Low-temperature dynamics of amorphous polymer surface and subsurface layers: Study by single molecule spectroscopy

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Abstract:

We present the first results of our single-molecule spectroscopy studies of low temperature spectral dynamics of single impurity molecules (SMs) introduced in surface and ultrathin subsurface layers of amorphous polymer films.

The system was thin films of amorphous polyisobutylene (of thicknesses 5-300 nm) supported on microscopic glass substrate. The fluorescent molecules of tetra-tert-butylterrylene (TBT) were used as spectral nanoprobes. We developed a procedure which allowed us to introduce TBT molecules directly upon the surface of polymer films or into subsurface layer of controllable depth of these films. We detected and analyzed zero-phonon spectral lines in individual optical spectra of single TBT molecules incorporated to surface layers of films under study and temporal evolution of these spectra over the time (spectral histories). The measurements were performed at T=4.5K.

It was found that in the case of TBT molecules deposited solely on the surface of amorphous polymer films the only broadband fluorescent spectra were detected. In the case of SMs incorporated a few nanometers (and even a fraction of nanometer) below the film surface the observed spectral picture was completely different and dependent on the depth of a doped layer. At very small depths zero-phonon lines of SMs were detectable, but their spectral widths were unusually larger than analogous widths of SMs located deeper. With increasing of depth, the zero-phonon spectral lines become narrower and at depth more than 100 nm they become comparable with the widths of SMs in bulky polymer. Spectral histories of SMs incorporated into near-surface layer of films were also different. They demonstrated more random and faster temporal behavior than histories of SMs introduced in bulky material. Additionally to reproducible jumps of zero-phonon line frequencies, caused by flipping two-level systems, irreproducible jumps and drifts of zero-phonon line frequencies were observed. These results clearly show the existence near the surface of amorphous polymer sample ultrathin layer with faster and richer than in the case of bulky material dynamics.