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SIMULATIONS OF ROTATIONAL DYNAMICS AND ELECTRONIC SPECTROSCOPY IN SUPERCRITICAL FLUIDS

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By

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ABSTRACT

Molecular dynamics simulations of diphenylbutadiene (DPB) and hydroxymethylstilbene (HMS) in supercritical CO₂ were performed in order to understand the role of solute-solvent interactions in determining solvation structure and rotational dynamics in supercritical solvents. A characteristic feature of solvation in supercritical solvents is the buildup of solvent density in the neighborhood of the solute – a phenomenon known as local density augmentation. Effects of density augmentation can be found in many solute-centered observables such as electronic spectral shifts and solvent-induced friction. Experimental measures of local densities derived from absorption shifts were compared to simulated shifts based on two simple models. Although neither accurately reproduced the magnitude of the absorption shifts measured in experiment, the density dependence of the simulated shifts was close to experiment. The augmentation deduced from these experimental data was close to the found in simulation. The simulations slightly underestimated the extent of density augmentation seen in experiment, following the pattern observed in prior studies. Following the examination of the solvation structure, the rotational dynamics of both solutes were analyzed and compared with two experimental studies performed by different researchers. Whereas both sets of experimental data showed a linear relationship between the rotation times of DPB and the bulk density, the data sets reported quantitatively different density dependent behaviors of the HMS rotation times. Succinctly, although both data sets implied that the rotation times of DPB

were ignorant of the local density augmentation, they didn't agree on whether or not the same was true for HMS. In order to try to understand these differences, the rotational friction was examined in simulation, as it characterizes the observed rotation times. Surprisingly, it was found that integral friction was linear in the bulk density, and therefore, was ignorant of the local density augmentation. However, a subsequent detailed examination of the time-dependent rotational friction in simulation showed why this is the case.

In order to obtain more quantitative agreement between simulated and experimental spectral shifts, simulation studies of anthracene in a series of representative liquid solvents were performed. Anthracene was chosen as it represents a simple case, where the solute-solvent interactions are dominated by dispersion interactions. As a result, the excited state intramolecular potential energy surface of the solute was model with a modified version of the ground state surface. In the excited state, the well-depths and sizes of the solute carbon atoms were scaled. Using this approach, the absorption shifts and widths of anthracene in the various solvents showed agreement to within 20% of experimental measurements. In addition, when pressure dependent simulations of anthracene in n-hexane were performed, the spectral shift model also showed good agreement with experimental absorption shifts and widths. When anthracene was simulated in the excited state, the resulting emission shifts calculated in simulation also showed good agreement with experiment. Unfortunately, the simulated emission widths agreed with experiment to no better than 30%. It was concluded that this relatively large error in the emission

widths was due to the functional form (Lennard-Jones) used to model the excited state. To address this result, several variations of the simulation shift model were adopted but failed to yield significantly improved correlations with experiment. Nevertheless, it was concluded that the spectral shift model used in simulation provided a useful prediction of experimental measurements.

The final study applied the spectral shift model optimized for anthracene in liquid solvents to simulations of anthracene in supercritical CO_2 and ethane. Simulated spectral shifts and widths were generally found to agree with experiment to within uncertainties. In addition, the augmentation derived from the simulation spectral shift calculations displayed modest agreement with experiment in ethane. On the other hand, the simulated shifts underestimated augmentation derived from experiment in CO_2 . The source of this discrepancy is not yet understood.

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Chapter 1

Introduction

It is a daunting task to try to imagine a world without solvents. From the most mundane industrial processes to the vital biochemical reactions that support life, solvents facilitate a variety of chemical processes, which would otherwise not be possible. In recent years, a special class of solvents, known as supercritical fluids, has been increasingly used in a host of industrial applications¹⁻³. This pervasiveness is due to the fact that the solvent properties of supercritical fluids are highly tunable⁴. Namely, above the critical temperature, the solvent can be continuously changed from a gas-like to a liquid-like state with only modest changes in pressure. In addition, because solvents, like CO₂, are environmentally benign and have critical temperatures close to room temperature, disposal and handling of these solvents is neither expensive nor hazardous. Therefore, it is easily understandable why supercritical fluids have been a boon to large-scale chemical processes.

Along side their remarkable macroscopic properties, supercritical fluids have a host of unique microscopic properties as well. Specifically, in region of the critical point, the solvent density around the solute is enhanced relative to the bulk density. This inhomogeneity produced by the solute is known as local density augmentation⁴, and can be viewed as a clustering effect. Because the local environment about the solute differs from the bulk, the solute's behavior is not that expected based on bulk solvent properties. It is precisely these phenomenona, namely local density augmentation and its coupling to solute energetics and dynamics, which is investigated in this thesis.

Chapter 2 contains a detailed study of diphenylbutadiene (DPB) and hydroxymethylstilbene (HMS) in supercritical CO₂. Choice of these systems was motivated by early measurements of rotational times by Anderton and Kauffman⁵. These authors found qualitatively different density dependences of the rotational times of these two solutes. In contrast, Biswas *et al.*⁶ have also measured rotation times of DPB and HMS in CO₂ and have found comparable rotation times at all densities. The simulation studies found in Chapter 2 help to decide on the correct experimental picture, as well as discern what role solute-solvent interactions play in the solvent distribution and solute rotational dynamics. In addition, because simulation gives insight into the microscopic mechanisms of rotational friction and how they give rise to the rotational behavior of the solutes, a deeper understanding of molecular rotations in supercritical solvents is achieved.

Most of what is known about solvation in supercritical fluids comes from spectroscopic measurements, and in particular data on electronic spectral shifts. Therefore, the ability of simulation to predict experimental spectral shifts is crucial to determining the accuracy of simulations. The problem, however, is that a rigorous computational treatment of these spectral shifts is unfeasible at the present time. As a result, approximate methods for calculating these shifts are indispensable. In Chapter 3, absorption and emission shifts of anthracene in various solvents are collected using MD simulations. The general approach taken is to model the difference between the ground and excited states of anthracene in terms of a simple change in the Lennard-Jones potentials⁷⁻¹⁰ specifying its interaction with its solvent surroundings. More specifically, the excited state well-depths and atomic sizes of the carbon atoms of anthracene are scaled. These scaling factors are determined by optimization over the various solvents to get the best agreement between simulated and experimentally measured shifts and widths. In Chapter 3, the applicability of such an approach, using the same scaling factors for all solvents, is investigated and the general behavior of the spectroscopic model is discussed.

Finally, Chapter 4 extends the spectroscopic approach laid out in Chapter 3 to supercritical systems. In particular, simulations of anthracene in CO_2 and ethane are performed, and the scaling parameters determined in Chapter 2 are used to predict absorption and emission shifts and widths of anthracene in these two solvents. In addition, Chapter 4 also discusses the differences between local density augmentation predicted by theses spectroscopic calculations and how they relation to the augmentation seen by the coordination number of the 1st solvation shell.

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Chapter 2

Solvation and Friction in Supercritical Fluids: Simulation-Experiment Comparison in Diphenyl Polyene/CO₂ Systems

I. Introduction

Over the past two decades, supercritical fluids have been increasingly used in a variety of industrial processes such as extractions and separations. They have also been used as a tool to understand and facilitate chemical reactions¹⁻³. Their almost ubiquitous presence may be attributed to their highly tunable properties as solvents. Above the critical temperature, the properties of supercritical fluids can be continuously changed from gas-like to liquid-like values with modest changes in pressure. In addition to their varied macroscopic characteristics, the microscopic distribution of solvent molecules in the near critical region has also been of considerable interest. In this region of the phase diagram, the distribution of solvent molecules is found to be inhomogeneous; the solvent tends to form regions of enhanced density that may be loosely described as solvent clustering^{4,5}. It is precisely this phenomenon, as well as its coupling to dynamic observables, that is of interest in the present thesis.

This present chapter focuses on the static and dynamic behavior of diphenylbutadiene (DPB) and hydroxymethylstilbene (HMS) in CO₂, and is based

upon previously published work[Patel, 2002 #6021]. In particular, the solvation structure and rotational behavior of these solutes are characterized. These particular systems were chosen for several reasons. First, and most importantly, Anderton and co-workers have experimentally determined rotation times for DPB and HMS in CO₂ as well as in a number of other liquid solvents⁶⁻⁸. Secondly, as noted by Anderton and Kauffman, these solutes have very similar mechanical properties; *i.e.* they have comparable dimensions and moments of inertia. The main difference between DPB and HMS is in their electrical characteristics. DPB has no dipole moment whereas the dipole moment of HMS is about 2.9 D⁷. As a result, differences in the observed solvation structure and rotational behavior may be attributed to differences in the electrical properties of these two solutes. Therefore, the contribution of solute-solvent electrical interactions in the compressible region of CO₂ can be evaluated on a microscopic basis by simulation.

Of particular interest is the coupling of the solvation structure to the rotational dynamics of DPB and HMS in CO₂. Through their measurements of rotation times, Anderton and Kauffman concluded that DPB does not induce any solvent clustering. However, owing to hydrogen bonding between HMS and CO₂, the authors conclude that solvent clustering is indeed present, and substantial, in the HMS/CO₂ system. These conclusions are based on the degree of non-linearity of the rotation times on the bulk density; the measured rotation times of DPB are not inconsistent with a linear density dependence, whereas the measured HMS rotation times by these authors are highly non-linear. In light of the fact that local density augmentation is

seen about solutes similar to DPB in a wide variety of solvents⁹, these conclusions are not anticipated. As a result, a large part of the current work is devoted to investigating local solvent structure. By understanding the solvent distribution and energetics around the solute, the connection between solvation and solute dynamics becomes more transparent. In order to get a quantitative handle on this coupling, the solvent friction is also investigated as it provides a numerical as well as a conceptual characterization of the rotational environment of the solute.

Biswas *et al.*¹⁰ also measured rotation times of DPB and HMS in CO₂. These authors reported rotation times in DPB and HMS that are not inconsistent with a linear density dependence. More importantly, though, the rotation times of Biswas *et al.* are similar for both DPB and HMS, in contrast to the reported rotation times of Anderton and Kauffman. It should be noted that the experimental work of Biswas *et al.* was completed after the work presented in this thesis. Nevertheless, these results place even more emphasis on the need to understand how the solvation structure affects the rotation times in the supercritical region.

The remainder of this chapter is divided into 5 sections. Section II covers the theoretical background. Here, the various calculations performed in simulation are motivated and described. In addition, some general discussion involving the phenomenon of local density enhancement in supercritical fluids is also provided. Section III presents special considerations when performing supercritical simulations. In general, near the critical density, solvent-solvent spatial correlations extend over large distances and there is also an associated slowing down of the dynamics. This

effect is considered in the context of precautions needed to ensure realistic simulation results. Section III also presents calculations of the shear viscosities and selfdiffusion constants of neat CO₂ used to test the suitability of the solvent model employed here. The model was parameterized to reproduce the co-existence curve for the pure liquid, and therefore, a gauge on the dynamic predictions of the solvent model is needed. The parameterizations of the solute models are given in Section IV. Both DPB and HMS have several conformations close, in energy, to the global minimum of the intramolecular potential energy surface. These conformations are discussed in relation to their effects on the solute dynamics as well as their effects on the solute-solvent energetics. Also in Section IV are the results of convergence and ensemble testing of the simulations. The microcanonical ensemble was chosen for these simulations. However, the effects of using a different thermodynamic ensemble are also investigated. The solvation structure results of the simulations are presented in Sections VA and VB. Section VA begins with a discussion of solvent distributions. The solvent distributions are explored using radial distribution functions as well as density contour maps. In addition, the effect of hydrogen bonding in the HMS/CO₂ system is also investigated. According to Anderton and Kauffman, the non-linear dependence of the HMS rotation times on the bulk density is due to solvent clustering induced by hydrogen bonding between HMS and CO₂, and therefore, the energetics of such an association is investigated. In Section VB, the simulated spectral shifts and local density augmentation is compared to experimental measurements¹¹. To the extent that the experimentally measured

spectral shifts are a direct measure of the coordination number, they are compared to the simulated coordination number as well as the simulated spectral shift. The simulation results on rotational dynamics are given in Section VC. Here, rotational times and correlation functions of the solutes are studied. These results are compared to experimental measurements^{8,10} in Section VD. The solvent friction, which gives rise to the observed dynamics, is discussed in Section VE. Here, it is found that the observed rotation times for DPB and HMS are a rather curious combination of attractive and repulsive contributions of the solute-solvent intermolecular potential. Finally, concluding remarks are given in section VI.

II. Theoretical Background

A. Local Density Augmentation

The phenomenon of local density augmentation has been observed for over a decade now⁴. This phenomenon is depicted in Figure 2.1, which shows the expected behavior of the 1st solvation shell population along an isotherm near the critical temperature. At low densities, the solvent has a characteristic gas-phase distribution about the solute. As the bulk solvent density is increased, the density of the 1st solvation shell increases faster than the corresponding increase in the bulk density. Sometime before the critical density is achieved, the situation is reversed and the increase in the local density is slowed. Finally, at high densities, the local and the



Figure 2.1: Schematic Representation of Local Density Augmentation.

bulk densities approach each other and increase at the same rate. Here, the characteristic dense-fluid distribution is achieved.

Although local density augmentation has been observed for some time now, a quantitative understanding of its roots has only recently been achieved[Egorov, 2000 #5428]. What is generally known is that there are at least two contributing factors: the isothermal compressibility and solute-solvent intermolecular potential.

Early attempts at understanding the basis of local density augmentation focused on the isothermal compressibility as the cause^{5,12}. At the critical point, the isothermal compressibility

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \tag{2.1}$$

of a fluid diverges. Here, ρ is the density, *P* is the pressure, and *T* is the temperature. By expanding the pressure in a Taylor series in density and the van der Waals parameters in temperature, the compressibility of a fluid near the critical point can be written as¹³,

$$\kappa_T \approx \frac{A}{\Delta T + B(\Delta \rho)^2}$$
(2.2)

where *A* and *B* are combinations of the expansion coefficients, ΔT is T- T_c , and $\Delta \rho$ is ρ - ρ_c . Eqn. 2.2 shows that in the vicinity of the critical point, the compressibility is still large. It should be noted that the width of the region about the critical density where the isothermal compressibility is large is dependent on *B*. This result is the main focus of the argument. Namely, as a result of the large compressibility, an

attractive solute may increase the number of solvent molecules in its vicinity at a relatively low free energy cost.

More recent studies^{14,9} have shown that there is another determinant of the local density augmentation: the solute-solvent intermolecular potential. Lewis *et al.* ⁹ have seen that even at isotherms well above the critical temperature, anthracene derivatives show significant local density augmentation for a range of solvents (non-polar, quadrupolar, and dipolar). Along a distant isotherm, the compressibility should not contribute appreciably to local density augmentation and therefore, there must be another contributing factor the density enhancement about the solute. In addition, Egorov¹⁴ has shown that by increasing the well depth of solute-solvent interaction (making it more attractive), the local density augmentation can be significantly increased.

Although both factors play a role in local density augmentation, they are distinct. In so far as the isothermal compressibility is concerned, it has been shown, if compressibility were the only factor contributing to the density enhancement, the correlation of density fluctuations would be the ultimate cause of the local density augmentation¹² (the isothermal compressibility is proportional to the static structure factor at zero wavenumbers, which in turn is the Fourier transform of the correlation of density fluctuations). However, in terms of the work done by Egorov and Lewis, there seems to be a more direct contribution owing to the strength of solute-solvent interactions, and it is clear that this contribution plays a large, if not dominant, role in determining the density enhancement in the region of the solute.

In and of itself, the local density augmentation is an interesting phenomenon. However, it is the effect of local density augmentation on other system observables that is the main concern of the present thesis. To be more specific, different solute observables are sensitive to different regions of the solvent. This distance dependence will then determine the effect that local density augmentation has on the observable of interest. It is this subtlety that is a large part of this study.

B. Spectral Shifts

In the current work, the spectral shifts of DPB, and HMS are calculated as probes of the local solvent environment.

$$h\Delta v_{abs} = \langle E(S_1) - E(S_0) \rangle_{S_0} \equiv \langle \Delta E \rangle_{S_0}$$

$$h\Delta v_{em} = \langle E(S_1) - E(S_0) \rangle_{S_1} \equiv \langle \Delta E \rangle_{S_1}$$

(2.3)

In Eqs. (2.3), $\langle E(S_i) \rangle_{S_j}$ is the solute-solvent interaction energy described by the S_i state parameters in the S_j equilibrium trajectory. Unfortunately, a rigorous computational treatment of the spectral shifts is still not practical in dense systems, and therefore, classical approximations in simulations are necessary to reproduce the experimental values. Several different methods are used to estimate ΔE and these methods are enumerated below. It should also be noted that all of the approaches are independent of any dynamical contributions to the spectroscopy, and therefore, report only on the configurational phase space of the system.

Model 1: Charge Difference

In some systems, such as those involving C153, electrical interactions between the solute and solvent dominate the spectroscopy and ΔE can be calculated by

$$\Delta E = \sum_{\alpha=1}^{N_u} \sum_{i=1}^{N_v} \frac{q_i \Delta q_\alpha}{r_{\alpha i}}.$$
(2.4)

Here, *u* refers to the solute, *v* refers to the solvent, *N* is the number of sites, *q* is the atomic charge, Δq is the charge difference $q(S_1)-q(S_0)$, and $r_{\alpha i} = |\mathbf{r}_{\alpha}-\mathbf{r}_i|$ is the distance between atoms α and *i*. The convention used is that the Greek and Latin indicies correspond to solute and solvent quantities respectively. Unfortunately, because the excited state charges on anthracene are very similar to the ground state charges, eqn. 2.4 does not yield useful results, as the subsequent spectral shifts are very small. Therefore, the results of this model, although calculated during the course of the simulation, are omitted from the reported results.

Model 2: Change in Lennard-Jones Parameter

The second model describes the spectral shift of the solute in terms of a change in the Lennard-Jones (LJ) well depth and size parameters. This method has been successfully used to reproduce spectra of jet-cooled complexes^{15,16} and is slighty adapted here. In this case, the energies are modeled as,

$$E^{(S)} = \sum_{\alpha=1}^{n_u} \sum_{i=1}^{N_v} 4\varepsilon_{\alpha i}^{(S)} \left[\left(\frac{\sigma_{\alpha i}^{(S)}}{r_{\alpha i}} \right)^{12} - \left(\frac{\sigma_{\alpha i}^{(S)}}{r_{\alpha i}} \right)^6 \right]$$
(2.5)

with

$$\sigma_{\alpha i}^{(s)} = \frac{1}{2} \left(\sigma_{\alpha \alpha}^{(s)} + \sigma_{i i}^{(0)} \right)$$

$$\varepsilon_{\alpha i}^{(s)} = \sqrt{\varepsilon_{\alpha \alpha}^{(s)} \varepsilon_{i i}^{(0)}}$$
(2.6)

taken as the combining rules for the mixed quantities. Here *S* refers to the electronic state, σ is the atomic diameter, ε is the well depth, and n_u is the number of chromophore atoms (atoms that contribute to the spectral shift) of the solute. The LJ parameters for the ground state solute and the solvent atoms are taken from various sources that are described in Chapter 2 Section IV.A of this thesis. On the other hand, the excited state well depths and atomic diameters of the solute are parameterized so as to reproduce the shifts and widths of anthracene in various liquid solvents. This process is described detail in the chapter on Anthracene simulations (*Insert Chapter and Section when written*).

Model 3: Perturbation Expansion

This method is a simplification of the method used by Shalev *et al.* to reproduce the spectral shifts of aromatic chromaphore-rare gas heteroclusters¹⁷. The starting point of this method is the second-order perturbation expansion of the energy difference between the S_1 and S_0 states of the solute interacting with a single solvent atom.

$$\Delta E_{A} = \sum_{\alpha \neq \beta} \sum_{i>0} \frac{\left| H_{\alpha 0,\beta i}^{'} \right|^{2}}{E_{\alpha} - \left(E_{\beta} + E_{i} \right)} - \sum_{\alpha \neq \beta} \sum_{i>0} \frac{\left| H_{00,\beta i}^{'} \right|^{2}}{-\left(E_{\beta} + E_{i} \right)}$$

$$H_{\alpha 0,\beta i}^{'} = \left\langle M_{\alpha} A_{0} \right| H^{'} \left| M_{\beta} A_{i} \right\rangle$$

$$(2.7)$$

Here, M_n is solute wavefunction for the nth electronic state, A_m is the solvent wavefunction for the mth electronic state, and E_n and E_m are the corresponding energies. The authors show that for a molecular solute and an atomic solvent, the electronic spectral shift may be expressed as

$$\Delta E = \sum_{i=1}^{N_{\nu}} \alpha_i e^2 \overline{F}_i \sum_{\beta=1}^{n_u} \sum_{\gamma=1}^{n_u} K^{(i)}_{\beta\gamma} G^{(i)}_{\beta\gamma} \text{ with } G^{(i)}_{\beta\gamma} = \frac{\mathbf{r}_{i\beta} \mathbf{r}_{i\gamma}}{r^3_{i\beta} r^3_{i\gamma}}.$$
(2.8)

Here, α_i and $\overline{F_i}$ are the electronic polarizability and ionization potential of the solvent atoms. $G_{\beta\gamma}^{(i)}$ is a geometric factor and $K_{\beta\gamma}^{(i)}$ is an electronic factor determined by the molecular orbitals (MO) used in the expansion of the excited and ground states of the solute. To be more precise, $K_{\beta\gamma}^{(i)}$ involves two single summations and two double summations over the MO coefficients. In the present work, $K_{\beta\gamma}^{(i)}$ is replaced by a sum exclusively over the MOs involved in the electronic transition, which is reasonably well described by a single $\pi\pi^*$ HOMO \rightarrow LUMO excitation (*needs footnote*). The electronic factor may now be written as,

$$K_{\beta\gamma}^{(i)} \approx \frac{Q_{\beta}Q_{\gamma}}{\varepsilon^{LUMO} - \varepsilon^{HOMO} - \overline{F_{i}}} \approx \frac{Q_{\beta}Q_{\gamma}}{hv_{gas} - \overline{F_{i}}}$$
(2.9)

where Q_{γ} is the transition monopole formed from the product of the HOMO and LUMO MO coefficients on atom γ ($Q_{\gamma} = C_{\gamma}^{HOMO} C_{\gamma}^{LUMO}$). This approximation leads to the final expression used in the calculation of the spectral shift.

$$\Delta E_{3} \approx f e^{2} \sum_{i=1}^{N_{v}} \sum_{\beta=1}^{n_{u}} \sum_{\gamma=1}^{n_{u}} \mathcal{Q}_{\beta} \mathcal{Q}_{\gamma} \frac{\mathbf{r}_{i\beta} \cdot \mathbf{r}_{i\gamma}}{r_{i\beta}^{3} r_{i\gamma}^{3}}$$

$$f \approx \frac{\alpha \overline{F}}{3(hv_{gas} - \overline{F})}$$

$$(2.10)$$

In eq. 2.10, the solvent molecules have been treated as independent sites with identical and independent atomic poalarizabilities; in the case of CO_2 , the atomic polarizability is taken as 1/3 of the molecular polarizability.

