# Emission Peak Shifts of a Dipolar Solute Dissolved in Nondipolar Solvents: A Quantitative Measure of Quadrupole−Dipole Interactions in Supercritical $CO_2$

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Solvents are often broadly categorized as polar and nonpolar, depending on solvent permittivity. However, some common nonpolar solvents such as benzene, supercritical $CO_2$, and 1,4-dioxane exhibit much larger polarity than that predicted from their permittivities. These solvents are unusual in that their polarities are not the result of dipolar charge distributions and are therefore more appropriately categorized as "nondipolar". Our recent studies of ADMA (1-(9-anthryl)-3-(4-*N*,*N*-dimethylaniline)propane) in liquids demonstrate that the ADMA sandwich heteroexcimer is an excellent probe for investigation of solvent−solute interaction. In this paper we present measurements of the emission spectra of ADMA in a series of nondipolar solvents and determined the excess stabilization energy experienced by ADMA in each of these solvents. These excess energies have been analyzed according to a new theory (Matyushov and Voth, *J. Chem. Phys.* **1999**, *111*, 3630), demonstrating that quadrupole−dipole interactions are responsible for the excess stability. Our measurements agree with theory, indicating the importance of the role of the length scale in quadrupolar stabilization. The excess solvent shifts observed in supercritical $CO_2$ are primarily the result of the quadrupolar nature of the solvent, calling into question assumptions often used in the analysis of local density augmentation.

## I. Introduction

The effect of solvent polarity on the electronic spectra of solutes is well-known. Normally, these effects are correlated with expressions obtainable from continuum theories approximating the solute as a dipole immersed in a continuum dielectric and expressed in terms of Onsager-like functions.[1] These expressions result from consideration of an ideal dipole solute immersed in a polarizable solvent that may also have a permanent dipole moment (both being characterized by the solvent dielectric constant) and often offer excellent correlations with the observed solvatochromic shifts in neat solvents.[2−4] Reynolds et al.[5] have investigated the validity of applying these continuum based models.

In applying dielectric continuum models several common solvents show a noticeable anomaly. For example 1,4-dioxane, benzene, and supercritical $CO_2$ have low dielectric constants but exhibit relatively large local polarities.[5−13] Reynolds et al.[5] demonstrate that these solvents belong to a general class of solvents that they define as "nondipolar" (as opposed to nonpolar solvents such as cyclohexane), most of which demonstrate some deviation from continuum models. Typically, solutes dissolved in these solvents exhibit a Stokes shift that exceeds the prediction of continuum theories, reflecting "excess stabilization" in excess of that predicted based on solute−solvent dipole−dipole interactions. Different explanations have been offered for these apparent deviations,[2,5,6,11] the most logical explanation being that a dipolar solute can interact with higher order multipoles of a solvent whose net dipole moment is near zero but that nevertheless have several polar bonds. Reynolds et al.[5] investigated the Stokes shift of coumarin 153 in a variety of nondipolar solvents and obtained a correlation between the magnitude of the Stokes shift and the solvent quadrupole moment. Not surprisingly, the "excess stabilization" characterized by the difference between the measured Stokes shift and the continuum prediction is most evident when the solvent's quadrupole moment is the leading finite term in the multipole expansion of the solvent charge distribution. Excess stabilization resulting from solute−solvent dipole−quadrupole interactions is the topic of this paper.

The "intuitive" correlation between the excess stabilization and the solvent quadrupole moment can be evaluated quantitatively on the basis of a recent theory developed by Matyushov and Voth,[14] referred to hereafter as the MV theory. We have recently undertaken an extensive investigation of solvatochromism of exciplex emission from ADMA (1-(9-anthryl)-3-(4-*N*,*N*-dimethylaniline)propane)[3] and confirmed the linear relationship between its solvent shift and the Lippert−Mataga (LM) solvent polarity function, *F*,

$$F = \frac{2(\epsilon - 1)}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (1)$$

where $\epsilon$ is the solvent permittivity and *n* is the solvent refractive index. In this paper we demonstrate that this relationship does not hold in solvents that are nondipolar, and we correlate the excess stabilization with the solvent quadrupole moment based on our interpretation of MV theory. Within the context of this theory, our results indicate that the effective quadrupole density is substantially lower than the bulk solvent density. When the density scaling predicted by MV theory is removed, we observe excellent agreement between the MV-predicted quadrupolar solvation energy and our measured excess stabilization energies for axially symmetric quadrupolar solvents. These results emphasize the sensitivity of quadrupolar solvent solvation energy to the details of the solvent charge distribution. The implications of these results for solvation in supercritical $CO_2$ are discussed in section V of this paper.

