

Chapter 8

Summary

Ultrafast spectroscopy of I_2 in solid Kr

The model system I_2 in Kr matrix is examined with femtosecond pump-probe spectroscopy to develop appropriate strategies for the strong system-bath coupling in the condensed phase. A novel evaluation scheme is presented that allows the extraction of information on potentials and dynamics directly from the experiment without the aid of simulations. The vibrational frequency ω_e and the anharmonicity $\omega_e x_e$ of the excited B state are measured over a wide energy range, although the absorption spectrum itself is structureless and contains no information except the Franck-Condon envelope. A one dimensional (1-D) representation of the multidimensional excited state potential is constructed.

It is shown that both pump and probe wavelength have to be optimized when vibrational frequencies are deduced from femtosecond-pump-probe spectra. The effect of the probe window on the measured frequency can exceed 7% in the case of I_2/Kr , which is on the order of the anharmonicity itself. In systems with even stronger interactions, where the wave packet is substantially broadened in energy space (e.g. in liquids with large fluctuations), the question of which part of the wave packet is probed will gain importance.

Snapshots of a wave packet trajectory near the dissociation limit are taken, which directly display the inelastic and nonlinear fragment cage ($I - Kr$) interaction. Vibrational relaxation rates that vary over three orders of magnitude are derived. In the strongest interactions, more than 50 phonons of the Kr lattice are created in a single collision. This is equivalent to 3000 cm^{-1} or 57% of the initial energy. Near the potential minimum the energy loss is only 1 phonon in 5 periods. Despite the strong interactions, vibrational coherences survive up to 10 ps. The interplay of vibrational relaxation and predissociation was further investigated in the diploma thesis of Markus Gühr. This work [115, 116] relies on the good knowledge of the energy dissipation rates derived here.

The experimental findings are compared to calculated potential energy surfaces (PES) and molecular dynamics (MD) simulations. The experiments suggest the use of multiple trajectories in order to derive an averaged 1-D potential that goes beyond the approximation of a frozen solvent cage.

Ultrafast photodynamics of ClF in solid rare gases

The molecule ClF isolated in solid rare gases Ar and Kr is established as a new model system that allows for analysis and control of the interplay of dissociation and recombination dynamics. On the spectroscopic side, the $A' \rightarrow X$ emission of ClF is analyzed and found to be a convenient measure of the concentration of recombining ClF molecules. The energetics of the ion-pair state Cl^+F^- in Ar is clarified in absorption and emission, which is essential for monitoring the recombination dynamics by fs-pump-probe spectroscopy with LIF detection. The spectroscopic characteristics of the F fragment after photodissociation of ClF in Ar and Kr and the respective quantum yields are compared to

previous experiments on F_2 dissociation. A laser control scheme is demonstrated, which reversibly shuttles F atoms from ClF to interstitial Kr sites and back to the Cl radical.

The evaluation scheme to derive vibrational relaxation rates from fs-pump-probe spectra is applied to ClF/Ar and Cl_2/Ar . Two different regimes of energy dissipation are found. The rate for high excitation energies of ClF/Ar in the B state exceeds 35% (2600 cm^{-1}) per period, and 40 phonons of the Ar lattice are created in one collision. Above the gas phase dissociation limit the interaction of the fragments with the cage is strong and the exponentially increasing dissipation rate displays the nonlinear nature of the interaction. Wave packets excited to the repulsive $^1\Pi$ state lose more than 50% of the energy in the first period. If the molecule is recombined and bound in the molecular potential, the vibrational relaxation is slow ($\sim 6\text{ cm}^{-1}$ or 0.2% per period). For Cl_2/Ar the rapid energy loss in the first collision is even stronger (60% per period), because Cl and Ar have nearly equal masses. The MD simulations predict shock-waves that quickly remove the energy from the excited molecule.

The ultrafast coupling of energy into the solvent modes shows up also in the oscillatory structure of the pump-probe spectra of the vibrational wave packets of ClF in Ar or Cl_2 in Ar . This is verified by molecular dynamics (MD) and two dimensional quantum simulations. The vibration of the Kr cage around an F fragment driven by ClF dissociation is observed. As a general result it is confirmed that the vibrational coherence is preserved over several periods when the energy from the initially excited molecule ("chromophore") is transferred to the solvent on an ultrafast timescale. The solvent cage is excited impulsively and performs coherent vibrations. A well defined geometry and timing of the interactions seem essential for preserved coherence. This may in future offer a route to coherent control in dissipative systems.

Ultrafast tilting of the molecular $Cl - F$ bond ($\tau_r = 1.2\text{ ps}$) in dissociation-recombination dynamics in Ar is monitored by polarization sensitive fs-pump-probe spectroscopy. The small fragment size and the isotropic cage (substitutional site) allow for skewed scattering events of F atoms with the cage atoms. The evaluation in terms of the ultrafast decay of the anisotropy is valuable for comparison with simulations, since the difficult calculation of ion-pair states is circumvented. It is verified that the $I - I$ bond experiences no angular reorientation in its axially symmetric double substitutional site. This situation in solid Kr differs from previous experiments in liquid Kr , where I_2 was found to rotate.

