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Watching How Molecules Orient in a Surface Forces Apparatus, Using Confocal Raman Spectroscopy SHAN JIANG, UIUC, Materials Science and Engineering Department, MINSU KIM, UIUC, Physics Department, SUNG CHUL BAE, STEVE GRANICK, UIUC, Materials Science and Engineering Department — Much is known about surface forces, less about where they come from. This laboratory is engaged in direct vibrational spectroscopic measurements of how molecules orient in confined geometries. Regarding force measurements, PDMS (polydimethylsiloxane) was a model system for many years. In this study, we describe direct experiments using a novel version of confocal Raman spectroscopy. This experiment allows direct measurement of how the PDMS molecules orient under confinment as well as under subsequent shear. When the thickness of the fluid film is less than the unperturbed radius of gyration of the polymer, we obtain two novel findings: (a) linewidth analysis of peaks reveals that vibrational relaxation times are perturbed in this confined geometry; (b) orientation of the chain backbone is not everywhere the same within the molecularly-thin film; domains of various orientation are observed instead.

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