C. Friction

Molecular friction is used to further understand the behavior of molecular rotations. Although the methods used to obtain the friction in this work are not novel, the interpretation and application of such methodologies is subtle, and therefore, deserves some comment. In general, dynamic rotational and translational behavior of molecules is interpreted via correlation times; that is, the time it takes the system variable of interest to become randomized. Physically, if attention is focused on a single molecule, its motion appears to be chaotic. This motion can be broken down into two components: 1) a systematic variation and 2) a random variation in the dynamic observable of interest. Mathematically, this separation of effects is embodied in the Langevin equation, where the notion of molecular friction is described by a systematic variation of the dynamic observable. Because the interest lies in understanding the correlation times, the friction, which can be related to the random force, becomes integral to understanding the randomization of the dynamic trajectory. Below is a generalization and quantification of the above ideas.

Translational Friction

The generalized Langevin equation (GLE) provides a convenient framework in which to analyze translational friction. The GLE for translational velocity of a solute, $\mathbf{v}(t)$ can be written as¹⁸,

$$m\frac{d\mathbf{v}}{dt} = -m\int_{0}^{t} d\tau \zeta_{v}(t-\tau)\mathbf{v}(\tau) + \mathbf{F}(t)$$
(2.11)

where m is the solute mass and $\mathbf{F}(t)$ is called the random force acting on the solute. The friction kernel, $\zeta_v(t)$, can be related to the random force via the second fluctuation dissipation theorem

$$\zeta_{\nu}(t) = \frac{\langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle}{3mkT}.$$
(2.12)

At this point, it should be noted that the term "random force" is a bit of a misnomer because the force is completely deterministic, and therefore, not at all random. $\mathbf{F}(t)$ appears to be a randomly fluctuating force with ζ_v being the systematic counterpart, from a phenomenological development. On the other hand, a rigorous development of the GLE¹⁹ shows that $\mathbf{F}(t)$ is orthogonal to A, where A is the variable being propagated by the Liouville operator. In the case of translational friction, this means that the random force has the translational motion of the solute projected out. However, if the solute is much more massive than the solvent, the approximation can be made that the dynamics of $\mathbf{F}(t)$ with a fixed verses free solute will be similar. The time dependent friction, appropriate for a given system, can be related to its velocity autocorrelation function¹⁸

$$\frac{dC_{\nu}}{dt} = -\int_{0}^{t} d\tau \zeta_{\nu} (t-\tau) C_{\nu}(\tau). \qquad (2.13)$$

Here, $C_{\nu} = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ is the velocity autocorrelation function. In general, one can form a memory function equation from any dynamical variable used to define a GLE such as eq. 2.13. However, the interpretation of the friction and random force then becomes a little more ambiguous. Taking the Laplace transform of eq. 2.13,

$$\widetilde{\zeta}_{v}(z) = \frac{1}{\widetilde{C}_{v}(z)} + zi$$
(2.14)

one can then solve for the frequency dependent friction. The time dependent friction can then be recovered by taking the inverse Laplace transformation²⁰. This use of the memory function equation provides a direct route from simulation to the time dependent friction.

Rotational Friction

Obtaining the rotational friction of a general polyatomic molecule is not straightforward. The difficulty stems from the fact that for an asymmetric solute, a rigorous, soluble GLE cannot be formed²¹. For a rigid, linear body however, the GLE is completely analogous to eq. 2.11.

$$I\frac{d\mathbf{\omega}}{dt} = -I\int_{0}^{t} d\tau \zeta_{\omega}(t-\tau)\mathbf{\omega}(\tau) + \mathbf{N}(t)$$

$$\zeta_{\omega}(t) = \frac{\langle \mathbf{N}(0) \cdot \mathbf{N}(t) \rangle}{2IkT}$$
(2.15)

In eq. 2.15, $\boldsymbol{\omega}$ is the angular velocity (in the molecular frame), $\zeta_{\boldsymbol{\omega}}$ is the rotational friction, *I* is the moment of inertia, and $N_{\boldsymbol{\omega}}$ is the random torque on the body. The corresponding memory function equation is identical to eq. 2.14, with the rotational variables substituted for the translational variables. For an asymmetric polyatomic molecule, a heuristic approach is adopted by defining a system of *independent* GLEs for rotation about each principal axis of the molecule.

$$I_{i} \frac{d\boldsymbol{\omega}_{i}}{dt} \equiv -I_{i} \int_{0}^{t} d\tau \zeta_{\omega}^{(i)}(t-\tau) \boldsymbol{\omega}_{i}(\tau) + \mathbf{N}_{i}(t)$$

$$\zeta_{\omega}^{(i)}(t) = \frac{\langle \mathbf{N}_{i}(0) \mathbf{N}_{i}(t) \rangle}{I_{i} kT}$$
(2.16)

Here, *i* refers to one of the three principal axes. Eqs. (2.16) are reasonable approximations in the limit of small coupling between angular velocity components. In particular, DPB and HMS are close to symmetric tops, and therefore, the expectation is that Eqs. (2.16) provide a useful measure of the time dependent friction on such systems.

D. Radial Distribution Functions

Radial distribution functions play a central role in describing intermolecular correlations in disordered systems. In the case of a random distribution of atoms, one may easily envision that the probability of finding a particle, P_2 , at a distance r_{12} from

another particle, P_1 , is simply proportional to density. However, if molecules interact, their positions become correlated and this probability changes. What follows is a general outline that can be found in almost any text that deals with statistical mechanics such as *The Theory of Simple Liquids*¹⁸.

To explore this question, consider the canonical ensemble and start with the definition of the probability of a single configuration which can be written as

$$P_{N}(r_{1},...,r_{N})\prod_{i=1}^{N}dr_{i} = \frac{\exp(-\beta U)\prod_{i=1}^{N}dr_{i}}{Z_{N}}$$
(2.17)

where Z_N is related to the partition function Q_N by $Z_N = Q_N / (N! \Lambda^{3N})$. In the above expression, $\beta = 1 / kT$, U is the potential energy, Z_N is called the configurational integral, and Λ is the thermal wavelength. The left-hand side of eq. 2.17 should look quite familiar as it is simply the probability that there is a particle in the volume dr_1 about r_1 , a particle in volume dr_2 about r_2 , and so on. The 2-particle correlation may now be written as,

$$P(r_1, r_2)dr_1dr_2 = \frac{dr_1dr_2 \int \prod_{i=3}^{N} dr_i \exp(-\beta U)}{Z_N}$$
(2.18)

where the coordinates of the other particles have been integrated out. The pair distribution function is now defined as

$$g(r_1, r_2) = V^2 \left(1 - \frac{1}{N}\right) \frac{\int \prod_{i=3}^N dr_i \exp(-\beta U)}{Z_N}.$$
 (2.19)

If the intermolecular potential is spherical, then $g(r_1,r_2) = g(r_{12}) = g(r)$. In this case, the pair correlation function is called the radial distribution function. In the thermodynamic limit, the normalization condition becomes

$$4\pi\rho \int dr r^2 g(r) = N \,. \tag{2.20}$$

The physical interpretation of the radial distribution function is that g(r) represents the probability of finding a particle at a given distance from another particle with respect to a random distribution of particles. More generally, there is now a connection between the equilibrium partition function and the radial distribution function. This intimate connection allows for many properties to be written in terms of integrals over g(r) and therefore makes the radial distribution function a powerful tool in understanding equilibrium properties.

Radial distribution functions of the sort just described are most useful for describing the structure of atomic fluids. Here, the interest is in the solvent structure surrounding a polyatomic solute. For this reason, the calculation of the radial distribution functions in this chapter is somewhat different than what is described above. If a single distribution function is desired, which will characterize the relative displacement of a solvent atom from the solute molecule, the definition of atomic separations must be modified to account for the non-spherical nature of the solutes studied. In order accomplish this, the smallest separation between a given solvent atom and any atom of the solute is the distance used in the calculation of the distribution shell distribution function. The resulting g(r) will be referred to as the "solvation shell distribution function", $g_{ss}(r)$, and by using such a distribution, the relative probability

of finding any solvent atom a given distance from the surface of the solute is calculated.

III. Supercritical Simulations

A. Convergence

Molecular dynamics simulations at state points near the critical point involve subtleties that are not present in liquid-phase simulations^{5,22}. Therefore, special attention must be paid to the simulation details in order to ensure the full convergence of simulation statistics.

As the critical point of the solvent is approached, the spatial correlations grow in extent. The correlations characteristic of critical behavior are manifested in a longranged tail of the radial distribution function

$$g(r) - 1 \sim r^{-1} e^{-r/\xi}$$
. (2.21)

As the correlation length, ξ , increases, the volume of the simulation box must also be increased so that the spectrum of density fluctuations is not truncated. In addition to the diverging correlation length, there is also a "critical slowing down" of dynamic system observables^{22,1,5} in the vicinity of the critical point. Maddox *et al.* have shown that this slowing down is due to the coupling of the local solvent environment to the long-range density fluctuations present in supercritical fluids, which implies that the solute dynamics are affected by this phenomenon. In terms of running an appropriate
simulation, the expectation is then simulation sizes and simulation lengths should be larger than those appropriate for standard liquid state studies.

B. CO₂ Simulation Model

The solvent model used here is the rigid "EMP2" model of Harris and Yung²³, which is parameterized to reproduce the experimental liquid-vapor coexistence curve, is used. The model parameters are provided in Table 2.1. Because this work, at least in part, focuses on the rotational behavior of DPB and HMS in CO₂, it is necessary to investigate the dynamic properties of this simulation model. In particular, the solvent self-diffusion coefficient (*D*) and the shear viscosity (η) are calculated from simulations of pure CO₂ in order to ascertain the frictional characteristics (in the hydrodynamic limit²⁴) of the solvent. The viscosity and diffusion constant are calculated via²⁵,

$$\eta = \frac{V}{kT} \int_{0}^{\infty} dt \left\langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \right\rangle, \quad \alpha \neq \beta$$
(2.22)

and

$$D = \frac{1}{3} \int_{0}^{\infty} dt \langle \mathbf{v}_{i}(t) \cdot \mathbf{v}_{i}(0) \rangle = \lim_{t \to \infty} \frac{1}{6t} \langle |\mathbf{r}_{i}(t) \cdot \mathbf{r}_{i}(0)| \rangle$$
(2.23)

where $P_{\alpha\beta}$ is an element of the pressure tensor, *V* is the system volume, **v**_i is the center of mass (COM) velocity of molecule *i*, **r**_i is the COM position of molecule *i*, and *t* is time.

| Atom | <i>ɛ/k</i> (K) | $\sigma(\text{\AA})$ | q (e) | m (g/mol) |
|------|----------------|----------------------|--------------|-----------|
| | | | | |
| 0 | 80.51 | 3.03 | -0.33 | 16 |
| С | 28.13 | 2.76 | 0.65 | 12 |

Table 2.1: CO₂ Parameters of Harris and Yung (Ref. 23).

The results of the viscosity and diffusion constant calculations are displayed in Figure 2.2 and Table 2.2. The calculated and experimental viscosities²⁶ show excellent agreement, with a maximum deviation of 5% at a simulated density of $1.05\rho_c$. The diffusion constant also exhibits good agreement with experimental values^{27,28}, however it is underestimated throughout the entire density range simulated. This difference implies that the simulation model overestimates the translational friction in the real system, and hence, slightly elevated rotational times of DPB and HMS might be anticipated.

For the rotational behavior of neat CO₂, the situation is reversed. Figure 2.3 shows a comparison between simulated and experimental²⁹ 1/e times for the molecular reorientation. The simulated values are calculated via,

$$C^{(L)}(t) = \langle P_L[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle$$
(2.24)

where **u** is a unit orientation vector along the molecular axis and P_L is the Legendre polynomial of order *L*. For all but the lowest experimental density, the simulation model underestimates the 1/e orientation times, which suggests that the rotational friction is underestimated. Nevertheless, the simulation model of Harris and Yung provides a reasonable representation of CO₂ dynamics in dense systems and is therefore adopted for use in the current work.



Figure 2.2: Comparison of Experimental and Simulated Shear Viscosities and Self-Diffusion Constants. Experimental results are plotted as solid lines and simulation results are plotted with filled circles. Experimental viscosity is from Ref. 26 and self diffusion constant is from Ref. 27.

| | η (mP) | | D $(10^{-8} \text{ m}^2 \text{ s}^{-1})$ | | |
|-------------------------|-----------------|------|---|---------|--|
| density (ρ/ρ_c) | sim | expt | sim | expt | |
| | | | | | |
| 0.25 | $0.161\pm.007$ | .17 | 17 ± 3 | 18/18 | |
| 0.63 | $0.241 \pm .12$ | .23 | $6.5\pm.6$ | 7.3/6.8 | |
| 1.05 | $0.33 \pm .02$ | .35 | $3.7 \pm .3$ | 4.3/3.8 | |
| 1.69 | $0.71 \pm .04$ | .69 | $1.7 \pm .2$ | 2.3/2.0 | |
| 2.00 | $0.96 \pm .05$ | 1.00 | $1.3 \pm .2$ | 1.5/1.5 | |

Table 2.2: Comparison of Experimental and Simulated Viscosities and Diffusion Constants for Neat CO_2 . Experimental viscosities are from Ref. (22) and experimental diffusion constants are from Ref. 27 (left) and Ref. 28 (right).



Figure 2.3: Comparison of Experimental and Simulated Rotation Times of Neat CO₂. Experimental data is shown as filled symbols and simulation data is shown as open symbols. Experimental data is from Ref. 29.

IV. Simulation Models and Details

A. DPB and HMS Parameters

The LJ parameters for DPB and HMS are taken from the OPLS force-field of Jorgensen and co-workers³⁰. The molecular geometries are obtained by both semiempirical³¹ (AM1) and *ab initio*³² (RHF/6-31G(d,p)) geometry optimizations. These calculations predict twisted minimum energy geometries with a torsional displacement, χ (Figure 2.4), of approximately 20°. Moreover, the local minima at 20° show only a slight preference over the planar geometry (< 1 kJ/mol). At 300 K, however, torsional displacements of 40° are easily attained. As a result, it is assumed that simulating the solutes in different local minima do not appreciably change the resulting trajectories. Hence, planar geometries of DPB and HMS are adopted in this study.

As seen in Figure 2.4, the methanol group in HMS also possesses a conformational degree of freedom. The figure labeled "IP" has the terminal hydrogen of the OH group extended away from the molecule and in the molecular plane while the figure labeled "OP" has this hydrogen pointed back towards the benzene ring and out of the molecular plane. AM1 calculations show a preference for the OP conformation over the IP conformation by about 10 kJ/mol. Unfortunately, it is unclear how this minimum will change in the presence of CO₂. For example, hydrogen bond donors will tend to prefer the OP configuration while hydrogen bond acceptors will prefer the IP configuration. To the extent that dipole-quadrupole



Figure 2.4: Molecular Geometries of DPB and HMS.

interactions are important³³ (*i.e.* HMS-CO₂) considerable attention must be given to the appropriate conformation of the methanol group in HMS. Simulations of both conformations of HMS in CO₂ were performed. The simulation results show a small difference in solvent configuration about the HMS methanol moiety. However, this difference does not appreciably affect the density augmentation or the rotational behavior of HMS, and therefore, the OP trajectory results are reported in this work.

The ground state atomic charges for DPB and HMS can be seen in Figure 2.5. The charges are obtained from electrostatic potential fits of the 6-31G(d,p) wavefunctions³⁴. From the magnitude of the charges, the expectation is that there will be significant electrical interactions between DPB and CO₂. Moreover, the HMS atomic charges are larger than the corresponding DPB atomic charges, and therefore, these interactions are predicted to be even greater in the HMS/CO₂ system. The ground state dipole moment of the simulated HMS is calculated to be 1.8 D. The experimental dipole moment is found to be $2.9 \pm .1$ D. In the simulation model of HMS, the bulk of the dipole moment is derived from the hydroxyl group, which might place the source of the discrepancy upon the HMS methanol conformation. AM1 calculations of the HMS dipole moment as a function of OH rotation about the C-O bond have a maximum value of 2.2 D (1.9 D for the IP geometry), which is still about 24% smaller than the experimental value. In addition, the simulated HMS has a dipole moment which is larger than those determined experimentally for similar molecules³⁵ shows that the simulated HMS has a dipole moment which is too large. The source of this deficiency is unknown. Finally, the excited state charges for DPB





Figure 2.5: Atomic Charges and Principle Reference Frames of DPB and HMS.

and HMS are similarly determined from AM1 calculations. Because the S_1 - S_0 charge differences are so small, the excited state dipole is only slight different than the ground state dipole moment.

Both DPB and HMS are expected to have similar rotational dynamics. Both molecules have very similar moments of inertia, and are close to the prolate limit $(I_{zz}^{-1} = I_{yy}^{-1} < I_{xx}^{-1})$, where *x*, *y*, and *z* are the principal axes (shown in Figure 2.5). Furthermore, the molecular dimensions are similar in the three principal directions. As a result, any significant deviations in the rotational characteristics of DPB from HMS must be related to the different electrical interactions with the solvent. This difference is noted by Anderton and Kauffman⁸ and forms the basis for their experimental study of these two solutes. Complete listings of DPB and HMS parameters are found in Tables 2.3 and 2.4 respectively and a comparison of molecular properties is found in Table 2.5.

B. Simulation Conditions

The MD simulations of DPB and HMS were carried out in the microcanonical (NVE) ensemble. DPB was simulated at nine different densities ranging from $0.2\rho_c$ to $2.0\rho_c$ while the HMS simulations were carried out at 5 different densities spanning the same range. The systems were equilibrated for 1 ns and the energy was chosen such that the average temperature is 311 K (about 7 K above the critical temperature of CO₂). Following equilibration, production runs were completed for a further 4 ns

| Atom | e/k | σ | q | т | Δa | Δε | 0 |
|------|--------|-------|--------|---------|--------|-------|--------|
| | (K) | (Å) | (e) | (g/mol) | (e) | (K) | (e) |
| | | | | , U | | | |
| С | 35.220 | 3.550 | -0.137 | 12.011 | 0.003 | 3.522 | -0.007 |
| С | 35.220 | 3.550 | -0.169 | 12.011 | -0.024 | 3.522 | 0.046 |
| С | 35.220 | 3.550 | 0.154 | 12.011 | 0.028 | 3.522 | -0.056 |
| С | 35.220 | 3.550 | -0.183 | 12.011 | -0.004 | 3.522 | 0.046 |
| С | 35.220 | 3.550 | -0.115 | 12.011 | -0.010 | 3.522 | -0.008 |
| С | 35.220 | 3.550 | -0.126 | 12.011 | 0.019 | 3.522 | 0.071 |
| Н | 15.100 | 2.420 | 0.131 | 1.008 | -0.003 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.127 | 1.008 | 0.003 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.133 | 1.008 | -0.004 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.124 | 1.008 | 0.001 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.126 | 1.008 | -0.006 | 0.000 | 0.000 |
| С | 38.240 | 3.550 | -0.232 | 12.011 | -0.019 | 3.824 | 0.148 |
| С | 38.240 | 3.550 | -0.093 | 12.011 | 0.017 | 3.824 | -0.118 |
| Н | 15.100 | 2.420 | 0.136 | 1.008 | 0.000 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.125 | 1.008 | -0.002 | 0.000 | 0.000 |
| С | 38.240 | 3.550 | -0.092 | 12.011 | 0.014 | 3.824 | 0.118 |
| С | 38.240 | 3.550 | -0.234 | 12.011 | -0.017 | 3.824 | -0.148 |
| Н | 15.100 | 2.420 | 0.123 | 1.008 | -0.002 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.138 | 1.008 | 0.000 | 0.000 | 0.000 |
| С | 35.220 | 3.550 | 0.148 | 12.011 | 0.028 | 3.522 | 0.056 |
| С | 35.220 | 3.550 | -0.165 | 12.011 | -0.003 | 3.522 | -0.046 |
| С | 35.220 | 3.550 | -0.131 | 12.011 | -0.011 | 3.522 | 0.008 |
| С | 35.220 | 3.550 | -0.136 | 12.011 | 0.019 | 3.522 | -0.071 |
| С | 35.220 | 3.550 | -0.121 | 12.011 | 0.003 | 3.522 | 0.007 |
| С | 35.220 | 3.550 | -0.170 | 12.011 | -0.024 | 3.522 | -0.046 |
| Н | 15.100 | 2.420 | 0.131 | 1.008 | -0.004 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.128 | 1.008 | 0.001 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.130 | 1.008 | -0.006 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.126 | 1.008 | -0.003 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.125 | 1.008 | 0.003 | 0.000 | 0.000 |

Table 2.3: DPB Atomic Parameters.

