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Rotation and Isomerization of Diphenylbutadiene and 4-(Methanol)Stilbene in Supercritical CO$_2$−A Re-Examination

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The rates of excited-state rotation and isomerization of *trans,trans*-1,4-diphenylbutadiene (DPB) and 4-(methanol)stilbene (HMS) in supercritical CO$_2$ ($T = 36$ °C, $\rho = 0.4-2\rho_c$) were measured using time-resolved emission methods. These measurements were prompted by a discrepancy between rotation times recently simulated for these systems (Patel, N.; Biswas, R.; Maroncelli, M. *J. Phys. Chem. B* **2002**, *106*, 3306−3318) and earlier experimental results. The present data show the rotation times of the two solutes to be approximately equal and linear functions of (bulk) solvent density, consistent with the simulations. The rate of isomerization of HMS decreases approximately linearly with solvent density, whereas the isomerization of DPB is remarkably insensitive to density.

In a recent paper,[1] we reported simulations of *trans,trans*-1,4-diphenylbutadiene (DPB) and 4-(methanol)stilbene (HMS) in supercritical CO$_2$ and compared the simulation results to experimental data on electronic spectral shifts[1] and solute rotation times.[2] Although good agreement was found for the spectral shifts and the local density augmentations they reflect, the situation with respect to rotational dynamics was less satisfying. Simulated rotation times were approximately linear functions of density and virtually identical in DPB and HMS. In contrast, the experimental rotation times of HMS showed a markedly nonlinear density dependence, and the rotation times in DPB were measured to be less than those of HMS, especially at the highest densities studied. Moreover, the experimental rotation times of DPB were uniformly smaller than the simulated times, by as much as 30% at the highest densities. This last discrepancy was considered to be serious because it implies that friction on rotational motion was overestimated by roughly a factor of 2 by the simulations. As discussed in detail in ref 1, such an error is unexpected in light of the fact that density augmentation and solvent properties related to friction are both reasonably captured by the simulation models. Beyond these quantitative differences, the distinction between DPB and HMS observed in experiment but not in simulation also led to quite different qualitative conclusions concerning the local environments of these solutes and the importance of hydrogen bonding in HMS/CO$_2$.

This unsatisfying state of affairs prompted us to reexamine the experimental rotation data. The rotation times used for comparison to simulation were obtained some time ago in a pioneering study by Anderton and Kauffman.[2] These authors employed a combination of fluorescence lifetime and steady-state anisotropy measurements to determine rotation times. Because such data can be influenced in unforeseen ways by scattering and impurity fluorescence, we decided to remeasure the rotation times in these systems via more direct measurements of time-resolved emission anisotropies.

Time-resolved data were obtained using the time-correlated single-photon-counting technique. The apparatus uses the tripled output of a mode-locked Ti:sapphire laser for excitation (300 nm) and a monochromator plus microchannel plate detection

system having an overall instrumental response of ~25 ps (fwhm). Details of this system and its use for measuring rotations in supercritical solvents have already been described.[3] Slight improvements in the stability of the laser system and in masking scattered light in the supercritical cell enabled more accurate data fitting here than originally reported. Thermal regulation of the supercritical cell and details of the samples and sample preparation are described in refs 1 and 4. All data were recorded at a temperature of 36.3 ± 0.1 °C.

Representative emission decays (359−367 nm) at a high density[5] are shown in Figure 1. As illustrated by these data, the width of the instrument response function (irf, 27 ps fwhm) is roughly the same as the time over which the parallel (‖) and perpendicular (⊥) emission decays differ, indicating that the rotation times of interest are close to and even shorter than the instrumental resolution available here. For this reason, we do not expect to determine accurately the time dependence of the anisotropy decays in the present measurements. Nevertheless, the resolution is sufficient that, given a value of the initial anisotropy r_0, such data do provide reliable, albeit noisy, estimates of rotation times.

