

# Chapter 5

## Conclusions

In this thesis, I address a question that is central to reaction dynamics: is it possible to control bond-selective dissociation using laser radiation? To tackle this problem, a scheme is proposed that relies on a new class of short laser pulses: *few-cycle* pulses. We have analyzed these pulses in terms of several half-cycle pulses, where a single half-cycle pulse can be considered a “kick” that imparts energy (or momentum, see Ref. [33]) to the molecular system. The few-cycle pulse mechanism that we propose is not only theoretically intriguing, it is also experimentally realistic. Half-cycle and few-cycle pulses can be generated with existing technology, and many experiments utilizing such pulses have already been suggested. For our simulations of wave packet dynamics, we have chosen two hydrogen-bonded anions and their neutral counterparts as model systems,  $\text{FHF}^-/\text{FHF}$  and  $\text{OHF}^-/\text{OHF}$ . These linear triatomic systems have few degrees of freedom, so a 2D model consisting of the symmetric and asymmetric stretching modes provides us with a realistic description of the vibrational motion involved in the dissociation of the bonds  $R_1$  and  $R_2$ .

For simulations of wave packet dynamics, 2D potential energy surfaces (PESs) were calculated for the anion and neutral species, and the permanent dipole surface was obtained for the anion. Due to the delocalized negative charge in the anionic species, the basis sets contained polarization and augmented diffuse functions for both the hydrogen and the heavy atoms. For  $\text{FHF}^-$ , QCISD/*d*-aug-cc-pVTZ was used to construct the PES and dipole surface (see Section 3.2), and for  $\text{OHF}^-$ , UMP4/6-31++G(d,p) was used (see Section 3.3). These methods were chosen primarily due to the quality of results of previous calculations performed at the same level of theory for similar systems. From the 2D PES, anharmonic wave functions (*cf.* Figures 3.4 and 3.10) and corresponding vibrational frequencies could be calculated for  $\text{FHF}^-$  (*cf.* Figure 3.4) and

OHF<sup>-</sup> (*cf.* Figure 3.10), as well as for the isotopomers FDF<sup>-</sup> (*cf.* Figure 3.5) and ODF<sup>-</sup> (*cf.* Figure 3.11). These calculated values were in good agreement with previous results for both FHF<sup>-</sup> and OHF<sup>-</sup> (*cf.* Tables 3.3 and 3.9, respectively). Simulated IR absorption spectra for FHF<sup>-</sup> and FDF<sup>-</sup> (Figure 3.6), could be compared to experimental data, but no experimental data is available for comparison with the IR absorption spectra of OHF<sup>-</sup> and ODF<sup>-</sup> (Figure 3.12) [169].

The first system, FHF<sup>-</sup>, has D<sub>∞v</sub> symmetry, so the dissociation products, (F + HF) and (FH + F) are chemically indistinguishable. With this first system, our goal was to design a few-cycle IR laser pulse that would induce dynamical symmetry breaking in the anion species [170]. The IR pulse excites a superposition of vibrational eigenstates, or a wave packet, consisting primarily of asymmetric stretching eigenstates. The motion of the wave packet corresponds to the oscillations of the center hydrogen between the heavy end atoms. When the wave packet is maximally displaced from the equilibrium position, an ultrashort (~5 fs) UV pulse is fired that photodetaches an electron, creating the neutral species (FHF) via a vertical excitation. The resulting wave packet on the neutral PES is now located at a region corresponding to predominantly one set of dissociation products, either (F + HF) *or* (FH + F), and continues to evolve preferentially along that product channel. Thus, the natural branching ratio of the system can be enhanced using a combination of few-cycle IR and UV pulses, in this case from 0.50 : 0.50 to 0.75 : 0.25 (*cf.* Figure 4.9).