| Atom | c/k | σ | a | m | Aa | A c/k | 0 |
|------|--------|-------|--------|-----------|--------------------|-------|--------|
| | (K) | (Å) | (e) | (g/mol) | <u>کانا</u> (e) | (K) | (e) |
| | (11) | (11) | (0) | (g, 1101) | (0) | | (•) |
| С | 35 230 | 3 550 | -0.107 | 12.011 | -0.003 | 3 523 | -0.016 |
| Č | 35 230 | 3 550 | -0.326 | 12.011 | -0.021 | 3 523 | 0.061 |
| Č | 35.230 | 3.550 | 0.275 | 12.011 | 0.011 | 3.523 | -0.097 |
| Č | 35.230 | 3.550 | -0.172 | 12.011 | 0.004 | 3.523 | 0.061 |
| Č | 35.230 | 3.550 | -0.279 | 12.011 | -0.020 | 3.523 | -0.018 |
| Č | 35.230 | 3.550 | 0.065 | 12.011 | 0.029 | 3.523 | 0.114 |
| Ĥ | 15.100 | 2.420 | 0.136 | 1.008 | -0.006 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.172 | 1.008 | 0.001 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.152 | 1.008 | -0.007 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.155 | 1.008 | 0.000 | 0.000 | 0.000 |
| С | 38.250 | 3.550 | -0.222 | 12.011 | 0.006 | 3.825 | 0.150 |
| Н | 15.100 | 2.420 | 0.149 | 1.008 | -0.002 | 0.000 | 0.000 |
| С | 38.250 | 3.550 | -0.385 | 12.011 | 0.002 | 3.825 | -0.158 |
| Н | 15.100 | 2.420 | 0.182 | 1.008 | -0.003 | 0.000 | 0.000 |
| С | 35.230 | 3.550 | 0.409 | 12.011 | 0.019 | 3.523 | 0.079 |
| С | 35.230 | 3.550 | -0.305 | 12.011 | -0.022 | 3.523 | -0.057 |
| С | 35.230 | 3.550 | -0.084 | 12.011 | 0.002 | 3.523 | 0.011 |
| С | 35.230 | 3.550 | -0.190 | 12.011 | 0.031 | 3.523 | -0.095 |
| С | 35.230 | 3.550 | -0.082 | 12.011 | -0.019 | 3.523 | 0.012 |
| С | 35.230 | 3.550 | -0.303 | 12.011 | 0.013 | 3.523 | -0.057 |
| Н | 15.100 | 2.420 | 0.153 | 1.008 | 0.001 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.132 | 1.008 | -0.004 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.141 | 1.008 | -0.008 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.128 | 1.008 | 0.001 | 0.000 | 0.000 |
| Н | 15.100 | 2.420 | 0.168 | 1.008 | -0.007 | 0.000 | 0.000 |
| С | 33.220 | 3.500 | 0.195 | 12.011 | -0.023 | 0.000 | -0.001 |
| Ο | 85.550 | 3.120 | -0.647 | 16.000 | 0.008 | 0.000 | 0.000 |
| Н | 15.100 | 2.500 | 0.068 | 1.008 | 0.007 | 0.000 | 0.000 |
| Н | 15.100 | 2.500 | 0.021 | 1.008 | 0.009 | 0.000 | 0.000 |
| Н | 0.000 | 0.000 | 0.402 | 1.008 | -0.003 | 0.000 | 0.000 |

Table 2.4: HMS Atomic Parameters.

| | Mass amu | <i>I_{xx}</i> amu Å ² | <i>I</i> _{yy} amu Å ² | I _{zz} amu Å ² | $egin{array}{c} L_x \ { m \AA} \end{array}$ | L_y Å | $egin{array}{c} L_z \ m{\AA} \end{array}$ | μ D |
|-----|-------------|---|--|---------------------------------------|---|---------|--|--------|
| | | | | | | | | |
| DPB | 206 | 198 | 3429 | 3627 | 16.3 | 7.2 | 3.6 | 0 |
| HMS | 210 | 205 | 3030 | 3223 | 15.5 | 7.2 | 4.2 | 1.8 |

Table 2.5: Comparison of Molecular Properties.

while statistics were sampled every 10 fs. In both cases, a 2 fs integration time step was used to propagate the equations of motion. The translational equations of motion were integrated using a Verlet type leap-from algorithm²⁵. For the rotational equations of motion, a quaternion approach²⁵ was adopted for the solute while a modified Gear algorithm was used for the solvent²⁵. Molecular interactions were computed with a site-site approach with applied minimum image boundary conditions using 864 solvent molecules. A 9 Å cut-off was used for solvent-solvent interactions. Although this may seem too small, the solute-solvent dipole-quadrupole and the solute-solute quadrupole-quadrupole coupling are weak and hence the ignored longrange interactions are negligible. As a test of the simulation algorithm conditions, further simulations of DPB in CO₂ were performed with the DLPOLY program³⁶ at a single reduced density of $0.626\rho_c$. These runs were performed in 1) the microcanonical ensemble (NVE) using an Ewald sum and 2) in the isobaricisothermal ensemble (NPT) with a 12 Å cut-off. The results are displayed in Table 2.6. Comparison of the NVE results shos that a 9 Å cutoff is sufficient here, as both the Ewald summation and the spherical cut-off simulations agree to within statistical uncertainties. In addition, the simulations performed in the NPT ensemble show good agreement with the temperature and pressure of the NVE simulations. What is different is the solute-solvent interaction energies and the simulation volumes. Both the Lennard-Jones and electrostatic interaction energies are about 5% higher in the NPT simulations, and at the simulated density, correspond to having an extra atom in the 1st solvation shell of the solute. The density corresponding to the volume of the

| | NVE: $R_{\text{cut}} = 9 \text{ Å}$ | NVE: Ewald | NPT: $R_{\text{cut}} = 12 \text{ Å}$ |
|-----------------------|--|------------------|--------------------------------------|
| //I.I.(kI/mol) | -54.60 ± 0.86 | -55 49 + 1 72 | -58 14 + 0 86 |
| U_{uv} -El (kJ/mol) | -6.57 ± 0.14 | -6.74 ± 0.28 | -7.12 ± 0.13 |
| <i>T</i> (K) | 311.2 ± 0.42 | 309.1 ± 0.93 | 310.0 ± 0.02 |
| P (MPa) | 8.4 ± 0.04 | 8.1 ± 0.08 | 8.4 ± 0.02 |
| $V(10^5{ m \AA}^3)$ | 2.15 | 2.15 | $2.01 \pm .014$ |

Table 2.6: Comparison of Simulation Conditions.

NPT simulations is about 7% higher than the NVE simulations, and so, the slightly higher interaction energies in the isothermal-isobaric simulations are arguably a result of this difference in the density. As a result, the conclusion is that the solvent environment about the solute is relatively independent of the tested simulation conditions.

C. Trajectory Convergence

As described in Section III.A of this chapter, convergence of the simulation trajectory requires special considerations owing to the long wavelength and slowly varying density fluctuations of the solvent. The temporal aspect of convergence of these simulations is discussed first. Plotted in Figure 2.6 is the normalized running time average of the 1st solvation shell population of DPB in CO₂ at a density of $0.626\rho_c$. At 4 ns, variation in the coordination number can still be seen. However, the amplitude of these variations is small (less than 0.5% of the value at 4 ns) and so the discrepancy between the average at 4 ns and the infinite time average should also be small. Therefore, the run lengths are assumed to be adequate for the current study.

Insofar as the spatial convergence of the simulations is concerned, experimental X-ray diffraction measurements³⁷ have determined the correlation length of CO₂ to be less than 15 Å for the range of densities simulated. At near critical densities, the box length of the simulations is about 50 Å, which implies that the full spectrum of density fluctuations is being truncated. In order to ascertain the degree of truncation, simulations of anthracene in a monatomic model of ethane were



Figure 2.6: Temporal Convergence of Coordination Number of DPB in CO₂ at $0.626\rho_c$. Running average of coordination number.

conducted at a density of $0.5\rho_c$. The choice of anthracene in ethane is a practical one; because the solute is modeled as a neutral monatomic species, calculations involving a large number of solvent molecules can be accomplished relatively quickly. Plotted in Figure 2.7 is the 1st solvation shell population as a function of the simulation size. From these simulations, a size convergence is anticipated at about 1000 solvent molecules. With respect to the simulations of DPB and HMS in CO₂, this means that they are too small by about 15% in the number of molecules simulated. However, the DPB and HMS simulations are assumed to yield meaningful results, because the small error in the number should have a negligible effect on the rotational and translational dynamics of the solute.

V. Results and Discussion

A. Solvation Structure: Simulation Results

Pictures of the DPB/CO₂ simulations spanning the density range $0.2\rho_c - 2.0\rho_c$ are seen in Figure 2.8. The cross sections are defined by the cylinder $r = [0, l_b/2]$ and z = [-5 Å, 5 Å] in the solute centered coordinate system, where l_b is the simulation box length at 2.0 ρ_c . At a density of $0.2\rho_c$, the solvent environment resembles a gas-phase system, as the attractive part of the solute-solvent interactions are the dominant force in determining the solvent distribution in this region. The mean free path is relatively large and therefore, solute-solvent collisions are infrequent. As the density is



Figure 2.7: Spatial Convergence of Coordination Number of Anthracene in Ethane.



Figure 2.8: Snapshots of DPB/CO₂ Simulations. Cylindrical cross sections are defined by $r = [0, l_b/2]$ and z = [-5 Å 5 Å].

increased, there are more solvent molecules in the vicinity of the solute, and therefore, the rate of molecular collisions increases. Near the critical density, as previously mentioned, there is an excess of solvent in the vicinity of the solute (This effect is maximized at $0.6\rho_c$, as will be shown later.). However, it is difficult to discern this excess from a single snap-shot because the solvent itself exhibits a broad range of densities. Hence, many snap-shots, encompassing the full distribution of solvent environments, would have to be studied in order to visualize the local density augmentation. Moving to a density of $2.0\rho_c$, the solvent has the characteristic liquid distribution. In this region, as solvent packing becomes the dominant effect determining the solvent environment, solute-solvent collisions occur with much greater frequency.

In order to get a more quantitative picture of the solvent distributions, relative density maps of the DPB and HMS simulations are plotted in Figures 2.9 and 2.10 for densities of $0.2\rho_c$ and $2.0\rho_c$ respectively. Figure 2.9 is studied first. For both DPB and HMS, the greatest enhancement of solvent density is above and below the aromatic planes of the molecules as seen in the *xz* and *yz* cross sections. In addition, HMS also exhibits a build-up of solvent density about the OH group, as proposed by Anderton and Kauffman⁸; this can be seen clearly in the *xy* and *xz* cross sections where the hydroxyl end of HMS shows a relative build-up of solvent molecules. However, compared to the density enhancement above and below the molecular π -system, the augmentation induced by the OH group is about ¹/₂ as effective. Also, as seen in the *xz* and *yz* cross sections, HMS shows slightly greater enhancement of the



Figure 2.9: Density Maps at $0.2\rho_c$. Shading denotes average densities of solvent atoms, relative to the bulk density. Grid lines are spaced at 0.5 Å intervals.



Figure 2.10: Density Maps at $2.0\rho_c$. Shading denotes average densities of solvent atoms, relative to the bulk density. Grid lines are spaced at 0.5 Å intervals.

solvent density about the solute. Previously, it was shown, Table 2.5, that DPB and HMS have very similar mechanical properties, and therefore, differences observed in the simulations of these two solutes would be attributable to the differences in their electronic characteristics. As a result, it is most likely the case that the greater augmentation seen in HMS is due to the larger atomic charges in the π -system (see Figure 2.5). Turning attention to Figure 2.10, at a reduced density of 2.0, the augmentation about DPB and HMS, as well as the difference in augmentation between these two solutes, is considerably muted compared to the low-density plots in Figure 2.9 (At a density of $2.0\rho_c$, it is assumed that there is no augmentation.). The picture of local density augmentation thus far agrees with physical intuition. Namely, as density is increased from a region where the attractive solute-solvent interactions dictate the solvent distribution, to a region where the solvent distribution is controlled by packing considerations, the augmentation about the solute is greatly diminished. In addition to the augmentation, Figure 2.10 also clearly shows that the solvation shells reflect the geometry of the solute, and hence, using what was previously termed $g_{ss}(r)$, is an accurate method by which to quantify the solvent distribution about the solute. This quantification of Figures 2.9 and 2.10 is the next facet of the solvent distribution to be discussed.

Plotted in Figure 2.11 are the solvation shell distribution functions for DPB/CO₂ spanning reduced densities of 0.2 to 2.0. These functions are essentially averages of the 3D distributions of Figures 2.9 and 2.10 averaged over solute-shaped regions of the solvent. As the bulk density of the system is increased, the first peak of



Figure 2.11: Solvation Shell Distribution Functions for DPB/CO₂. See Chapter 2 Section II D for description of $g_{ss}(r)$. The inset shows the density dependence of the global and local maxima of $g_{ss}(r)$, denoted by r_1 and r_2 respectively.

 $g_{ss}(r)$ decreases and the second solvation shell begins to form at an intermolecular separation of about 7 Å. Once again, the interpretation of $g_{ss}(r)$ is that it reflects the probability of finding a solvent atom at a given distance from the surface of the solute relative to a random distribution of solvent atoms. Therefore, the density dependent behavior of the 1st peak in $g_{ss}(r)$ in Figure 2.11 implies that as the bulk density of the system is increased, the relative probability of finding a solute atom within the first solvation shell decreases. This observation is contrary to the physical picture of dense liquids where the global maximum of g(r) increases with the bulk density of the system. This behavior of the 1st peak in the radial distribution function has been seen before^{38,39}, and therefore, although the behavior is contrary to dense liquid behavior, it is somewhat anticipated. The inset in Figure 2.11 shows the density dependence of the first peak of $g_{ss}(r)$. Here, at high densities, the turnover behavior can be seen, as the system begins to behave like a dense liquid. At low to moderate densities, however, the 1st peak in the solvation shell distribution function is monotonically decreasing. Therefore, there does not seem to be any special dependence on the relative displacement from the critical density. On the other hand, the density dependence of the second peak in the solvation shell distribution function, again in the inset of Figure 2.11, does show a non-monotonic dependence on the bulk density. This result makes sense if the strength of the solute-solvent interactions is considered; solute-solvent intermolecular interactions dominate at small separations in $g_{ss}(r)$. At larger distances, the strength of the solute-solvent interactions diminishes and the structure of the bulk fluid is determined by the solvent-solvent interactions.

Therefore, in the region of the second maximum in $g_{ss}(r)$, the solvent-solvent spatial correlations, which are dependent upon the relative displacement of the bulk density to the critical density, are dominating the structure of $g_{ss}(r)$, and hence, the behavior seen in the inset of Figure 2.11 is understandable. This result can be arrived at more quickly if eq. 2.22 is considered. Namely, as the critical density is approached from either above or below, the correlation length diverges and the tail of the radial distribution function becomes infinitely long.

The comparison of the DPB and HMS solvation shell distribution functions is made in Figure 2.12. In analogy to Figures 2.9 and 2.10, at low density, there is a greater probability (about 15%) of finding a solvent atom close to HMS compared to DPB. At high density, as was previously seen in the density maps, there is no real distinction between the solvation shell distribution functions for either solute.

With the solvent distribution explored, focus is now placed upon the energetics of these distributions in DPB and HMS. Table 2.7 shows the static quantities of interest. The coordination number is shown in the second column of Table 2.7. At low densities, HMS shows a larger coordination number than does DPB. However, this difference is small (about 9%) and quickly drops to under 2% as the bulk density is increased. On the other hand, the HMS solute-solvent interaction energy, U_{UV} , is greater than that of DPB by about 40% at a reduced density of 0.25. The interaction energy is composed of two parts: 1) the contribution from the Lennard-Jones potential and 2) the contribution for the Coulomb potential. Because the Lennard-Jones potential is short ranged and the coordination number of the DPB



Figure 2.12: Comparison of DPB and HMS Solvation Shell Distribution Functions. See Chapter 2: Section ID for description of $g_{ss}(r)$.

| density | N_1 | - <i>U</i> _{UV} | $-U_{UV}(LJ)$ | $f_{ m el}$ |
|------------------|-------|--------------------------|---------------|-------------|
| ρ/ρ _c | | kJ/mol | kJ/mol | |
| | | DPB | | |
| 0.25 | 20 | 31.1 | 27.4 | 0.12 |
| 0.47 | 35 | 101 | 45.9 | 0.11 |
| 0.63 | 41 | 126 | 53.8 | 0.11 |
| 0.80 | 45 | 140 | 58.4 | 0.11 |
| 1.05 | 55 | 187 | 71.0 | 0.10 |
| 1.48 | 64 | 236 | 83.0 | 0.10 |
| 1.69 | 71 | 265 | 91.2 | 0.10 |
| 1.90 | 77 | 292 | 98.6 | 0.10 |
| 2.00 | 80 | 306 | 102. | 0.10 |
| | | HMS | | |
| 0.25 | 22 | 55 | 29.6 | 0.18 |
| 0.63 | 42 | 126 | 54.3 | 0.17 |
| 1.05 | 54 | 183 | 69.7 | 0.16 |
| 1.69 | 69 | 257 | 88.3 | 0.16 |
| 2.00 | 79 | 299 | 100. | 0.16 |

Table 2.7: Solute-Solvent Energetics. The columns labeled N_1 and U_{UV} contain the coordination number of the first solvation shell and the solute-solvent interaction energy respective. The column labeled U_{UV} (LJ) contains the contribution from the Lennard-Jones potential to the total interaction energy and the column labeld f_e contains the fraction of the total interaction energy due to electrostatic contributions.

and HMS systems is similar, the difference in U_{UV} must be due to the Coulombic interaction potential. The Lennard-Jones contribution to U_{UV} , U_{UV} (LJ), is plotted in third column of Table 2.7 and the differences seen in the coordination number are indeed reflected in this contribution to the total solute-solvent interaction energy. On the other hand, the fraction of the total interaction energy that comes from the Coulombic contribution, f_{el} , is systematically higher in HMS than in DPB. Therefore, the differences in the solvation energetics of HMS and DPB are due to the dipolequadrupole coupling present in HMS/CO₂.

As a final aspect of the solute-solvent energetics, the strength of hydrogen bonding interactions is explored. Shown in Figure 2.13 are the local minima of HMS and CO₂ found by two-molecule Monte Carlo methods⁴⁰, in the combined potential energy surface. The hydrogen bonding structure is labeled 1, the two non-hydrogen bonding structures are labeled as 2 and 3, and shown in panel 1, is a structure which is a cooperative effect between the hydroxyl dipole and the ring charges on HMS. From the inset table of Figure 2.13, it is clear that the pure hydrogen bonding structure, 4, is not the global minimum. In addition, while the structure at the global minimum does involve hydrogen bonding, the difference in terms of interactions energies between this structure and the others is small (about 1-2 *kT*). This observation, taken together with the fact that the non-hydrogen bonding structures are more numerous than those involving hydrogen bonding, it is not surprising that the effect of hydrogen bonding between HMS and CO₂ is small in this study of the solvation structure. In particular, if the atomic charges on the terminal hydroxyl



Figure 2.13: Two-Molecule Local Minima from Monte Carlo Calculations.

group of HMS are ignored, a local minimum of 13 kJ/mol, within $\frac{1}{2} kT$ of the global minimum, is still found corresponding to structure 1. As a result, the electrical differences observed between DPB and HMS solvation energetics are attributed to the increased atomic charges in the π -system of the solute and do not have an appreciable contribution from hydrogen bonding

B. Solvation Structure: Experimental Comparison of Absorption Shifts

Comparison to experimental results¹¹ is made through absorption measurements and calculations. A direct comparison of simulated absorption shifts to the experimentally observed shifts, as well as a comparison of the augmentation derived from these shifts is made. Table 2.8 contains the shift results. For both DPB and HMS, Δv_2 , eq. 2.6, systematically underestimates the magnitude of the absorption shift while Δv_3 , eq. 2.11, overestimates the magnitude. However, both Δv_2 and Δv_3 predict the shift of DPB to be greater than that of HMS over the entire density range, is as observed in experiment. Unfortunately, the degree to which the shifts in DPB and HMS differ is also underestimated by the simulations. For example, at a reduced density of 2.0, experimental measurements show a 40% difference between the shifts of the two solutes while simulation predicts a difference of about 16.5%. However, the more important facet of the calculated absorption shifts is not their quantitative agreement with experiment, but their qualitative agreement. If the shifts have the same density dependence, regardless of the magnitude, the augmentation calculated from the curves will be equivalent, as will be discussed shortly. In Figure 2.14 are

| density | Δv_2 | Δν3 | Δv_{exp} | $\Delta v_2/N_1$ | $\Delta v_3/N_1$ |
|------------------|------------------|------------------|------------------|------------------|------------------|
| ρ/ρ _c | cm ⁻¹ |
| | | D | PB | | |
| 0.25 | 128 | 574 | | 6.4 | 28.7 |
| 0.47 | 218 | 972 | 769 | 6.2 | 27.8 |
| 0.63 | 257 | 1138 | 772 | 6.3 | 27.8 |
| 0.80 | 277 | 1225 | 853 | 6.2 | 27.2 |
| 1.05 | 345 | 1515 | 1013 | 6.3 | 27.5 |
| 1.48 | 406 | 1759 | 1244 | 6.3 | 27.5 |
| 1.69 | 445 | 1926 | 1324 | 6.3 | 27.1 |
| 1.91 | 486 | 2091 | 1421 | 6.3 | 27.2 |
| 2.01 | 506 | 2168 | 1482 | 6.3 | 27.1 |
| | | HI | MS | | |
| 0.25 | 122 | 560 | | 5.5 | 25.5 |
| 0.63 | 226 | 1014 | | 5.4 | 24.1 |
| 1.05 | 293 | 1296 | 758 | 5.4 | 24.0 |
| 1.69 | 377 | 1636 | 946 | 5.5 | 23.7 |
| 2.01 | 433 | 1863 | 1065 | 5.5 | 23.6 |

Table 2.8: Comparison of Experimental and Simulated Absorption Shifts.



ure 2.14: Comparison Between Experimental and Simulated Absorption Shifts. The experimental data is displayed as closed triangles. The simulation data is displayed with open symbols; Δv_2 (eq. 2.6) is plotted with circles and Δv_3 (eq. 2.11) is plotted with squares. Shifts are normalized to their value at $2\rho_c$. Experimental data is from Ref. 11.

the absorption shifts normalized to their value at $2.0\rho_c$. The situation is similar to what is seen in the absolute shifts. Namely, both Δv_2 and Δv_3 predict a higher degree of non-linearity in the density dependent shifts of HMS compared to DPB as seen in experiment. Unfortunately, Δv_2 and Δv_3 also underestimate the non-linearity for both solutes. Now the question is how is do these differences affect the augmentation derived from the absorption shifts?

