Two-dimensional Electronic Spectroscopy of Controlled Isolated Systems

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Synopsis Phase-modulated pump-probe spectroscopy is capable of detecting non-linear signals even from dilute samples. We currently implement a phase-modulated two-dimensional electronic spectroscopy setup to measure 2D spectra of doped helium nanodroplets. The 2D spectra will be used to investigate coherent processes in complex molecules.

Two dimensional electronic spectroscopy (2DES) is a powerful tool to study coherences and correlations on ultrafast time scales. Until now, 2DES has been limited almost exclusively to condensed phase studies. Our aim is to apply 2DES to controlled isolated systems by using doped helium nanodroplet beams. Helium nanodroplets provide the dopant with a cold environment and minimal perturbation, which are ideal conditions to study the behavior of an individual system in a well-controlled environment.

However, the target density in doped helium droplet beams is several orders of magnitude lower than in bulk condensed phase samples. Furthermore, 2DES depends on the third order response of the sample to the incident light. Together, this leads to particularly small signals. We adapt a phase modulation technique combined with lock-in detection to overcome this issue [1]. This technique has already shown significant sensitivity improvements for coherent pump-probe spectroscopy in helium nanodroplets [2].

One advantage of 2D spectroscopy is that in the 2D spectra homogeneous and inhomogeneous broadening mechanisms are readily disentangeled. For this reason, 2D spectroscopy has been used to characterize the dynamics of solvents such as the ultrafast rearrangement dynamics of water [3]. In a similar way, 2DES may be used to get more insights into the helium droplet properties when doped with different species.

We currently implement the experimental setup and do initial characterization measurements.

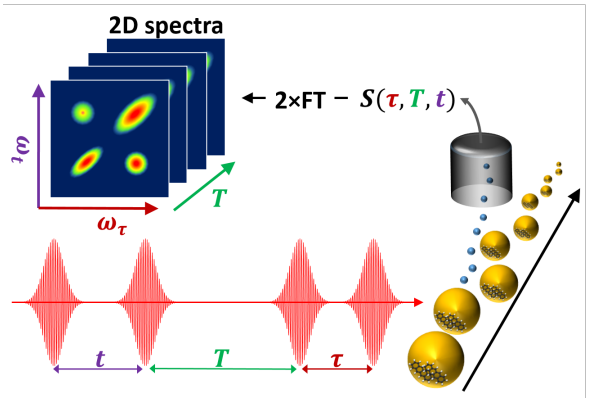

Figure 1. Schematic of the experiment without phase modulation. A train of four fs-pulses is used to excite the dopant within the droplets. The excited state population is then measured by photo ionization or fluorescence. The resulting signal is Fourier transformed with respect to the inter pulse delays τ and t yielding 2D-spectra at different times T.

References

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