Femtosecond resolved imaging of torsion in a chiral molecule

Laser induced alignment of molecules dissolved in superfluid He nanodroplets

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LASER CONTROL OF CHEMICAL REACTIONS
Safed
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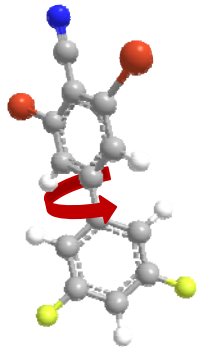
Femtosecond resolved imaging of torsion in a chiral molecule

Purpose of this part of the talk

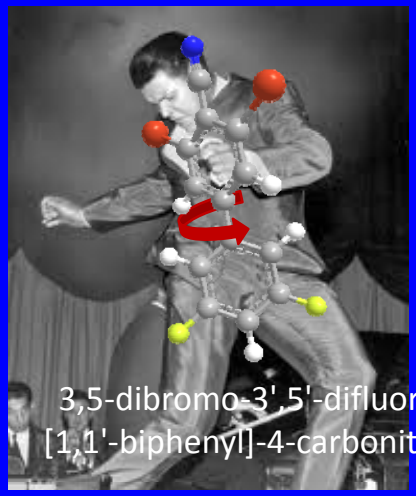
Show that it is possible to image
an important normal-vibration
in a complex molecule
on its natural time and length scale

by fixing the molecule in space
and image two molecular moieties
using femtosecond timed
Coulomb explosion

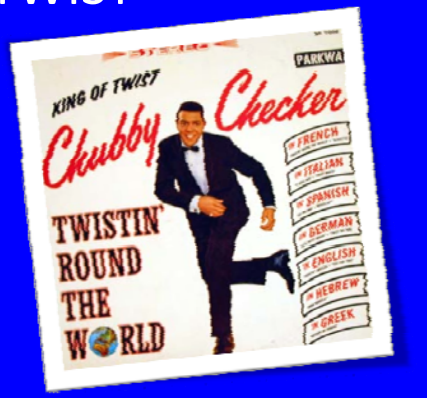


HOLD-AND-TWIST

HOLD & TWIST

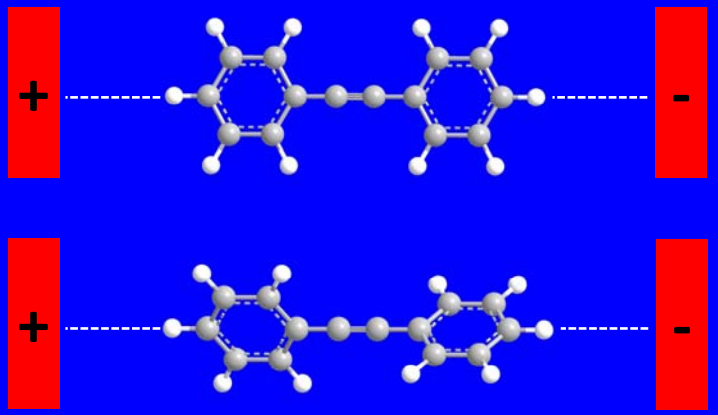


3,5-dibromo-3',5'-difluoro-
[1,1'-biphenyl]-4-carbonitrile

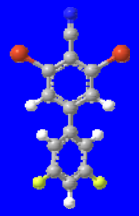


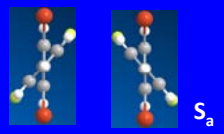
Why twisting (torsion) ?

(Ultrafast) Molecular switches



Why twisting (torsion) ?

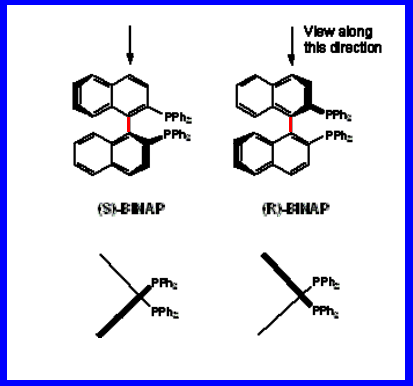


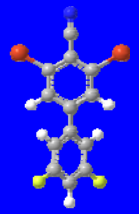


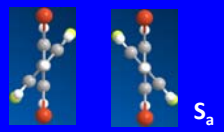
Spiral stairs

Why twisting (torsion) ?

Handedness determines function







Nobel Prize in Chemistry 2001: Noyori.

Why twisting (torsion) ?

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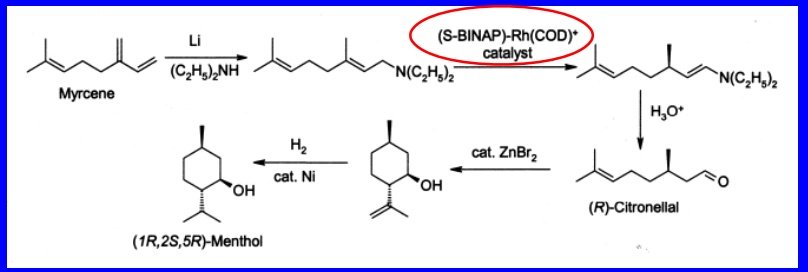

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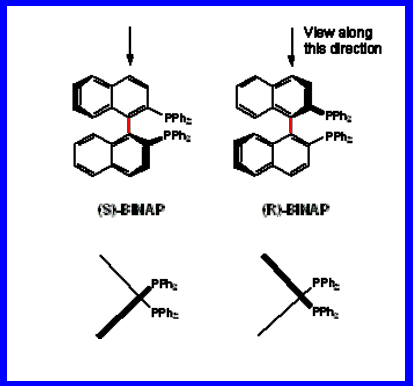
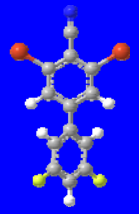
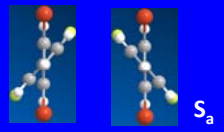
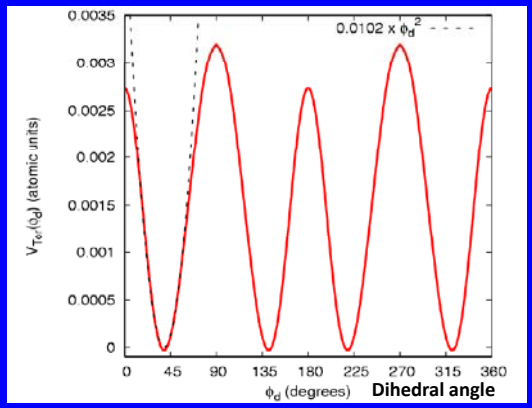




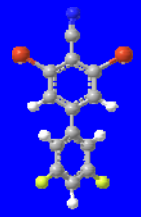


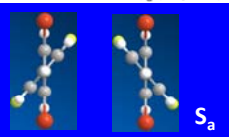
Nobel Prize in Chemistry 2001: Noyori.