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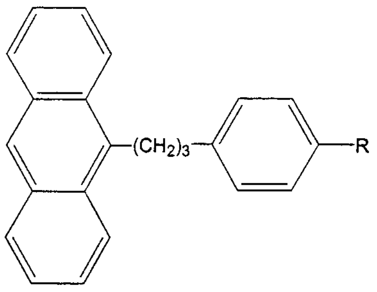

**Figure 1.** Structure of ADMA (R = $N(CH_3)_2$) and APP (R = H).

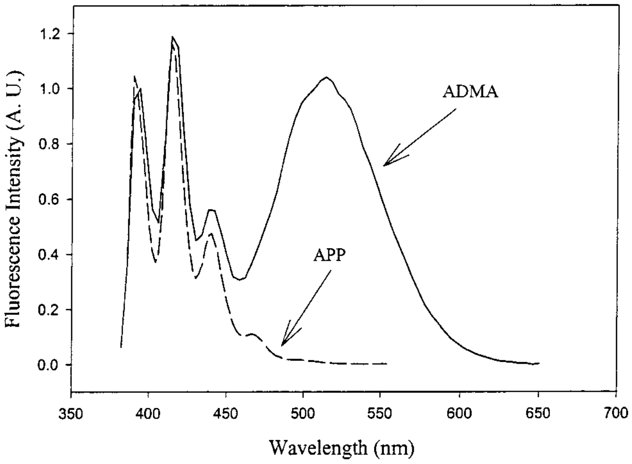

**Figure 2.** Fluorescence spectra of ADMA and APP in dioxane, illustrating their similarity in the 400−480 nm region. The prominent feature in the 480−580 nm region of the ADMA spectrum is emission from the sandwich heterexciplex conformation of the molecule.

## II. Experimental Section

ADMA and APP (1-(9-anthryl)-3-phenylpropane, Figure 1) were synthesized by the method outlined previously.[3,15] The liquid solvents were obtained in the purest commercially available form, degassed with argon, and used without further purification. All sample concentrations were $10^{-5}$ M. Ethylene, carbon dioxide, and fluoroform where obtained in their purest form from Air Products and used without further purification.

The fluorescence spectra of the solutions were collected in a home-built scanning T-format fluorometer. The emission was collected with a photomultiplier tube through one arm, and the fluorescence at a fixed wavelength was collected synchronously and simultaneously through the other arm to correct for fluctuations in the emission intensity due to sample and instrumental conditions. The emission slit widths were set at 1.5 nm giving 3 nm resolution. The liquid solutions were thermostated at 25 °C, while the temperatures of the supercritical fluids were all set to $T_r \sim 1.01$ (34.1 °C for $CO_2$ and 30.0 °C for $C_2H_4$ and $CHF_3$). The densities of the supercritical fluids are 898.5 kg/m$^3$ for $CO_2$, 420 kg/m$^3$ for $C_2H_4$, and 1054 kg/m$^3$for $CHF_3$. The supercritical solution samples were prepared in a custom-made high-pressure cell[15] of our own design.

## III. Results

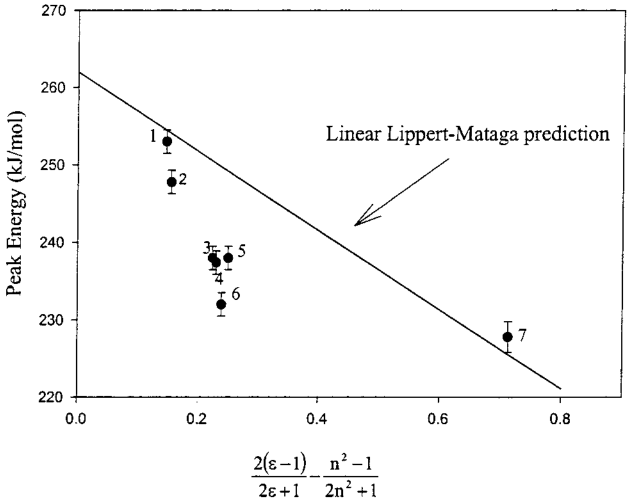

**Figure 3.** Peak energies of the ADMA sandwich heteroexcimer dissolved in nondipolar solvents plotted against the Lippert−Mataga polarity function. The line is the result of a linear regression analysis of peak shifts measured in nonpolar and dipolar solvents. The numbers in the plot match the solvents in Table 1.

