STUDY OF MOTIONAL DYNAMICS IN COMPLEX FLUIDS BY VERY HIGH-FIELD, VERY HIGH-FREQUENCY EPR (VHF-EPR)

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Very High-field/high-frequency electron paramagnetic resonance (VHF-EPR) has the potential of allowing us to address important questions about fundamental processes in glass-forming systems as the glass transition is approached. We present experimental VHF-EPR spectra taken with a resistive magnet based high field (25 Tesla) EPR spectrometer at different frequencies (525.4275 and 670.463 GHz) over a temperature range from 200 K to 410 K. Two nitroxide spin probes, perdeuterated 2,2, 6,6-tetramethyl-4-methyl aminopiperidinyl-N-oxide (MOTA), and 3,3-dimethyloxazolidinyl-N-oxy-2,3-5a-cholestane (CSL) were used in this VHF-EPR study of the glass former ortho-terphenyl (OTP).

1 Introduction

Recently, Freed and co-workers have provided new insights into the approach to the glass transition with their Electron Paramagnetic Resonance (EPR) study at 9.4 T and 250 GHz of the glass forming hydrocarbon fluid OTP, using a range of nitroxide spin probes of different sizes and shapes.[1-5] EPR of nitroxide spin probes in liquids plays an important role in the study of glass forming liquids: Although the spectra arise from individual spin-bearing molecules, they are very sensitive to the interactions between the spin probe and its surroundings, and this leads to useful information about the dynamics in the host liquid.

The spin probe rotational rates can be categorized into three different regimes: The "fast motional regime" (fmr), the "slow motional regime" (smr) and the "rigid limit regime" (rl). In the fmr (at relatively high temperatures), only rotational rates and no details of the dynamics can be deduced from the EPR spectrum. The sensitivity of the spectrum to the microscopic details of molecular dynamics is particularly enhanced upon cooling, *i.e.*, in the smr, which makes this regime highly desirable to study. In the rl, the spectrum loses its sensitivity to the dynamics.

Because the dynamics in complex liquids involve individual and collective modes of reorientation which occur on different time scales, it is very important to perform EPR experiments over a wide range of magnetic fields and frequencies. By performing the EPR experiment at higher frequencies (and magnetic fields), the effective time-scale of the experiment becomes shorter, so relatively faster liquid motions fall into the EPR smr. This is one significant advantage for extending these

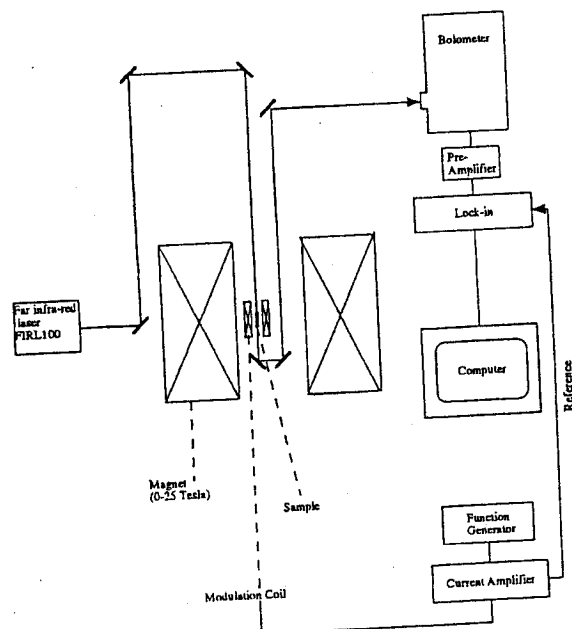

454

Figure 1: A block diagram of the spectrometer.

experiments to higher fields. In addition, by working at high frequencies, as compared to conventional microwave frequencies, one achieves much better orientational resolution, and this greatly enhances the sensitivity to the motional model.

2 Experimental

A Very High-Field EPR (VHF-EPR) spectrometer has been built recently and is now operational at the National High Magnetic Field Laboratory. The spectrometer is based on a highly homogeneous 25 T resistive magnet, known as the "Keck" magnet, with a field homogeneity (at 25 T) of 10 ppm over 1 cm dsv, without shimming. The source of microwaves is a CO_2 pumped far infra-red laser (FIRL 100, Edinburgh Instruments) that offers a series of discrete frequencies starting at 160 GHz up to 7 THz. However, being limited by the low output power at the lower frequency end and the detector sensitivity at the high end, it is mainly used to span the high frequency regime from 400 GHz to 3 THz. An indium antimonide hot electron bolometer is used as the detector, and the sample probe is a single pass transmission probe with field modulation.[6] A block diagram of the spectrometer is given in Fig. 1.

