ANALYSIS OF FEMTOSECOND PUMP-PROBE SPECTRA IN THE CONDENSED PHASE: DYNAMICS AND POTENTIALS OF I_2 IN RARE GAS MATRICES

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We present a scheme to directly extract molecular dynamics and potentials from femtosecond pump-probe-spectra in the condensed phase[a]. As a model-system we consider the well studied I_2 molecule isolated in a Kr matrix, since it shows up to 32 oscillations of the molecule despite relaxation and predissociation. The method can be applied to more complicated systems, if several oscillations of one mode can be measured. It is complementary to sophisticated simulations and yields intuitive understanding of pump-probe spectra.
Due to the coupling to many degrees of freedom of the bath atoms, the electronic absorption spectrum is broad and completely unstructured. Using femtosecond pump-probe spectroscopy, the molecular vibrations can be observed in the time domain as oscillations in the LIF-signal. Vibrational frequency, anharmonicity and a rate of energy dissipation can be read directly off the spectra. Using independently tunable pump and probe pulses (from noncollinearly pumped OPAs) we measured a set of spectra covering a wide range of excitations of the B-state. The systematic variation of pump and probe wavelengths allows to seperate predissociation, relaxation, dephasing and dispersion of the molecular wavepacket. Interesting details of the probe process are revealed.

[a] Bargheer, K. Donovang, P. Dietrich and N. Schwentner, *J. Chem. Phys.* **111** (1999) 8556-8564