Typical spectra of APP and ADMA are shown in Figure 2. The difference spectra reveal a Gaussian peak that is assigned to emission from an intramolecular charge-transfer configuration of ADMA. (See ref 3 for deatils of the spectral analysis.) The photochemistry of ADMA has been examined in great detail.[4,16−21] ADMA in the excited state undergoes a charge transfer to form an intramolecular complex. In nonpolar and moderately polar solvents this "heteroexcimer"[4,19−21] is most stable when it obtains a sandwich-like conformation. The "sandwich heteroexcimer" (SH) is emissive, extremely long-lived (>100 ns in the absence of $O_2$),[15,18,19] and has a large dipole moment (~12 D).[22] Thus, its emission is extremely sensitive to solvent polarity.

The ADMA SH emission peak energy in nonpolar and dipolar (even hydrogen bonding) solvents can be adequately described by the relationship[3,4]

$$E_p\ (\mathrm{kJ/mol}) = -51.104[F] + 262 \qquad (2)$$

where $F$ is given by eq 1. The first term on the right is solvent dependent, and the second term represents the peak energy in a vacuum and agrees well with the emission spectra of ADMA in supersonic jets.[23] Because the heteroexcimer emission peak energies are reasonably linear in $F$, we surmise that the ground state dipole moment is approximately zero.[1] It is important to note that eq 2 does not describe the Stokes shift, but rather the charge transfer exciplex emission peak energy. Exciplex emission only derives from the folded conformation, and this folded form is not stable in the ground state, making Stokes shift measurements impossible. Coulombic attraction holds the exciplex in the folded form, and as a result the emissive species is not very flexible. The solvatochromic peak shifts can be referenced against the exciplex emission peak energy of the isolated molecule. Contribution from internal motion occurs in both isolated molecule and solvated environments. This effect may be manifest in the peak width but should not effect the average peak energy. Therefore, the difference between the $E_p$ in a given solvent and the $F = 0$ intercept (262 kJ/mol) can be taken as the solvation energy of ADMA in that solvent. Furthermore, these results indicate that ADMA behaves as an ideal nonpolarizable dipole solute, as is required for comparison with MV theory.

Figure 3 plots the heteroexcimer emission peaks against $F$ in a series of nondipolar solvents. Results for supercritical fluoroform, a dipolar solvent, are also included. The straight line is the result of our previous work in nonpolar and dipolar solvents.[3] The nondipolar solvents exhibit a sizable deviation

**TABLE 1: Peak Positions of the ADMA Sandwich Heteroexcimer (SH) in Nondipolar Solvents Together with Solvent Properties**[a]

| solvent | SH peak (nm) | $\sigma$ (Å) | $\langle Q\rangle$ | $\langle\langle Q\rangle\rangle$ | $\langle\langle Q\rangle\rangle/\langle Q\rangle$ | $\epsilon$ | $n$ |
|---|---|---|---|---|---|---|---|
| ethylene (1) | 473.4 | 4.5 | 2.434 | −2.434 | −1.0 | 1.62 | 1.27 |
| $CO_2$ (2) | 483.9 | 4.3 | 5.46 | 5.46 | 1.0 | 1.55 | 1.21 |
| benzene (3) | 504.1 | 5.3 | 8.35 | 8.35 | 1.0 | 2.27 | 1.50 |
| tetrafluorobenzene (4) | 502.7 | 7.5 | 13.36 | −12.14 | −0.90 | 2.1 | 1.407 |
| toluene (5) | 502.0 | 5.6 | 7.92 | −7.92 | −1.0 | 2.37 | 1.5 |
| 1,4-dioxane (6) | 516.3 | 5.3 | 11.68 | ∼-0.01 | ∼0.001 | 2.21 | 1.42 |
| fluoroform (7) | 525.3 | | | | | 7.32 | 1.16 |

