Chapter 7

ClF in Ar

7.1 DIM-Potentials and Interactions

For CIF in Ar the potentials were calculated as described in chapter 4, taking into account the asymmetry of the molecule.

$$\hat{H}_{total} = \underbrace{H_{mol}^{ClF} + V_{SO}^{ClF}}_{ClF} + \underbrace{\sum_{Cl,F} \sum_{k} U_{(Cl,F),k}^{DIM}(r_{(Cl,F),k}, \gamma_{(Cl,F),k})}_{(Cl,F)-Ar} + \underbrace{\sum_{k,l} V_{Ar_k-Ar_l}}_{Ar-Ar}$$

The method for implementing ClF in an argon matrix using the DIM approach is similar to that described for Cl₂ in chapter 6. Again the Valence Bond basis set, consisting of 36 states, is constructed as described in section 4.2. Cl has the electronic configuration $1s^22s^22p^63s^23p^5$, F $1s^22s^22p^5$.

Ab initio calculations for ClF with and without spin orbit coupling were performed by A.B. Alekseyev [74], and those potentials were associated with the appropriate valence bond wavefunction. The gas phase potentials of ClF are shown in Fig. 7.3. The ground state has a dissociation energy of 2.59 eV in comparison of 2.49 eV for Cl₂. The ³ Π state shows a dissociation energy of 0.33 eV and is thus bound slightly stronger than the same state of Cl₂ with a dissociation energy of 0.23 eV. The ¹ Π state shows a very shallow minimum of 0.01 eV for $r_{Cl-F} = 6.5$ a_0 , whereas for Cl₂ this state shows no such minimum.

To this the spin-orbit coupling elements are added, using the derivation for the matrix elements of section 4.4 with the two different coupling constants for chlorine (0.109 eV) and fluorine (0.05 eV), respectively. Again l,s-coupling is assumed for the separated halogen atoms. Interaction with the argon atoms is included, taking to account the distance between each of the halogen atoms and the angle between the molecular orbital containing the electron hole and each of the argon atoms. The potentials for F-Ar were taken from ab initio calculations performed by G. Chaban [75], which are steeper in for shorter intramolecular distances than those determined by Aquilanti et al. [76], see Fig. 7.1, potentials for Cl-Ar see Fig. 6.1.



Figure 7.1: F-Ar interaction: Σ and Π potentials. Experimental values (Aquilanti, [76]): Σ (dashed line), Π (dotted line), ab initio calculations by G. Chaban: Σ (squares) and Π (circles)

The Σ -state shows a minimum of 0.013 eV at $r_{F-Ar} = 5.86 a_0$, the Π -state only a very shallow minimum of 0.006 eV at $r_{F-Ar} = 6.8 a_0$. Both potentials are repulsive for smaller internuclear distances.

The Ar-Ar interaction is described using potentials from Aziz et al. [50]. After diagonalization of the Hamiltonian, including all these interactions, the adiabatic potentials will be obtained at each timestep, see section 2.

7.2 Geometry

CIF occupies a single substitutional site in the lattice. The simulations were performed in a box containing 257 atoms, corresponding to 3 unit cells in each direction.



Figure 7.2: Orientation of CIF in Ar: alignment to {111} direction. Cl and F are pointing to triangular windows, respectively.

The molecule was aligned on the {111} direction of the crystal as shown in Fig. 7.2, pointing to the same triangular windows as F_2 in Ar, see Fig. 1.3. In this orientation, dissociation of the molecule is possible, in contrast to the orientation in {011} direction, where the molecule points to a four-atomic window, but after photodissociation and subsequently opening of this window hits the next argon atom on this axis and recombines in the initial cage [81]. The equilibrium distance for the ground state of ClF in the Ar matrix is r_{Cl-F} = 3.01 a₀. The center of mass is shifted slightly to $R_{ClF} = 0.1$ a₀, due to the stronger repulsion of the chlorine from the surrounding matrix atoms. Taking the initial location of the removed argon atom as origin of the cartesian coordinate system, this means that the atomic fragments are not symmetric with respect to the origin. The Cl will be shifted towards this origin and the F atom will be shifted more in z-direction, see Fig. 7.2.