Torsional potential

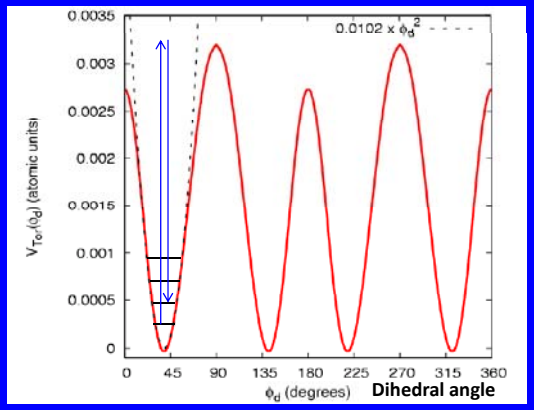


8 kJ/mole
= 80 meV

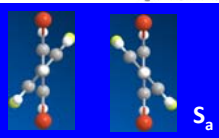




Torsion induced by stimulated Raman transitions



Torsion has by far the largest Raman cross section of all normal mode vibrations



R_a S_a

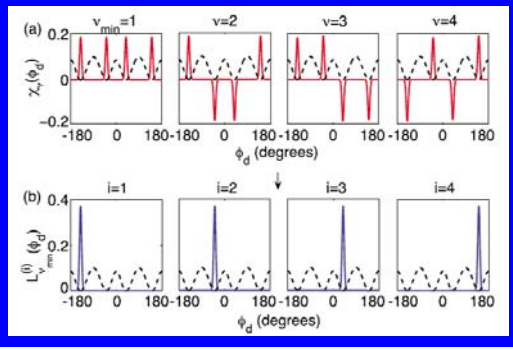
Theoretical treatment

$$i\partial_t \Psi(\Phi;\phi_d,t) = [T_d + V_{tor}(\phi_d) + V_{kick}(\Phi;\phi_d,t)]\,\Psi(\Phi;\phi_d,t)$$

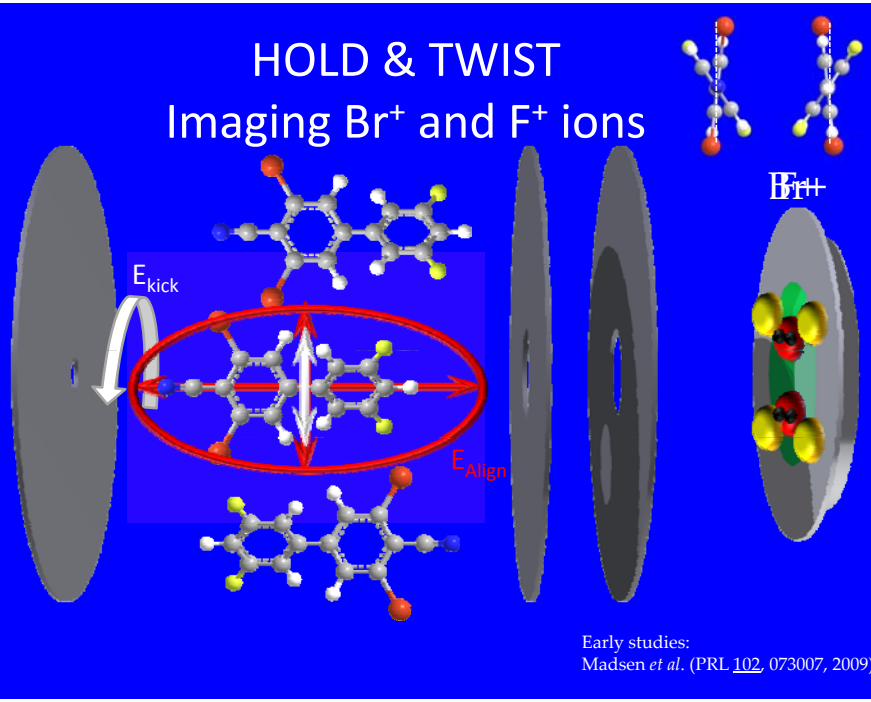
$$T_d = -\frac{I_{Br^+} + I_{F^+}}{2I_{Br^+}I_{F^+}}\frac{\partial^2}{\partial\phi_d^2}$$

$$V_{kick}(\Phi,\phi_d,t) = -\frac{1}{4}F_0^2(t)[\alpha_{xx}(\phi_d)\cos^2(\Phi+\eta\phi_d) + \alpha_{yy}(\phi_d)\sin^2(\Phi+\eta\phi_d) - 2\alpha_{xy}(\phi_d)\cos(\Phi+\eta\phi_d)\sin(\Phi+\eta\phi_d)]$$

Initial (localized) states

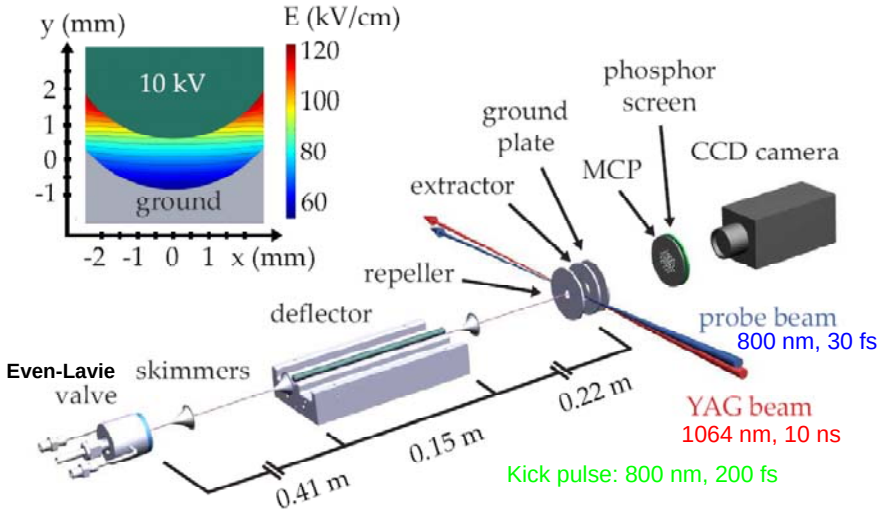


HOLD & TWIST
Imaging Br^+ and F^+ ions



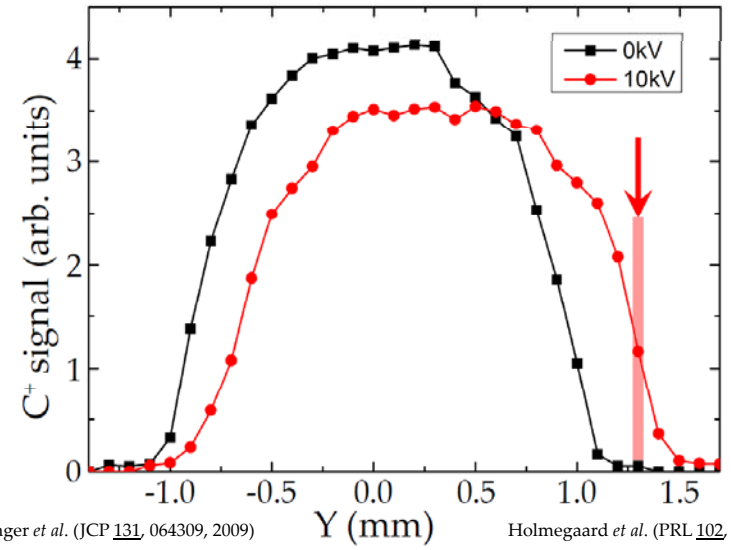
Early studies:
Madsen *et al.* (PRL 102, 073007, 2009)