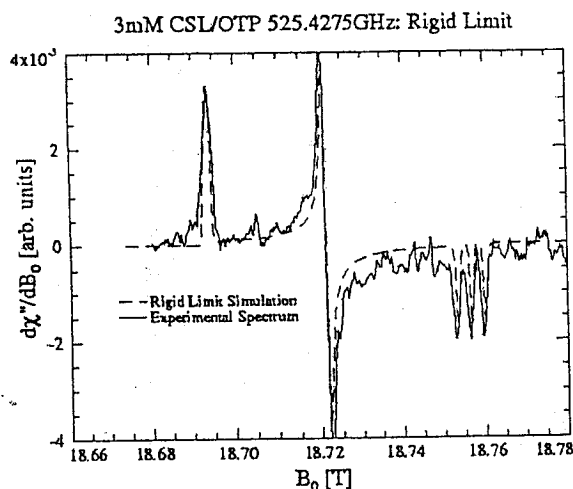3mM CSL/OTP 525.4275GHz: Rigid Limit

Figure 2: Rigid limit EPR spectra of 3 mM CSL in OTP at 525.4275 GHz and 228 K.

3 Results and discussion

The observed and simulated EPR spectra of 3 mM CSL in OTP at 525.4275 GHz and 228 K are shown in Fig. 2. The following rigid limit parameters were determined for the g and A (hyperfine) tensors from a fit that uses an isotropic Brownian diffusion model with a diffusion rate of 10^6 sec^{-1}: g_x = 2.009027 ± 0.000002, g_y = 2.006020 ± 0.000002, g_z = 2.002251 ± 0.000002, A_x = 0.591 ± 0.002 mT, A_y = 0.369 ± 0.002 mT, and A_z = 3.380 ± 0.002 mT. The linewidth of the rigid limit simulation has been artificially reduced to allow the reader to distinguish the fit from the data.

Figure 3 shows the average rotational diffusion rate, denoted as R^0 for consistency with Earle et al.,[1] for 3mM CSL in OTP at 670.463 GHz, the average rotational rate for 1mM MOTA in OTP at 525.4275 GHz, and the average rotational rates determined for the same MOTA and CSL systems at 250 GHz by Earle et al.[1] The solid symbols in the figure are results of measurements from the HF-EPR laboratory at Cornell University. It is worth noting that the rotational diffusion rates determined in both laboratories but at different frequencies are in agreement. The higher frequency data also show results for the higher temperatures. They indicate that activated behavior for R^0 observed at 250 GHz continues into the higher temperature region, although some reduction of this activation energy may take place for CSL. This high temperature regime is one where simple Brownian motion (with only small effects from the dynamic cage[1-4]) should apply, and where R^0 should obey the η/T dependence in OTP[1] (η is the shear viscosity), characterized by the Stokes-Einstein-Debye (SED) law.[8] Experiments at lower temperatures at the higher frequencies are expected to provide more information with which to test the microscopic models of dynamics.[1]
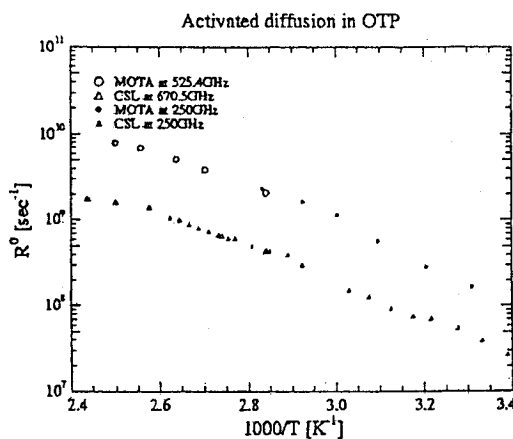
Activated diffusion in OTP

Figure 3: Average rotational diffusion rates as a function of temperature.

Acknowledgments

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