williams, R. C.; Scheraga, H. A. *Biopolymers* **1990**, *30*, 929.
(33) Westbrook, J. D.; Krogh-Jespersen, K. ESPPAC, a semiempirical electronic structure program for the calculation of excited-state properties, Rutgers University, 1989.
(34) Kitchen, D. B.; Hirata, F.; Westbrook, J. D.; Levy, R. M.; Kofke, D.; Yarmush, M. *J. Comput. Chem.* **1990**, *11*, 1169.