Experimental Setup



Molecular deflection

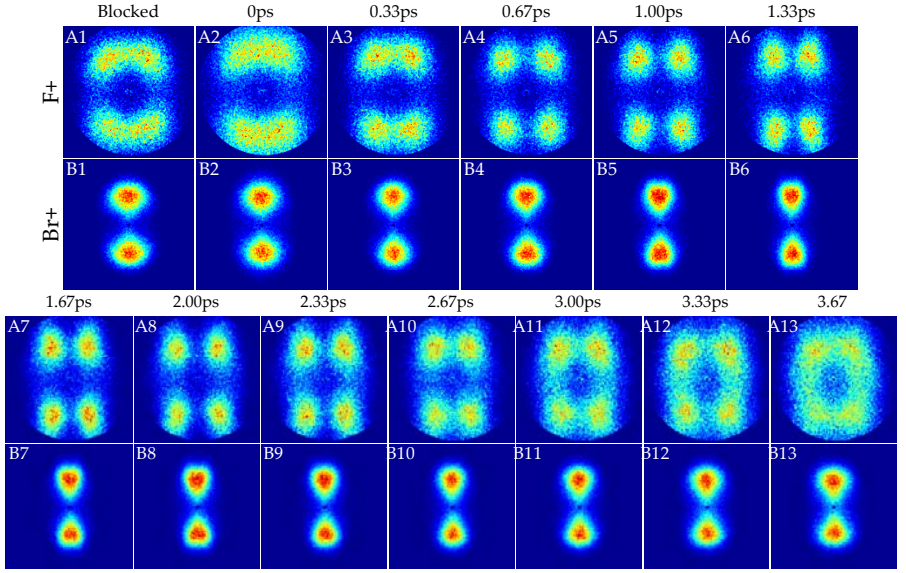
Rotational state-selection



Filsinger *et al*. (JCP 131, 064309, 2009)

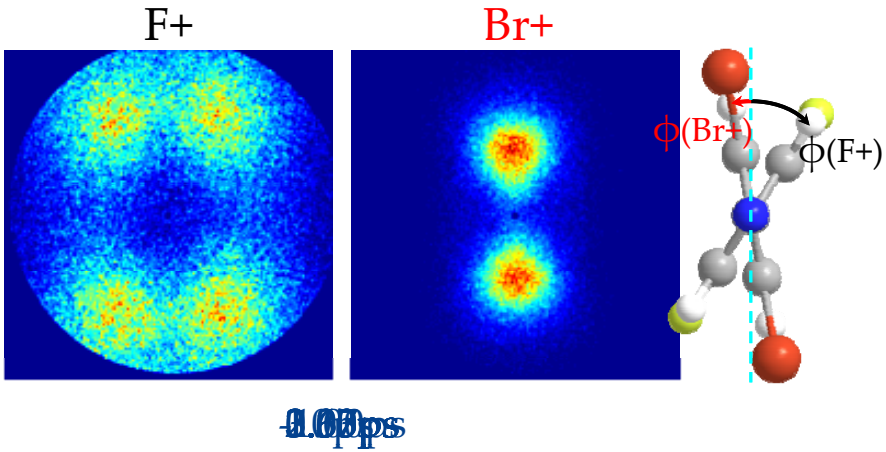
Holmegaard *et al*. (PRL 102, 023001, 2009)

Imaging Torsional Motion (0 - 4 ps)



Hansen *et al*. J. Chem. Phys. **136**, *204310* (2012)

Imaging Torsional Motion (0 - 4 ps)



Hansen *et al*. J. Chem. Phys. **136**, *204310* (2012)

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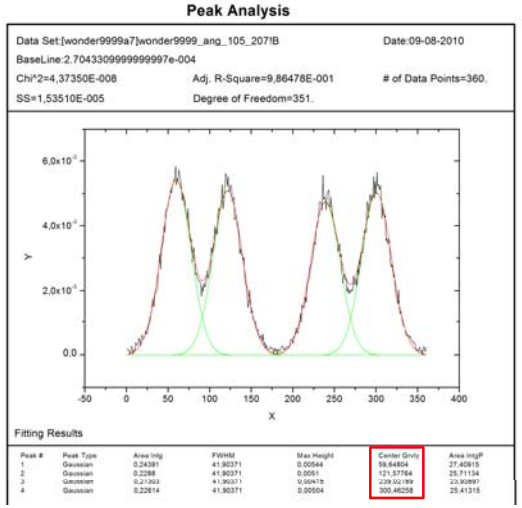
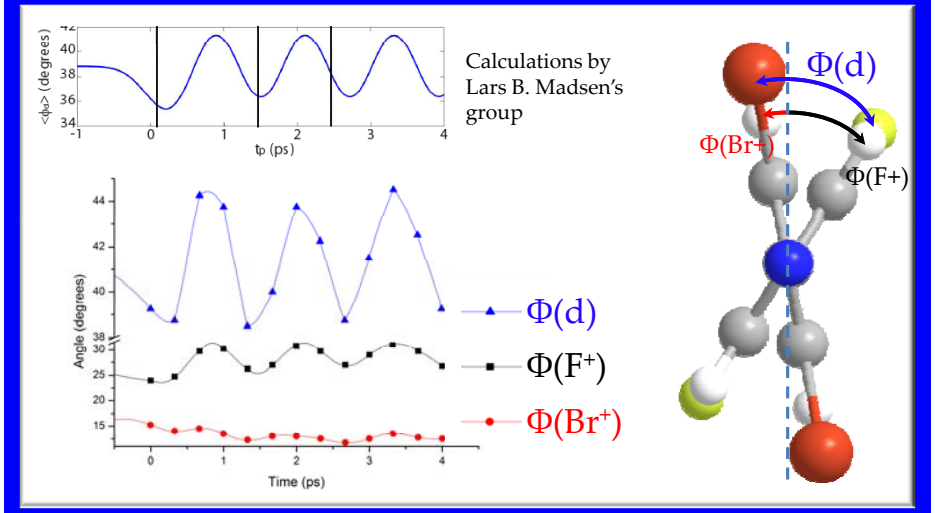
iNANO

