

A RATIONAL COHERENT CONTROL SCHEME APPLIED TO THE SOLVENT INDUCED PREDISSOCIATION OF BR₂ IN SOLID AR

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In order to manipulate the predissociation dynamics of a chromophore-bath system (here Br₂ embedded in a crystalline Ar environment) we excite and probe it with appropriately shaped femtosecond pulses. A sequence of five phase-stabilized ultrashort pulses allows in a first step to prepare out the coherent population in the inflow channel (here the covalent B state) from a dominant incoherent contribution (A state) strongly coupled to the motion of the solvent atoms [1]. The driving process for this excitation cleaning is constructive interference between subsequently excited wave packets by subpulses building up the pulse train [2]. Only those parts of the excited population preserving vibronic phase memory contribute to the interference term. We observe coherence times of about 1.2 ps, which is surprisingly long concerning condensed phase systems. In a second step we open the predissociation channel by steering the phases of the pulses and selecting this way the solvent phonon contributions. These are responsible for the efficient predissociation as predicted by recent results of quantum calculations [3]. Our rational control scheme is based on the available spectroscopic information on the system [4]. We directly write it into the spectrum of an ultrashort excitation pulse using a typical pulse shaper unit with a liquid crystal display as an active device. This way we generate in the chromophore spectral combs matching either the spectral positions of the chromophore's vibrational levels or those originating from phonon excitation. In the time domain that corresponds to the generation of excitation pulse trains where the spectral selection is stored in the temporal phases of the subpulses.

Frequency resolved spectra show that the reaction dynamics is restricted to a sharp spectral region [4]. Therefore, the duration of excitation and probe pulses has to be optimized in order to provide the required spectral resolution of the process without destroying the dynamical character of the excitation. We show experimentally and in combination with gas phase simulations how the pulsewidth affects the quality of monitoring the reaction's fast time evolution.

References

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