Imaging complexes in helium droplets with Coulomb explosion

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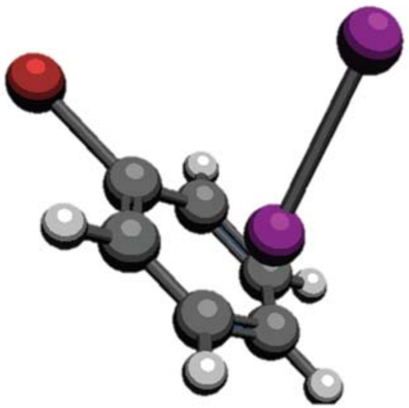
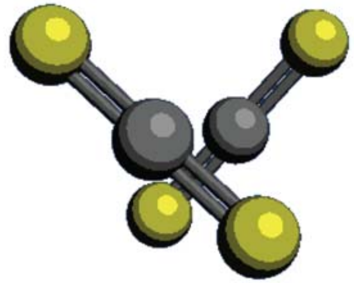
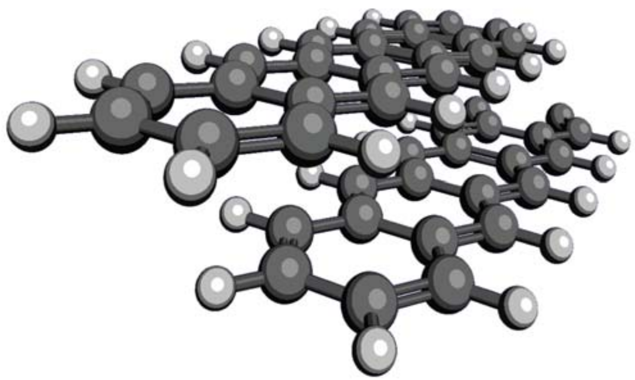
Dimers and complexes

Our goal is to measure the structure and dynamics of weakly-bound complexes in droplets

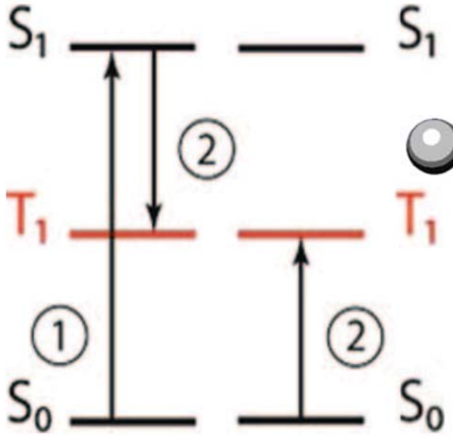


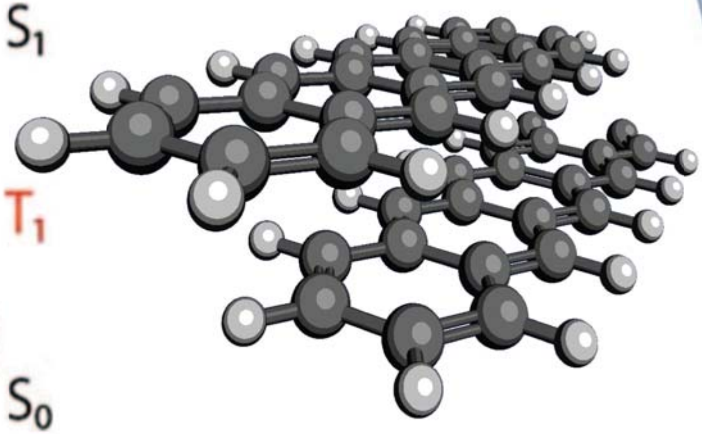




Dimers and complexes

One major goal is to study the dynamics of singlet fission





Coulomb explosion imaging

We want to look at complex systems
➔ High resolution spectroscopy?