Extracting the F^+ and Br^+ splits from the images

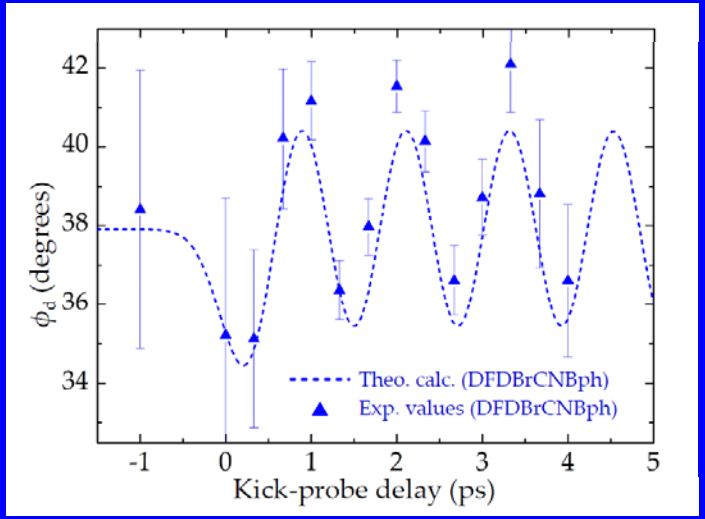


EXTRACTING THE DIHEDRAL ANGLE



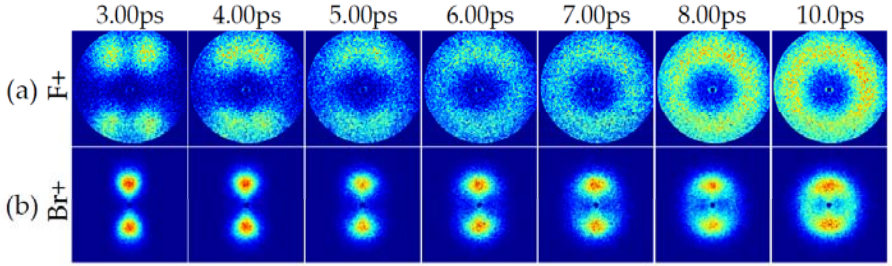
Hansen *et al*. J. Chem. Phys. **136**, *204310* (2012)

EXPERIMENTS vs CALCULATIONS

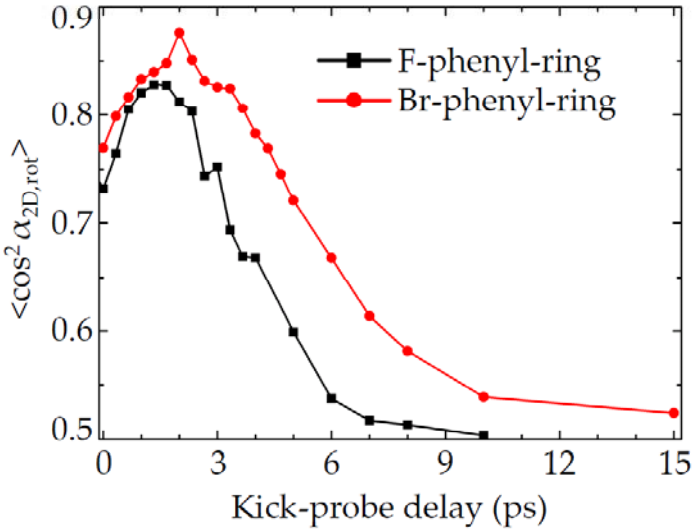


Hansen *et al*. J. Chem. Phys. **136**, *204310* (2012)

Long time behaviour (4 - 10 ps)



Long time behaviour
Dephasing of the phenyl rings



Long time behaviour
Dephasing of the phenyl rings

Rotational state of
Each phenyl ring
i = F, Br

$$\Psi_i(\phi_i, t) = \sum_{J_i} c_{J_i} \frac{1}{\sqrt{2\pi}} e^{iJ_i\phi_i} e^{-i\frac{J_i^2}{2I_i}t},$$

Time dependence
of observables

$$\cos\left(\frac{2J_i+1}{2I_i}t\right)$$

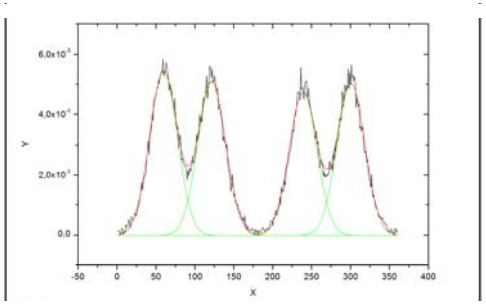
Dephasing time

$$\sim \frac{\mathbf{I_i}}{\mathbf{2J_i+1}}$$

The two rings dephase
at a ratio

$$r = \frac{\tau_{F^+}}{\tau_{Br^+}} = \frac{I_{F^+}}{I_{Br^+}} \cdot \frac{2J_{Br^+}+1}{2J_{F^+}+1}$$

Covariance analysis of
angular correlations in ion images



Covariance analysis of
ion time-of-flight spectra

Science 246, 1029 (1989)

Covariance Mapping: A Correlation Method Applied to Multiphoton Multiple Ionization

L. J. Frasinski, K. Codling, P. A. Hatherly

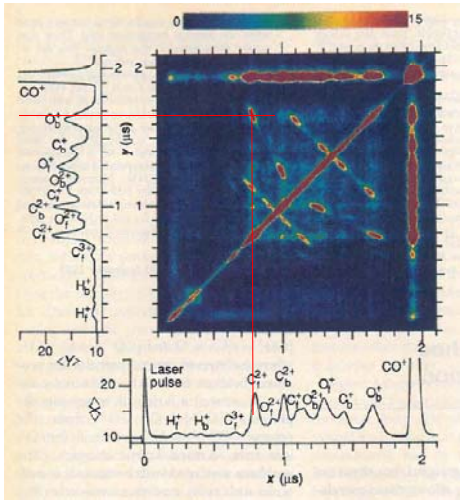
In some cases there are hidden correlations in a highly fluctuating signal, but these are lost in a conventional averaging procedure. Covariance mapping allows these correlations to be revealed unambiguously. As an example of the applicability of this technique, the dynamics of fragmentation of molecules ionized by an intense picosecond laser are analyzed.

Covariance analysis of
ion time-of-flight spectra

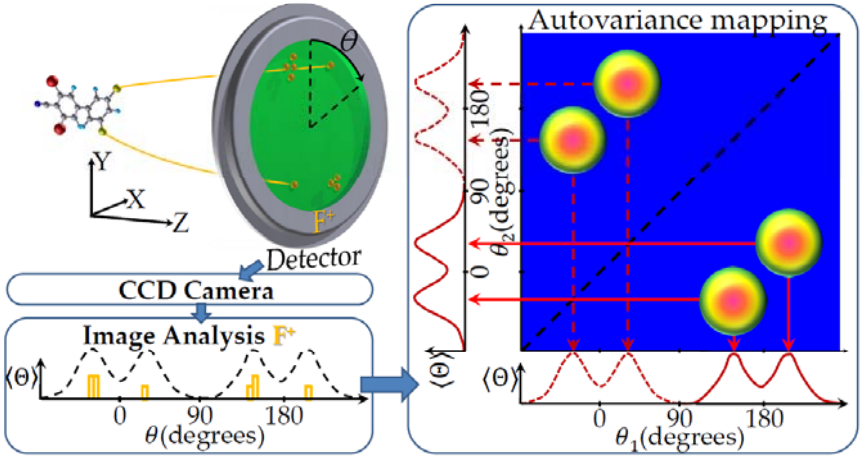
$CO + N\ h\nu \rightarrow CO^{3+} + 3\ e^-$