The symmetry of the system is C_{3v} and is thus reduced from that for F_2 in Ar (D_{3d}) for the same orientation in the crystal.

7.3 Potentials

Fig. 7.3 shows the adiabatic potentials of CIF with fixed center of mass, compared to the gas phase potentials (panel a)). Spin-orbit coupling will lift the degeneracy, see for example the ${}^{3}\Pi_{u}$ states, which are the lowest states above the ground state. Embedding the molecule in an argon matrix will cause the potential to bend up at $r_{Cl-F} \geq 5.3 a_{0}$, due to the repulsive Ar-X,Y interaction when the fragments are approaching the cage wall. This leads to nearly degeneracy of the different states and as a second effect, the repulsive potentials are stabilized.



Figure 7.3: Potentials for CIF: gas phase without spin-orbit coupling(top), gas phase including spin-orbit coupling (center), in Ar, aligned along {111} (bottom)

The ground state shows a potential minimum at $r_{Cl-F} = 3.0 a_0$, correspond-

ing to a potential energy of -3.09 eV. The ${}^{3}\Pi$ states are bound with a potential minimum of -0.62 eV at $r_{Cl-F} = 3.82a_{0}$, while the ${}^{1}\Pi$ states show a potential minimum at 4.01 a_{0} , corresponding to 0.13 eV. They are quasi-bound states, because in the matrix environment, dissociation is hindered.

7.3.1 Matrix shift



Figure 7.4: Potentials for CIF in gas phase (solid lines) compared to CIF in Ar (dashed lines). Bottom to top: ground state, ${}^{3}\Pi$, ${}^{1}\Pi$.

From Fig. 7.4 the effect of the matrix on the potentials of the CIF molecule can be seen. The solid shift $\delta \omega_s = \omega_s - \omega_{gas}$ for the ground state is 0.14 eV, corresponding to a red shift of 4 %. This value is larger than that for the other halogens or interhalogen compounds determined by Jacox [52], but still in an appropriate range. The change of the vibrational frequencies $\delta \omega / \omega$ is expected to be very small, but especially for the Π states it can be seen that the potential is seriously deformed.

7.4 2d-Potential Surfaces

For CIF as an asymmetric molecule, there are two degrees of freedom which have to be taken into account. Fig. 7.5 shows the adiabatic potential energy surfaces of the three important states: the ground state ${}^{1}\Sigma$ (X), the first optically allowed state ${}^{1}\Pi$ (C) and the energetically lowest triplet state ${}^{3}\Pi$ (B), which couples to the singlet Π state.

The potentials were calculated along the CIF center-of-mass coordinate R_{ClF} and the internuclear bond distance r_{Cl-F} . The horizontal lines show the cuts through the surfaces at equilibrium geometry in the ground state, which will lead to a presentation like Fig. 7.3. The second potential minimum on the right presents the case where the F-atom has left the initial cage and is located between the first and the second argon window, see Fig. 7.2. The larger chlorine is not able to leave the cage, because of the repulsion from the window. This is reflected in the small value of R_{ClF} at large internuclear distances.



Figure 7.5: 2-Dimensional potentials for CIF Ar, aligned in {111} direction of the crystal. R_{ClF} is the center-of-mass coordinate, r_{Cl-F} the internuclear distance. Contour lines are spaced by 0.2 eV starting at 0.2 eV ($^{1}\Sigma$) nd 2.6 eV (Π -states). The solid lines depict one-dimensional cuts at the minimum position of R_{ClF} in the ground state.

7.5 Dynamics of ClF in Ar



Figure 7.6: Potential energy curves of CIF in gas phase (A) and embedded in an argon matrix (B), aligned in {111} direction.