[a] Peak positions are obtained from the method described by Khajehpour and Kauffman.[3] The Lennard-Jones hard sphere diameters ($\sigma$) are obtained from the references indicated in the text. Effective axial quadrupole moments are calculated with eqs 9 and 10 using the data of Reynolds et al.[5] with the exception of (1) which was calculated using the data of Maroulis.[26] Dielectric constants and refractive indices are found from the literature[35−41]

from the linear prediction indicating an excess stabilization over that predicted from dipole−dipole interactions. When a real solvent charge distribution is well characterized by dipole and quadrupole moments, the solvation energy, $E_s$, of an ideal nonpolarizable dipole solute can be partitioned into three terms,

$$E_s = E_d + E_n + E_q \tag{3}$$

where $E_d$ includes contributions of the solvent permanent dipole to the dipole−dipole interaction energy, $E_n$ includes contributions from solvent induced dipole to the dipole−dipole interaction energy, and $E_q$ is the dipole−quadrupole interaction energy. The LM polarity function accounts for the sum of $E_d$ and $E_n$ for ADMA. Thus, in nondipolar solvents the difference between the experimental peak energy and the peak energy predicted by eq 1 (the "excess stabilization energy") is $E_q$. Values of the peak emission energies are given in Table 1 along with calculated values of the solvent quadrupole moments.[5] The results exhibit a correlation between excess stabilization energy and solvent quadrupole moment. We now proceed to analyze this correlation using a recent theory of solvation by a dipolar−quadrupolar solvent.

## IV. Matyushov−Voth Theory and Analysis

MV theory models a solute as an ideal dipole at the center of a hard sphere and the solvent as a hard sphere with both an ideal dipole and an ideal quadrupole at its center. The solvent quadrupole is idealized as an axially symmetric quadrupole that can be characterized by the scalar quantity $Q$. Repulsive solvent−solute interactions are modeled as hard sphere interactions, and attractive interactions are modeled as the sum of only two terms in the multipole expansion of the interaction: a solute dipole−solvent dipole term (referred to hereafter as the d−d interaction) and a solute dipole−solvent quadrupole term (referred to hereafter as the d−q interaction). MV theory is formulated as a perturbation expansion of the chemical potential, which is written in terms of the resulting multipole expansion of the solute−solvent interaction energy. The method of Padé approximants is used to find the first two nonvanishing terms in the expansion. Approximate expressions for the solvation energy resulting from each of the two types of interactions can be extracted from the chemical potential (see eqs 30−38 in ref 14), offering a method to compare stabilization from d−d interactions to stabilization from d−q interactions.

Matyushov and Voth[14] offer an approximate expression for the ratio of the quadrupolar to dipolar solvation energies, which is advantageous because numerous complex factors are eliminated from the calculation, including several integrals over radial distribution functions. The ratio of the quadrupolar solvation energy, $E_q$, to the dipolar solvation energy, $E_d$, is approximated as

$$\frac{E_q}{E_d} \approx \frac{y_q I_6^{(2)}}{y_d I_4^{(2)}} \approx 2.0\frac{(Q)^2}{(m)^2\sigma^2} r_{0s}^{-4/3} \tag{4}$$

where $m$ is the solvent dipole moment, $r_{0s} = R_0/\sigma + 0.5$, $R_0$ is the solute radius, and $\sigma$ is the hard sphere diameter of the solvent. The first equality is written in terms of the so-called "dipole density" ($y_d$) and "quadrupole density" ($y_q$). The $I_n(2)$ are integrals over the solvent−solute radial distribution function and are responsible for the approximate dependence of eq 4 on $r_{0s}$. This expression derives from the ratio of the d−d and d−q energies (eqs 36 and 37 in ref 14) by retaining only the leading terms in each expression, and it does not include solvent polarizability. Vath et al. have presented a straightforward means of extending MV theory to account for solute dipole−solvent induced dipole interactions by including a polarizability term to the dipole density.[24] The multipole densities are given by the expressions

$$y_q = \frac{2\pi}{5kT}\frac{Q^2}{\sigma^2}\rho_q \tag{5}$$

$$y_{d.n} = \frac{4\pi}{9kT}m^2\rho_d + \frac{4\pi}{3}\rho_d\alpha = \frac{\epsilon - 1}{\epsilon + 2} \tag{6}$$

The original theory was written without the polarizability term in eq 6. The second equality in eq 6 reflects the Debye relationship between solvent bulk dielectric properties and molecular properties. After inclusion of the polarizability, the ratio of energies reads

$$\frac{E_q}{E_d + E_n} = \frac{y_q I_6^{(2)}}{y_{d.n} I_4^{(2)}} \tag{7}$$

We distinguish the dipole density, $\rho_d$, from the quadrupole density, $\rho_q$, in order to facilitate our subsequent analysis of the experimental results. $E_d + E_n$ is characterized by the solvent dependent term in eq 2 because this term reflects the solvation energy of ADMA, as discussed in section III.

