MAR08-2007-020078

Abstract for an Invited Paper
for the MAR08 Meeting of
the American Physical Society

Earle K. Plyler Prize Talk: Stark Realities

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Stark spectroscopy is the effect of an electric field on a spectrum. Measurements of the Stark effect give information on the change in dipole moment and polarizability for a spectroscopic transition. The great majority of Stark effect measurements have been and still are made in the gas phase where spectroscopic transitions are very narrow and a Stark splitting can be readily measured. There are many fewer examples of Stark spectroscopy measurements in condensed phases, largely because of the perceived difficulty of applying a large electric field. While this is the case for liquid samples, where molecular alignment and low breakdown voltages complicate the measurement, it is simple to immobilize the molecule of interest, either by embedding it in a thin polymer film or by freezing the solvent. The latter is completely general and any sample that forms a high quality optical glass, including protein samples, can be studied. In this talk I will present an overview of applications of Stark effects to diverse systems. We divide the phenomenon into two broad classes: classical Stark effects, where the applied field acts as a perturbation shifting a transition; and non-classical Stark effects, where the applied field affects the intrinsic absorption lineshape and/or populations of states. Classical Stark effects provide quantitative information on the dipolar nature of excited states for electronic or vibrational transitions. Once calibrated, the spectroscopic transition can be used to probe electric fields in organized complex systems such as proteins and changes in those fields accompanying mutations, catalysis, ligand binding and folding. Vibrational Stark effects are particularly useful in this context, and this has led to diverse strategies for introducing unique and sensitive probes for electrostatic fields in proteins. Non-classical Stark effects embrace the many effects that electric fields can have on reaction dynamics, particularly involving electron transfer, either photoinduced or in mixed valence systems. For such systems, the electric field can alter the absorption or emission lineshape substantially because the potential surface depends upon the field and the spectrum depends on the shape of the potential. Examples of each type will be presented.