Fig. 7.6 shows the possible processes for CIF embedded in an argon matrix, compared to the gas phase. While in the latter case photoexcitation to the ${}^{1}\Pi$ state would lead to dissociation, the bending of the potential due to the environment results in different reaction channels, like discussed in chapter 1.1, compare to Fig. 1.1. Dissociation or recombination with or without state transitions could be expected. Experimentally it could be shown, that this system shows a ultrafast spin-flip during the first 500 fs [78], leading to recombination in the bound ${}^{3}\Pi$ state. 50 % of this spin flip occurs in the first stretching of the molecule, which will take 250 fs [16]. This phenomenon was also found in simulations of HCl in Ar [79, 80] or F₂ in Ar [22]. While intersystem crossing is expected to occur on a picosecond timescale, it happens on a subpicosecond timescale for molecules in rare gas environments. The classical trajectory simulation, performed as for Cl₂ was supplemented by the calculation of coupling elements for the particular states ${}^{1}\Sigma$, ${}^{1}\Pi$ and ${}^{3}\Pi$ to estimate the role and timescale of electronic transitions.

Another interesting feature of the system is the influence of the environment on the dissociation of the molecule. The fragments of CIF in alignment to the $\{111\}$ direction point to three-atomic windows, respectively. The barrier for leaving the

cage is different for the Cl and the F fragment, as shown in Fig. 7.7. This will lead to different photodissociation dynamics, depending on the initial excitation energy. Here the cage effect as discussed in section 1.2, see Fig. 1.4 can be compared to the perfect caging observed in the case of Cl_2 in Ar, with respect to the different fragments, Cl and F.



Figure 7.7: Potential energy barriers of Cl of F fragments for leaving the initial cage. The distance r_{Cl-F} is elongated artificially by fixing one of the fragments on its initial position in the lattice and then shifting the other fragment to the next cage.

7.5.1 Excitation to the ${}^{1}\Pi$ State

First the molecule was excited from the minimum of the ground state potential to the ${}^{1}\Pi$ state with 4.644 eV excitation energy.

Fig. 7.8 shows the internuclear distance r_{Cl-F} and the distances of Cl and F, respectively, after exciting the molecule to the ¹ Π state. From the upper panel it can be seen that the bond is stretching in the first 110 fs to 6.2 a₀, then contracting again, until after 250 fs nearly the original bond length is reached. A second elongation follows, but this time to a larger internuclear distance of 6.8 a₀ after 400 fs. After decreasing again, the bond stretches to 9 a₀, which corresponds to the fluorine atom leaving the cage.

The displacements of the Cl and F fragments are shown in panel b) and c) of Fig. 7.8. The kinetic energy of the fluorine is larger than that of the chlorine



Figure 7.8: Internuclear distance r_{Cl-F} and displacements of the Cl and F atom from their initial locations after excitation of ClF to the C-state (${}^{1}\Pi$).

atom, because of the momentum conservation $m_F v_F = -m_{Cl} v_{Cl}$. The F atom, which is moving in positive direction with respect to the center of the coordinate system, is reaching its first maximum after excitation at 4.1 a_0 after 135 fs, while the chlorine atom is only 1.6 a_0 after 95 fs. The shorter Δr of the Cl is due to the stronger repulsion between Cl and Ar, compared to F-Ar. The chlorine atom is reflected from the window atoms and will invert its direction and following the fluorine molecule. A collision will happen when the chlorine has already passed its initial coordinates. In the next bond stretch, the fluorine is moving to larger distances of 5 a_0 after 400 fs, while the chlorine is not even reaching the displacement of the first stretching, but proceeds in the following bond contraction even slightly more in the direction of the fluorine. After a second collision, the fluorine atom is now proceeding through the first window, until stopped by the second window after 850 fs, while the chlorine atom is not able to pass through the window.