$CO^{3+} \rightarrow C^{2+} + O^+$

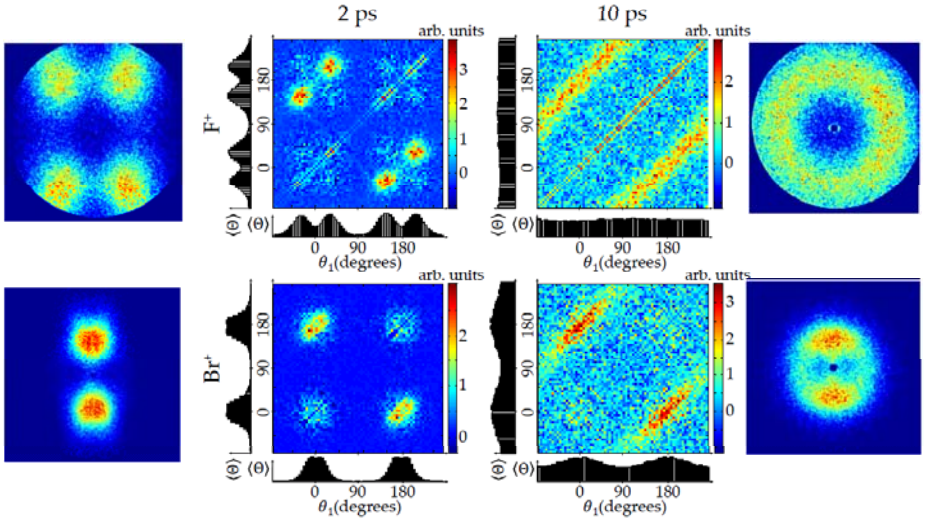
$$C(x,y) = \langle (X - \langle X \rangle)(Y - \langle Y \rangle) \rangle =$$
$$\langle XY \rangle - \langle X \rangle \langle Y \rangle =$$
$$\langle X(x)Y(y) \rangle - \langle X(x) \rangle \langle Y(y) \rangle$$
$$= \frac{1}{N} \sum_{i=1}^{N} X_i(x) Y_i(y) -$$
$$\left[\frac{1}{N} \sum_{i=1}^{N} X_i(x)\right] \left[\frac{1}{N} \sum_{i=1}^{N} Y_i(y)\right]$$



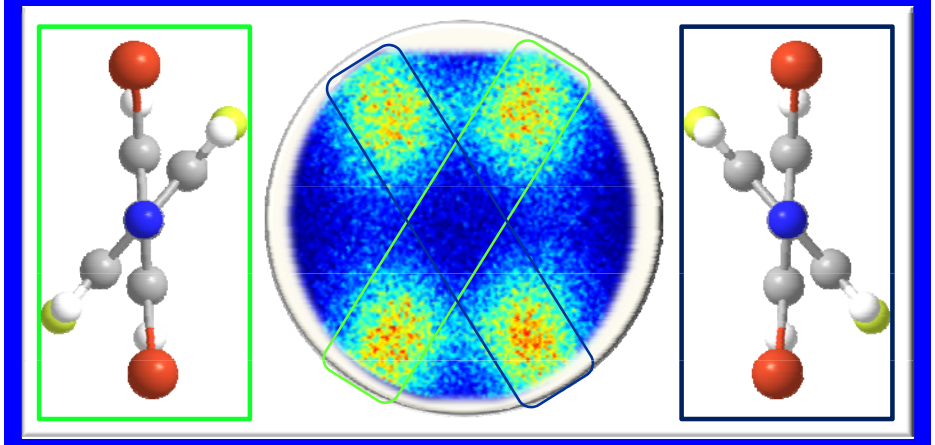
Covariance analysis of angular correlations in ion images



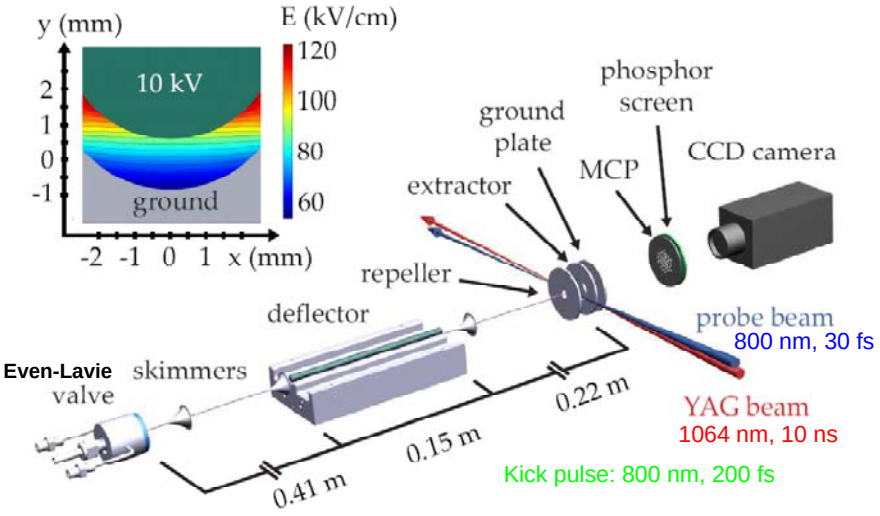
Covariance analysis of angular correlations in ion images



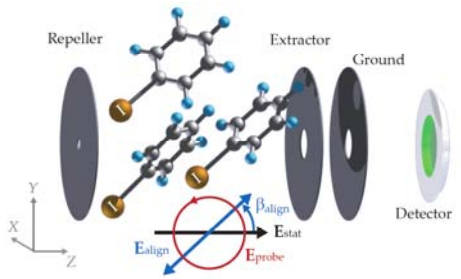
Enantiomeric resolution? Is the molecule oriented?

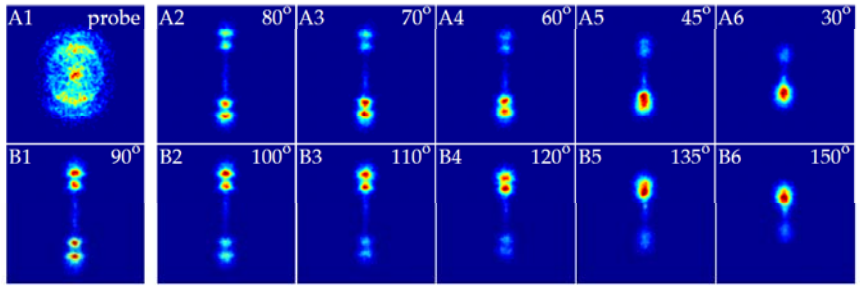


Experimental Setup

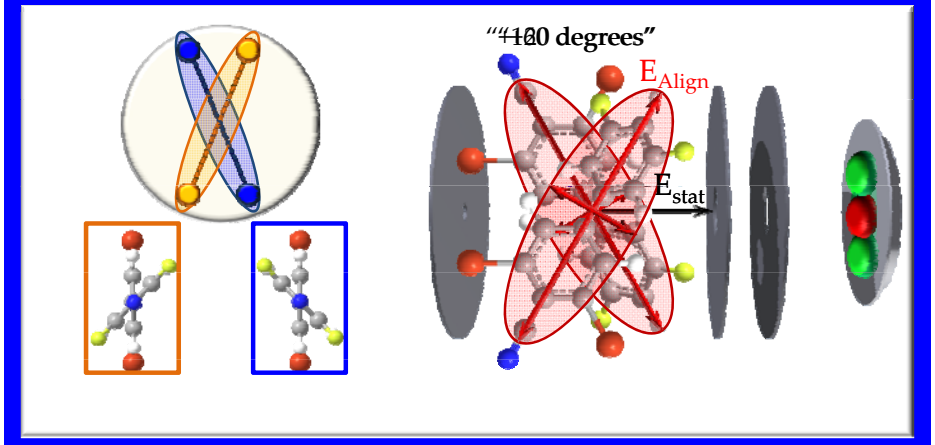


Orientation by a combined
Strong laser field and a weak static electric field





Enantiomeric resolution?
Is the molecule oriented



People

Experiment

Jonas Lerche Hansen

Jens H. Nielsen

Theory

Lars Bojer Madsen

Christian Brun Madsen

Quantum chemistry

Mikael P. Johansson

Synthesis

Troels Skrydstrup

Anders Lindhardt

Laser induced alignment of molecules dissolved in superfluid He nanodroplets

Laser induced alignment (and orientation) of isolated molecules

- Works well – because:

