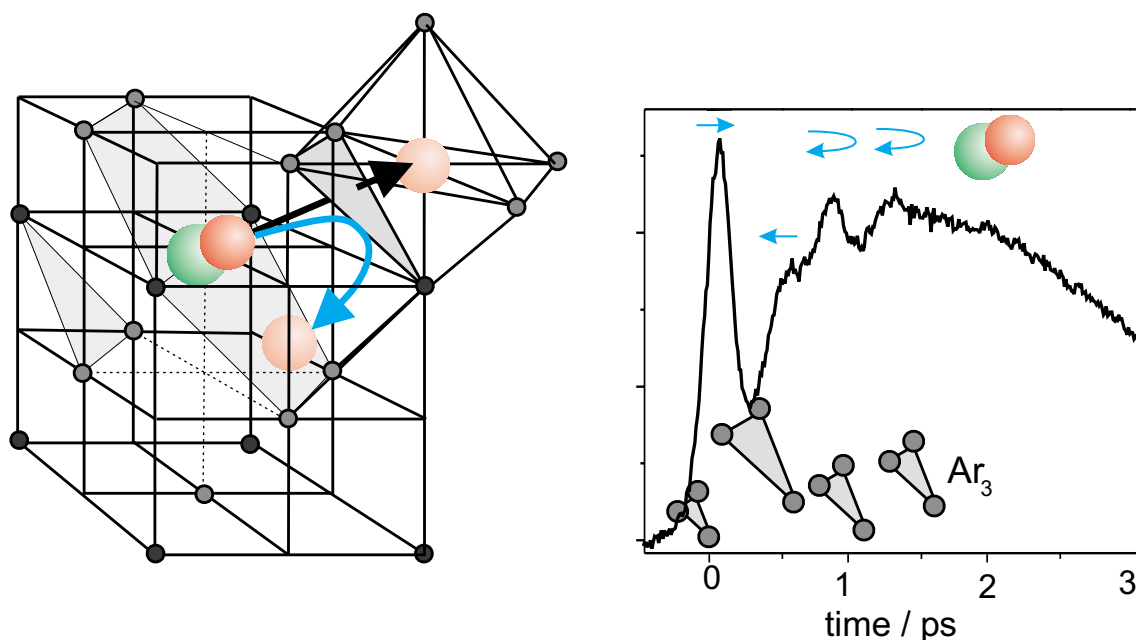


Ultrafast photodynamics in condensed phase: ClF, Cl₂ and I₂ in solid rare gases



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Ultraschnelle Photodynamik in kondensierter Phase: ClF, Cl₂ and I₂ in Edelgasfestkörpern

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Abstract

This thesis is part of a project that deals with photochemistry in the condensed phase and is embedded in the collaborative research center "Analysis and Control of Ultrafast Photoinduced Reactions" (SfB 450). Halogens and interhalogens (I_2 , Cl_2 and ClF) in rare gases solids are investigated as model systems by femtosecond-pump-probe spectroscopy.

Coherent wave packet dynamics of I_2 with a period of $T \sim 350$ fs can be observed for more than 10 picoseconds after photoexcitation, despite the strong interactions of the molecule near the dissociation limit with the crystalline Kr matrix. With this system, a novel evaluation scheme for pump-probe spectra is developed and tested, which permits the construction of effective one dimensional potentials of excited electronic states (B and E). An average trajectory of I_2 is measured to visualize the dissipative wave packet dynamics, and vibrational relaxation rates are determined from different signatures of the pump-probe spectra. Near the minimum of the potential, the energy loss is less than 1% per period, but it grows beyond 50% above the gas phase dissociation limit.

The molecules ClF and Cl_2 are examined in Ar and Kr matrices with pump-probe spectroscopy for the first time. The wave packet dynamics of an F fragment that exits the solvent cage is observed in real time. The time for direct cage exit is measured to be $t_{exit} = 250$ fs. Besides the dissociation, the competing recombination of the molecular fragments displays rich dynamics. Above the dissociation limit, the ClF molecule loses more than 35% of its kinetic energy in the first period, whereas the rate slows down to 0.1% near the minimum of the potential. Experimental results evidence a strong coupling of singlet and triplet states, which forces the molecule to recombine into the lowest electronically excited states. Although the spin-orbit coupling of the light atoms Cl and F is weak, the spin-flip occurs in less than $t_f = 500$ fs. Wave packet dynamics persist despite these strong interactions. The scattering of fragments by the cage is compared for molecules with similar electronic states but different isolation geometries in the lattice. A photoselected orientation of the ClF bond in the isotropic Ar cage (single substitutional) is destroyed within $\tau_d = 1.2$ ps, whereas I_2 remains aligned in the fixed cylindrical Kr cage (double substitutional). In co-doped $ClF/Cl_2/Ar$ matrices, the ratio of excited Cl^+Cl^- vs. Cl^+F^- is controlled with a contrast of 1 : 250, using a double-pulse sequence.

The systematic variation of pump and probe wavelength allows for a definite interpretation of the experiments without the aid of calculations, which makes the results particularly valuable for the comparison to the simulations which are simultaneously developed within the SfB 450.

In advance, the spectroscopy of ClF in Ar and Kr was clarified and dissociation yields were measured. Two NOPAs were constructed to provide tunable fs-pulses. The commercial design was improved to double their efficiency. In addition, the implementation of a flexible variant of the FROG technique permits the characterization of the pulse duration and phase of fs-pulses from the IR to the UV.