The windows start opening after 60 fs, as can be seen from Fig. 7.9, faster for the fluorine and slightly slower for the chlorine windows. The opening of the windows is enforced in the second collision. Comparing to Fig. 7.6, the barrier for the F atom due to the cage atoms is now lowered. In the next oscillation, the fluorine is able to pass through the windows and enters the next cage. This is consistent with the mechanism of *delayed* exit, as discussed in section 1.2 and

is consistent to simulations of F_2 in an argon matrix [75]. This classification is valid, because in contrast to a *forced* exit, there is no rearrangement of the window atoms like shown in Fig. 1.4. In the case of the chlorine the barrier is still too high and it remains in the original cage. So for the chlorine even in this geometry the caging is *perfect*. This could be expected by comparing the different barriers for the cage exit for F or Cl, respectively, shown in Fig. 7.7. The barrier for the F atom in the rigid potential is 1.95 eV, compared to 7.1 eV for the Cl atom.



Figure 7.9: Displacements of the window atoms for the F-windows (dashed) and the Cl-windows (straight) with respect to their initial positions.

The other argon atoms in the vicinity of the cage are only weakly affected by the photodissociation of the chromophore. As expected, after dissociation the fluorine atom approaches the second window and hits the center of the second window, which will then start to open.

Fig. 7.10 shows the sketch of a trajectory leading to the dissociation/cage exit of the fluorine atom.

7.6 Spin-flip

The simulations of the previous section were performed on the C-state, neglecting the experimentally observed ultrafast spinflip, which has to be taken into account by implementing a mechanism for the intersystem crossing. From the experiment



Figure 7.10: Trajectory for the dissociation of CIF after excitation to the C-state.

there is evidence that this spin-flip will take place during the first bond elongation of the chromophore. From Fig. 7.11 it can be seen, that after excitation the potential energy will decrease, due to the repulsive forces experienced by the atomic fragments. The atomic fragments are accelerated, until a bond length of 4 a_0 is reached and the repulsion from the surrounding argon atoms cause the potential to rise. At 110 fs, where the first maximum of bond elongation is reached, the states are nearly degenerated.

In the DIM formulation discussed in chapter 4, the spin-orbit matrix elements couple the different states of the molecule. At distances $\leq 5a_0$, the energy gap between the ${}^{1}\Pi$ and ${}^{3}\Pi$ state is large in comparison with the V_{SO} . At larger distances the energy gap is decreasing, until $V_{SO} \geq (V_{1\Pi} - V_{3\Pi})$. Now with the spin-orbit coupling as dominant contribution, the system can undergo a state transition from the singlet to the triplet state. From the classical calculations performed here, the spin-orbit coupling will exceed the difference in the potential energy $V_{SO} \geq (V_{1\Pi} - V_{3\Pi})$ at an internuclear bond distance of 5.6 a_0 , which is reached after 72 fs.

In addition, the wavefunction was propagated along the trajectory using



Figure 7.11: Eigenvalues of the DIM Hamiltonian along a trajectory for the dissociation of CIF after excitation to the C-state.

Runge-Kutta algorithm. The nonadiabatic couplings between X-¹ Π and ¹ Π –³ Π states were calculated like described in chapter 5. By this the probability of a state transition could be estimated. Fig. 7.12 shows that at a distance of 5.3 a_0 there exists a coupling between the ¹ Π and ³ Π state, increasing the probability of a hop, while the coupling between the ground and the triplet state is much lower, the same as the coupling between the ground and the excited state. The nonadiabatic coupling depends on the velocity of the nuclei, described by the vector $\dot{\mathbf{R}}$, see section 5.5. The term \mathbf{d}_{kj} can be calculated using eq. 5.45. It depends also on the energy gap between the states. In regions, where the energetic gap between the potentials of the states decrease, in this case for $r_{Cl-F} \geq 5.3a_0$, the denominator will decrease, leading to an enhanced coupling between the states, thus enhancing the probability of a state transition. In the full dimensional calculation, this distance was reached after already 60 fs, see Fig. 7.12. One reason for the decrease in time could be that the excitation process is too simple, changing instantly from the ground to the ¹ Π state.

By this the effect of a more realistic excitation by laser pulses is neglected: the finite duration of the laser pulse corresponds to a uncertainty in frequency $\Delta \nu$. On the excited state, this bandwidth results in a broad distribution of the wavepacket. This could lead to a longer time for the wavepacket to reach the relevant internuclear distances discussed above.