Matyushov and Voth point out that the d−d contribution to solvation will be dominant for dipolar solvents, and in most cases the d−q contribution to solvation in these solvents will be difficult to isolate. However, nondipolar solvents ($m \approx 0$) such as those examined in this study can clearly engender substantial solvation in excess of the d−d contribution. In these cases, the d−q contribution to the solvation energy can be found by combining eqs 5−7. Recognizing that $\epsilon = n^2$ for nondipolar solvents, $E_d + E_n = -51.104(n^2 - 1)/(2n^2 + 1)$ and $y_{d,n} =$

$(n^2 - 1)/(n^2 + 2)$ to give

$$E_{\text{q.nondipolar}} = K\frac{Q^2\rho_{\text{q}}}{\sigma^2}\cdot r_{0\text{s}}^{\ 4/3}\frac{n^2+2}{2n^2+1} \cong K\frac{Q^2\rho_{\text{q}}}{\sigma^2}\cdot r_{0\text{s}}^{\ -4/3} \quad (8)$$

The second equality reflect the fact that the ratio of refractive index terms is nearly constant (±5%) over the broad range of refractive index values used in this study. Equation 8 expresses the contribution of the d−q interaction to the stabilization energy.

Before proceeding further, a discussion of the scalar quantity $Q$ is in order. Formally, $Q$ is the projection of the quadrupole tensor onto the solvent molecule axis of symmetry ($Q_{zz}$), which is also the dipole axis. Nonaxial quadrupoles cannot be characterized by a single quantity, and are often characterized by an "effective axial quadrupole moment" defined as

$$\langle Q\rangle^2 = Q_{zz}^{\ 2} + \frac{1}{3}(Q_{xx} - Q_{yy})^2 = \frac{2}{3}(Q_{xx}^{\ 2} + Q_{yy}^{\ 2} + Q_{zz}^{\ 2}) \quad (9)$$

This expression (and eq 10) is derived in the quadrupole principal axis system. The first equality in eq 9 (and eq 10) is written to highlight axial ($Q_{zz}$) and nonaxial ($Q_{xx} - Q_{yy}$) contributions to $\langle Q\rangle$. The second equality derives from the traceless property of the quadrupole tensor. Note that an axial quadrupole has $Q_{xx} = Q_{yy}$, thus $\langle Q\rangle = Q_{zz}$, as is expected. However, the effective axial approximation is not always appropriate. Gubbins et al.[25] point out that eq 9 is derived from consideration of the second-order perturbation expansion of the interaction potential between two multipoles. The third-order term results in another definition for the effective quadrupole moment

$$\langle\langle Q\rangle\rangle^3 = Q_{zz}^{\ 3} - Q_{zz}(Q_{xx} - Q_{yy})^2 = \frac{4}{3}(Q_{xx}^{\ 3} + Q_{yy}^{\ 3} + Q_{zz}^{\ 3}) \quad (10)$$

and while this definition gives $\langle\langle Q\rangle\rangle = Q_{zz}$ for an axial quadrupole, it is also clear that in general $\langle\langle Q\rangle\rangle \neq \langle Q\rangle$. Thus, it is impossible to identify a single scalar quantity that can characterize a nonaxially symmetric quadrupolar charge distribution to all orders in perturbation theory, though such a quantity does exist (i.e., $Q_{zz}$) for an axially symmetric quadrupole. For this reason, MV theory is derived using the axial quadrupole assumption and can only be applied to solvents with axially symmetric or nearly axially symmetric quadrupoles. As the above discussion indicates, use of an effective axial quadrupole moment may be inappropriate for nonaxially symmetric solvents. Gubbins et al.[25] suggest that deviation of the ratio $\langle\langle Q\rangle\rangle/\langle Q\rangle$ from unity provides a useful test of the symmetry of a quadrupolar charge distribution. We have applied this test to various solvents in order to carefully assess the efficacy of MV theory for predicting solvation energies of ADMA in nondipolar solvents. In Table 1 we list the calculated values of $\langle Q\rangle$ and $\langle\langle Q\rangle\rangle$ used in this analysis.[5,26] These draw heavily from the careful and extensive work of Reynolds et al.[5] The table indicates that the effective axial approximation is applicable for ethylene, carbon dioxide, benzene, and toluene. We have also studied 1,2,4,5-tetrafluorobenzene (TFB) and dioxane, two solvents that cannot be approximated as axially symmetric, for contrast. In the case of dioxane, we examine this solvent in light of the so-called "dioxane anomaly" that reflects the large disparity between continuum dielectric predictions and measured solvatochromic shifts commonly observed in this solvent.