Three methods are applied to extract rotation times from such polarized emission decays. The first method uses simultaneous iterative recovolution fitting of the parallel and perpendicular data to a model consisting of single-exponential population and anisotropy decay functions. Examples of this type of fit are shown in Figure 1. The second method involves sequential reconvolution fitting of the magic angle and parallel emission decays. The magic angle decay is first fit to a single-exponential function to determine the population decay time. This lifetime is then used in a constrained fit of the parallel emission data to a biexponential function. In this fit, one time constant is fixed at the magic angle value, the relative amplitudes of the two components are fixed, and only the time constant of the second component is varied to determine the rotation time.[6] The final method of analysis does not involve fitting. Instead, the difference between the parallel and perpendicular decays is integrated and ratioed to the integral of their (weighted) sum to obtain the equivalent of a steady-state anisotropy. The advantage of using time-resolved data in this manner rather than steady-
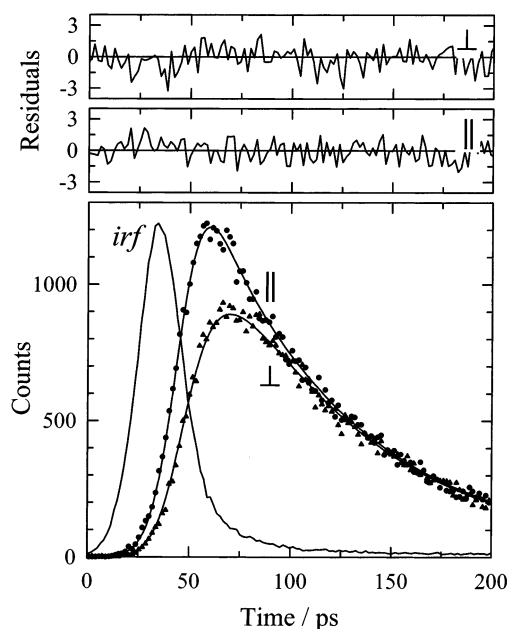
Figure 1. Representative polarized emission decays of DPB in CO_2. The data shown here were recorded at the highest density studied, $2.0\rho_c$ ($T = 36.3$ °C, $P = 324$ bar[5]). The curve labeled irf is the instrument response function obtained from Rayleigh scattering ($\lambda_{em} = \lambda_{exc} = 300$ nm) by the supercritical solvent. Circles and triangles show the emission decays (363 nm) polarized parallel (∥) and perpendicular (⊥), respectively, to the excitation polarization. The smooth curves drawn through these points are the result of simultaneous fitting of the data to a single-exponential population and anisotropy model. Weighted residuals of the fits are shown in the upper panels.

Figure 2. Fluorescence lifetimes (top panel) and rotation times (bottom panel) of DPB in CO_2 as functions of solvent density. The open circles in the bottom panel are experimental rotation times determined using the methods described in the text. The filled triangles are simulated times from ref 1, and the line is the best fit to these data. X denotes the $1/e$ time of the free rotor orientational correlation function.

Figure 3. Fluorescence lifetimes (top panel) and rotation times (bottom panel) of HMS in CO_2 as functions of solvent density. See the caption to Figure 2 for details. The dashed line reproduces the linear regression to the simulated DPB rotation times from Figure 2 to show the near equality of the rotation times of the two solutes.

state data is that one integrates only over the small time window where fluorescence occurs (~500 ps). This windowing helps discriminate against any solvent or impurity emission that could be present in weakly fluorescent samples such as these. (Time-resolved data also have the advantage that any excitation or Raman scattering, if present, is usually clearly visible in the data.) In all three analyses, we account for the bias in parallel versus perpendicular detection efficiencies by matching the decays at times greater than 100 ps. In all cases, the initial anisotropies are fixed at values of $r_0 = 0.39$ for DPB[7–9] and 0.34 for HMS.[10]

Measured fluorescence lifetimes and rotation times are plotted as functions of CO_2 density in Figures 2 and 3. The short lifetimes observed here (top panels) reflect the excited-state trans−cis isomerization of DPB and HMS. Under the present conditions, the inverse decay times directly measure the rates of these reactions.[8,11] In the case of HMS, the lifetime increases approximately linearly with solvent density, by ~35% for a 3-fold increase in (bulk) solvent density. We note that the range of local densities spanned by these experiments is considerably less than the range of bulk densities. The local density surrounding HMS is estimated to vary by less than a factor of 2 over the range of conditions observed.[1] However, even in terms of local densities, the lifetime of HMS is a rather weak function of density. In the case of DPB, there is no observable change in the lifetime with density. The lifetime remains 68 ± 1 ps over the entire range $0.4–2\rho_c$. Similar behavior was noted previously by Kauffman and co-workers,[12,7] who found a density-invariant decay time of 61 ± 3 ps for DPB in CO_2.