Excitation to the singlet state $^1\Pi$ and probing the bound triplet states $^3\Pi$ evidences the ultrafast nonadiabatic transition to the lowest excited electronic states, unequivocally for ClF/Ar , Cl_2/Ar and I_2/Kr . This transition involves an ultrafast spin-flip. It is surprising that it occurs on the femtosecond timescale also in small molecules like ClF , although the intramolecular spin-orbit interaction is weak. The effect was predicted for F_2/Ar by nonadiabatic MD simulations. The accumulation of population in the bound triplet state within $\tau_f = 500\text{ fs}$ observed in the experiment, is in quantitative agreement with these simulations. It is an upper limit for the spin-flip time, since it measures the time for dissociation plus spin-flip plus recombination.

The cage exit of F fragments after excitation of ClF/Kr is monitored in real time. The time to reach the nearest interstitial O_h site is $\tau_{exit} = 250\text{ fs}$, and an indirect cage exit after 1 ps is observed especially for warm Kr matrices. These results are in excellent agreement with the simulations of F_2/Ar .

A double-pulse control scenario is demonstrated in mixed $Cl_2/ClF/Ar$ solids. Variation of the time delay between a pump and a control pulse switches between the fluorescences of Cl^+Cl^-/Ar and Cl^+F^-/Ar with a very good contrast ratio of 1:250. In these experiments the excited state population of the ion-pair species is controlled. The mechanism exploited in this scheme is ultrafast vibrational relaxation. A wave-packet-timing control in a Tannor-Kosloff-Rice scheme is also demonstrated on a timescale of 50 fs.

Setup for ultrafast spectroscopy

In the experimental setup two major achievements were made. Two non-collinear optical parametric amplifiers (NOPAs) were built for the generation of tunable sub 30 fs pulses. Their efficiency was doubled in comparison to the commercially available ones. With this improvement two experiments with four independently tunable femtosecond pulses can run simultaneously, while a considerable fraction of laser power is retained for a third experiment.

The characterization of the femtosecond pulses was extended in a flexible setup that can be used to characterize pulses from the infrared to the ultraviolet spectral region by Frequency Resolved Optical Gating (FROG). The cross-correlations can be taken in situ, simultaneously with the pump-probe experiment.

Future Prospects

Cage exit dynamics

The cage exit dynamics of F fragments deserve further experimental investigation on the femtosecond timescale. Two directions of investigation are very promising. First, experiments on the cage exit after excitation to the $^1\Pi$ state should be performed. Up to now, experiments with this excitation were accomplished only in Ar and with a probe laser that records the recombination dynamics. They were analyzed in chapter 7.6 with focus on the spin flip. It was shown that the 1.5 eV higher excess energy is absorbed by the matrix within one or two periods. The 2-D quantum simulations presented in Fig. 7.10 demonstrate a greatly enhanced exit probability, if the Ar is pre-excited. This implies that a large effect of the excess energy on the cage exit dynamics can be expected, as this leads to large amplitude motion of the rare gas atoms. These experiments should be carried out in Kr .

The second direction that should be pursued is cage exit in multiply doped Ar matrices. The ArF excimer states lie too far in the UV but co-doping with Kr or Xe can be used to detect the F fragments. Then the shuttling of the F atom from Cl to the co-dopand (e.g. Xe) and back can be followed on the femtosecond timescale. It will be interesting to compare the results of ultrafast experiments in different matrices, since already the static bleaching experiments showed an increase of the permanent dissociation efficiency by an order of magnitude on going from Ar to Kr .

New Molecules

The molecule $ClXeF$ was observed after photolysis of ClF in Xe matrices [95]. The same experiments that tried to produce $ClKrF$ were unsuccessful. However, calculations show that this molecule is bound by 0.4 eV in the linear configuration and there is a barrier to the formation of $ClF + Kr$ [97]. Since the bleaching experiments show that ClF is effectively dissociated, it is expected that the $ClKrF$ molecule can be generated with properly chosen pulse parameters. In any case it will be very interesting to analyze the formation of either $ClKrF$ or $ClXeF$ in real time with femtosecond pulses.

Active control of molecular dynamics

The active control of molecular dynamics in these model systems will be pursued in several ways. Strong infrared laser pulses will be used to align molecules with the polarization vector of the light field [224]. The feasibility has been demonstrated in the gas phase [225, 226], and the experiments on the statistical reorientation of the ClF bond (chapter 7.5.3) show a way to measure the ultrafast alignment of molecules also in the condensed phase.

The use of double pulses or tailored pulses from a pulse-shaper will be used to actively control the interplay of solute-solvent-solute interaction that was demonstrated in this thesis. The idea is to prepare wave packets with appropriate timing that exploit the coherence of the molecular vibration and the cage motion, e.g. to enhance the cage exit.