Kurzfassung

Diese Arbeit ist in einem Projekt entstanden, das sich mit Fragestellungen der Photochemie in der kondensierten Phase beschäftigt und in den Sonderforschungsbereich SFB 450, "Analyse und Steuerung ultraschneller photoinduzierter Reaktionen" eingebettet ist. Als Modellsysteme werden Halogene und Interhalogene (I_2 , Cl_2 und ClF) in Edelgasfestkörpern mit Femtosekunden-Pump-Probe Spektroskopie untersucht.

Trotz der starken Wechselwirkung des I_2 -Moleküls nahe der Dissoziationsgrenze mit der kristallinen Kr -Matrix bleibt eine kohärente Wellenpaketdynamik mit einer Periode von $T \sim 350$ fs über 10 Picosekunden nach der Photoanregung erhalten. Für die Auswertung der Pump-Probe Spektren wird an diesem System ein neues Schema entwickelt und erprobt, das die Konstruktion effektiver eindimensionaler Potentiale von angeregten elektronischen Zuständen (B und E) gestattet. Die dissipative Wellenpaketdynamik des Moleküls wird an einer gemessenen Trajektorie sichtbar gemacht, und verschiedene Signaturen der Ultrakurzzeitspektren dienen der Bestimmung von Schwingungsrelaxationsraten. In der Nähe des Potentialminimums beträgt die Energieabgabe weniger als 1% pro Periode, steigt aber im Bereich der Gasphasendissoziationsgrenze auf Werte über 50% an.

Zum ersten Mal werden die Moleküle ClF und Cl_2 in Ar - und Kr -Matrix mittels Pump-Probe Spektroskopie untersucht. Für ClF in Kr wird die Wellenpaketdynamik beim Austritt eines Fragmentes (F) aus dem Umgebungskäfig zeitaufgelöst beobachtet. Die gemessene Zeit für den direkten Käfigaustritt beträgt $t_{exit} = 250$ fs. In Konkurrenz zur Dissoziation steht die Rekombination der Molekülfragmente, die eine reichhaltige Dynamik aufweist. Oberhalb der Dissoziationsgrenze verliert ClF über 35% der kinetischen Energie in der ersten Periode, während die Rate im Potentialminimum auf 0,1% pro Schwingung sinkt. Die experimentellen Ergebnisse belegen eine starke nicht-adiabatische Kopplung von Singulett- und Triplettzuständen, die das Molekül sehr schnell in die niedrigsten elektronisch angeregten Zustände relaxieren läßt. Das Umklappen des Spins erfolgt in weniger als $t_f = 500$ fs, obwohl die Spin-Bahn-Kopplung bei leichten Atomen wie Cl und F schwach ist. Trotz dieser starken Wechselwirkungen ist eine Wellenpaketdynamik zu beobachten. Das Streuverhalten der Fragmente am Käfig von geometrisch unterschiedlich eingebauten Molekülen mit ähnlichen elektronischen Zuständen wird verglichen. Wenige Stöße der Fragmente mit dem isotropen Ar -Käfig (einfach substituiert) zerstören eine photoselektierte Ausrichtung der ClF -Bindung innerhalb von $\tau_d = 1,2$ ps, während I_2 in seinem zylindrischen Kr -Käfig (zweifach substituiert) starr ausgerichtet bleibt. In gemischt dotierten $Cl_2/ClF/Ar$ -Matrizen läßt sich mit einer Doppelpulsfolge das Verhältnis von angeregtem Cl^+Cl^- gegenüber Cl^+F^- und deren Fluoreszenz mit einem Kontrast von über 1:250 steuern.

Durch systematische Variation der Wellenlängen von Pump- und Probe-Pulsen wird mit den Experimenten eine eindeutige Interpretation erarbeitet, ohne dabei auf Rechnungen zurückzugreifen. Die Ergebnisse sind deshalb besonders geeignet für den Vergleich mit den im SFB 450 parallel laufenden Simulationen.

Die Spektroskopie von ClF in Ar und Kr sowie die Bestimmung der Dissoziationsausbeuten stellen wichtige Vorarbeiten dar. Der Aufbau von zwei neuen NOPAs zur Erzeugung der fs-Pulse resultierte in einer Verdopplung der Effizienz gegenüber dem kommerziellen Gerät. Zudem wurde eine flexible Variante der FROG-Technik implementiert, mit der sich fs-Pulse vom infraroten bis zum ultravioletten Spektralbereich bezüglich ihrer Pulsdauer und Phase charakterisieren lassen.

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Abbreviations

Ti:Sa - titanium doped sapphire
SHG - second harmonic generation
(PG)-FROG - (polarization gate)-frequency resolved optical gating
NOPA - non-collinear optical parametric amplifier
LIF - laser induced fluorescence
CARS - Coherent anti-Stokes Raman scattering
DIM - diatomics in molecules
DIIS - diatomics in ionic systems
CI - configuration interaction
MD - molecular dynamics
PES - potential energy surface
RKR - Rydberg-Klein-Rees
fs - femtosecond ($10^{-15} s$)
ps - picosecond ($10^{-12} s$)
 a_0 - Bohr radius $5.292 \times 10^{-11} m$

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