This insensitivity to solvent density over such a wide density range is remarkable. One might attribute this behavior to the fact that the reaction approaches the transition state limit and is thus independent of solvent friction over the density range
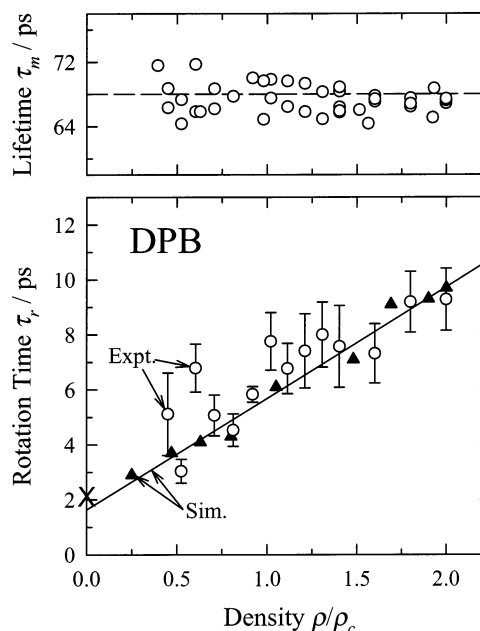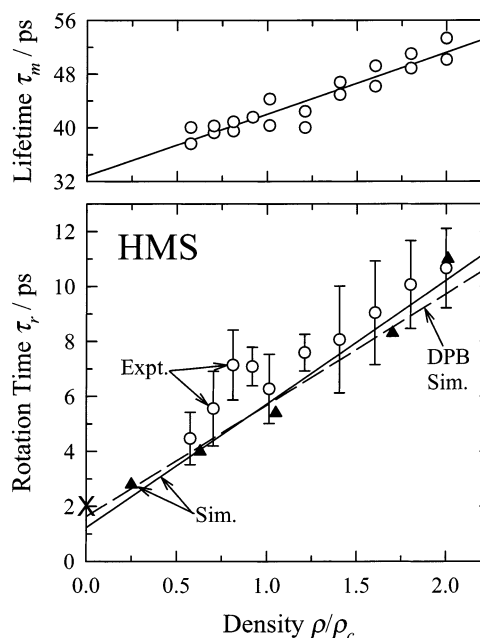
studied. However, the barrier height for DPB isomerization is known to be sensitive to both solvent polarity[13−15] and electronic polarizability.[8] It is therefore likely that the apparently simple behavior displayed here actually hides significant but opposing density trends in the energetic and frictional effects on the isomerization rate. Similar considerations might also pertain to the case of HMS, rendering the density dependence weaker than might have been anticipated.

Measured rotation times (open circles) are displayed in the bottom panels of Figures 2 and 3. The points denote the averages

of the three analysis methods described above for each of two or three data sets and the error bars are the standard deviations of the mean of these six to eight values for each density. Although there is considerable uncertainty in these rotation times, they behave as anticipated, decreasing significantly with decreasing solvent density and approaching the free rotor limit (X) at the lowest densities studied. The rotation times measured here are generally larger than those measured by Anderton and Kauffman.[2] In the case of DPB, our data roughly parallel these earlier data. For HMS, on the other hand, the pronounced nonlinear density dependence reported in ref 2 is not reproduced, but the rotation times agree at the highest densities. We do not know the origins of these differences; however, given the more direct nature of the measurements made here, we believe that the present data are preferable. These new data also lead to much more satisfactory agreement with the simulation results, denoted by the filled triangles and the linear regressions (solid lines) in Figures 2 and 3. To within the corresponding uncertainties, the experimental rotation times appear to be roughly linear functions of density, as do the simulation results. In addition, the rotation times for HMS and DPB are the same to within experimental uncertainties, also as predicted by simulation. We therefore conclude that the simulations reported in ref 1 do not grossly misrepresent the friction present in the DPB/CO$_2$ system. Rather, they provide a description of DPB and HMS in CO$_2$ that semiquantitatively accounts for both the observed spectral shifts[1] and, as shown here, the experimental rotation times. The qualitative interpretation of these simulations should therefore be a reliable guide to the molecular details of solvation in these systems.

References and Notes

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