Dissociation dynamics were also studied for the heavy isotopomer, FDF<sup>-</sup> in Section 4.3.6, for which a mass-related scaling factor was used to re-optimize the laser parameters needed to achieve dynamic symmetry breaking (*cf.* Figure 4.11) [171]. Due to the lower frequency of the asymmetric stretching vibration, the frequency of the IR pulse,  $\omega_{\text{IR}}$ , must be lowered with respect to that of FHF<sup>-</sup>. Also, the pulse duration,  $t_p$ , and time at which the UV pulse is applied,  $t_{0,\text{UV}}$ , between the IR and UV pulse must be extended according to the mass-related scaling factor to account for the slower dynamics of the deuterated isotopomer. For these simulations of FHF<sup>-</sup> and FDF<sup>-</sup>, wave packet dynamics, the linear molecule was assumed to lie along the space-fixed  $Z$  axis.

For non-optimal orientations, the efficiency of the IR + UV laser pulses was also examined (see Section 4.3.7). An optimal yield of spatially separated molecular products (FH) and atomic products (F) is observed when the molecule is oriented in the  $+Z$  or  $-Z$  laboratory directions, whereas for perpendicular molecular orientations, the laser pulses are inefficient at displacing the wave packet and therefore at spatially separating the molecular and atomic products. Nonetheless, for the fraction of optimally oriented molecules, a spatial separation of molecular and atomic dissociation products is

obtained [172].

The second model system,  $\text{OHF}^-/\text{OHF}$ , is asymmetric, such that two distinct sets of dissociation products exist,  $(\text{O} + \text{HF})$  and  $(\text{OH} + \text{F})$ . Preliminary calculations indicate that achieving a spatial separation of these products requires control over the molecular orientation throughout the duration of the dissociation process. Our first challenge with this system was, therefore, to control molecular orientation (see Section 4.4.1). For these simulations, a rigid rotor model, neglecting spin angular momentum, was used to approximate the rotational motion of the non-vibrating molecule [173]. We optimized a half-cycle pulse (HCP), a special type of few-cycle pulse containing one predominant unipolar field peak, with small tails of opposite polarity. In the non-adiabatic limit, the pulses are short ( $\sim 300$  femtoseconds) compared to the rotational period ( $\sim 50$  picoseconds) of the molecule. When the laser is turned on, the molecule exchanges units of angular momentum with the field. This field-matter interaction gives rise to a rotational wave packet in angular momentum space that is composed of several rotational (rigid rotor) eigenstates. The initial isotropic distribution of the wave function is replaced by a wave function restricted in angular space, but which oscillates with the rotational period. After the field has been removed, the composition of the rotational wave packet is constant, but the phases of the individual rotational states continue to clock on the time scale of the rotational period of the system. Therefore, oscillatory recurrences of molecular orientation is conserved as long as coherence in the wave packet is maintained—even after the orientation field has been removed. Since molecular orientation is observed on the scale of picoseconds, these rotational coherences, or revivals, offer relatively long windows of time during which femtosecond laser experiments can be carried out. Temperature effects on the molecular orientation were also studied, since higher temperatures broaden the angular distribution and therefore reduce the degree of molecular orientation. Nonetheless, for temperatures lower than 20 K, a moderately low degree of molecular orientation is still observed (*cf.* Figure 4.21).

After investigating molecular orientation under field-free conditions in Section 4.4.1, we proceeded to address the challenge of selectively breaking the strong and weak bonds of  $\text{OHF}^-$  in Section 4.4.2; for this investigation we considered a non-rotating, 2D vibrational model of  $\text{OHF}^-$  [174]. When  $v_{00}$  of  $\text{OHF}^-$  is propagated on the neutral PES under field-free conditions, a branching ratio of 0.84:0.16 for  $(\text{O} + \text{HF}):(\text{OH} + \text{F})$  is observed. In other words, the O–H bond is much weaker than the H–F bond. The question we ask, therefore, is whether this natural branching ratio can be changed using few-cycle laser pulses. To address this problem, an IR + UV pulse sequence was optimized for each dissociation pathway, and wave packet propagations were carried out. After each pulse sequence, the branching ratio of the wave packet on the neutral PES was calculated. For