In general, the augmentation from any system observable, which is assumed to be proportional to the bulk density in the liquid region, is calculated via the following definition:

$$LDA \equiv \rho_{eff} - \rho = \frac{\chi(\rho)}{m_{ref}} - \rho$$

$$m_{ref} = \frac{\chi(\rho_{ref})}{\rho_{ref}}$$
(3.1)

where χ is a system observable and ρ_{ref} is taken as 2.0 ρ_c (see Figure 2.1). As mentioned above, the consequence of such a definition is that any observable that is simply proportional to local density will also report the same amount of local density augmentation. In terms of the simulated absorption shifts, Table 2.8 shows the ratios of Δv_2 and Δv_3 to N_1 . The superficial conclusion is that the augmentation calculations based on the absorption shifts and those based on the coordination number will be identical. More subtly, and more importantly, the implication is that the calculated absorption shifts are a more or less direct measure of the coordination number and are therefore of the density augmentation present in the system. With this in mind, the comparison of calculated and experimental augmentation is displayed in Figure 2.15.


Figure 2.15: Comparisons of Local Density Augmentation ($\rho_{eff} - \rho$) Serived From Experiment and Simulation. Augmentation calculated from experimentally observed and simulated absorption shifts are plotted with filled triangles and open circles respectively. Experimental data is from Ref. 11.

For simulated values, augmentation derived from the coordination number is plotted for the reasons described above. Simulation predicts a greater maximum augmentation in HMS/CO₂ than in DPB/CO₂. In addition, both simulation and experiment predict a maximum augmentation at a reduced density of about 0.6, which is in agreement with other studies^{41,9} on a variety of systems. However, although the simulated data agrees with experiment within estimated uncertainties, the augmentation seen in simulation is systematically underestimated for both solutes. In particular, the maximum augmentation in simulation is about 17% lower than experiment for DPB and about 20% lower for HMS. For this reason, possible sources of error are considered.

There are two main sources of error. First of all, it should be noted that the spectral shift calculations used in simulation are completely additive and therefore, the proportionality with the coordination number is not unexpected. However, a rigorous treatment of the electrical interactions involves many-body contributions⁴². Along these lines, Stratt and Adams have considered⁴³ incorporation of such many-body effects, assuming that the shifts may decomposed in to 2 parts: 1) A repulsive part which is indeed additive and 2) a dielectric contribution which is collective. It is this latter non-additive contribution, neglected in the current description of the absorption shifts, which is expected to break the observed proportionality between the coordination number and the shift. This observation suggests that the experimentally measured absorption shift is not entirely a measure of the coordination number. Rather, it is related to the coordination number in a non-trivial manner, and so, the

discrepancy seen between the augmentation derived from N_1 and the experimental shifts does not imply that the simulations are not capturing the augmentation of the real system. Instead, the hope is that the problem lies in the calculation of the shifts themselves. The second possible source of error has been commented on in Section II C. Namely, it was shown, Figure 3.4, that the system sizes of DPB and HMS are probably about 15% too small. Increasing the system size, would probably increase the amount of augmentation seen in the simulation. However, the error in the total number is small, and therefore the error in the coordination number will be even smaller. So it is most likely the case that the error in the system size is not the dominating factor contributing to the discrepancy seen between simulation and experiment. In order to sort out this difference, more study is needed, and it is hoped that the inclusion of the polarization modes sheds some light on this problem.

C. Dynamics: Rotation Times

With the solvation structure of both DPB/CO₂ and HMS/CO₂ explored, attention is focused on the dynamics of these solutes. To begin, the orientational correlation functions (eq. 2.24) of the solute are investigated and both L = 1 and L = 2functions are considered. The interpretation of L = 1 is straightforward because $P_L(x)$ = x. Namely, the persistence (or lack thereof) of a given orientation is what is being measured. The interpretation of the correlation of higher order Legendre polynomials is not as intuitive, however, many experiments such as those used to measure the rotation time DPB and HMS in CO₂ actually report on the L = 2 function. The orientational correlation functions, at L=2, are displayed in Figure 2.16. The corresponding correlation functions of HMS are not included as they are similar to the DPB results. In addition, the free rotor decays (broken lines) are also plotted. As expected, the correlation functions slow with increasing density, with the free rotor function bounding the decays from below at early times. At times greater than 1 ps, the correlation functions depart significantly from the free rotor limit. Taken together with the fact that the simulated decays are well described by exponentials (or a sum of exponentials), and therefore contain only a small Gaussian contribution, these observations imply that even at low densities, the orientational motion of the solutes are diffusive in nature. So at a reduced density of 0.25, where the static picture of the solvation structure resembles that of the gas phase, solute-solvent collisions are still frequent enough to destroy the inertial character of the rotational motion at early times. Figure 2.5 also shows that the decay of the *x* principle axis is much slower than the decays of the *y* and *z* axes, which are similar to one another.

D. Dynamics: Experimental Comparison of Rotation Times.

Although the orientational correlation functions themselves are interesting, it is actually the integral orientation time,

$$\tau_{\alpha}^{(L)} = \int_{0}^{\infty} dt C_{\alpha}^{(L)}(t)$$
(3.2)



Figure 2.16: Orientational Correlation Functions (L=2) of DPB/CO₂ at Reduced Densities of 0.25, 1.0, and 2.0. Solid lines denote simulation results. Dashed lines denote the free rotor limit obtained from angular velocity distributions computed during simulation.

of these decays which can be compared to experiment. Simulated values for both $\tau_{\alpha}^{(1)}$ and $\tau_{\alpha}^{(2)}$ are listed in Table 2.9. Comparison to experiment is made in Figure 2.17. Because the transition moment of both solutes lies along the x principle axis, $\tau_x^{(2)}$ is what is measured in experiment. From Figure 2.17, the simulated integral times (filled circles) for both solutes are seen to be approximately linear in the bulk density, and extrapolate to the free rotor correlation times, which are denoted as "+" in the figure. As an aside, the integral time of a free rotor is actually infinite (for certain values of L) because once the initial angular velocities are known, the trajectory is known for all time. As a result, the 1/e time, the time it takes for the correlation to decay to 1/e, is used as the free rotor time here. For the x axis, at higher densities, the comparison is justified because these decays are well represented by single exponentials and so the integral time is equal to the 1/e time. For the other principal axes, the decays are represented as double exponentials, and though the comparison of the extrapolated integral time to the 1/e time is not absolutely correct, it provides a useful gauge of zero density predictions. The simulated rotation times of DPB and HMS are nearly equal at all but the highest density simulated. With respect to DPB, the experimental data of Anderton and Kauffman⁸ is also not inconsistent with a linear density dependence, however the integral times are systematically lower than predicted by simulation. For HMS, the data of Anderton and Kauffman is qualitatively different from the simulation predictions in that the integral times show a highly non-linear density dependence. The authors ascribe this difference to the

| density | ${	au}_{x}^{(1)}$ | $	au_{y}^{(1)}$ | $	au_z^{(1)}$ | $	au_{x}^{(2)}$ | $	au_{y}^{(2)}$ | $	au_z^{(2)}$ | D_{tr} | |
|---------------|-------------------|-----------------|---------------|-----------------|-----------------|---------------|-----------------------|--|
| ρ/ρ_c | ps | ps | ps | ps | ps | ps | $Å^2 \text{ ps}^{-1}$ | |
| DPB | | | | | | | | |
| 0.00 | 3.4 | 1.2 | 1.2 | 2.1 | 0.8 | 0.8 | | |
| 0.25 | 5.6 | 2.8 | 2.7 | 2.9 | 1.3 | 1.5 | 5.4 | |
| 0.47 | 8.4 | 4.2 | 5.1 | 3.7 | 2.0 | 2.1 | 2.6 | |
| 0.63 | 10.0 | 5.1 | 5.6 | 4.1 | 2.0 | 2.5 | 1.8 | |
| 0.80 | 12.0 | 5.6 | 5.9 | 4.3 | 2.2 | 2.4 | 1.3 | |
| 1.05 | 16.0 | 6.3 | 6.8 | 6.1 | 2.9 | 2.9 | 1.2 | |
| 1.48 | 19.0 | 8.4 | 9.1 | 7.1 | 3.4 | 4.1 | 0.88 | |
| 1.69 | 25.0 | 10.0 | 11.0 | 9.1 | 4.0 | 4.9 | 0.69 | |
| 1.90 | 27.0 | 12.0 | 13.0 | 9.3 | 4.4 | 5.2 | 0.58 | |
| 2.00 | 29.0 | 11.0 | 13.0 | 9.7 | 4.6 | 5.6 | 0.56 | |
| HMS | | | | | | | | |
| 0.00 | 3.2 | 1.2 | 1.2 | 2.0 | 0.8 | 0.8 | | |
| 0.25 | 4.1 | 3.2 | 4.1 | 2.8 | 1.5 | 1.7 | 5.0 | |
| 0.63 | 11.0 | 5.1 | 4.8 | 4.0 | 2.0 | 2.3 | 1.8 | |
| 1.05 | 13.0 | 6.5 | 8.0 | 5.4 | 2.8 | 2.9 | 1.1 | |
| 1.70 | 22.0 | 10.0 | 10.0 | 8.3 | 3.8 | 4.5 | 0.67 | |
| 2.01 | 33.0 | 14.0 | 13.0 | 11.0 | 4.8 | 5.1 | 0.38 | |

Table 2.9: Integral Rotation Times and Translational Diffusion Coefficients.



Figure 2.17: Comparison of Experimental and Simulated Integral Times. Simulation data is displayed as filled circles. Experimental measurements of Anderton and Kauffman⁸ are displayed as open triangles. Experimental measurements of Biswas *et al.*¹⁰ are displayed as open squares.

fact that the hydroxyl group on HMS induces a solvent clustering about the solute, and therefore, removes the linear behavior of the integral times with bulk density that would be otherwise observed (as evidenced by the DPB times). In terms of the discussion in Section V.A of this chapter, it is difficult to see how the terminal OH group is able to effect this kind of change in the rotation time. Namely, the augmentation about the hydroxyl group in HMS is small compared with the augmentation above and below the molecular plane, and therefore, the effect of hydrogen bonding on the rotation times should be masked by the greater augmentation present elsewhere about the solute. This is also the reason why the simulated rotation times for DPB and HMS are similar.

Biswas *et al.*¹⁰ have also measured rotation times of DPB and HMS in supercritical CO₂ and these results are also displayed in Figure 2.17. For both solutes, agreement, to within anticipated uncertainties, between simulation and experimental data is shown. More importantly, the HMS rotation times measured by Biswas *et al.* can be viewed as being linear in density, in sharp contrast to the data by Anderton and Kauffman. It should be noted that the two sets of experimentally determined rotation times use different methods to extract the desired information and each of these methods have their inherent difficulties^{10,11}. Because the Perin method⁴⁵ used by Anderton and Kauffman incorporates time-resolved information collected only at the magic angle, and then uses the steady state anisotropy and limiting anisotropy to calculate the rotation time, it is a somewhat indirect route. Therefore, in light of the discussion on solvation structure and the fact that Biswas *et* *al.* directly measured anisotropy decays, the Biswas *et al.* times are preferred to the data of Anderton and Kauffman.

It is still a curiosity that the simulated rotation times of both solutes do not show the same type of non-linearity in the bulk density as do other system observables like the the coordination number. Insofar as the solute-solvent interaction energy is dominated by contributions from the 1st solvation shells (Table 2.7) the expectation is that this region of the solute provides an almost complete description of the rotational environment of the solute. It is therefore reasonable to conclude that if there is augmentation present in the 1st solvation shell, then the rotational behavior of the solute should reflect on this augmentation. However, as can be seen from Figure 2.17, both DPB and HMS have rotation times that are roughly linear in the bulk density. As a result, it is clear that a deeper look at the rotational behavior of DPB and HMS is needed in order to understand the microscopic reasons why the rotation times seems to be ignorant of the density inhomogeneities about the solutes.

E. Dynamics: Friction

It is important to reconfirm that the roughly linear dependence of τ_x^2 on density extends to other measures of rotational and translational friction. In addition, it might be the case that the L = 1 rotation times, which are a more direct measure of the solute angular displacement, might be more sensitive to the solvent environment and thereby more likely to show evidence of augmentation. Figure 2.18, which



Figure 2.18: Rotation Times and Translational Diffusion Constants for DPB/CO₂. In the top two panels, the x, y, and z rotation times are plotted with open circles, filled triangles, and open squares respectively. The free rotor time is denoted as as "+".

shows the L = 1 and L = 2 rotation times of DPB for each principle axis, addresses these two issues. Again, because the results for DPB and HMS are similar, only the DPB results are shown. These values are also listed in Table 2.9. All of the rotation times are approximately linear functions of the bulk density. This result, although unsatisfying, is anticipated based on the previous results described in Section D. Namely, rotations which displace the *y* and *z* unit vectors of the molecular reference frame must also displace solvent above and below the molecular plane, and because only an isolated rotation about the *z* axis is ignorant of solvent augmentation, the expectation is that the rotation times for all principle axes should be qualitative similar. Assuming, as is often done in experiment, that $\tau_i^{(L)}(\rho) - \tau_{i,fr}^{(L)}$ provides a measure of the rotational friction, the linear dependences shown in Figure 2.18 imply that frictions is approximately proportional to bulk density.

The same conclusion holds for translational friction. The bottom panel in Figure 2.18 and Table 2.9 show the inverse of the translational diffusion constant, D_{tr} , computed from simulation, which is proportional to the translational friction in the diffusive limit²⁴. In light of the considerable augmentation, this result, although seemingly contrary to physical intuition, does support the conclusion that the rotational results obtained are not spurious. In fact, it is clear that if the rotation times of DPB and HMS are to be understood, a deeper look at the friction is required. For this reason, the time dependent friction is analyzed next, in the hopes that the decomposition of the friction leads to an appropriate explanation of the behavior depicted in Figure 2.18.

A complete description of friction involves $\zeta(t)$, the time-dependent friction. The normalized components of the time dependent rotational friction and the translational friction are plotted in Figure 2.19. These curves are generated using the methods described in Chapter 2, Section II.D. The time-dependent friction functions have been averaged into low-, mid-, and high-density curves to partially average out numerical noise in the inverse Laplace transformation. The initial fast decays of the time-dependent friction are to a good approximation invariant to the bulk density. This fast initial decay is due to the repulsive part of the solute-solvent interaction potential: at small intermolecular separations, small changes in distance lead to large changes in the force and torque and therefore cause the correlation of these variables to decay quickly (see Eqns. (2.12) and (2.16)). Therefore, it is fair to characterize repulsive solute-solvent interactions as binary in nature. On the other hand, the long time decay of the time dependent friction does seem to show a non-trivial density dependence. The slow decay is controlled by the attractive part of the solute-solvent potential, where the potential does not have a comparatively large derivative. The fact that there is a significant density dependence to this long-time tail means that it is determined by collective solvent motions, in contrast to the binary behavior of the fast decay.

In order to characterize the time-dependent friction, it is convenient to be able to calculate the correlation times of the friction decays. However, because of noise present in these decays, the times calculated by straightforward integration will not be sufficiently accurate. Nevertheless, these times can still be accurately calculated



Figure 2.19: Time-Dependent Rotational and Translational Friction Functions. The time dependent friction is averaged into low, mid, and high density decays as described in the text. The low density decay is plotted with a solid line while the mid and high density decays are plotted with broken and dotted-dashed lines respectively.

without using the explicit time-dependent decays. The correlation time, τ_{ζ} , is related to the integral friction, ζ , through the relation $\tau_{\zeta} = \zeta / \zeta_0$, where ζ_0 is the time-zero friction (*i.e.* the amplitude of $\zeta(t)$ at t = 0). The amplitude, ζ_0 , can be calculated from eq. 2.16. At t = 0, there is no difference between the random and real forces so the amplitude can be obtained directly from simulation. Insofar as the integral time is concerned, by taking the limit of eq. 2.14 at zero frequency it can be shown that $\zeta = \tau_{\omega}^{-1}$. Therefore, the friction decay is not needed in order to obtain the correlation time. Clearly, such a characterization is not very complete in that it ignores the detailed time evolution of the friction decay. However, insofar as the dynamics of interest are diffusive, the approximation is justified in that these dynamics are governed by the integral friction. It is therefore necessary to take a short diversion in order to establish to what extent this picture is an accurate representation of the rotational behavior of DPB and HMS in CO₂.

Rotational correlation functions for diffusive dynamics can be obtained via the following relations⁴⁶,

$$C_{\alpha}^{(1)}(t) = \exp[-(3D_{rot} - D_{\alpha})t]$$
(2.25)

$$C_{\alpha}^{(2)}(t) = \left(\frac{1}{2} + \frac{3(D_{rot} - D_i)}{4\Delta}\right) \exp\left[-\left(6D_{rot} + 2\Delta\right)t\right] + \left(\frac{1}{2} - \frac{3(D_{rot} - D_i)}{4\Delta}\right) \exp\left[-\left(6D_{rot} - 2\Delta\right)t\right]$$
(2.26)

$$\Delta = \sqrt{D_x^2 + D_y^2 + D_z^2 - D_x D_y - D_x D_z - D_y D_z}$$
(2.27)

where D_{rot} is the average rotational diffusion coefficient and D_{α} is the rotational diffusion coefficient for the α principle axis, which can be obtained via the Stokes-Einstein-Debye relation²⁴

$$D_{\alpha} = \frac{kT}{I_{\alpha}\zeta_{\alpha}}.$$
(2.28)

Shown in Figure 2.20 are the ratios of correlation times predicted for the limit to those determined by simulation. In general, the simulated correlation times are larger than those obtained assuming purely diffusive behavior. However, for reduced densities of 0.5 and higher, these deviations are less than 20%, suggesting that a diffusive description of rotational motion is valid for all but the lowest density simulated. In addition to the correlation times, the decays of the correlation functions are shown in Figure 2.21 (the diffusive calculations have be shifted for clarity). For the x principle axis, reduced densities of 0.63 to 2.0 are plotted and for the y and z principle axes, correlation functions are shown for reduced densities of 1.0 to 2.0. For $C_x^{(2)}$, the diffusive calculation predicts an effectively exponential decay that is well reproduced by simulation. Similarly, the simulated $C_{y}^{(2)}$ and $C_{z}^{(2)}$ correlation functions show a decay which follows the bi-exponential prediction of eq. 3.4 to within estimated uncertainties. Therefore, a diffusive description of rotational motion again seems to be valid. It should also be stated that all of the L = 1 correlation functions, which are not shown, are all well described by single exponential functions in the diffusive limit as well as by simulation. For the lowest densities, the shapes of the diffusive decays are not reproduced by simulation, as might have been anticipated



Figure 2.20: Ratio of Correlation Times From Simulation and Diffusive Predictions. The ratios of the x, y, and z correlation times are plotted with open circles, open squares, and filled triangles respectively. The diffusive calculations are as described in the text. For clarity, only the error bars for the z-components are displayed.



Figure 2.21: Comparison of Orientational Correlation Functions from Simulation and Diffusive Predictions. The simulated correlation functions are plotted with solid lines and the diffusive predictions are plotted with dashed lines. Curves predicted by the diffusive model (as described in the text) have been vertically shifted for clarity.

from Figure 2.20. Because the coupling between angular variables is not anticipated to change significantly with density, the dominating contribution to the error is attributed to the fact that the diffusive description ignores the detailed time dependence of the friction, and not to the fact that an approximate GLE is used. Therefore, as hoped, a diffusive picture is reasonable approximation and focus is now returned to the characterization of the solvent friction.

Shown in Figure 2.22 are the components of the solvent friction (the translational case is treated analogously to the rotational case). In the top left panel, the integral friction is plotted along with the scaled coordination number (note that the x component of the integral friction is also scaled for clarity). As expected from the orientation times, the rotational integral friction is linear in the bulk density, as is the translational friction constant. Obviously, the curvature seen in the coordination number is not mimicked in the integral friction as physical intuition would have suggested. However, the friction amplitudes, upper right plot of Figure 2.22, do show the same non-linearity as does the coordination number, indicating that the amplitudes are sensitive to the density enhancement around the solute. This point is more quantitatively displayed in the bottom left panel. Here, the ratio of the coordination number to the friction amplitude, normalized to its value at a reduced density of 2, is plotted as a function of density. Although some variation is seen, the difference is everywhere less $\pm 5\%$, except for the *z* component of the friction amplitude. The larger departure shown by the z component of the integral friction, is understandable because isolated rotation of the solute about the z axis in the



Figure 2.22: Components of Friction. In all cases, the *x*, *y*, and *z* components of the friction are plotted as filled circles, open squares, and filled triangles respectively. The panels labeled ζ , and $\zeta(t = 0)$ contain the integral friction and the time-zero friction amplitude respectively. The panel label $\zeta(0)/N_1$ show the ratio of the coordination number to the time-zero friction amplitude, normalized to the ratio at a reduced density of 2. The final panel, labeled as τ_{ζ} , shows the density dependent correlation time of the friction decays. Here, the translational components are plotted as open diamonds.

molecular reference frame is relatively ignorant of any effects of density enhancement (see Figures 3.6 and 3.7). The fact that the friction amplitudes have the same qualitative density dependence is understandable because, as has already been discussed, the short time behavior of the friction decay is due to binary solute-solvent repulsive interactions. Therefore, solvent molecules outside the first solvation shell contribute insignificantly to the friction amplitude.

As a final aspect of the solvent friction, the correlation times of these decays are considered in the bottom right panel of Figure 2.22. Here, it is shown that the correlation times are increasing functions of density. Returning to Figure 2.19, it has already been shown that the initial friction decays are relatively invariant to the bulk to the bulk density. As a result, the density dependence of the integral friction can be attributed to differences in the long time tails of these correlation functions. Again, the long time behavior is a result of the collective attractive solute-solvent interactions. Therefore, the linearity seen in the integral friction is not suggesting that the rotational and translational dynamics are ignorant of the local density enhancement. Instead, it is a cancellation effect between the rapidly fluctuating binary solute-solvent repulsive interactions and the slowly varying collective solute-solvent attractive interactions that brings about the linearity seen in the integral friction.

VI. Conclusion

The current study has explored the solvation structure and rotational dynamics of DPB and HMS in CO₂. Insofar as the solvation structure is concerned, it was shown that both DPB and HMS show evidence of local density augmentation. This augmentation was shown to be localized above and below the molecular plane of both solutes. In addition, although hydrogen bonding was seen in the HMS/CO₂ system, the net effect is negligible when compared to augmentation seen elsewhere. Twomolecule Monte Carlo simulations showed that although the hydrogen bonding structure between HMS and CO₂ is the global minimum on the intermolecular potential energy surface, there are many other minima within 1-2 kT of the global minimum. Also, DPB induced slightly less augmentation than HMS. In light of the two-molecule Monte Carlo calculations, the source of this difference was determined to be the larger atomic charges on the fluorophore atoms of HMS with respect to DPB.

