THEORY OF TIME DEPENDENT FLUCTUATIONS IN SINGLE MOLECULE SPECTROSCOPY

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Single molecule spectroscopy reveals fascinating fluctuation behaviors, not observed in standard spectroscopies, for example spectral jumps, blinking, photon bunching and anti bunching. We investigate the theory of time dependent fluctuations of single molecule fluorescence. In particular the relation between spectral diffusion, found in many single molecule experiments, and photon counting statistics. It is shown that Mandel's Q parameter, describing fluorescence intensity fluctuations, is related to a three-time dipole correlation function describing the dynamics of the molecule coupled to its environment. Our approach, based on linear response theory, generalizes the Wiener–Khintchine formula, which gives the average number of fluorescence photons in terms of a one time dipole correlation function. An exact solution for Q is found, for a single molecule undergoing a simple Kubo-Anderson spectral diffusion process. In the slow and fast modulation limits our results reduce to simple expressions describing super Poissonian photon statistics. For the slow modulation case our approach describes well single molecule spectroscopy experiments in a low temperature glass.

- E. Barkai, Y. Jung and R. Silbey *Theory of Single Molecule Spectroscopy: Beyond the (ensemble) Average* **Annual Review of Physical Chemistry** invited review and http://www.nd.edu/ jbarkai/
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