  • Isolated molecules rotate freely

  → Laser pulses can create (broad) coherent superpostions of rotational eigenstates

- Works particularly well when:

  • Molecules are cooled to low rotational temperatures or, even better, few (a single) quantum state is selected

Laser induced alignment of molecules in a solvent ?

• Molecules in a solvent are not characterized by free rotation

• Even if a rotational wave packet is created collisions would destroy it quickly

• The laser pulse also interacts with the solvent

- Laser induced alignment may be sensitive to the numerous mechanisms not present in gas phase

- Laser induced alignment may be hindered by the numerous mechanisms not present in gas phase

Choose a special solvent: Superfluid liquid helium droplets

Unique properties:

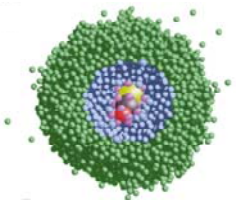
• Superfluid: Molecules can (apparently) rotate freely

• Robust environment

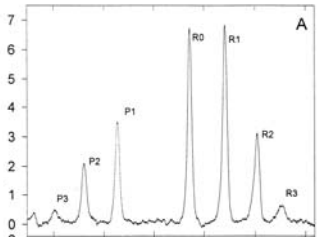
• Dissolved molecules thermalize to the cold environment (0.37 K for ^{4}He)

• Wide range of molecules can be embedded

• Bose condensate

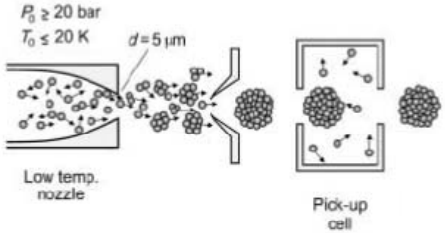


IR absorption spectrum of OCS



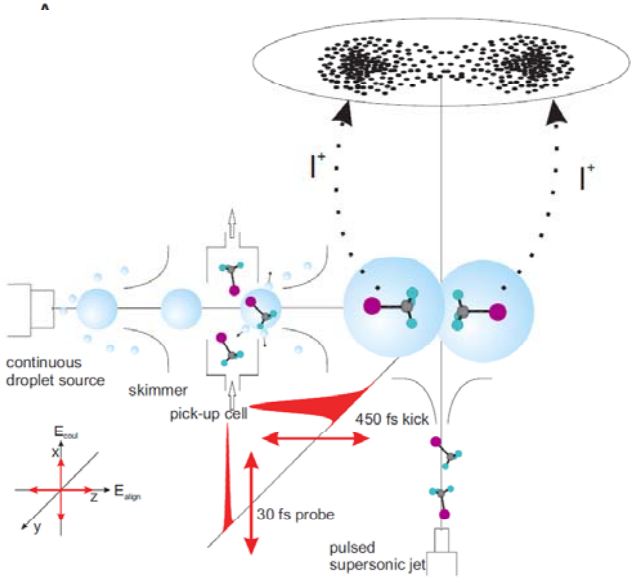
Science **279** 2083 (1998)

