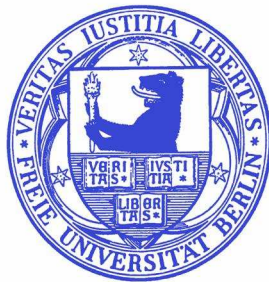


**Theory of using
few-cycle IR and UV laser pulses
to
control the orientation
and selective dissociation of
hydrogen-bonded anions**



INAUGURAL – DISSERTATION
zur Erlangung des Doktorgrades
der Freien Universität Berlin
Fachbereich Biologie, Chemie, Pharmazie

vorgelegt von

Nadia Elghobashi

aus Huntsville, Alabama

2005

Erstgutachter: Prof. Dr. J. Manz
Zweitgutachter: PD Dr. Leticia González
Tag der Disputation: 31 Oktober 2005

Contents

1	Introduction	1
1.1	Overview	1
1.2	Infrared laser-mediated photodissociation	3
1.3	Control of molecular orientation	5
1.4	Triatomic hydrogen-bonded systems	7
1.5	Goals of this thesis	9
1.6	Structure of thesis	10
2	Theory	13
2.1	The time-independent Schrödinger equation	13
2.1.1	Born-Oppenheimer approximation	14
2.1.2	Electronic Schrödinger equation	14
2.1.3	Nuclear Schrödinger equation	15
2.2	Solving the Schrödinger equation	17
2.2.1	Solutions to the electronic problem	17
2.2.2	Solving the nuclear problem	28
2.2.3	Numerical approaches to solving the vibrational problem	30

2.3	The time-dependent nuclear Schrödinger equation	35
2.3.1	Time-dependent Hamiltonian	35
2.3.2	The origin of $\hat{\mathbf{V}}^{ext}(t)$: interaction of the electric dipole with an electro- magnetic field	40
2.3.3	Properties of the electric field	42
2.3.4	Autocorrelation function and absorption cross-section	44
2.3.5	Numerical methods for solving the time-dependent Schrödinger equation .	45
2.4	Angular momentum	49
2.4.1	Commutation rules	49
2.4.2	Angular momentum observables	50
2.4.3	Coupling of two angular momentum vectors	52
2.5	The rigid rotor	56
2.5.1	Wave functions and eigenenergies	56
2.5.2	Linear triatomic molecule ABC	58
2.5.3	Orienting a linear rigid rotor in a laser field	64
3	Quantum chemistry and vibrational spectra	71
3.1	Hamiltonian for a linear triatomic molecule	71
3.2	FHF ⁻ /FHF	74
3.2.1	Potential energy and dipole surfaces	74
3.2.2	Geometry optimization and rotational constant	76
3.2.3	Eigenenergies and vibrational frequencies	78
3.2.4	Isotope effects: FDF ⁻	81

3.2.5	IR absorption spectra of FHF^- and FDF^-	86
3.3	OHF/OHF^-	89
3.3.1	Potential energy and dipole surfaces	89
3.3.2	Geometry optimization and rotational constant	92
3.3.3	Eigenenergies and vibrational frequencies	94
3.3.4	Isotope effects: ODF^-	97
3.3.5	IR absorption spectra of OHF^- and ODF^-	100
4	Quantum dynamics and control	103
4.1	Approach	104
4.2	Time-dependent Schrödinger equation for a coupled two-level system	104
4.2.1	Half-cycle IR orientation pulse	106
4.2.2	Few-cycle IR pulses	106
4.2.3	UV pulses	110
4.3	Results for FHF^-/FHF	112
4.3.1	1D model	112
4.3.2	Three half-cycle pulses	115
4.3.3	Extension to 2D model	115
4.3.4	Smooth \sin^2 pulse	117
4.3.5	Combined IR and UV laser pulses	117
4.3.6	Isotope effects: dynamics of FDF^-	118
4.3.7	Spatial distribution of products	122
4.4	Results for OHF^-/OHF	128

4.4.1	Half-cycle pulses (HCP) to control molecular orientation	128
4.4.2	Breaking the strong and weak bonds	135
4.5	Assumptions and sources of error	141
5	Conclusions	149
A	Moment of inertia for a linear triatomic molecule	155
B	2D vibrational eigenenergies for FHF^-, FDF^-, OHF^-, and ODF^-	159
C	Symbols, conversions, and atomic units	161
	List of Figures	168
	List of Tables	177
	Bibliography	180

Abstract

The focus of this work is controlling orientation and bond-selective dissociation of hydrogen-bonded anions of the type XHY^- using ultrashort, “few-cycle” laser pulses. For these quantum dynamical simulations, two triatomic hydrogen-bonded anions and their neutral counterparts, FHF^-/FHF and OHF^-/OHF , are chosen as model systems.