In order to gauge the accuracy of the simulation predictions, spectral shifts were computed and compared to experimental measurements. Although the normalized experimentally determined spectral shifts agreed with simulation to within uncertainties, the systematic underestimation of the experimental shift by simulation is some cause for concern, as this underestimation has been seen previously⁴¹. The source of the error comes from the degree of non-linearity of the spectral shift in the bulk density; the experimental shifts are more non-linear than the simulated shifts. The models used here to calculate spectral shifts are sums over independent contributions from individual solvent molecules. As such, the predict shifts that are simply proportional to the coordination number. It is likely that this observed proportionality is the cause of the disagreement between experiment and simulation. The current simulated shifts are completely additive, whereas a more thorough treatment would involve non-additive contributions⁴². By including such contributions, Stratt and Adams⁴³ showed that this leads to about a 10% increase in the calculated augmentation. It will be the focus of future work to include these contributions in the simulation model.

The simulated rotation times of DPB and HMS were found to be 1) linear in the bulk density and 2) nearly equivalent to each other. These simulation results, while not inconsistent with the experimental work of Biswas *et al.*, showed poor agreement with the experimental results of Anderton and Kauffman⁸. Although the simulated rotation times of DPB may arguably agree, to within uncertainties, with the values reported by Anderton and Kauffman, the corresponding rotation times of HMS differ considerably. In particular, simulation does not predict the large degree of nonlinearity seen in the experimentally measured rotation times of HMS. Anderton and Kauffman ascribe this non-linearity to clustering about HMS induced by hydrogen bonding. Simulations of the solvation structure show that, within the context of the simulation models, hydrogen bonding plays a small role in the overall solute-solvent energetics. Therefore, the effect of hydrogen bonding on rotational dynamics is expected to be nominal. Better agreement between simulation and experiment is seen when compared to the measured rotation times of Biswas *et al.* These measured rotations times for DPB and HMS are not inconsistent with a linear density dependence and these times agree with simulation within uncertainties. More importantly, the rotation times of Biswas *et al.* are similar for both DPB and HMS. This similarity is predicted by simulation, but not by the rotation times of Anderton and Kauffman. Due to the more direct nature of the measurement made by Biswas *et al.*, these times are preferred. Therefore, the conclusion is that there is not much different about the rotational dynamics between these two solutes.

The most interesting aspect of this work comes from the investigation of solvent friction. The friction is used characterize the rotational environment of the solutes. Because the rotational environment of the solute is almost exclusively determined by the 1st solvation shell distribution, it is reasonable to conclude that the rotation times of the solutes should report on the local density enhancement. Simulation results showed that, contrary to physical intuition, the integral friction is linear in the bulk density and not the local density. By decomposing the friction into a friction amplitude and an integral time, it becomes clear why the rotation times are seemingly ignorant of the local density enhancement. Namely, this decomposition showed that the amplitudes did mimic the non-linearity of the coordination number. In addition, correlation times of the time-dependent friction also showed a non-linear density dependence. The variation in the amplitude was shown to be a result of shortranged, binary solute-solvent interactions and the variation in the friction correlation time was shown to be a result of the long-ranged, collective solute-solvent interactions. As a result, it was shown that it is the cancellation of these two effects,

namely the attractive and repulsive parts of the solute-solvent intermolecular potential, which produces the observed linearity of the rotation times, and therefore, the observed rotation times are only seemingly ignorant of the local density augmentation.

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Chapter 3

Modeling the Electronic Spectral Shifts of Anthracene in Liquid Solvents

I. Introduction

Clearly, without a comparison to experiment, the accuracy of simulation results cannot be gauged. This connection, between experiment and simulation, is often made by spectroscopic investigation. In solution, experimental electronic spectral shifts can be used to characterize both the local solvent environment as well as solute dynamics, and therefore supply a wealth of information that can be compared with simulation predictions. From a simulation standpoint however, spectral shifts are not easily attainable, as a rigorous computational treatment of the spectroscopy is still not practical in condensed phase systems. Therefore, there is an ever present need for approximate models used to compute spectral shifts of solutes in solution.

One recent approach to modeling the spectroscopy of non-polar systems is to represent the exited state of the solute by the ground state Lennard-Jones functions with modified atomic radii and well depths¹⁻⁴. The motivation for such a heuristic approach is that if the ground state simulation trajectories are evolved on a Lennard-Jones potential energy surface, then it is not unreasonable to assume that the excited state of the solute can be model by the same function, with the change in parameters

accounting for the change in the nuclear and electronic polarizabilities of the solute in the excited state.

The current chapter investigates the use of such an approach to model the spectroscopy of anthracene in a wide range of solvents. Section II A describes the details of how spectral shifts are calculated from simulation data. In Section II B, the solvent models used here are described along with some tests of their accuracy for representing the pure solvents. Section III B discusses the general predictions of the spectral shift model. Specifically, how changes to the model parameters influence the spectral shifts and widths is examined for a typical case. The results obtained by fitting the model parameters are then presented and discussed in Section III C. This section starts with a discussion on the predictions. The ability of the spectral shift model to account for the pressure-dependence of the experimental spectra in two solvents is also examined. Finally, the model predictions for emission spectra are compared to experiment and the applicability of such calculations as a whole are discussed within the framework of linear response

II. Methods

A. Spectral Shift Model

Experimentally, the absorption shift is defined by

$$h\Delta v_{1,0} = \Delta v_{1,0}^{(\text{soln})} - \Delta v_{1,0}^{(\text{gas})}$$
(3.1)

where $\Delta v_{1,0}^{(\text{soln})}$ is the spectral shift of the solute in solution and $\Delta v_{1,0}^{(\text{gas})}$ is the analogous quantity in the gas phase. The corresponding expression for the emission shift can be obtained by interchanging the subscripts 0 and 1 in eqn. 3.1. In addition to the shifts themselves, the widths of the absorption and emission peaks in experiment and simulation are compared. The widths are significant in that they report on the distribution of interactions about the solute.

The starting point for the spectral shift calculations performed in this chapter is the definition of the Lennard-Jones solute-solvent site-site interaction potential,

$$U_{\alpha i}^{(s)}(r_{\alpha i}) = 4\varepsilon_{\alpha i}^{(s)} \left[\left(\frac{\sigma_{\alpha i}^{(s)}}{r_{\alpha i}} \right)^{12} - \left(\frac{\sigma_{\alpha i}^{(s)}}{r_{\alpha i}} \right)^{6} \right]$$
(3.1)

where ε and σ are the interaction well depth and diameters respectively and *S* is the electronic state of the solute. The convention adopted in this chapter is that Greek and Latin indexes correspond to solute and solvent atoms respectively. The absorption shift can be written as,

$$h\Delta v_{1,0} = \left\langle \sum_{\alpha} \sum_{i} \left[U^{1}_{\alpha i}(r_{\alpha i}) - U^{0}_{\alpha i}(r_{\alpha i}) \right] \right\rangle_{0}$$
(3.2)

and the definition of the square width is given as,

$$\left(\delta\Delta v_{1,0}\right)^2 = \left\langle \left(\Delta v_{1,0}\right)^2 \right\rangle - \left\langle \Delta v_{1,0} \right\rangle^2 \tag{3.3}$$

where the angular brackets denote the ensemble average and where it is understood that the corresponding emission shifts and widths can be calculated by interchanging the subscripts 1 and 0. Finally, the excited-state Lennard-Jones parameters used in eq. 3.1 are given in terms of the ground state parameters,

$$\sigma_{\alpha i}^{(1)} = \left(1 + \delta_{\alpha \phi} x\right) \sigma_{\alpha i}^{(0)}$$

$$\varepsilon_{\alpha i}^{(1)} = \left(1 + \delta_{\alpha \phi} y\right) \varepsilon_{\alpha i}^{(0)}$$
(3.4)

where x and y are scaling parameters, ϕ is a fluorophore atom on the solute (with respect to anthracene, the fluorophore atoms are the carbon atoms), and δ is the kronecker delta. The scaling parameters, x and y, are optimized in order to obtain the best agreement between simulated and experimentally measured shifts and widths for a range of solvents.

Although the interaction potentials used to generate the simulated ground state trajectories are computed using the standard Lorentz-Berthelot combining rules,

$$\sigma_{\alpha i}^{(s)} = \frac{1}{2} \left(\sigma_{\alpha \alpha}^{(s)} + \sigma_{i i}^{(0)} \right)$$

$$\varepsilon_{\alpha i}^{(s)} = \sqrt{\varepsilon_{\alpha \alpha}^{(s)} \varepsilon_{i i}^{(0)}}$$
(3.5)

it is computationally advantageous to adopt a different scheme for the calculation of spectral shifts. If eq. 3.5 is used to define the two-body interaction potential, each variation in the scaling parameters x and y requires the analysis of the entire simulation trajectory for each solvent used in the fitting. However, if a geometric mean is used to define both $\sigma_{ai}^{(s)}$ and $\varepsilon_{ai}^{(s)}$,

$$\sigma_{\alpha i}^{(s)} = \sqrt{\sigma_{\alpha \alpha}^{(s)} \sigma_{i i}^{(0)}}$$

$$\varepsilon_{\alpha i}^{(s)} = \sqrt{\varepsilon_{\alpha \alpha}^{(s)} \varepsilon_{i i}^{(0)}}$$
(3.6)

the solute and solvent contributions to the shift and width can be factored, greatly reducing the amount of computation needed to generate the spectral shifts and widths. Taking eq. 3.6 as the combining rules, and defining

$$\omega_{\alpha}^{(s)} = 4\sqrt{\varepsilon_{\alpha\alpha}^{(s)}} (\sigma_{\alpha\alpha}^{(s)})^{6}$$

$$\zeta_{\alpha}^{(s)} = -4\sqrt{\varepsilon_{\alpha\alpha}^{(s)}} (\sigma_{\alpha\alpha}^{(s)})^{3}$$
(3.7)

$$w_{i} = \sqrt{\varepsilon_{ii}^{(0)}} (\sigma_{ii}^{(0)})^{6}$$

$$z_{i} = \sqrt{\varepsilon_{ii}^{(0)}} (\sigma_{ii}^{(0)})^{3}$$
(3.8)

the expression for the spectral shift is found to be

$$\left\langle h\Delta\nu\right\rangle = \sum_{\alpha} \left(\Delta\omega_{\alpha}\left\langle W_{\alpha}\right\rangle + \Delta\zeta_{\alpha}\left\langle Z_{\alpha}\right\rangle\right) \tag{3.9}$$

with

$$W_{\alpha} = \sum_{i} \frac{W_{i}}{r_{\alpha i}^{12}}$$

$$Z_{\alpha} = \sum_{i} \frac{Z_{i}}{r_{\alpha i}^{6}}$$
(3.10)

and where $\Delta \omega_{\alpha} = \omega_{\alpha}^{(1)} - \omega_{\alpha}^{(0)}$ and $\Delta \zeta_{\alpha} = \zeta_{\alpha}^{(1)} - \zeta_{\alpha}^{(0)}$. Also, the expression for the average squared shift, which is needed to calculate the spectral widths via eq. 3.3, is

$$\left\langle \left(h\Delta\nu\right)^{2}\right\rangle = \sum_{\alpha} \left(\Delta\omega_{\alpha}\Delta\omega_{\beta}\left\langle W_{\alpha}W_{\beta}\right\rangle + 2\Delta\omega_{\alpha}\Delta\zeta_{\beta}\left\langle W_{\alpha}Z_{\beta}\right\rangle + \Delta\zeta_{\alpha}\Delta\zeta_{\beta}\left\langle Z_{\alpha}Z_{\beta}\right\rangle\right).$$
(3.11)

The advantage of using a geometric mean as the combining rules for both Lennard-Jones parameters now becomes clear; the entire simulation trajectories only need to be analyzed once during the whole fitting procedure. By computing and storing W_{α} , Z_{α} , $W_{\alpha}Z_{\beta}$, $W_{\alpha}W_{\beta}$, $Z_{\alpha}Z_{\beta}$ averaged over solvent configurations, the shift and width can be easily recomputed for any value of the scaling parameters.

Operationally, absorption shifts are calculated as follows. Simulate anthracene in its ground state in various solvents and collect the simulation trajectories. From the simulated trajectories, form the sums listed in eqns. 3.10 and complete the appropriate averaging. From and initial guess of x and y, use eqns. 3.4 and 3.6 to calculate excited state Lennard-Jones parameters of the flurophore atoms on anthracene and then use eqns. 3.9 and 3.11 to calculate the absorption shift and width of anthracene in the various solvents. The final step is to vary the scaling parameters, using a Levenberg-Marquardt⁵s minimization of χ^2 (χ^2 is a measure of the goodness of fit), in order to get the best simultaneous fit of the absorption shifts and widths across all of the different solvents. In order to obtain the emission shifts, anthracene is simulated with the excited state parameters determined by fitting the absorption shifts. By interchanging the subscripts 1 and 0 in eqns. 3.2 and 3.3, and by changing the sign of the scaling parameters, the simulated emission shifts and widths can be calculated. It should be noted that there is no need for fitting here, as both the ground and excited state parameters for anthracene were determined from the absorption shifts.

B. Simulation Models and Details

The ground state geometry of anthracene was obtained via RHF calculations⁶ using the 6-31G* basis set. Ground state charges were obtained from Merz-KollmanSingh (MKS) fitting of the MP2/6-31G(d) electrostatic potential. Anthracene excited-state charges were obtained from ESP fits of AM1/CI calculations⁷. Lennard-Jones parameters of anthracene were taken from the OPLS parameterization of benzene⁸. Solvent models of acetone⁹, acetonitrile (ACN)^{10,11}, CCl4¹², CHCl₃⁹, CS2¹³, cyclohexane (CHEX)^{14,15}, dimethylsulfoxide (DMSO)¹⁶, n-hexane (NHEX)¹⁷, perfluoro-n-hexane (PFH)¹⁸, and tetrahydrofuran (THF)¹⁹ were selected from available literature models, based on their ability to reproduce liquid state thermodynamic properties. The Lennard-Jones parameters of the solvent models can be found in Table 3.1 and the solute parameters and geometry can be found in Table 3.2.

In the current work, two simulation models of both acetonitrile and cyclohexane were considered. The first acetonitrile model, denoted $ACN^{(1)}$ was parameterized by Edwards *et al.*¹⁰ in order to reproduce the dielectric properties of liquid acetonitrile. The second model, denoted as $ACN^{(2)}$, was parameterized by Jorgensen and Briggs¹¹ in order to reproduce thermodynamic and structural data of the pure liquid. Both models, in an effort to improve computational efficiency, use a united atom representation of the methyl group. The important difference is that the dipole moment of the Edwards *et al.* model, 4.14 D, is larger than the dipole moment of the simulation model used by Jorgensen and Briggs, 3.44 D. As expected, the model of Edwards *et al.* does better at reproducing the experimentally measure dipole moment, 3.92 D²⁰, as it is parameterized to reproduce the dielectric properties of liquid acetonitrile.

| Solvent | Legend | Atom/Site | $\sigma(\text{\AA})$ | <i>ε / k</i> (K) | <i>q</i> (e) |
|--------------------|--------|------------------------|----------------------|------------------|-----------------|
| | | | | | |
| Acetone | 1 | С | 3.75 | 53 | 0.300 |
| | | 0 | 2.96 | 106 | -0.424 |
| | | CH ₃ | 3.91 | 81 | 0.062 |
| ACN ⁽¹⁾ | 2a | CH ₃ | 3.76 | 104 | 0.15 |
| | | С | 3.65 | 76 | 0.28 |
| | | Ν | 3.20 | 86 | -0.43 |
| ACN ⁽²⁾ | 2b | CH_3 | 3.60 | 191 | 0.269 |
| | | С | 3.40 | 50 | 0.129 |
| | | Ν | 3.30 | 50 | -0.398 |
| CCl ₄ | 3 | С | 3.80 | 25 | 0.248 |
| | | Cl | 3.47 | 134 | -0.062 |
| CHCl ₃ | 4 | СН | 3.80 | 40 | 0.420 |
| | | Cl | 3.47 | 151 | -0.140 |
| CS_2 | 5 | С | 3.35 | 51 | 0.000 |
| | | S | 3.52 | 183 | 0.000 |
| CHEX-UA | 6a | CH_2 | 3.91 | 59 | 0.000 |
| CHEX-AA | 6b | С | 3.50 | 33 | -0.12 |
| | | Н | 2.50 | 15 | 0.06 |
| DMSO | 7 | 0 | 2.80 | 36 | -0.540 |
| | | S | 3.40 | 120 | 0.540 |
| | | CH_3 | 3.80 | 148 | 0.000 |
| NHEX | 8 | С | 3.50 | 33 | -0.180 / -0.120 |
| | | Н | 2.50 | 15 | 0.060 |
| PFH | 9 | С | 3.50 | 33 | 0.360 / 0.240 |
| | | F | 2.95 | 27 | -0.120 |
| THF | 10 | 0 | 3.00 | 86 | -0.500 |
| | | RCH ₂ -OR | 3.80 | 59 | 0.250 |
| | | -CH ₂ -ROR- | 3.91 | 59 | 0.000 |

Table 3.1: Solvent Parameters.

| Atom | X (Å) | Y (Å) | <i>ɛ</i> /k (K) | $\sigma(\text{\AA})$ | <i>q</i> (e) | M (g/mol) | Δ <i>q</i> (e) |
|------|-------|-------|-----------------|----------------------|--------------|-----------|----------------|
| | | | | | | | |
| С | -3.63 | 0.72 | 35.22 | 3.55 | -0.11 | 12.01 | 0.01 |
| С | -2.47 | 1.40 | 35.22 | 3.55 | -0.22 | 12.01 | -0.01 |
| С | -1.21 | 0.71 | 35.22 | 3.55 | 0.14 | 12.01 | 0.01 |
| С | 0.00 | 1.39 | 35.22 | 3.55 | -0.30 | 12.01 | -0.01 |
| С | 1.21 | 0.71 | 35.22 | 3.55 | 0.14 | 12.01 | 0.01 |
| С | 2.47 | 1.40 | 35.22 | 3.55 | -0.22 | 12.01 | -0.01 |
| С | 3.63 | 0.72 | 35.22 | 3.55 | -0.11 | 12.01 | 0.01 |
| С | 3.63 | -0.72 | 35.22 | 3.55 | -0.11 | 12.01 | 0.01 |
| С | 2.47 | -1.40 | 35.22 | 3.55 | -0.22 | 12.01 | -0.01 |
| С | 1.21 | -0.71 | 35.22 | 3.55 | 0.14 | 12.01 | 0.01 |
| С | 0.00 | -1.39 | 35.22 | 3.55 | -0.30 | 12.01 | -0.01 |
| С | -1.21 | -0.71 | 35.22 | 3.55 | 0.14 | 12.01 | 0.01 |
| С | -2.47 | -1.40 | 35.22 | 3.55 | -0.22 | 12.01 | -0.01 |
| С | -3.63 | -0.72 | 35.22 | 3.55 | -0.11 | 12.01 | 0.01 |
| Н | -4.57 | 1.24 | 15.10 | 2.42 | 0.13 | 1.01 | 0.00 |
| Н | -2.47 | 2.48 | 15.10 | 2.42 | 0.14 | 1.01 | 0.00 |
| Н | 0.00 | 2.47 | 15.10 | 2.42 | 0.15 | 1.01 | 0.00 |
| Н | 2.47 | 2.48 | 15.10 | 2.42 | 0.14 | 1.01 | 0.00 |
| Н | 4.57 | 1.24 | 15.10 | 2.42 | 0.13 | 1.01 | 0.00 |
| Н | 4.57 | -1.24 | 15.10 | 2.42 | 0.13 | 1.01 | 0.00 |
| Н | 2.47 | -2.48 | 15.10 | 2.42 | 0.14 | 1.01 | 0.00 |
| Н | 0.00 | -2.47 | 15.10 | 2.42 | 0.15 | 1.01 | 0.00 |
| Н | -2.47 | -2.48 | 15.10 | 2.42 | 0.14 | 1.01 | 0.00 |
| Н | -4.57 | -1.24 | 15.10 | 2.42 | 0.13 | 1.01 | 0.00 |

Table 3.2: Anthracene Parameters.
Both cyclohexane simulation models employed in these simulations are a result of the OPLS parameterization by the Jorgensen research group. The first cyclohexane model employed, denoted CHEX-UA, is a united atom representation¹⁴ in which each CH₂ group is modeled as a single interaction site. The second model, denoted CHEX-AA, is an all-atom representation of cyclohexane¹⁵. In addition to the obvious difference in the number of interaction sites, atomic charges are present in the all-atom but not in the united-atom representation, however, the effect of these atomic charges is negligible in the present simulations.

Prior to solute+solvent simulations, simulations of the neat solvents were performed in order to gauge the accuracy for reproducing the properties of these solvents under ambient conditions (298 K and 1 atm). Each liquid was equilibrated from a lattice for at least 200 ps prior to four production runs of 100 ps each. The number of molecules simulated for each system is listed in Table 3.3 and was chosen to provide approximately the same simulation size for all solvents (box length of about 34 Å). All of the solvent models were rigid and the equations of motion were integrated with the DLPOLY²¹ program suite using quaternion parameters. Periodic boundary conditions were imposed with a spherical truncation of Lennard-Jones interactions at 12 Å. For dipolar solvents, an Ewald sum²² was used to represent long-range electrical interactions. Solute+solvent simulations were performed under identical conditions. For the production runs, however, simulation configurations were stored every 400 fs to allow for calculation of the spectral shifts.

| Solvent | Number | V _m (sim) [cm ³ /mol] | V _m (exp) [cm ³ /mol] | Error (%) | ΔH _{vap} (sim) [kJ/mol] | ΔH _{vap} (exp) [kJ/mol] | Error (%) |
|--------------------|--------|--|--|--------------|--|--|--------------|
| | | | | | | | |
| Acetone | 351 | 75 | 74 | 1.8 | 31.3 | 30.5 | 0.5 |
| $ACN^{(1)}$ | 490 | 53 | 53 | 0 | 38.9 | 33.2 | 17.1 |
| ACN ⁽²⁾ | 490 | 54 | 53 | 2.8 | 32.7 | 33.2 | 1.6 |
| CCl_4 | 267 | 97 | 97 | 0.2 | 32.3 | 32.4 | 0.6 |
| CHCl ₃ | 322 | 80 | 81 | 0.4 | 31.7 | 31.3 | 1.5 |
| CS_2 | 428 | 61 | 61 | 0.1 | 27.7 | 27.5 | 0.7 |
| CHEX-UA | 239 | 106 | 109 | 2.3 | 35.7 | 33.3 | 7.2 |
| CHEX-AA | 239 | 110 | 109 | 0.7 | 34.9 | 33.3 | 4.7 |
| DMSO | 364 | 71 | 71 | 0.4 | 54.5 | 52.9 | 3 |
| NHEX | 254 | 133 | 132 | 1.1 | 32.7 | 31.5 | 3.8 |
| PFH | 255 | 207 | 201 | 2.7 | 31 | 32 | 3 |
| THF | 355 | 81 | 82 | 0.9 | 32.5 | 31.8 | 2.1 |

Table 3.3: Liquid Simulation Results and 1 atm and 298 K. Estimated uncertainties in the simulated molar volumes and enthalpies of vaporization are much less than 1% for all of the solvents listed, except for PFH where the uncertainty in the enthalpy of vaporization is about 12%. Experimental values were taken from Ref. 20.

