Molecular Motion of Aromatic Molecules Covalently Attached to Silica Surfaces: Surface Coverage Dependence. Edward W. Hagaman, A. C. Buchanan, III, and M. K. Kidder, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Large rotational diffusion rates have been determined for silica-attached 1-pyrene at the solid/air interface through time-dependent fluorescence anisotropy measurements. Diffusion rates $D_{\parallel}$ and $D_{\perp}$ were determined to be 4×10^6 and 2×10^6 s^{-1}, respectively, by treating the motion of the attached moiety as an oblate ellipsoid of rotation. ^{13}C NMR measurements on solid, silica-attached benzene-1-^{13}C, (surface coverage = 0.017 mmol g^{-1}, corresponding to derivatization of 1% of the surface silanols) gave remarkable, high-resolution spectra. A lower limit for the rate of phenyl group motion was estimated to be 1.5×10^5 s^{-1}, consistent with the fluorescence anisotropy data measured for silica-attached 1-pyrene. In this work the motional behavior and line width dependence of silica-attached aromatics as a function of surface coverage are examined using solution and solid state NMR.

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