Geometry optimizations of FHF^- and OHF^- are performed at QCISD and UMP4 levels of theory, respectively, to obtain equilibrium bond lengths and rotational constants. For the triatomic molecules, two-dimensional (2D) potential energy surfaces (PES) and dipole surfaces are constructed in bond coordinates, R_1 and R_2 . The molecules are assumed to retain a collinear geometry with $C_{\infty v}$ symmetry throughout all simulations. From the PES, 2D vibrational wave functions are calculated, as well as anharmonic symmetric and asymmetric vibrational stretching frequencies. Isotope effects are studied for the deuterated species, FDF^- and ODF^- . Absorption spectra are simulated and the frequencies and intensities of the resulting peaks are analyzed and compared with experimental data, as well as with vibrational frequencies obtained from the 2D wave functions.

The challenge of controlling molecular orientation prior to bond-selective dissociation is treated explicitly for OHF^- with rotational wave packet simulations. A single half-cycle IR pulse of nearly one field polarity is applied to orient the molecule in the direction of the laser field. Resulting rotational wave packet dynamics are analyzed to measure the degree of molecular orientation. Even after the field is removed, moderate molecular orientation is periodically obtained for several picoseconds. These rotational revivals appear on the time scale of the rotational period, and they recur as long as coherence in the wave packet is maintained.

To control bond-selective dissociation of the pre-oriented FHF^- and OHF^- anions, few-cycle infrared (IR) pulses are designed to induce bond compressions and extensions in the anion species. In this context, isotope effects are also examined for the heavier isotopomer FDF^- . These pulses are constructed out of several half-cycle IR pulses, such that each half-cycle drives the oscillatory motion of the center hydrogen atom between the heavy end atoms. For FHF^- and FDF^- , this IR pulse gives rise to dynamical symmetry

breaking. When the resulting wave packet has reached the turning point of its oscillation, a well-timed, ultrashort UV pulse is applied to the anion. The UV pulse detaches an electron from the anion and vertically excites the wave packet to a bond-selective region of the neutral PES. Branching ratios of the resulting dissociation can be calculated.

For FHF^- , this few-cycle IR + UV pulse scheme enhances the natural branching ratio of $(\text{FH} + \text{F}):(\text{F} + \text{HF})$ from 0.50:0.50 to 0.75:0.25. For the heavier isotopomer FDF^- , the adjusted pulse parameters give rise to an even larger $(\text{FD} + \text{F}):(\text{F} + \text{DF})$ branching ratio of 0.80:0.20. In OHF^- , a natural branching ratio of $(\text{O} + \text{HF}):(\text{OH} + \text{F})=0.84:0.16$ is enhanced to 0.95:0.05. Breaking the strong HF bond is challenging, and with re-optimized IR + UV pulses, the branching ratio can only be enhanced marginally in favor of the products $\text{OH} + \text{F}$ to 0.80:0.20.

The spatial separation of dissociation products for FHF^- is also investigated for a range of molecular orientations in the space-fixed laboratory frame. For molecular orientations in the $+Z$ or $-Z$ laboratory directions, one obtains an optimal yield of spatially separated molecular (FH) and atomic (F) products.

To summarize, this thesis investigates the orientation and bond-selective dissociation of the model systems FHF^- and OHF^- with a control scheme based on ultrashort, few-cycle IR and UV laser pulses.

Acknowledgments

This thesis presents the work that I completed between February 2002 and June 2005 at the Freie Universität Berlin, at the Institut für Chemie und Biochemie. I would like to express my thanks to many people who have supported me throughout the past three and a half years.

I am grateful to my advisors, Jörn Manz and Leticia González, not only for their guidance and supervision, but also for their kindness, patience, and commitment to teaching.

I thank Tamar Seideman for re-introducing me to angular momentum in quantum mechanics and being an excellent mentor in this field. I am also very grateful to Bretislav Friedrich, who kindly took much time to discuss the theory of angular momentum with me and to raise many intriguing questions.

I am grateful to my experimental partners in the AG Wöste, Knut Asmis and Cristina Kaposta, who were always helpful and willing to answer questions regarding the laser experiments.

I would also like to thank Markus Oppel, Oliver Kühn, and Holger Naundorf for reading parts of my thesis and making useful comments.

To the AG Manz, present and past: thank you for making the working environment so friendly and open. I would like to extend a special thanks to Jürgen Full, David Ambrosek, Mohamed Shibl, and Ingo Barth—thank you for being such kind office mates.

I am grateful to the Deutsche Forschungsgemeinschaft, Graduiertenkolleg 788, “Hydrogen bonding and hydrogen transfer”, and to Werner Gans, for providing me with the resources and infrastructure with which to conduct research from February 2002 to January 2005. I also thank the Berliner Programm zur Förderung der Chancengleichheit für Frauen for financial support from January 2005 to June 2005.

Finally, I would like to tell my family, and especially my dear parents, how much they have meant to me, despite the thousands of kilometers between us.