III. Results and Discussion

A. Checks on Solvent Models

Clearly, the accuracy of the spectral shift calculation depends, in part, on the faithfulness with which the solvent models reproduce the ground state energetics. To judge their accuracy in this context, results of the pure solvent simulations are listed in Table 3.3. The data here shows these models accurately reproduce experimental molar volumes, differing by about 3% at the maximum. The enthalpies of vaporization, on the other hand, compare less favorably. The acetonitrile model of Edwards *et al.* overestimates ΔH_{vap} by 17% while the model of Jorgensen and Briggs underestimates ΔH_{vap} by only about 2%. This difference stems from the fact that the simulation models were parameterized to reproduce different characteristics of the pure fluid (the model of Jorgensen and Briggs was parameterized to reproduce the enthalpy of vaporization). Although calculations based on both models of acetonitrile are presented, the model of Jorgensen and Briggs is preferred. The simulation model of CHEX-UA also overestimates the enthalpy of vaporization, by about 7%. Monte Carlo/NPT simulations¹⁴ of OPLS cyclopentane and benzene at STP show good agreement with experimentally determined vaules of ΔH_{vap} , and therefore, the expectation was that the model would be suitable for the present purposes. The inclusion of explicit hydrogen atoms into the molecular description in CHEX-AA slightly reduces the error in the predicted enthalpy of vaporization. This observation is not surprising, as the all atom model adds another 2 parameters that may be adjusted to better reproduce experimental results. The literature has an abundance of

simulation potentials for cyclohexane^{23,24}, however, the OPLS models, CHEX-UA and CHEX-AA, provide a good balance between accuracy and computational expense.

B. General Freatures of the Spectral Shift Model

Before looking at the results of fitting experimental data, it is instructive to look at the general behavior of the spectral shift model. To accomplish this, anthracene+CHEX-UA is taken as a representative system, and the behavior of the shifts and widths is examined as a function of the scaling parameters x and y.

Plotted in Figure 3.1 are the iso-shift and iso-width contours of the anthracene+CHEX-UA absorption as functions of $\sigma^{(1)}/\sigma^{(0)}$ and $\varepsilon^{(1)}/\varepsilon^{(0)}$. The behavior of the widths is readily understandable. Namely, the global minimum occurs at $(\sigma^{(1)}/\sigma^{(0)}, \varepsilon^{(1)}/\varepsilon^{(0)}) = (1,1)$, where the difference potential is identically zero. The oval contours of the width are elongated along the $\varepsilon^{(1)}/\varepsilon^{(0)}$ axis because changes in the well-depth only serve to increase the curvature of the well, as opposed to changes in the atomic diameter which displace the global minimum the global minimum of the difference potential (This will be elaborated upon later). The behavior of the shift contours is a little more subtle. The contours correspond to a slightly parabolic surface in three dimensions. Along the $\varepsilon^{(1)}/\varepsilon^{(0)}$ axis, there are no extrema. However, using eqn. 3.14, an extremum along the $\sigma^{(1)}/\sigma^{(0)}$ axis is found at

$$\frac{\sigma^{(1)}}{\sigma^{(0)}} = \left(\frac{U_{tot}^{(att)}}{2U_{tot}^{(rep)}}\right)^{\frac{1}{3}}$$
(3.12)



Figure 3.1: Absoprtion Iso-shift and Iso-width Contours for Anthracene in CHEX-UA. Solution for best fit across solvents is shown with an "*". Iso-shifts and widths are shown in solid and broken lines respectively. Units in cm⁻¹.

where $U_{tot}^{(att)}$ and $U_{tot}^{(rep)}$ are the total solute-solvent interaction energies arising from the r^{-12} and r^{-6} contributions to the ground state Lennard-Jones potential respectively. Therefore, the trough in the three dimensional surface occurs at eqn. 3.12 for any value of the scaling parameter y. As with the widths, scaling the interaction welldepth does not change the global minimum, and so the fact that there is a trough along the $\varepsilon^{(1)}/\varepsilon^{(0)}$ axis is not very surprising. These qualitative features not withstanding, the important observation here is that in general, the ε scaling dominates changes in the absorption shift whereas the σ scaling dominates changes in the absorption width.

The optimum scaling parameters, determined by fitting across all solvents, are denoted by the "*" in Figure 3.1. In order to characterize the behavior of the spectral shift model about this point in $\sigma\varepsilon$ -space, cross-sections of the shift and width surfaces are plotted in Figures 3.2 and 3.3 respectively. In Figure 3.2, the change in the absorption shift is nearly linear for physically extreme changes in both σ and ε . Also from this figure, it is more easily seen that changes in the well-depth have a more profound impact on the spectral shift than do the corresponding changes in the atomic radius. Of course, as was already stated, the opposite is true when looking at variations in the width, as evidenced by Figure 3.3. Here, the absorption widths are seen to pass through a minimum at $(\sigma^{(1)}, \varepsilon^{(1)}) < (\sigma^{(0)}, \varepsilon^{(0)})$. However, in the region of the optimum solution for the scaling parameters, the change in the width is approximately linear in both *x* and *y*. The main conclusion to be drawn is that while changes of σ/σ_0 by ± 0.01 and $\varepsilon/\varepsilon_0$ of ± 0.1 about the optimum solution do not change



Figure 3.2: Variation of the Absorption Shift of Anthracene in CHEX-UA with the Scaling Parameters $\sigma^{(1)}/\sigma^{(0)}$ and $\varepsilon^{(1)}/\varepsilon^{(0)}$. Dashed lines in upper panel denote extent of $\sigma^{(1)}/\sigma^{(0)}$ scaling.



Figure 3.3: Variation of the Absorption Width of Anthracene in CHEX-UA with the Scaling Parameters $\sigma^{(1)}/\sigma^{(0)}$ and $\varepsilon^{(1)}/\varepsilon^{(0)}$. Dashed lines in upper panel denote extent of $\sigma^{(1)}/\sigma^{(0)}$ scaling.

the simulated widths by more than experimental uncertainties (about 30 cm⁻¹)²⁵, the same cannot be said for the uncertainties in the absorption shifts (about 50 cm⁻¹)²⁵. This result is important in that it comments on the behavior of the shift model when the optimum scaling parameters are determined during the course of the fitting procedure. That is to say, uncertainties in the experimental spectral shifts, which dictate the search area in $\sigma\epsilon$ -space, correspond to a wide range of simulated shifts and therefore, experimental uncertainties in the shifts are far more damaging than uncertainties in the widths.

At this point, it is instructive to take a deeper look at the absorption shifts and consider how they are composed of attractive and repulsive contributions. In general, the spectral shift of a solute can be written in terms of the atom-atom radial distribution function as

$$h\Delta v = \sum_{\alpha} \sum_{i} 4\pi \rho_{i} \int_{0}^{\infty} dr r^{2} \Delta U_{\alpha i}(r) g_{\alpha i}(r)$$
(3.13)

where, once again, α runs over the solute sites and *i* runs over the solvent sites. In the case of anthracene, all of the solute fluorophore atoms are identical. Similarly, for CHEX-UA, all of the solvent atoms are identical. Therefore, eqn. (3.13) can be simplified considerably,

$$\Delta v = 56\pi \rho \int_{0}^{\infty} dr r^{2} \Delta U_{\phi v}(r) g_{\phi v}(r)$$
(3.14)

where ϕv refers to the fluorophore-solvent atom interaction pair. The utility of eqn. 3.14 is that it allows the total shift to be decomposed into contributions from the

attractive and repulsive parts of the Lennard-Jones difference potential²⁶.

Specifically, because r and g(r) are everywhere greater than zero, the differential form of eqn. 3.14 is only less than zero when the difference potential is less than zero. For CHEX-UA, the attractive and repulsive contributions to the shift are given by the expressions below,

$$h\Delta v = h\Delta v_{rep} + h\Delta v_{att} \tag{3.15}$$

$$h\Delta v_{rep} = 56\pi\rho \left(\sqrt{y}(x+1)^{6} - 1\right) \int_{0}^{\infty} dr r^{2} U_{\phi\nu}^{(rep)}(r) g_{\phi\nu}(r)$$

$$h\Delta v_{att} = 56\pi\rho \left(\sqrt{y}(x+1)^{3} - 1\right) \int_{R}^{\infty} dr r^{2} U_{\phi\nu}^{(att)}(r) g_{\phi\nu}(r)$$
(3.16)

where $U_{\phi}^{(rep)}(r)$ and $U_{\phi}^{(att)}(r)$ are the r^{-12} and r^{-6} components of the ground state Lennard-Jones interaction potential. This dissection of the shift into attractive and repulsive contributions is depicted in Figure 3.4. The top and middle panels of the figure show the radial distribution function and the difference potential for anthracene+CHEX-UA and the bottom panel shows the differential shift. At small intermolecular separations, where the magnitude of the difference potential is large, the radial distribution function is relatively small, and hence so is the positive ("repulsive") contribution to the shift. As g(r) reaches its global maximum, the difference potential is approximately at it's global minimum, thereby maximizing the negative ("attractive") contribution to the shift. Specifically, in the case of CHEX-UA, the repulsive and attractive contributions are found to be -240 cm⁻¹ and 1270 cm⁻¹ respectively. While this is an interesting observation, the more important point is that the repulsive and attractive contributions to the spectral shift cannot be varied



Figure 3.4: Dissection of the Spectral Shift of Anthracne in CHEX-UA. Plotted in the top and middle panels are the anthracene-CHEX-UA radial distribution function and Lennard-Jones interaction potential respectively. Plotted in the bottom panel is the distance dependent differential shift.

independently. That is to say, by scaling x or y, both the attractive and repulsive contributions to the spectral shift are also scaled.

As a final aspect of the general behavior of the spectral shift model, the line shapes of the absorption bands are examined. Plotted in Figure 3.4 are the line shapes obtained when the scaling parameters are varied about the optimum value of $(\sigma^{(1)}/\sigma^{(0)}, \varepsilon^{(1)}/\varepsilon^{(0)}) = (0.02, 0.21)$ as depicted in Figure 3.1. From the upper panel of Figure 3.4, the line shape of the absorption band with $(\sigma^{(1)}/\sigma^{(0)}, \varepsilon^{(1)}/\varepsilon^{(0)}) = (0.02, 0.21)$ is seen to be approximately Gaussian. As the scaling of the atomic size increases or decreases from this value, the line shapes become increasingly asymmetric, with an elongated tail. This asymmetry is attributable to the asymmetry of the Lennard-Jones difference potential. The bottom panel of Figure 3.4 shows the variation in line shapes with the scaling parameter y. Because scaling $\varepsilon^{(0)}$ scales the well-depth, the symmetry of the difference potential in the region of the global minimum is only slightly affected, and therefore, changes in $\varepsilon^{(1)}/\varepsilon^{(0)}$ do not have a dramatic effect on the shape of the absorption band.

C. Comparison to Experimental Spectra

With the general behavior of the spectral shift model well characterized, focus is now placed on how well these calculations reproduce experimental observations. Namely, the question asked is how well can a single parameterization of $\sigma^{(1)}/\sigma^{(0)}$ and $\varepsilon^{(1)}/\varepsilon^{(0)}$ predict the spectral shift of anthracene in various solvents?



Figure 3.5: Simulated Line Shapes of the Absorption Bands of Anthracene in CHEX-UA.

The comparison between experimental²⁵ and simulated absorption shifts and widths is made in Figure 3.6 and in Table 3.4 with the scaling $(\sigma^{(1)}/\sigma^{(0)}, \epsilon^{(1)}/\epsilon^{(0)}) = (0.02, 0.21).$ At the outset, it should be mentioned that although the scaling factors of the fluorophore-solvent interaction parameters are somewhat larger than others have employed^{1,3} (for example, Heidenrich *et al.*³ scaled the carbon-argon pair well-depth and diameter by 12% and 1%, respectively, in order to model the spectroscopy of perylene-argon clusters in the gas phase), the overall variation in parameters is still modest. The correlation of experimental and simulated shifts thus calculated is shown in the upper panel of Figure 3.2. With the exception of CS_2 (#5) and PFH (#9), the error in the calculated absorption shifts is less than 20%. The situation is similar when the experimental and simulated absorption widths are compared, as in the bottom panel of Figure 3.2. However, in this case, the widths of $CCl_4(#3)$ as well as CS₂ and PFH differ from the experimental measurements by more than 30%. The estimated experimental uncertainties in the shifts and widths are 50 cm⁻¹ and 30 cm⁻¹ respectively. As a result, although the simulated shifts are generally beyond these uncertainties, the simulated widths generally are not. In addition, the χ^2 value determined during the fitting procedure was 4.12, and because χ^2 much greater than 1 implies that the difference between the experiment and simulation is outside the margin of statistical uncertainties, the general conclusion is that the simulated predictions do not agree with the experimental measurements. However, it is not clear whether better agreement with experiment is to be expected. In particular, although simulations of the pure solvents predict enthalpies of vaporiation and molar



Figure 3.6: Correlation of Experimentally Measured and Simulated Absorption Shifts and Widths. The CS_2 data was not included in the fitting but are included as predictions. Experimental uncertainties in the shifts and widths are ± 50 cm-1 and ± 20 cm-1 respectively. Estimated uncertainties in the simulation data are less than 1% of the value. Labeling scheme can be found in Table 3.1. Experimental data is from Ref. 25.

| solvent | Δν (exp) cm ⁻¹ | $\Delta v (sim) cm^{-1}$ | error % | δΔv (exp) cm ⁻¹ | $\frac{\delta\Delta\nu(sim)}{cm^{\cdot1}}$ | error % | | |
|-------------------------------------|------------------------------|--------------------------|------------|-------------------------------|--|------------|--|--|
| | | | | | | | | |
| Absorption ($x = 0.02, y = 0.21$) | | | | | | | | |
| CS_2 | 1840 | 1250 | 32 | 160 | 140 | 13 | | |
| DMSO | 1240 | 1050 | 16 | 160 | 130 | 17 | | |
| CCl_4 | 1230 | 1020 | 17 | 170 | 120 | 30 | | |
| CHCl ₃ | 1170 | 1300 | -11 | 160 | 150 | 7 | | |
| THF | 1050 | 1000 | 5 | 140 | 130 | 6 | | |
| CHEX-UA | 1000 | 1030 | -3 | 120 | 120 | -4 | | |
| CHEX-AA | 1000 | 1000 | -1 | 120 | 90 | 25 | | |
| acetone | 940 | 900 | 4 | 140 | 130 | 8 | | |
| ACN ⁽¹⁾ | 930 | 1050 | -13 | 140 | 150 | -1 | | |
| ACN ⁽²⁾ | 930 | 1080 | -16 | 140 | 140 | 0 | | |
| NHEX | 930 | 930 | 0 | 110 | 90 | 19 | | |
| PFH | 460 | 690 | -51 | 60 | 80 | -24 | | |
| Emission ($x = -0.02, y = -0.21$) | | | | | | | | |
| DMSO | 1530 | 1300 | 14 | 200 | 120 | 39 | | |
| CCl_4 | 1440 | 1260 | 13 | 220 | 100 | 53 | | |
| CHCl ₃ | 1400 | 1600 | -14 | 180 | 130 | 25 | | |
| THF | 1240 | 1250 | 0 | 150 | 110 | 26 | | |
| CHEX-AA | 1100 | 1260 | -14 | 130 | 110 | 11 | | |
| acetone | 1180 | 1130 | 4 | 160 | 120 | 26 | | |
| ACN ⁽¹⁾ | 1170 | 1300 | -11 | 160 | 120 | 25 | | |
| ACN ⁽²⁾ | 1170 | 1340 | -15 | 160 | 130 | 20 | | |
| NHEX | 1030 | 1110 | -8 | 120 | 90 | 30 | | |
| PFH | 500 | 840 | -65 | 80 | 80 | -1 | | |

Table 3.4: Experimental and Simulated Spectral Shifts and Widths. Experimental values were taken from Ref. 25.

volumes that are close to experiment, there is no measure of how well these simulation models capture the solute-solvent interactions present in the real systems. In addition, because modeling the spectral shift via a change in Lennard-Jones parameters is only an approximate model²⁷, the degree to which these calculations can accurately reflect the excited state solute-solvent interactions is not known. Therefore, while a uniform parameterization of the solute Lennard-Jones parameters in the modeling of the excited state of anthracene is appealing, it cannot be stated for certain whether or not a uniform parameterization is beyond the abilities of the spectral shift model described here.

Insofar as CS_2 and PFH are concerned, the rather large disagreements between experiment and simulation are not unanticipated. In order to understand the possible sources of error in the spectral shift model, it is useful to view the observed shifts from a different perspective. If the solvent is viewed as a dielectric continuum, and the solute is represented by a point dipole in a spherical cavity, the spectral shift may be written as^{28,29},

$$\Delta v = A[f(\varepsilon) - f(n^2)] - Bf(n^2)$$
(3.17)

$$f(x) = \frac{x-1}{x+2}$$
(3.18)

where ε and *n* are the dielectric constant and the refractive index of the medium respectively. Here, the factors *A* and *B* are fit parameters and have been determined to be 170 cm⁻¹ and 4100 cm⁻¹ respectively. Moreover, because *B* is almost 25 times as large as *A*, the electronic polarizability is by far the dominating contribution to the overall shift. As a result, the omission of the nuclear polarizability in the present description of the spectral shift, eq. 3.9, is not at all damaging. However, to be as accurate as possible, the small correction for the nuclear polarizability has been subtracted from the experimentally determined spectral shifts prior to fitting the scaling parameters x and y and these adjusted values are already reflected in Table 3.4.

Plotted in Figure 3.7 is the correlation of dielectric continuum predictions and experimentally measured^{30,31} absorption shifts. The majority of the solvents are well described by a single correlation. On the other hand, predictions for CS_2 are underestimated by a large amount. It is left as a curiosity that the spectroscopic behavior of CS₂ apprears to be distinct from that of the other solvents, and therefore, the experimental shifts and widths are not included in the parameterization of the scaling parameters in eqns. 3.4. In addition to CS_2 , the perfluorinated solvents are also seen to exhibit a fundamentally different spectroscopic behavior from the majority of the solvents plotted in Figure 3.7, although as group, these prefluorinated solvents are well represented by a single correlation. This observation is not new³¹⁻³³ and it has been suggested that the different behavior seen in perfluorinated solvents derives from a different balance of repulsive and attractive contributions to the solutesolvent interactions relative to their hydrogenated analogues³². Although these differences are known to exist, they are important in the parameterization of the scaling variables x and y because they test the spectroscopic model's ability to account for a wide range of shift magnitudes.



Figure 3.7: Correlation of Experimentally Measured Absorption Shifts Using a Dielectric Continuum Theory. CS_2 and perfluoronated solvents are represented by filled squares and filled triangles respectively. All other solvents are represented by circles. Non-polar solvents, aprotic solvents, and alcohols are plotted as black, grey, and open symbols respectively. Experimental data is from Refs. 30 and 31.

Regardless of the special cases of CS₂ and PFH, the spectral shift model as a whole is clearly failing to capture the range of different solute-solvent interactions spanned by the various solvents, at least within experimental uncertainties. Therefore, the attractive and repulsive contributions to the spectral shift (eqn. 3.16) are examined for all of the solvents, in the hopes that it will shed further light on possible source of error. The repulsive and attractive contributions are shown in Table 3.5. With the exception of CHEX-AA, NHEX, and PFH, the average repulsive contribution to the shift is about 260 cm⁻¹ with a standard deviation of about 13% and the average attractive contribution is about 1332 cm⁻¹ with a standard deviation of about 11%. Considering only CHEX-AA, NHEX, and PFH, the averaged repulsive and attractive contributions are 68 cm⁻¹ and 941 cm⁻¹. Clearly then, the solvents can be sorted into two groups based on the ratio of repulsive to attractive contributions of the spectral shift. The most obvious difference between these two groups is that the simulation models of CHEX-AA, NHEX, and PFH all have hydrogen atoms modeled explicitly, whereas the other solvent models, where applicable, use the OPLS united atom representation. As a result, it would seem that the breaks down into attractive and repulsive contributions is quite sensitive to the specific solvent model chosen, despite the fact that the net shifts and widths are not.