Figure 7.12: Coupling d_{jk} between ground-³ Π (dashed), ground-¹ Π (dotted), ³ Π -¹ Π (solid) states (top) in comparison to the potential energy curves of ¹ Σ (solid), ³ Π (dotted), ¹ Π (dashed).

7.7 Discussion

The state transition or ultrafast spin-flip, has been found experimentally and exact quantum calculations of a two state system, taking into account the excited singlet and triplet states, were performed on the 1d-potentials derived in this work [16].

The results achieved by classical simulations and the coupling terms found by propagation of the wavefunction show that at larger Cl-F distances $\geq 5.3a_0$ a state transition from the ${}^{1}\Pi$ to the ${}^{3}\Pi$ state has to be expected. The main contribution to the ClF potentials in this region is due to the repulsion from the argon windows located on the z-axis, leading to nearly degeneracy of the potential energy curves. As discussed in the previous section, the probability of a state transition depends on the energy gap between the states, the velocity of the atoms and of the off-diagonal coupling elements of the Hamiltonian. The spin-orbit terms couple the potential energy surfaces and become dominant if the energy separation of the states becomes smaller than V_{SO} . This behaviour is reflected by the mixing angle η [16]:

$$tan(2\eta) = \frac{V_{SO}}{\frac{1}{2}(V_{1\Pi} - V_{3\Pi})}$$
(7.1)

This value is shown in Fig. 7.13. At internuclear distances $r_{Cl-F} \leq 5.3a_0 \eta$ is

relatively small, while for larger distances the potentials are nearly degenerated, decreasing the denominator of equation 7.1, while the spin-orbit coupling is taken as a constant value. This results in a rapid increase of η for $r_{Cl-F} \geq 5.3a_0$.



Figure 7.13: Mixing angle η as defined in Eq. 7.1.

Fig. 7.14 shows the wave packet motion after excitation to the ${}^{1}\Pi$ state [16], calculated in reduced dimension (only two states are taken into account), but with full quantum mechanical dynamics simulation. After 12 fs there is a wave packet building up in the initially excited state, propagating according to the bond elongation. At 72 fs, the wavepacket is also building up in the triplet state. The resulting change in population can be seen in Fig. 7.15.

The photoexcitation is carried out with a rather sharp laser pulse with $\tau = 30$ fs, corresponding to a full width half minimum of 15 fs. This pulse is shorter than in the experiment, to avoid side-effects like the interference of the wavepacket. In this model simulation, 10 % of the ground state population is transferred initially to the optically allowed ¹ Π state. Already after 36 fs it can be seen from Fig. 7.14 and Fig. 7.15 that the population of the triplet state is rising. This intersystem crossing is very effective, and so after 75 fs nearly 50 % of the initially excited population can be found in the ³ Π state.

The results found in this quantum calculation fit nicely to the results from the classical/semiclassical simulations performed in this work. The quantum



Figure 7.14: Wave packet dynamics after excitation of the ${}^{1}\Pi$ state. The solid and dashed lines correspond to the singlet and triplet wavepacket, respectively. Snapshots are taken at t = 12, 36 and 72 fs. Excitation was simulated with a $\tau =$ 30 fs laser pulse ($\lambda = 318$ nm). Calculations performed by M.V. Korolkov [16]



Figure 7.15: Time evolution of the singlet and triplet state population corresponding to the wave packet dynamics after excitation to the ¹ Π state, Fig. 7.14. The pulse envelope profile is depicted by the shaded area ($E_0\mu_{1}\Sigma_{\Pi} = 0.002E_h$). Taken from [16]

calculations are not including the dynamics of the potential, with respect of lowering the potential barrier along the Cl-F stretching coordinate, but as was shown, the influence of the Ar window motion is very weak during the first bond elongation of the chromophore, see Fig. 7.9. So in the time prior to the collision with the cage, the center-of-mas and the relative motions are decoupled. After the collision with the cage, the 1d-model is not appropriate anymore, because then the Ar₃ stretching of the windows will influence the dynamics.