Molecules dissolved in liquid helium nanodroplets



10^3-10^8 He atoms per droplet

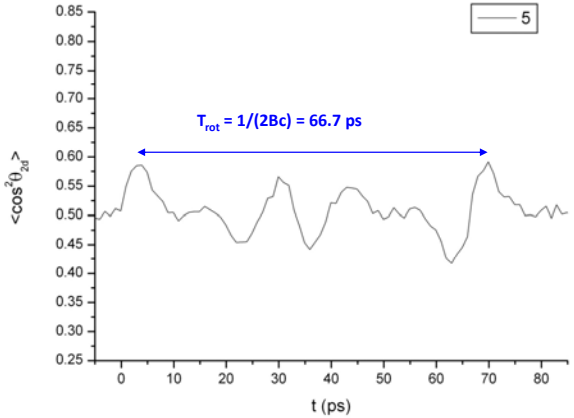
Experimental setup



Alignment of isolated molecules

Methyliodide CH_3I

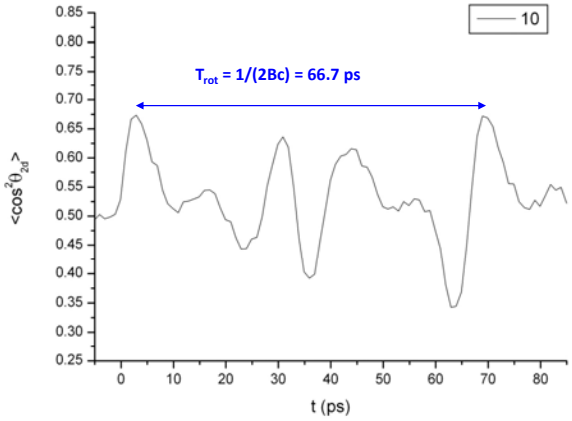
I_{align} = 4.0 x 10^{11} W/cm^2



Alignment of isolated molecules

Methyliodide CH_3I

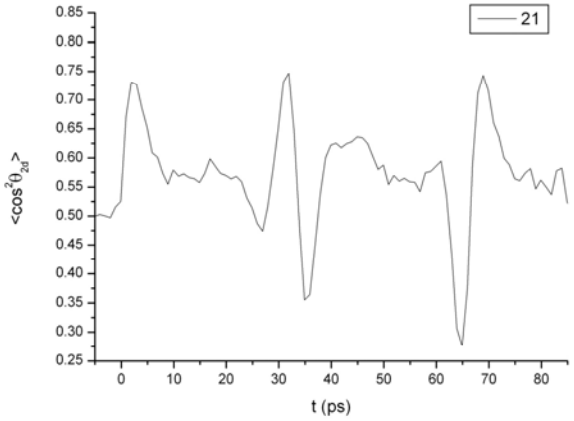
I_{align} = 8.0 x 10^{11} W/cm^2



Alignment of a isolated molecules

Methyliodide CH_3I

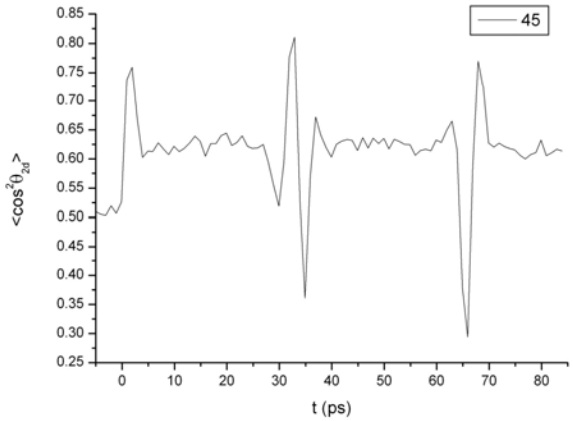
I_{align} = 1.7 x 10^{12} W/cm^2



Alignment of isolated molecules

Methyliodide CH_3I

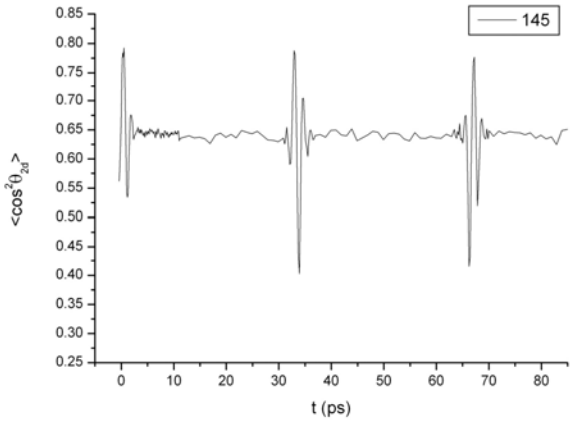
$I_{align} = 3.6 \times 10^{12}$ W/cm^2



Alignment of isolated molecules

Methyliodide CH_3I

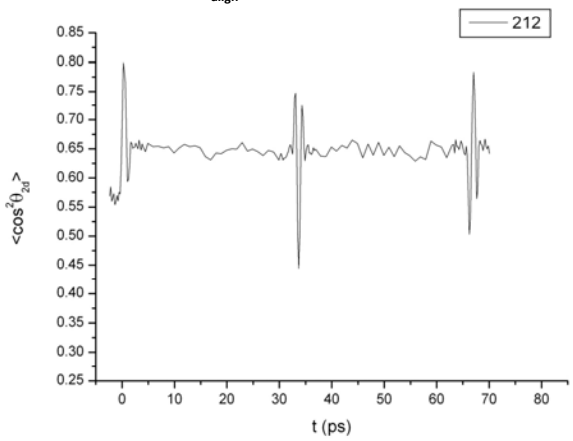
$I_{align} = 1.2 \times 10^{13}$ W/cm^2



Alignment of isolated molecules

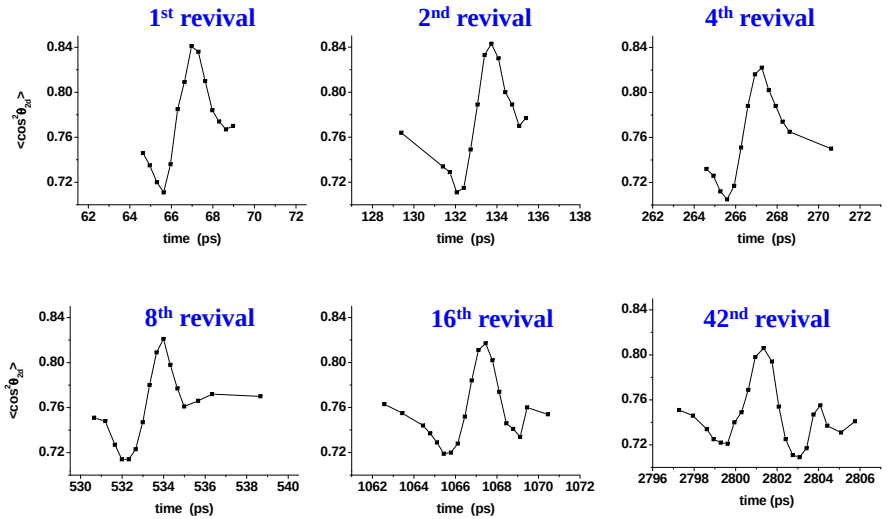
Methyliodide CH_3I

$I_{align} = 1.7 \times 10^{13}$ W/cm^2



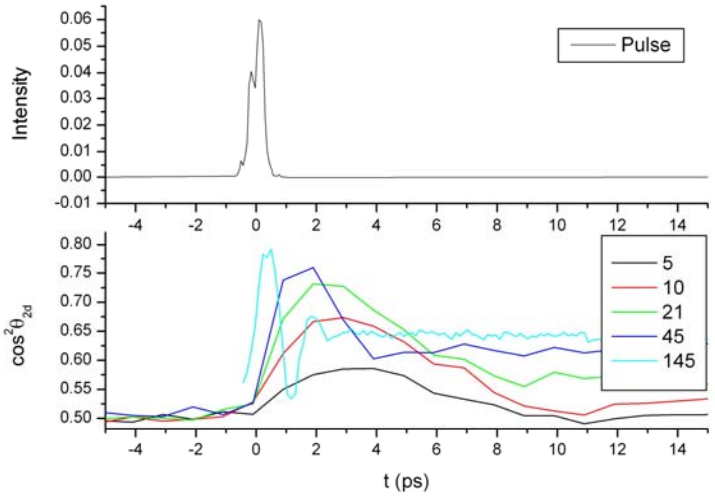
Lots of revivals !