Because simulation data is available for both united atom and all-atom models of cyclohexane, these models are compared in order to resolve the differences seen in their spectroscopic behaviors. The attractive contribution to the spectral shift of anthracene in CHEX-UA and CHEX-AA differ by about 13% whereas the repulsive

| Solvent | Δv_{tot} cm ⁻¹ | Δν _{rep} cm ⁻¹ | $-\Delta v_{att}$ cm ⁻¹ | Δv_{att} / Δv_{rep} |
|--------------------|-----------------------------------|---------------------------------------|------------------------------------|-------------------------------------|
| | | | | |
| acetone | 900 | 200 | 1110 | 5.5 |
| ACN ⁽¹⁾ | 1040 | 290 | 1330 | 4.7 |
| ACN ⁽²⁾ | 1070 | 300 | 1370 | 4.6 |
| CCl_4 | 1020 | 220 | 1230 | 5.7 |
| CHCl ₃ | 1300 | 300 | 1590 | 5.4 |
| CHEX-UA | 1030 | 240 | 1270 | 5.4 |
| CHEX-AA | 1010 | 80 | 1090 | 13.4 |
| CHEX-AA: C-C | 640 | 10 | 650 | 65.1 |
| CHEX-AA: C-H | 370 | 80 | 450 | 5.5 |
| CS_2 | 1240 | 280 | 1520 | 5.5 |
| DMSO | 1050 | 280 | 1320 | 4.8 |
| NHEX | 930 | 70 | 1000 | 14.3 |
| PFH | 690 | 50 | 740 | 14.1 |
| THF | 1000 | 250 | 1250 | 5.0 |

Table 3.5: Decomposition of the Spectral Shifts into Attractive and Repulsive Contributions. CHEX-AA: C-C denotes the shift contribution from the solute-solvent carbon-carbon pair interaction. CHEX-AA: C-H denotes the shift contribution from the solute-solvent carbon-hydrogen pair interaction. contribution differs by about 60%. Therefore, focus is placed on understanding the short ranged spectroscopic differences between these two solvent models. Shown in Figure 3.8 is the decomposition of the spectral shift for CHEX-UA and CHEX-AA. Insofar as CHEX-AA is concerned, the explicit modeling of the hydrogen atoms of the solvent serves to distance the solute-solvent carbon-carbon separation with respect to CHEX-UA, as evidenced by the plots of the radial distribution functions. Moreover, the slope of $g_{C,H}(r)$ departs from zero more slowly than does $g_{C,ME}(r)$. Even if the $g_{C,H}(r)$ and $g_{C,H}(r)$ are averaged, the early behavior $g_{C,H}(r)$ still dominates the rise from zero. It is precisely this fact, namely that CHEX-UA overestimates the steepness of the repulsive part of the potential, which gives rise to the greater repulsive contribution to the spectral shift of anthracene in CHEX-UA relative to CHEX-AA. Therefore, although the united atom models qualitatively capture, in an average sense, the component of the spectral shift derived from attractive intermolecular interactions, the short-distance repulsive contribution is not well reproduced. It would then seem that for the present purposes, the all atom model solvent model is preferable.

As mentioned earlier, although a single parameterization of the anthracene Lennard-Jones scaling factors is desired, the spectroscopic modeling embodied in eqns. 3.9 and 3.11 cannot account for all of the variations in solute-solvent interactions as depicted in Figure 3.2 and Table 3.4. Therefore, it logical to ask whether or not the current spectroscopic model can account for the pressure dependent spectral shifts, where the intermolecular potential function does not vary.



Figure 3.8: Dissection of the Spectral Shift of Anthracene in CHEX-UA and CHEX-AA. Shown in the top and middle panels are the radial distribution functions and the interaction potential for anthracene-cyclohexane respectively. Shown in the bottom panel is the distance dependent differential shift. The united atom representation is plotted with a solid line. The all atom hydrogen and carbon contributions are plotted with dotted-dashed and dashed lines respectively.

The correlation of the pressure dependent absorption shifts and widths of anthracene in CS₂ and n-hexane are shown Figure 3.9 and Table 3.6. Here, simulated pressures of 0.001, 5, and 10 kbar are compared with experimental results^{34,35}. For nhexane, good agreement is found between the experimentally measured absorption shifts and those predicted by simulation. For all three pressures, the errors in the simulated shifts are less than 6% while the errors in the widths are less than 15%. However, for CS₂, the situation is quite different. Clearly, simulation underestimates both the experimental shifts and widths of anthracene in CS_2 by a significant amount. Re-parameterization of the scaling factors, using the density dependent CS_2 data, reduces the error in the simulated shifts, however, only slightly improves the correlation of the absorption widths. It is only when x is forced to be less than zero in the density dependent re-parameterization of the scaling factors that the correlation of both the shift and width in CS_2 improves markedly. From a physical standpoint, it is not clear why decreasing the atomic size of the fluorophore atoms on anthracene should help the shift and width correlation seen in Figure 3.9. However, from the previous discussion of the differential shifts, it can be argued why this might be the case in the context of the present spectral shift model. For the scaling parameters (x,y) = (-0.08, 0.7370), the inequality

$$0 > \frac{\sqrt{y+1}(x+1)^6 - 1}{\sqrt{y+1}(x+1)^3 - 1}$$
(3.19)

holds true. As a result, the fluorophore-solvent difference potential is everywhere less than zero, and therefore, entirely attractive. In terms of the differential shift, this



Figure 3.9: Correlation of Pressure Dependent Absorption Shifts and Widths of Anthracene in CS₂ and n-hexane. n-hexane and CS₂ data are displayed with circles and triangles respectively. Filled symbols represent predictions based on solvent parameterization of the scaling factors. Grey and open symbols denote predictions based on re-parameterization of the scaling factors for the density dependent data forcing $\sigma^{(1)}/\sigma^{(0)} > 1$ and $\sigma^{(1)}/\sigma^{(0)} < 1$ respectively ($\sigma^{(1)}/\sigma^{(0)} < 1$ not computed for n-hexane). Experimental data is from Refs. 34 and 35.

result implies that there is no positive contribution to the total absorption shift and hence, suggests that spectral shift model overestimates the repulsive contribution for the density dependent parameterization of CS_2 when x > 0. As the density of the system is increased, the short distance rise in the radial distribution function becomes steeper, thereby increasing the repulsive contribution to the absorption shift in CS_2 when x > 0. As a result, the simulation model increasingly underestimates the shift at high densities. This behavior is clearly seen in Figure 3.9. It is hypothesized that because the repulsive contribution to the spectral shift is small in n-hexane (Table 3.5), *x* does not have to be less than zero because the differential shifts is almost exclusively attractive.

As a test of the spectroscopic model in the excited state, the predictions for anthracene emission are examined. For these calculations, trajectories in equilibrium with S_1 are used where the S_1 parameters of anthracene are defined eqns. 3.4 and 3.5 with the scaling parameters shown in Table 3.4. Results are plotted in Figure 3.10 and listed in Table 3.4. The simulated emission shifts differ from experiment by no more than 15%, which would suggest that the current modeling of the excited state potential energy surface of anthracene is at least approximately correct. On the other hand, with the exception of cylcohexane, the emission widths agree to no better than 25%. In addition, it is interesting to note that simulation predicts the widths to be larger in absorption, than in emission, whereas in experiment, the opposite relationship is observed. This result, however unfortunate, sheds some light on the deficiency of the spectroscopic model. Insofar as the emission shifts are concerned,



Figure 3.10: Correlation of Experimentally Measured and Simulated Emission Shifts and Widths. Experimental uncertainties in the shifts and widths are ± 50 cm-1 and ± 30 cm⁻¹ respectively. Estimated uncertainties in the simulation data are less than 1% of the value. Labeling scheme can be found in Table 3.1. Experimental data is from Ref. 25.

the implication is that the global minimum of the solute-solvent excited state potential energy surface is to a good approximation captured by the current spectroscopic modeling defined by eqns. 3.9 and 3.11. Conversely, because the simulated emission widths vary significantly from the experimental measurements, it may be the case that a Lennard-Jones function is not suitable for reproducing the curvature of the potential energy surface in the neighborhood of the global minimum. As a result, the agreement seen in the absorption and emission shifts while qualitatively satisfying, suggests eqns. 3.9 and 3.11 is not an accurate representation of the solute-solvent interactions in the excited state.

As a final test of the spectral shift model, the linear response predictions of the experimental and simulated data can be compared. If excited state of the solute can be described as a small perturbation of the ground state, then the absorption and emission shifts can be related to the widths by the following equation⁴,

$$\left(\delta\Delta v_{abs} + \delta\Delta v_{em}\right) = 2kT\Delta\Delta v \tag{3.20}$$

where *k* and *T* are Boltzmann's constant and temperature respectively, and where $\Delta \Delta v$ is the Stokes shift, is defined by: $\Delta \Delta v = \Delta v_{em} - \Delta v_{abs}$. Plotted in Figure 3.11 is the comparison of the linear response estimates from experiment and simulation. The proportionality between $\delta \Delta v_{abs} \delta \Delta v_{em}$ and $\Delta \Delta v$ was found to be 1.1kT and 0.58kT for experiment and simulation respectively. Clearly, neither the experimental nor the simulation results are at the linear response limit, however, this is not a cause for concern. The more important result is that the simulation spectral shift model is far more non-linear than the experimental results indicate it should be. Although part of



Figure 3.11: Linear Response Estimates from Experiment and Simulation. Experimental and simulation data are shown as filled and open symbols respectively.

the deviation of the simulation model comes from the absorption data, the greater contributor to the smaller slope seen in Figure 3.11 is the behavior of the emission model. Because the widths are directly related to the curvature of the difference potential in the region of the global minimum, these observations suggest that the repulsive contribution to the spectral shift is over-estimated. The well of the interaction potential in the excited state is too narrow.

In light of the above results, a thee effect of three modifications to the difference potential were explored. The first involved allowing the parameters of the hydrogen atoms on anthracene to change upon excitation. This modification allowed for two more scaling parameters in the fitting routine of the absorption shifts. However, this approach did little to improve the quality of fit for both the absorption shift and width correlations to experiment. The next approach was to allow the atomic parameters of the solute carbon atoms to vary differently based on symmetry. Anthracene has 4 distinct carbon atom types which imply 8 different scaling factors. Once again, this modification did not significantly change the absorption correlations.

The final attempt at modifying the spectral shift model employed the Mie potential,

$$U_{\alpha i}^{(S)}(r_{\alpha i},n) = \left(\frac{\varepsilon_{\alpha i}^{(S)}}{n-m}\right) \left(\frac{n^{n}}{m^{m}}\right)^{\frac{1}{n-m}} \left[\left(\frac{\sigma_{\alpha i}^{(S)}}{r_{\alpha i}}\right)^{n} - \left(\frac{\sigma_{\alpha i}^{(S)}}{r_{\alpha i}}\right)^{m} \right]$$
(3.21)

instead of the standard Lennard-Jones function. This potential can be considered as a generalized Lennard-Jones potential, which can be recovered from eqn. 3.21 by choosing (n,m) = (12,6). In the current implimentation, *m* is fixed at a value of 6,

while *n* was allowed to vary. The Mie potential is advantageous in that the relative repulsive and attractive contributions can be varied by simply varying *n* and *m*. This variation is shown in Figure 3.12, with the choice $(\sigma, \varepsilon) = (1,1)$. Although the ground state trajectories are evolved on the standard Lennard-Jones potential energy surface, the absorption shifts and widths were calculated from the Mie form using the same value of *n* in both the ground and excited states. For values of *n* close to 12, little change was observed in the predicted absorption shifts and widths. However, insofar as an accurate model of the excited state potential energy surface of anthracene is concerned, it is difficult to draw conclusions without the corresponding emission predictions from simulation. What can be said definitively, though, is that the Mie potential does no better at incorporating the variety of solute-solvent interactions into a unified anthracene potential as does the standard Lennard-Jones function, which is used in the integration of the simulation trajectories.

IV. Conclusions

This chapter has explored using changes in the solute Lennard-Jones parameters to model the absorption and emission spectroscopy of anthracene in various solvents. In Section B, the general behavior of the simulation model was investigated. It was shown that while scaling ε dominated changes in the absorption shift, changes in the absorption widths are dominated by scaling σ . By dissecting the absorption shifts into attractive and repulsive contributions, it was shown that the



Figure 3.12: Scaled Mie Potentials for Several Values of n (m = 6).

contribution from the attractive part of the Lennard-Jones potential is greater than the repulsive contribution, for the best fit *x* and *y*. More importantly, the dissection showed that by modeling the spectral with a change in Lennard-Jones parameters, the attractive and repulsive contributions to the overall spectral shift cannot be varied independently. In this section it was also shown that the line shapes of the absorption bands were more dependent on changes in the atomic diameters. Scaling the well depths also has an effect on these line shapes, however, compared with changes in the atomic diameters, these changes are insignificant.

The comparison of the experimental to simulated spectral shifts and widths showed that the spectral shift model embodied in eqns. 3.9 and 3.11 is unable to account for all of the differences in the solute-solvent interactions. In particular, the shifts and widths of CS_2 and PFH were shown to be especially difficult to predict. With respect to PFH, it was stated that others³¹⁻³³ had observed that the spectroscopic behavior of solutes in perfluorinated solvents is fundamentally different from the behavior in the analogous hyrogentated solvents, possibly owing to a different balance of attractive and repulsive interactions. In order to try to understand why the scope of different solute-solvent interactions was not captured by a single parameterizaion, the simulated absorption shifts were dissected into repulsive and attractive contributions. Although this dissection did not shed additional insight into the root of the problem, it showed that the all-atom and united-atom models of cyclohexane behave fundamentally differently. Due to the fact that the spectral shift model is unable to account for a wide variety of interactions with a single parameterization of *x* and *y*, it was decided to see if the model could account for the pressure dependent behavior of the absorption shift, where the intermolecular potential parameters do not change. For n-hexane, the absorption shifts and widths were well reproduced by the simulation model over a pressure range of 0.001 kbar to 10 kbar with *x* and *y* taken from the parameterization determined in the liquid solvent fits. The predictions for anthracene in CS₂ were considerably different from experimental values. Re-parameterization of the scaling variables over the pressure dependent CS₂ produced absorption shifts and widths which agreed well with simulation so long as *x* was chosen to be less than 0. As a result, it was suggested that the spectral shift model with x > 0 overestimated the repulsive contribution to the absorption shift of anthracene in CS₂.

The emission shifts were examined next, as they test the integrity of the spectral shift model in the excited state. Using the excited state Lennard-Jones parameters determined by the scaling factors *x* and *y*, excited state trajectories were computed and the emission shifts were calculated by changing the sign of these scaling factors. Qualitative agreement with experimentally determined emission shifts was obtained. The emission widths, on the other hand, compared less favorably. Examination of the linear response predictions showed that both experimental and simulated shifts and widths were far from the linear response limit. It was then concluded that because the emission shifts are reasonable well reproduced by simulation, the global minimum of the solute-solvent potential energy surface is

captured by the spectral shift model. However, because the emission widths are underestimated in simulation, the curvature of the potential energy surface in the region of the global minimum is not capture by the current spectroscopic modeling; in particular, the width of the well in simulation is too narrow. As a result, it was suggested that principle failure of the current spectral shift model is that it overestimates the repulsive contribution to the spectral shifts.

Finally, due to the apparent failure of the spectral shift model so far employed, variations on the spectral shift model were examined. Allowing the solute hydrogen radii and well depths to change during the course of the fitting procedure did little to change the quality of fit of the simulated absorption data to the experimental data. Furthermore, allowing for different solute carbon atoms to scale independently, based upon symmetry, like-wise failed to improve the correlation between simulated and experimental absorption shifts and widths. The last variation attempted was to use a generalized Lennard-Jones potential, the Mie potential, in the calculation of the spectral shifts and widths. Once again, the absorption results were only marginally improved.

The main result of this chapter is that while the modeling the spectral shifts with a Lennard-Jones difference potential is appealing, a unique parameterization of the scaling factors apparently does not account for the wide variety of solute-solvent interactions. However, it is also true that the solvent models used in simulation are parameterized to reproduce the characteristics of the bulk fluid, and therefore, it is not certain that the anthracene-solvent interactions present in the real system are necessarily captured by simulation. Arguable it may also be that the Lorentz-Berthelot combining rules used in simulation are not an accurate representation of the pair solute-solvent interactions. In addition, because the emission widths were found to be too small, it is most likely the case that the functional form of the difference potential is in error, and not the approach in general. However, without further density dependent simulations and emission predictions, it will be difficult to speculate on the true utility of the approach.
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Chapter 4

Simulation Studies of Density Augmentation and Solvation in Anthracene/C₂H₆ and Anthracen/CO₂ Supercritical Systems

I. Introduction

The work contained in this chapter represents an extension of the work contained in Chapter 3. In particular, focus is placed on the ability of the Lennard-Jones shift model (eqns.3.9 and 3.11) to predict the spectral shift of anthracene in supercritical CO_2 and ethane. The motivation for this study comes from Chapter 2, where it was shown that the local solvent densities (the solvent densities in the 1^{st} solvation shell) observed in simulations of DPB and HMS in supercritical CO₂ were smaller than those deduced from experiment. This observation appears to generally hold true when such comparisons are made to experimental estimates derived from electronic spectral shifts¹. Because most experimental information about local density is derived from electronic spectral shift measurements, it is critical that the source of this discrepancy be understood. Two possibilities exist: First, if the experimental spectral shifts are proportion to the local density, as simple models would suggest, then simulation is simply underestimating the extent of density augmentation. Alternatively, if the experimental shifts are not proportional to the local density, then simulation might be capturing the local density, and it may just be that the interpretation of the spectral shifts is in error. In either case, the answer to this question is of paramount importance.

The rest of the chapter is laid out as follows. In Section II, details of the simulation models are given. In Section III, the correlation between experimental and simulated absorption and emission shifts of anthracene in CO_2 and ethane are examined. Subsequently, the augmentation derived from these shifts, as well as other simulated observables are discussed. In addition, the feasibility of using the Lennard-Jones shift model is also examined in the context of weakly polar and non-polar systems. Finally, the extent to which the simulated and experimental observables relate to the physical augmentation present in the system is investigated. Finally, concluding remarks and possible future research avenues are given in Section IV.

II. Solvent models and Simulation Details

Descriptions of the anthracene and CO₂ simulation models can be found in Chapters 2 and 3 respectively. For ethane, a diatomic united-atom model was taken from the work of Martin and Siepmann², who optimized the parameters to reproduce the vapor-liquid coexistence curve. These authors decided on values of 3.75 Å and 98 K for σ and ε/k respectively, with a bond length of 1.54 Å.

Ground state simulations of anthracene in CO_2 and ethane were performed in the NPT ensemble at a temperature of 310 K using a modified version of the DLPOLY³ program. Constant pressure and temperature were achieved using a Hoover barostat and thermostat⁴. CO₂ simulations were conducted at 7 different pressures, spanning a range of 5-33 MPa. For ethane, 7 different pressures were also simulated, however covering a range of 3-22 MPa. Simulations in CO₂ and ethane contained 992 and 984 solvent molecules respectively. In both solvents cubic periodic boundary conditions were applied, and the equations of motions were integrated at 2 fs intervals with a Verlet-type algorithm using quaternion parameters. For CO₂, electrostatic forces were truncated at 12 Å⁵. The solvent model of ethane has no atomic charges.

Prior to production runs, each simulation was equilibrated for 1 ns. Subsequently, production runs of 4 ns were completed for each pressure. Each production run was comprised of 8 runs, 500 ps in length, and statistics were collected every 10 fs. Excited state simulations were performed under identical conditions to the ground state simulations. The excited state anthracene Lennard-Jones parameters were taken from Chapter 2. In particular, the carbon atom parameters in the excited state were taken as $1.02\sigma^{(0)}$ and $1.21\varepsilon^{\Box(0)}$, where $\sigma^{(0)}$ and $\varepsilon^{\Box(0)}$ are the ground state values.

III. Results and Discussion

A. Solvation Energies

Displayed in table 4.1 are the density dependent solute-solvent interaction energies of anthacene in CO_2 and ethane. In the ground state, the solvation energies in CO_2 are about 14%-30% higher than in ethane. This difference might be thought to arise due to the quadrupole-quadrupole interaction between CO_2 and anthracene,

| Pressure MPa | $ ho ho_{ m c}$ | - <i>U</i> _{lj} (S ₀) kJ/mol | -U _{el} (S ₀) kJ/mol | $N_1(S_0)$ | - <i>U</i> _{lj} (<i>S</i> ₁) kJ/mol | $N_1(S_1)$ |
|-----------------|------------------|--|--|------------|--|------------|
| | | | | | | |
| | | | CO ₂ | | | |
| 5.02 | 0.24 | 23 | 3 | 17 | 27 | 19 |
| 7.90 | 0.55 | 44 | 4 | 35 | 51 | 37 |
| 8.61 | 0.81 | 52 | 5 | 43 | 61 | 45 |
| 8.89 | 1.11 | 60 | 6 | 50 | 71 | 53 |
| 9.43 | 1.31 | 65 | 6 | 54 | 76 | 57 |
| 13.30 | 1.63 | 73 | 7 | 61 | 83 | 62 |
| 32.59 | 1.97 | 83 | 7 | 70 | 94 | 71 |
| | | | C_2H_6 | | | |
| 3.26 | 0.24 | 19 | | 8 | 24 | 9 |
| 4.97 | 0.49 | 33 | | 15 | 41 | 16 |
| 5.61 | 0.72 | 49 | | 22 | 62 | 25 |
| 5.75 | 1.01 | 57 | | 26 | 67 | 27 |
| 5.85 | 1.24 | 59 | | 27 | 67 | 27 |
| 8.60 | 1.65 | 65 | | 29 | 74 | 30 |
| 22.23 | 2.01 | 74 | | 33 | 84 | 34 |

Table 4.1: Simulated Solvation Energies in CO_2 and Ethane. The columns labeled U_{lj} and U_{el} contain the solute-solvent Lennard-Jones and Coulombic interaction energies. The column labeled N_1 denotes the number of atoms in 1st solvation shell. Densities were taken from simulations of the pure solvents (Ref. 9) at the pressures listed in column 1.

which is not present in the case of the ethane solvent. However, the Coulombic contribution to the ground state interaction energy in CO_2 accounts for only about 10% of the total interaction energy, which means that the Lennard-Jones contribution is about is still about 5%-25% higher than in ethane. In addition, although the anthracene- CO_2 interaction well-depth is, on average, smaller than the anthracene-ethane well-depth, the coordination number is about 50% higher (the coordination number is defined here as the number of *atoms* in the 1st solvation shell⁶). Therefore, the higher solute-solvent interaction energy in CO_2 relative to ethane is a reflection of the fact that CO_2 packs more efficiently around anthracene than does ethane.

In the excited state, the situation is similar. The Lennard-Jones interaction energies are about 5%-20% and the coordination number is about 50% higher in CO₂. Relative to the ground state simulations, the Lennard-Jones interaction energies increase by about 15% and 20% in CO₂ and ethane respectively, however, there is a change of only about 5% in the coordination number at all but the lowest density. This observation is attributed to the fact that in the excited state, the fluorophoresolvent contact radii are increased by 1% whereas the well-depths are increased by 10%. As a result, although there is little change in the coordination number, the significant scaling in the pair-interaction strengths leads to significantly increased solvation energies.

