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"Molecular spectrometers" in the condensed phase: local THz-FIR response from femtosecond fluorescence

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We examine dye molecules whose color depends on the polarity of the environment. Following fast optical excitation, their fluorescence band typically red-shifts by 0.5 eV on femtosecond to nanosecond time scales. This "dynamic Stokes shift" reflects the joint molecular and environmental reorganisation of the system. Solvation dynamics has been studied for decades in the hope that the dynamics of the environment itself can be extracted. We contribute with two research lines: (1) development of rigid polar solvation probes whose vibrational response is removed from that of water, for example, and (2) fluorescence techniques which measure the dynamic Stokes shifts more precisely. Two results will be shown. The frequency-dependent permittivity $\varepsilon(\omega)$ of water surrounding N-Methyl-6-Quinolone is extracted up to about 100 cm^{-1} from the time-resolved fluorescence shift R(t). The key consists in an analytical connection $\varepsilon(\omega) \quad \rightarrow$ R(t) which is needed for data fitting. Measurements with the cryoprotectant disaccharide trehalose in water serve to establish the method. Its unique feature is locality, *i.e.* the possibility to measure $\varepsilon(\omega)$ around a supramolecular structure with a covalently connected or embedded probe. THz vibrational activity of a biopolymer is thus measured locally, on the effective length scale for polar solvation, with an embedded molecular probe. For this purpose 2-hydroxy-7-nitro-fluorene was linked into a 13mer duplex opposite an abasic site. The NMR solution structure shows that the fluorene moiety occupies a well-defined position in place of a base-pair. The dynamic Stokes shifts for solution in H_2O and D_2O are quantified. Their difference is much larger than expected for free water, suggesting that only bound water is observed. A weak 26 cm^{-1} spectral oscillation of the emission band is observed which is not present when the probe is free in solution, and is therefore caused by the supramolecular structure (DNA and hydration water).