Methyliodide CH_3I



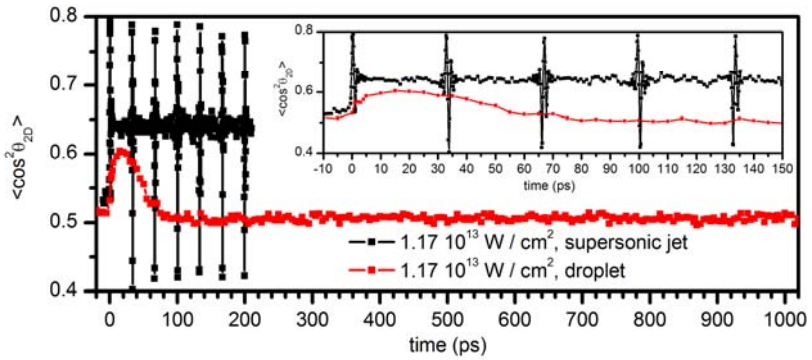
Alignment of isolated molecules

Early time dynamics



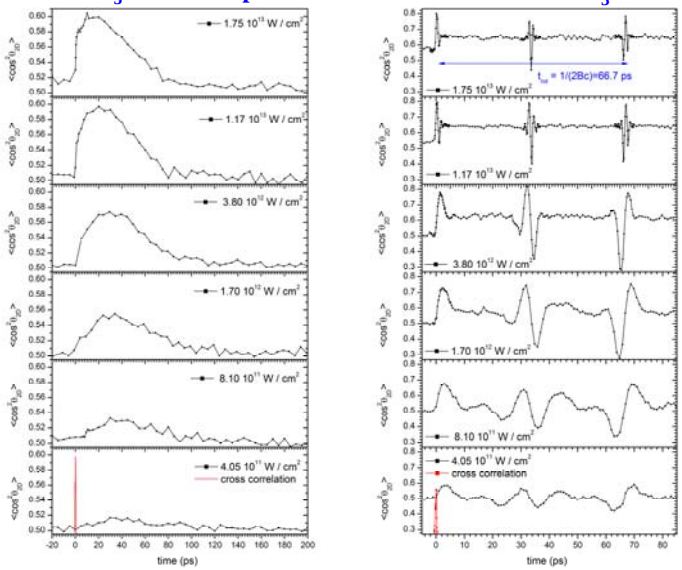
Alignment of molecules in He droplets

CH_3I

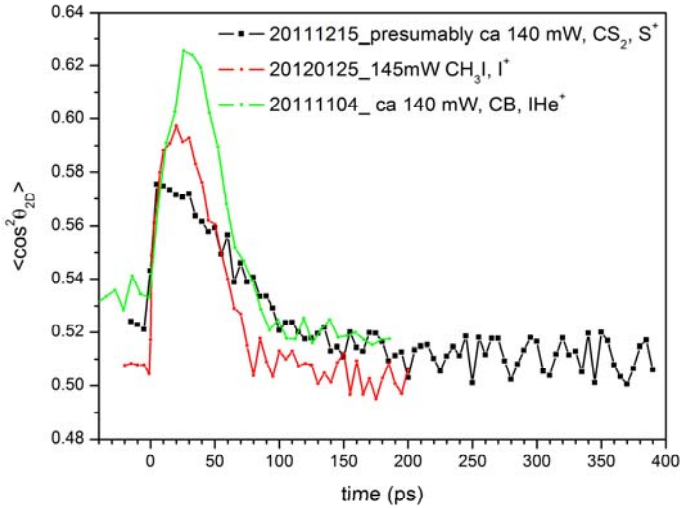


Dependence on kick pulse intensity

CH_3I in He droplets | **Isolated CH_3I**



Dependence on solvated molecule



- **No dependence on the droplet size (1000 – 11,000 He atoms)**

Theoretical treatments so far

(Not of molecules in He droplets)

PRL 95, 113001 (2005) PHYSICAL REVIEW LETTERS week ending 9 SEPTEMBER 2005

Intense Laser Alignment in Dissipative Media as a Route to Solvent Dynamics

S. Ramakrishna and Tamar Seideman*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

(Received 27 December 2004; published 7 September 2005)

We extend the concept of alignment by short intense pulses to dissipative environments within a density matrix formalism and illustrate the application of this method as a probe of the dissipative properties of dense media. In particular, we propose a means of disentangling rotational population relaxation from decoherence effects via strong laser alignment. We illustrate also the possibility of suppressing rotational relaxation to prolong the alignment lifetime through choice of the field parameters. Implications to several disciplines and a number of potential applications are proposed.

THE JOURNAL OF CHEMICAL PHYSICS 136, 184302 (2012)

Quantum and classical approaches for rotational relaxation and nonresonant laser alignment of linear molecules: A comparison for CO_2 gas in the nonadiabatic regime

J.-M. Hartmann[1,a)] and C. Boulet[2]

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[2]*Institut des Sciences Moléculaires d'Orsay (ISMO) CNRS (UMR 8214), Université Paris-Sud, Bât. 350, Orsay F-91405, France*

(Received 9 January 2012; accepted 6 April 2012; published online 9 May 2012)

Theoretical treatments so far

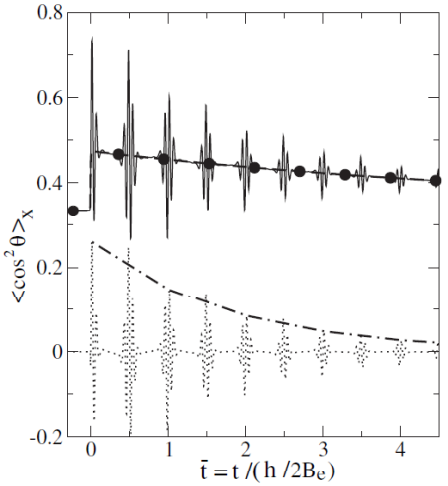
Ramakrishna and Seideman, PRL 2005

Effect of environment:

Decoherence and population decay after the pulse is switched off

→ Affects the amplitude but not the period of the revivals

- Correlations between the molecule and the droplet atoms are neglected



Our results are not captured by the published theoretical work

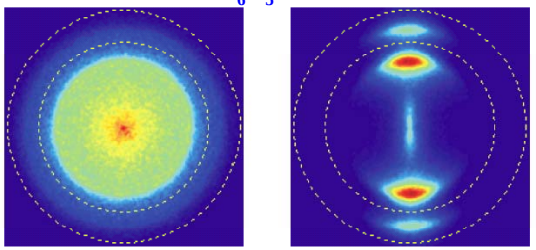
- The kick pulse may not excite the eigenstates of the molecule-droplet system (instead an entangled state)

- M may not be conserved (as in the gas phase) due to exchange of angular momentum during the kick pulse

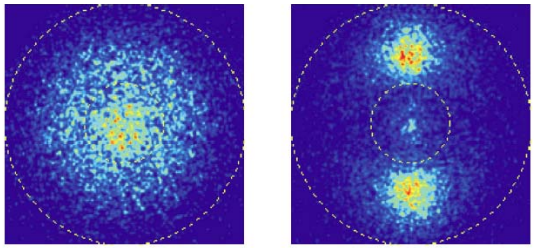
- M-scrambling (during and after the kick pulse) + onset of population decay
→ alignment decays towards an isotropic value

Adiabatic alignment

Isolated C_6H_5I Molecules

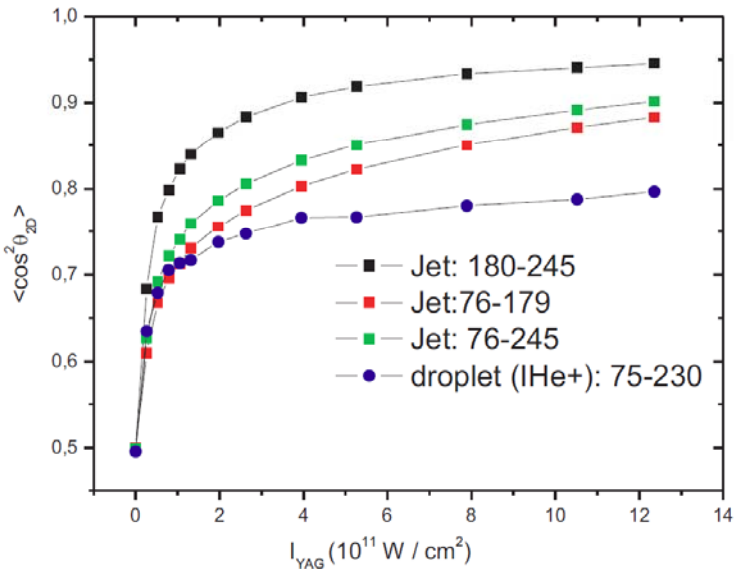


C_6H_5I molecules in He droplets



Adiabatic alignment

C_6H_5I



Outlook

- Molecular frame reactions dynamics of molecules in a solvent

- Use rotational dynamics of molecules to learn about the He droplets

People

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