The density dependence of the solute-solvent interaction energies, as well as the coordination number, is displayed in Table 4.2. Listed in this table are the ratios of the densities to the simulation observables. Furthermore, these ratios have been

| $ ho / ho_{ m c}$ | U _{1j} /ρ (S ₀) kJ/mol | $U_{\rm el}/ ho(S_0)$ kJ/mol | $N_1/\rho(S_0)$ | U _{lj} /ρ(S ₁) kJ/mol | $N_1/\rho(S_1)$ |
|--------------------|--|------------------------------|-----------------|---|-----------------|
| | | | | - | - |
| | | C | O ₂ | | |
| 0.24 | 2.2 | 2.8 | 2.0 | 2.3 | 2.1 |
| 0.55 | 1.9 | 2.1 | 1.8 | 1.9 | 1.9 |
| 0.81 | 1.5 | 1.7 | 1.5 | 1.6 | 1.6 |
| 1.11 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 |
| 1.31 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| 1.63 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| 1.97 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| | | C_2 | H ₆ | | |
| 0.24 | 2.1 | | 2.1 | 2.4 | 2.3 |
| 0.49 | 1.9 | | 1.8 | 2.0 | 2.0 |
| 0.72 | 1.9 | | 1.9 | 2.1 | 2.1 |
| 1.01 | 1.5 | | 1.5 | 1.6 | 1.6 |
| 1.24 | 1.3 | | 1.3 | 1.3 | 1.3 |
| 1.65 | 1.1 | | 1.1 | 1.1 | 1.1 |
| 2.01 | 1.0 | | 1.0 | 1.0 | 1.0 |

Table 4.2: Density Dependence of the Solvation Energies in CO_2 and Ethane. The tabulated values have been normalized to their high density ratios. The columns labeled U_{lj} and U_{el} contain the solute-solvent Lennard-Jones and Coulombic interaction energies. The column labeled N_1 denotes the number of atoms in 1st solvation shell.

normalized to their high density values in order to facilitate a comparison between observables. The fact that the ground state normalized ratios of N_1 are not identical indicates that the coordination number is not proportional to density. This observation reflects the presence of density augmentation, as the local solvent density changes at a different rate from the bulk density. This same trend is observed in ground state ratio of U_{li} in both CO₂ and ethane. However, because the ratios of U_{li} are roughly equivalent to the ratios of N_1 , the solute-solvent interaction energy is seen to be linearly dependent on the local density, and as a result, it can be said that U_{lj} and N_1 are proportional. On the other hand, in CO₂, the ratios of U_{el} are larger than the ratios of U_{li} and N_1 , especially at lower densities. This implies that U_{el} has a more non-linear density dependence than does the coordination number. This can be understood in terms of the intermolecular potential functions. To begin, the Lennard-Jones potential is the dominating contribution to the solvation structure, and therefore, determines the radius of the 1st solvation shell. In addition, because this potential is a short-ranged potential, the solute-solvent interaction energy is predominantly determined by the population of solvent molecules within the 1st solvent shell. Furthermore, because the maximum in the radial distribution function almost coincides with the global minimum in the Lennard-Jones interaction potential, the contributions of all molecules in the 1st solvation shell to the total Lennard-Jones interaction energy are roughly similar, a proportionality between U_{lj} and N_1 is not unanticipated. With respect to the Coulomb potential, it is either everywhere positive or everywhere negative for a solute-solvent site-site interaction pair, depending on the on the sign of the product charges. As a result, there is some cancellation of contributions to the total electrostatic energy, and hence, U_{el} represents a more collective quantity than does the Lennard-Jones energy.

In the excited state simulations, the non-linearity of U_{lj} and N_1 are slightly increased in both CO₂ and ethane at lower densities, although the proportionality between them is preserved. This observation is likely due to the fact that in the excited state simulations, there is an increase in the Lennard-Jones interaction energy.

B. Comparison of Spectral Shifts to Experiment

The comparison of the absorption shift calculations to experimental data⁷ is shown in Table 4.3 and Figure 4.1. In both CO₂ and ethane, the estimated uncertainties in the shifts and widths are about 50 cm⁻¹ and 30 cm⁻¹ respectively. The simulated shifts in CO₂ are within 10% of experiment at low to moderate densities, however, as the density is increased, the simulated shifts systematically overestimate experiment. The predicted widths, on the other hand, show good agreement with experiment over the entire density range. However, it should be noted that the uncertainty in experiment is about 25% of the measured width, and therefore, there is a large margin of error. In addition, to within uncertainties, experimental absorption shifts in CO₂ and ethane are nearly the same, with the shifts in CO₂ being larger by about 10%. Other things (*i.e.* the molecular polarizability) being equal, because CO₂ is quadrupolar, the spectral shift of anthracene in CO₂ is expected to lead to slightly larger shifts. However, because this difference should be small based on the strength

| $ ho ho_{ m c}$ | $\Delta v (exp)$ cm ⁻¹ | δ∆ν (exp) cm ⁻¹ | $\Delta \nu (\Delta lj)$ cm ⁻¹ | $\delta\Delta\nu (\Delta lj) \ cm^{-1}$ |
|------------------|--------------------------------------|-------------------------------|--|---|
| | | | | |
| | | CO_2 | | |
| 0.24 | | | 193 | 88 |
| 0.55 | 420 | 130 | 379 | 116 |
| 0.81 | 460 | 130 | 456 | 118 |
| 1.11 | 500 | 120 | 524 | 117 |
| 1.31 | 510 | 120 | 573 | 111 |
| 1.63 | 550 | 120 | 640 | 110 |
| 1.97 | 610 | 120 | 724 | 111 |
| | | C_2H_6 | | |
| 0.24 | | | 160 | 80 |
| 0.49 | | | 290 | 100 |
| 0.72 | 410 | 130 | 430 | 130 |
| 1.01 | 450 | 130 | 500 | 100 |
| 1.24 | 480 | 130 | 510 | 100 |
| 1.65 | 590 | 110 | 560 | 100 |
| 2.01 | 670 | 110 | 640 | 100 |

Table 4.3: Comparison of Experimental and Simulated Absorption Shifts in CO₂ and Ethane. $\Delta v(exp)$ denotes experimental shifts from Ref. 7 and $\Delta v(\Delta lj)$ denotes shifts from the simulation spectral shift model.



Figure 4.1: Comparison of Experimental and Simulated Absoprtion Shifts and Widths. Experimental and simulation data are plotted with filled and open circles respectively. Absorption shifts and widths are plotted with circles and triangles respectively. Experimental data is from Ref. 7.

of quadrupole-quadrupole coupling, it is expected to fall within experimental uncertainties. Simulation, on the other hand, predicts the shift in CO_2 to be up to 25% larger than in ethane. However, this magnitude of error was previously observed with anthracene shifts in liquid solvents (Chapter 3), and therefore, it cannot be concluded that the increased shift in CO_2 , relative to ethane, is a significant result.

The results of the emission shift calculations and the comparison to experiment⁷ are listed in Table 4.4 and plotted in Figure 4.2. These results are similar to what was seen with the absorption shifts, but emission shifts in both CO_2 and ethane are overestimated by the simulations. Given the performance of the model for predicting emission shifts in liquid solvents (Chapter 3), the level of agreement displayed here is not unexpected. It is important to note that although the magnitudes of the experimental and simulated emission shifts may not agree numerically, they are, roughly speaking, proportional. What this implies, then, is that although quantitative agreement is not achieved, simulation qualitatively captures the variation of the emission shift with density. It is this density dependence that is most important for estimating local densities, as discussed next.

C. Local Density Augmentation

Recall that local density augmentation characterizes an increased solvent density in the vicinity of the solute relative to the bulk fluid. This solute-induced density change can be loosely described as a clustering effect. It is important to differentiate between the "effective" augmentation reported by an observable such as

| $ ho ho_{ m c}$ | $\Delta v (exp)$ cm ⁻¹ | δΔν (exp) cm ⁻¹ | Δν (Δlj) cm ⁻¹ | $\begin{array}{c} \delta\!\Delta\nu(\Delta\!lj)\\ cm^{\text{-1}} \end{array}$ | |
|------------------|--------------------------------------|-------------------------------|------------------------------|---|--|
| | | | | | |
| | | CO_2 | | - | |
| 0.24 | | | 250 | 100 | |
| 0.55 | 430 | 140 | 480 | 120 | |
| 0.81 | 500 | 140 | 580 | 130 | |
| 1.11 | 550 | 130 | 680 | 130 | |
| 1.31 | 570 | 130 | 720 | 120 | |
| 1.63 | 610 | 130 | 790 | 110 | |
| 1.97 | 680 | 130 | 900 | 110 | |
| | | C_2H_6 | | | |
| 0.24 | | | 230 | 100 | |
| 0.49 | 430 | 140 | 390 | 120 | |
| 0.72 | 500 | 140 | 590 | 120 | |
| 1.01 | 530 | 130 | 630 | 110 | |
| 1.24 | 570 | 140 | 640 | 110 | |
| 1.65 | 650 | 120 | 710 | 100 | |
| 2.01 | 720 | 120 | 800 | 100 | |

Table 4.4: Comparison of Experimental and Simulated Emission Shifts in CO₂ and Ethane. $\Delta v(exp)$ denotes experimental shifts from Ref. 7 and $\Delta v(\Delta lj)$ denotes shifts from the simulation spectral shift model.



Figure 4.2: Comparison of Experimental and Simulated Emission Shifts and Widths. Experimental and simulation data are plotted with filled and open circles respectively. Absorption shifts and widths are plotted with circles and triangles respectively. Dashed curves denote simulation absorption data. Experimental data is from Ref. 7.

a spectral shift and the "physical" augmentation, defined directly in terms of solvent number densities. It is chosen to define "physical" augmentation in terms of the 1st solvation shell coordination number, N_1 . Mathematically, this is embodied in the following definition

$$LDA_{phys} = \rho_{phys} - \rho = \frac{N_1(\rho)}{\left(\frac{dN_1}{d\rho}\right)_{\rho=2}} - \rho$$
(4.1)

where when $\rho > 2$, N_1 is assumed to be proportional to the bulk density and ρ_{phys} is the local density of solvent molecules in the first solvation shell. It can be seen from eqn. 4.1, that any observable that is proportional to the coordination number will report the same augmentation. That is, quantitative agreement between observables is not necessary to obtain identical values for the augmentation, what is important is that they display the same normalized density dependence.

Local densities derived from experimental data depend on some assumed relationship between the observable and density in the absence of density inhomogeneities. Although the relationship can be complicated, in the case of anthracene, it is expected that the electronic spectral shifts should be simply proportional to density⁸. For the purposes of the present chapter, it can be assumed that the experimentally measured shifts should relate to augmentation in the manner described in eqn. 4.1 with N_1 replaced with Δv . Such effective LDA estimates will be examined next, using other simulation observables in addition to the spectral shifts. These effective estimates of LDA are defined by the following relation

$$LDA_{eff} = \rho_{eff} - \rho = \frac{\chi_1(\rho)}{\left(\frac{d\chi_1}{d\rho}\right)_{\rho=2}} - \rho$$
(4.1)

where χ represents some system observable and when $\rho > 2$, χ is assumed to be proportional to the bulk density.

Listed in Table 4.5 and plotted in Figure 4.3 are the simulation results of the augmentation reported by different observables in CO₂. In the ground state simulations, the Lennard-Jones interaction energy is seen to report essentially the same augmentation as does the coordination number. This is not surprising as these two observables were shown to be proportional in Table 4.2. Moreover, there is also a proportionality between the spectral shift calculation and the number. Because the spectral shift calculation is similar to the calculation of the Lennard-Jones interaction energy (*i.e.* they are described by the same expression), and because there is only a small scaling of the fluorophore-solvent contact radii, this result is not unanticipated. The largest departure from physical augmentation in the simulated system is seen in the Coulombic interaction energy, and the source of this non-proportionality between U_{el} and N_1 was discussed above.

In the excited state simulations of anthracene in CO_2 , the Lennard-Jones interaction energy and the simulated emission shift report approximately the same amount of augmentation as does the coordination number. In addition, when compared with the ground state simulations, roughly the same degree of augmentation is predicted, and because the coordination number changes, on average, by only 5% from the ground to the excited state, this result is not unexpected.

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| - | S ₀ | | | | S_1 | | | | |
|---------------------|----------------|------|----------|-----------------|-----------------------|---------|------|----------|-----------------------|
| $\rho/\rho_{\rm c}$ | Δv(exp) | N1 | U_{lj} | U _{el} | $\Delta v(\Delta lj)$ | Δv(exp) | N1 | U_{lj} | $\Delta v(\Delta lj)$ |
| | | | | | | | | | |
| CO_2 | | | | | | | | | |
| 0.24 | | 0.25 | 0.29 | 0.44 | 0.28 | | 0.28 | 0.32 | 0.31 |
| 0.55 | 0.81 | 0.45 | 0.49 | 0.63 | 0.48 | 0.70 | 0.48 | 0.52 | 0.51 |
| 0.81 | 0.67 | 0.42 | 0.43 | 0.53 | 0.44 | 0.66 | 0.45 | 0.47 | 0.47 |
| 1.11 | 0.49 | 0.30 | 0.31 | 0.37 | 0.32 | 0.49 | 0.37 | 0.38 | 0.38 |
| 1.31 | 0.34 | 0.23 | 0.24 | 0.27 | 0.25 | 0.36 | 0.27 | 0.27 | 0.28 |
| 1.63 | 0.14 | 0.10 | 0.10 | 0.13 | 0.11 | 0.16 | 0.10 | 0.10 | 0.10 |
| 1.97 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | | С | $_2H_6$ | | | | |
| 0.24 | | 0.25 | 0.27 | | 0.27 | 0.32 | 0.31 | 0.33 | 0.32 |
| 0.49 | | 0.40 | 0.42 | | 0.41 | 0.49 | 0.48 | 0.49 | 0.49 |
| 0.72 | 0.51 | 0.63 | 0.63 | | 0.63 | 0.77 | 0.77 | 0.77 | 0.77 |
| 1.01 | 0.33 | 0.55 | 0.55 | | 0.57 | 0.58 | 0.58 | 0.58 | 0.58 |
| 1.24 | 0.21 | 0.36 | 0.36 | | 0.37 | 0.37 | 0.36 | 0.36 | 0.37 |
| 1.65 | 0.11 | 0.11 | 0.11 | | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 |
| 2.01 | 0.00 | 0.00 | 0.00 | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Table 4.5: Comparison of Augmentation Derived From Experimental Spectral Shifts and Simulation Observables. The columns labeled U_{lj} and U_{el} contain the solutesolvent Lennard-Jones and Coulombic interaction energies. The column labeled N_1 denotes the number of atoms in 1st solvation shell. $\Delta v(exp)$ denotes experimental shifts from Ref. 7 and $\Delta v(\Delta lj)$ denotes shifts from the simulation spectral shift model.



Figure 4.3: Augmentation Derived From Ground and Excited State Simulation Observables in CO₂. Augmentation from 1st solvent shell population (N_1) and Lennard-Jones solute-solvent interaction energy (U_{lj}) are plotted with filled and open circles respectively. Results of the simulation spectral shift model and the Coulombic solute-solvent interaction energy are plotted with filled and open triangles respectively. Smooth curves are fits of the simulation data to a 4-parameter Weibull function.

In ethane, Figure 4.4 and Table 4.5, both the excited and ground state simulations show that the augmentation derived from both the spectral shift calculations and the Lennard-Jones interaction energies are similar to the coordination number. However, in the case of ethane, the excited state simulations predict larger augmentation than do the ground state simulations. As was the case in CO₂, the excited state Lennard-Jones interaction energies are larger, on average, by only about 6% in the excited state. However, in contrast to CO₂, where the LDA in S_0 and S_1 are the same, in ethane there is a significant increase in the LDA in S_1 when compared with the S_0 . Based upon the changes in the excited state Lennard-Jones parameters, it is not certain why this is the case, however as will be discussed below, this observation might be due to the proximity of the simulation state point to the critical point.

Comparison of the simulated shifts of anthracene in CO_2 and ethane show that at medium densities, the augmentation in ethane is larger than in CO_2 . Although it cannot be stated definitively why this may be the case, one possible cause is the state point of the simulations. Plotted in Figure 4.5 are the partial molar volumes of anthracene calculated from the ground state simulations in CO_2 and ethane,

$$\widetilde{V}_{U}^{*} = \left(\frac{\partial \widetilde{V}}{\partial n_{U}}\right)_{n_{v},P,T}$$
(4.2)

where n_U and n_V are the moles solute and solvent molecules respectively, \tilde{V} is the molar volume, P is the pressure, and T is the temperature. In simulation, the partial molar volumes were calculated by taking the difference between system volumes of



Figure 4.4: Augmentation Derived from Ground and Excited State Simulation observables in Ethane. Augmentation from 1st solvent shell population (N_1) and Lennard-Jones solute-solvent interaction energy (U_{lj}) are plotted with filled and open circles respectively. Results of the simulation spectral shift model are plotted with filled triangles. Open diamonds in S_1 denotes augmentation derived from N_1 in S_0 . Solid curves are fits of the CO₂ simulation data to a 4-parameter Weibull function. Broken lines connect C₂H₆ simulation data points.



Figure 4.5: Partial Molar Volumes of Anthracene from Simulation. Results from CO₂ and ethane are plotted in filled and open circles respectively.

the solute-solvent and pure solvent simulations⁹. From the figure, it is seen that the magnitude of the partial molar volume of anthracene is, generally, much larger in ethane. While this result reflects the fact that within the context of the simulation models the solute-solvent interactions are more attractive in ethane, it does not imply that the cause is due to the closer proximity of the ethane simulation to the critical point. However, the fact that the partial molar volumes are greater in ethane is consistent with the possibility that the simulations in ethane are closer to the critical point than the simulations in CO_2 . As a result, this possibility cannot be ruled out.

The augmentation derived from experimentally measured spectral shifts^{7,8,10} of anthracene in CO_2 and ethane are shown in Figure 4.6, and are listed in Table 4.5. In this figure, the augmentation derived from the experimental shift data of Ito and Maroncelli⁷ is plotted with circles. The augmentation derived from the emission data of Zhang *et al.*¹⁰ and Lewis *et al.*⁸ have been averaged together and plotted with a solid line (the error bars located at the peak of these curves denotes the spread of the averaged data at this point). While the data of Ito and Maroncelli was obtained at higher resolution, the data of Zhang *et al.* and Lewis *et al.* are composed of more measurements. As a result, augmentation derived from both sets of data is displayed. In addition, because the differences seen in the augmentation derived from the experimental absorption and emission shifts of Ito and Maroncelli are within uncertainties, these results are not compared to each other. Instead, focus is placed on the comparison between experiment and simulation. Furthermore, the comparison to



Figure 4.6: Comparison of Augmentation Derived from Experiment and Simulation. Augmentation derived from experimental absorption and emission shifts (Ref. 7) are plotted with filled and open circles respectively. Augmentation derived from the simulated 1^{st} solvent shell population (N_1) in S_0 and S_1 are plotted with filled and open triangles respectively. Solid lines denote averaged experimental emission data from Refs. 8 and 10.

simulation is made in terms of the coordination number, as a result of the proportionality of simulation observables established above.

With respect to CO_2 , both the absorption and emission shifts show roughly the same amount of augmentation. With respect to simulation, the coordination number shows much less augmentation than experiment, which means the same result is obtained when the augmentation derived from experiment is compared with the augmentation derived from the simulated spectral shifts. There are two possible sources for the disagreement in the simulated shift and experiment. First, it may be the case that the experimental shifts are not proportional to the population in the first solvation shell. On the other hand, it is also a possibility that simulation is just not capturing the physical augmentation of the experimental system. If the first of these possibilities is the major contributor to the observed discrepancy, then it is the case that the simulation shift model is not suitable to describe the spectral shift of anthracene in CO_2 , as it reports the same augmentation as the coordination number. Of course, the difference could also stem from a contribution of the two factors.

With respect to the experimental shifts in ethane, the measured augmentation is found to be slightly larger in emission than in absorption, which was also shown in simulation. At lower densities, the difference in augmentation from the coordination numbers in the ground and excited state simulations, underestimates experiment. However, it is worth pointing out that the experimental uncertainties in the shifts of anthracene in ethane are significant in this region, and so simulation may indeed agree with experiment throughout the entire density range. The experimental spectral shifts are proportional to the simulated coordination number, and hence, the simulation shift model seems to quantitatively capture the spectroscopic behavior of anthracene in ethane. The most pressing question, at this point, is do the Coulombic interactions in CO_2 lead to the observed disagreement between simulation and experiment. Unfortunately, this is left as a point for future work, and cannot be answered here.

IV. Conclusions

In the current chapter, the ability of the simulation spectral shift model to reproduce experimentally measured absorption and emission shifts of anthracene in CO_2 and ethane has been investigated. It was shown that in absorption, the magnitude of the spectral shifts and widths were reasonably well captured by the simulation shift model in both CO_2 and ethane.

With respect to the derived augmentation from simulation observables, in both ethane and CO_2 , the spectral shift model was found to be proportional to both the solute-solvent interaction energy as well as the coordination number. The proportionality of these observables is not unexpected, as the dominant contribution to the Lennard-Jones interaction energy come from the 1st solvent shell population. In the CO_2 simulations, however, the Coulombic interaction energy was found be more non-linear in density than the coordination number. Once again, because the Coulombic interaction energy is a more collective quantity than the Lennard-Jones

interaction energy, a proportionality with the coordination number is not expected. What was left as observation was the fact that in simulation, the augmentation in ethane was larger than in CO_2 .

Insofar as the experimental data is concerned, the general results were reflected in simulation. First of all, as in simulation, the local density augmentation in CO₂ derived from experiment is roughly equivalent in absorption and emission. On the other hand, the amount of augmentation derived from the simulated coordination number underestimated experiment. As a result, it was concluded that neither quantitative nor qualitative agreement was obtained between experiment and simulation in CO₂. In ethane the emission shifts reported slightly larger augmentation than did the absorption shifts. With respect to the simulation shift model, quantitative agreement was obtained with simulation. And hence, it was concluded that the spectral shift model, to a good approximation, accurately captured the experimentally observed spectral shifts in ethane.

In closing, it is important to reiterate the most important question asked in this chapter: Are the experimental absorption and emission shifts a direct measure of the physical augmentation in the system? The work contained in this chapter answers this question in part. Namely, in non-polar systems, the spectral shift model showed good agreement with experiment. On the other hand, this question still lingers in the case of weakly polar systems.

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