To approximate the solvent molecules as spheres, we have made use of the Lennard-Jones hard sphere diameters of the pertinent molecules[27−30] with two exceptions. The radius of ADMA in the sandwich heteroexcimer state has been calculated from continuum models and is ~4.32 Å.[3] No hard sphere values are available for TFB, but its van der Waals diameter (6.1 Å) can be calculated using the method of Bondi.[31] According to Hirschfelder[28] the van der Waals diameter is approximately 81% of the Lennard-Jones hard sphere diameter, and we have scaled the radius of TFB to reflect this difference. All solvent radii used in our analysis are reported in Table 1.

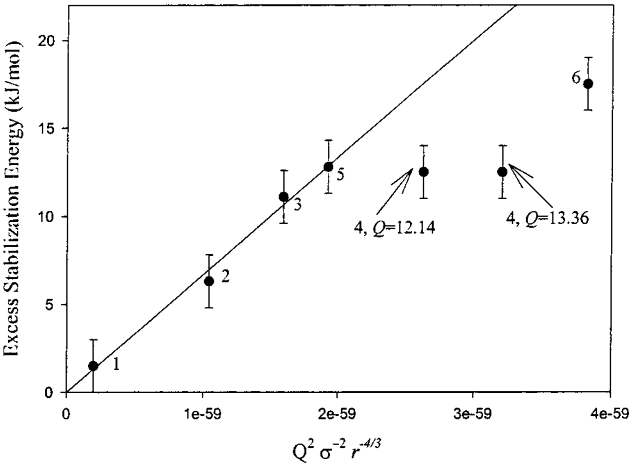

**Figure 4.** Excess solvation energy plotted against the density independent quadrupole function. The line is a linear regression fit of the solvents for which the effective axial approximation holds. The two points for 1,4-tetrafluorobenzene represent the different effective quadrupole calculations. The dotted line represents the excess stabilization energy if all quadrupoles in the first solvation shell take part in stabilizing the dipole.

Figure 4 exhibits a plot of excess stabilization energy versus $Q^2\sigma^{-2}r_{0\text{s}}^{\ -4/3}$. Three comments are in order regarding this plot. First, it demonstrates a linear relationship for the axially symmetric solvents. This result is consistent with the MV prediction and helps to corroborate that validity of this theory. Second, TFB and dioxane do not fall on the line, suggesting a failure of MV theory for nonaxially symmetric quadrupolar solvents. This result is not unexpected, and we discuss this fact below. Finally, the slope of this line is expected to equal $K'\rho_{\text{q}}$ according to eq 8, and the linear relationship indicates that $\rho_{\text{q}}$ is effectively constant within the context of MV theory. We have found that the use of the bulk density as a solvent dependent variable in this factor deteriorates the linear relationship, and we have used this observation to suggest that $\rho_{\text{q}}$ may not reflect the bulk density of solvent molecules, but rather the number of solvent molecules that are poised to significantly interact with the solute dipole moment. Such a scenario may result from deviations of real solvent and solute molecules from the spherical symmetry utilized in MV theory, as discussed below. Oftentimes the spherical approximation is found to be acceptable in dielectric continuum theories, but when quadrupolar interactions are at play, the reduced length scale of the interaction may render these systems more sensitive to nonspherical charge distributions.