the breaking of the easy bond (O + HF), we can enhance the natural branching ratio of 0.84 : 0.16 to 0.95 : 0.05 (*cf.* Figure 4.23, (a)-(e)). Breaking the HF bond and reversing the branching ratio is more difficult since the neutral PES strongly favors the O + HF products. The re-optimized laser pulses lower the ratio from 0.84 : 0.16 to 0.80 : 0.20, thereby marginally increasing the product ratio of OH + F (*cf.* Figure 4.23, (a')-(e')).

Many questions raised in this thesis should be investigated further. In the case of OHF<sup>-</sup>/OHF, a ro-vibrational model should be considered explicitly by constructing a Hamiltonian to calculate ro-vibrational eigenstates. Next, simulations of wave packet dynamics should be repeated for the extended model system using a three-pulse scheme: (1) IR HCP to orient the system, (2) IR few-cycle pulse to induce symmetry breaking, and (3) UV few-cycle pulse to photodetach an electron and excite to the neutral PES. Such simulations in ro-vibrational space would not only elucidate the dynamics of the real system, but they would also provide a more accurate framework within which experimentalists could design a similar approach. Extending the 2D vibrational model to a 3D model to include the bending vibration would also improve the accuracy of the vibrational frequencies and could possibly alter the dissociation dynamics. Since spin angular momentum was neglected in the rigid rotor model, it should be considered in future studies to study the effect of spin-orbit coupling on the rotational wave packet dynamics.

Also, vibrational transitions within the neutral PESs were not considered during the wave packet simulations, *i.e.* the permanent dipole moment  $\mu_n$  was set equal to 0. One should examine the effect on the dissociation dynamics for  $\mu_n \neq 0$ . In the future, control schemes could be designed that rely on the manipulation of vibrations in the neutral species to enhance bond-selective dissociation along the desired fragmentation channel. Furthermore, the transition dipole moment  $\mu_{an} = \mu_{na}$  between the anionic and neutral PESs was set equal to 1 within the Condon approximation. In the future, one could calculate the value of  $\mu_{an} = \mu_{na}$  and repeat the simulations to determine the effect of non-constant transition dipole moments.

Another interesting and critical aspect of few-cycle pulses is the role of the absolute carrier phase, an issue that was discussed in detail in Section 4.5. For a better understanding of the sensitivity of the few-cycle pulse mechanism to the carrier phase, simulations should be carried out in which the phase of the IR pulse is systematically varied.

In addition to the few-cycle laser scheme proposed in this thesis, new mechanisms should be contemplated to control bond-selective dissociation. For example, an intense

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“hole-burning” UV laser could be used to excite impulsively a small portion of the original ground state wave function to an excited electronic state [175]. Because of the resulting “hole” in the electronic ground state, the remaining population is coherent but no longer stationary. The dynamics of the created wave packet could be harnessed to induce excitations of the population to bond-selective regions of the upper electronic state. For example, when the momentum or position of the ground state wave packet is optimal, a second UV laser could be fired to transfer population vertically to the upper electronic surface. For certain laser pulse conditions, the “hole” can also be refilled [175]. The advantage of this mechanism over one involving IR and UV pulses is that the same UV laser can be fired twice. Such schemes could provide an elegant method for achieving selective dissociation.

In the future, one could also consider mechanisms that involve excited electronic surfaces. In this thesis, only the ground electronic states of both the anion and the neutral species were included in the model. However, one could investigate control schemes that rely on intermediate transitions to low-lying electronic states. For example, preliminary time-dependent density functional theory (TD-DFT) calculations on the system  $\text{FHF}^-$  indicate several excited electronic states in the vicinity of the ground electronic state of neutral FHF [169]. In the future, one could include those electronic states which have significant oscillator strengths associated with them.

