Chapter 8

Summary

The photodissociation dynamics of diatomic molecules embedded in a rare gas environment was investigated theoretically. Emphasis was placed on the guest-host dynamics with respect to the different orientation of the two model systems Cl_2 and ClF in Ar.

Potentials and interactions were derived using the Diatomics in molecules approach. Classical MD simulations were used to describe the dynamics of the system.

8.1 Cl_2 in Ar

The model system Cl_2 in Ar was investigated with emphasis on the guest-host interaction after photoexcitation of the chromophore molecule. First, the equilibrium geometry was determined, which shows the chlorine molecule on a disubstitutional site, oriented in {110} direction of the lattice. In this geometry, the molecular axis is pointing directly to argon atoms forming the cage. The other atoms of the cage were classified to different groups, which showed some influence on the dynamics of the system. The influence of the chromophore was shown to result in small displacements of these groups of atoms in the equilibrium geometry of the system.

Different channels for energy dissipation in the lattice were observed in the simulations. While the excitation to the energetically higher C-state showed the initialization of a shock wave as a primary effect, the excitation to the B-state leaves the molecular fragments with lower initial energy. Model calculations with different excitation energies, corresponding to different Cl-Cl bond lengths, were

performed to simulate the vibrational relaxation of the chromophore with respect to the matrix dynamics. Two different channels for energy dissipation in the lattice were found for excitation above and below the bound part of the potential in the B-state. For excitation above the potential well, the energy dissipation is similar to the C-state excitation, were the main part of the momentum of the molecular fragments is transferred to the argon atoms in direction of the molecular axis. Here the energy loss is pronounced, due to the effective transfer of momentum in a direct collision with the cage atoms. For excitation into the bound part of the potential, a different channel for energy dissipation was found, no direct collision will occur, due to the restriction of the maximal Cl-Cl bond length by the intermolecular potential. The energy loss is much less pronounced than in the case of higher excitations and is much more influenced by the anharmonicity of the potential. Energy is lost at the inner turning point, at smaller intermolecular distances. At this time the belt atoms, which span a rectangular window around the center of mass of the chromophore, but in layers above and below, have moved into the free space left by the dissociating guest molecule. The momentum is now transferred to this group of cage atoms, but less efficiently. The total energy of the chromophore in the excitations into the bound part of the potential is much more sensitive to rearrangements of the caging atoms, as could be seen in the total energy of Cl_2. The experimentally observed change in the relaxation rates (large for high excitations and much less for relaxation in the bound part of the potential) are consistent with the found mechanisms for energy relaxation. Additionally, the excitation spectrum for this system [20] showed a very weak coupling for the vibrational levels in the bound part of the potential and the same effect was found in the calculations performed in this work.

The experimental observations for similar systems like I_2 in Kr or Br_2 in Ar showed the appearance of a long living phonon mode, which should result from a excitation of host atoms located in the vicinity of the guest molecule. Indications were given, that this mode could be initialized by the photoexcitation of the chromophore and connected to this an expansion of the molecular wave function, like suggested in the DECP mechanism. The equilibrium geometry for Cl_2/Ar in the B-state was determined, which showed new equilibrium positions for especially the window and phonon atoms. After photoexcitation of Cl_2, especially the phonon atoms will experience a force until they finally oscillate around their new equilibrium positions. This oscillation is coupled to that of the belt atoms and shows a period in the range of that found for the surviving phonon

mode.

State transitions were not included in the dynamics simulations of Cl_2 in Ar, but evidence is given from the experiment and from quantum calculations, that population is transferred from the initially excited $^1\Pi$ (C) state to the $^3\Pi$ (B) state, indicating a usually forbidden spin-flip reaction.

8.2   ClF in Ar

The second model system was simulated for comparison of the different kind of lattice dynamics due to the different orientation of the guest molecule in the lattice. ClF occupies a single substitutional site and was aligned to the {111} direction of the lattice, with the fragments pointing to triangular windows, enabling the investigation of cage exit and dissociation. The photodissociation dynamics showed that for the chlorine atom the energy for cage exit is still too high in this orientiation, so the caging will be perfect. The fluorine atom, on the other hand, transfers some of its energy to the window atoms and by this initializes a Ar_3 stretching mode. This stretching leads to the opening of the windows and connected to this a lowering of the potential barrier, enabling exit of the initial cage. The energy dissipation in the lattice is much less effective as in the case of perfect caging and mainly the window atoms are driven by the chromophore dynamics.

As a first step to estimate the tole of electronic transitions, the nonadiabatic coupling elements were calculated. The adiabatic potential surfaces in this approach are coupled by the spin-orbit terms, the interaction with the argon atoms as small (Cl,F)-Ar distances, which leads to a significant decrease of the energy separation between the states, and by the nonadiabatic coupling elements. Comparison of the spin-orbit coupling and the energy gap between the initially excited $^1\Pi$ and the energetically lower $^3\Pi$ state showed that the value of SOC exceeds the energy gap at a distance of $r_{Cl-F} > 5.6$ a_0, enhancing the coupling between these states. The nonadiabatic coupling elements, derived by the method suggested by Tully [27] showed in addition a large coupling for $r_{Cl-F} > 5.3$ a_0, where the energy gap between the two states decreases. This distance is reached after 60 fs simulation time. Exact quantum simulations including one dimensional energy curves for the singlet and triplet Π state calculated in this from this work proposed a population transfer of 50 % from the singlet to the triplet state after

75 fs, which lies well in the time regime indicated by the appearance of spin-orbit and nonadiabatic coupling elements.

The classical simulations performed here were used to provide insight into the fundamental processes of photodissociation dynamics of small molecules embedded in condensed phases. Emphasis was placed on the guest-host interactions, which lead to interesting results for energy relaxation and -dissipation and for the initialization of shock waves. The systems ClF and Cl_2 were compared with respect to different caging mechanisms and the importance of coupling between particular adiabatic states was estimated.

To describe the experimentally observed features like the ultrafast spin-flip this method has to be extended, for instance, by the implementation of Tully's surface hopping method.