These calculations show a mechanism for the ultrafast spin-flip, observed in the experiment. Recently, a control scheme for the population transfer to the singlet or the triplet state, respectively, was developed by M.V. Korolkov and J. Manz, based on this model system [82].

Including the surface hopping mechanism in the semiclassical simulations performed in this work will have the advantage of the 'dynamical' potential and will lead to a proper description of the dynamic on longer time scales.

This has been done before for the system F_2 in Ar [23], where 2-d quantum simulations were compared to the semiclassical calculations using the DIM method in combination with the surface hopping mechanism. Fig. 7.16 shows snapshots of the dynamics in the system F_2 in Ar after photoexcitation, comparing the wavepacket motion with an ensemble of trajectories.

First the density of the wavefunction, shown by contour lines on the left panel, is located at the potential minimum of the ground state. The excited state potential $V_e(x,y)$ has three potential minima, corresponding to different locations of the atomic fragments. The orientation is in {111} direction, as in the case of CIF. Thus the first minimum belongs to a small F-F distance, the molecule is located in the original cage (I). To reach the second minimum (II), the atomic fragments have to leave the original cage and by this passing the first windows in the direction of the molecular axis. Consequently the third minimum (III) belongs to a location of the F atoms after passing through the second window.

After excitation, the F-F bond starts elongating, due to the repulsive part of the potential, and the wavepacket spreads. After already 80 fs, the wavepacket is repelled from the potential wall of V_e . This process belongs to the F-atoms hitting the center of the first window and thus transferring some momentum to these argon atoms. Now the windows start to open, which will enable the wavepacket to pass through. The same was found for the system CIF in Ar using classical trajectory simulations. If the initial energy of the atomic fragments



10 15 20 25 F - F

10

10 15 20 25 F - F

 $t = 220 \text{ fs } \omega = 0.24 \text{ a.u.}$

15 20 F - F

 $t = 300 \text{ fs} \ \omega = 0.24 \text{ a.u.}$

25

Ar₃

Ar₃

Ar3



 $t = 80 \text{ fs } \omega = 0.24 \text{ a.u.}$

Figure 7.16: Snapshots of the wavepacket dynamics of F_2 in Ar (left) compared to an ensemble of trajectories (right) using DIM/surface-hopping algorithm, taken from [23]

is not sufficient to overcome the potential barrier, they will be reflected and recombine. As recently as the windows have opened to some extend, the F atom is able to leave the initial cage. Quantum classical simulations, which included the system F_2 in 255 Ar in full dimension, showed the same behaviour for an ensemble of trajectories. Here it could be shown that exact quantum calculations and quantum-classical simulations using DIM/surface-hopping are in very good agreement for the time in which the 2d-model used in the exact quantum calculations is valid. In the case of F_2 in Ar this means the first 200-300 fs, after this the remaining degrees of freedom have to be taken into account for a proper description of the system.

By this, the systems ClF or F_2 are well comparable. The necessity for opening the windows prior to cage exit could be seen from the classical calculations performed in this work. The lattice dynamics is different to the case of Cl₂ in Ar, where after photodissociation a large amount of energy is transferred to the cage atoms. The transfer of momentum to the triatomic windows in the system CIF/Ar is much less efficient and the energy stays local for a longer time. Except for the window atoms, only very small displacements of the lattice atoms could be observed in the simulations, only after approx. 800 fs, when the fluorine leaves the initial cage and approaches the second window, while at the same time the atoms of the first (opened) window are reflected from the argon atoms belonging to the next shell. All these different contributions are very small compared to the influence of the window atoms. While Cl_2 in Ar showed a perfect caging, here delayed cage exit is possible, at least for the F atom. The Cl atom still is not able to overcome the potential barrier of the cage, since the windows are not able to open to such extent that the potential becomes sufficiently low for the Cl atom to leave. The mechanism found in [23] could be confirmed to some extend, because the classical simulations still show the lack of state transitions, which could be found in the experiment.