## V. Discussion

**Quadrupole Density.** The linear plot depicted in Figure 4 allows us to assess the assumption of a constant number density of quadrupoles involved in the solute dipole-solvent quadrupole interaction. The equation of the correlation line is $E_{\text{q}} = 6.68 \times 10^{62}Q^2\sigma^{-2}r_{0\text{s}}^{\ -4/3}$, and a value of $\rho_{\text{q}} = 2.40 \times 10^{27}\ \text{m}^{-3}$ can be extracted from the slope by careful analysis of eqs 4−8. The analysis of Suppan[32] demonstrates that the first solvation shell accounts for most of the solute−solvent dipolar interaction. Quadrupolar interactions are much shorter range than dipolar interactions, therefore the first solvation shell approximation should still be valid. Considering benzene as a typical solvent, the volume of the first solvation shell is approximately $3.36 \times 10^{-27}$ m$^3$ corresponding to ∼23 solvent molecules calculated from the number density of benzene ($6.7 \times 10^{27}$ m$^{-3}$). The above value for $\rho_q$ indicates that ∼7 molecules take part in the interaction. This disparity may be due to the large charge separation in ADMA (on the order of a few angstroms), and thus the point dipole approximation might be inappropriate. Alternatively, whereas ADMA is very well approximated by a sphere for the longer range dipolar interactions, quadrupolar interactions are much shorter range and it is conceivable that only a few well poised molecules in the first solvation shell interact with the sandwich heteroexcimer.

**Nonaxial Quadrupoles.** The deviations of 1,4-dioxan**e** and 1,2,4,5-tetrafluorobenzene from linearity is expected because the effective axial quadrupole approximation is invalid for these solvents. On the other hand, though TFB and 1,4-dioxane are not linearly correlated with the axially symmetric solvents, MV theory does predict a smaller stabilization for TFB than for 1,4-dioxane, which is consistent with experimental data. This is not the case when $\sigma$ and $r_{0s}$ are omitted from the calculation, and this observation offers another corroboration between MV theory and experiment.

The nature of the deviations of 1,4-dioxane and 1,2,4,5-tetrafluorbenzene from the linear prediction offer interesting insight into the validity of effective quadrupole approximation. Gubbins et al.[25] point out that there is no definition for a “universal effective quadrupole moment”. Figure 4 demonstrates that using $\langle\langle Q\rangle\rangle$ instead of $\langle Q\rangle$ for 1,2,4,5-tetrafluorobenzene in the quadrupolar function gives a result that is closer to the linear fit, demonstrating that using higher order perturbation terms might define a more realistic effective quadrupole moment for approximating the molecule as a point quadrupole. In the case of 1,4-dioxane, however, the difference between $\langle\langle Q\rangle\rangle$ and $\langle Q\rangle$ is extremely large, demonstrating that approximating 1,4-dioxane as a point quadrupole is always inappropriate. Geerlings et al.[33] demonstrate that each of the ether moieties in 1,4-dioxane can be modeled as a point dipole. Their simulations indicate that a dipolar solute dissolved in 1,4-dioxane effectively interacts with only one of the solvent dipoles, and the solute experiences a reaction field similar to a solvent having a dielectric constant of approximately 7. Figure 3 is consistent with this result, suggesting that the short length scale of quadrupolar interactions may have a profound influence on experimental observables.

**Supercritical $CO_2$.** The implications of this result for supercritical fluid science is highly significant. Figure 3 demonstrates that the dipolar supercritical solvent fluoroform adheres to the prediction of dielectric continuum models. Thus, the ADMA heteroexcimer peak energy in supercritical fluoroform is consistent with eq 1. On the other hand, $CO_2$ exhibits a deviation from the linear prediction with a magnitude that can be well characterized by its quadrupolar solvation energy. This highlights the fact that the large quadrupole moment of $CO_2$ coupled to its small size is responsible for its remarkable solvation properties. This result is significant for researchers analyzing local density augmentation in supercritical fluid solvents, and neglect of quadrupolar solvation can lead to erroneous conclusions regarding the local solvent density.

We have attempted to demonstrated that quadrupole−dipole interactions are responsible for the enhanced stability observed in the electronic spectra of molecules dissolved in nondipolar molecules. We have demonstrated the effects of the length scale-upon the observed stability, accounting for the different stabilities observed by molecules having similar quadrupole moments. These results indicate that quadrupole−dipole stabilization effects are extremely short-range and therefore only influence processes that occur in the near vicinity of the dipole. The results of this analysis demonstrates that $CO_2$ behaves as a quintessentially quadrupolar solvent and the various anomalies one can observe in its behavior can be interpreted as such. This work is consistent with our previous work, which addresses the importance of the interaction length scale on solvent mediated kinetic effects in reactions in supercritical $CO_2$.[15,34]

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