But…
For dynamics, we need femtosecond time resolution

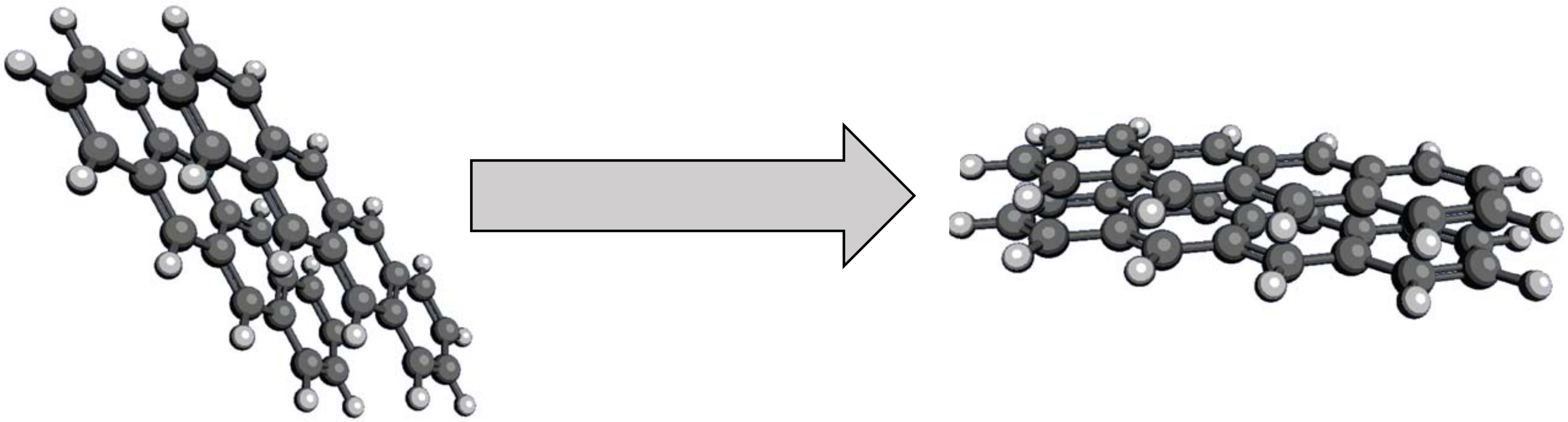
$$\Delta E \, \Delta t \geq \frac{1}{2} \hbar$$

We need a method based on imaging, not spectroscopy

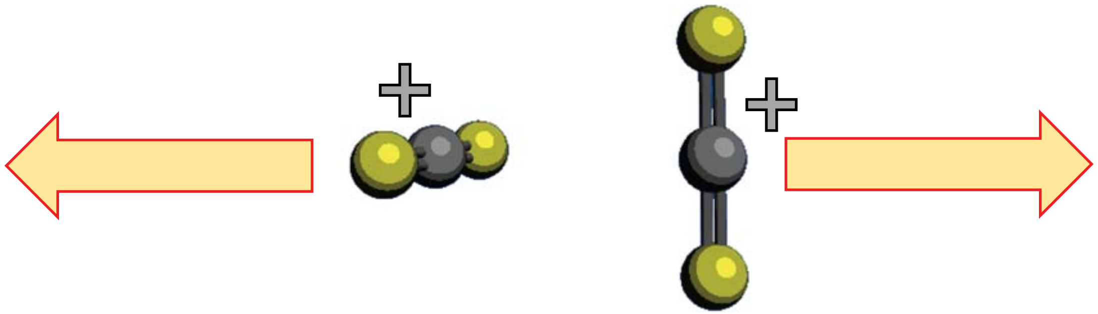
Coulomb explosion imaging

We combine two tools to do this

1) Laser induced alignment



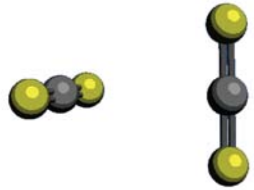
2) Coulomb Explosion Imaging



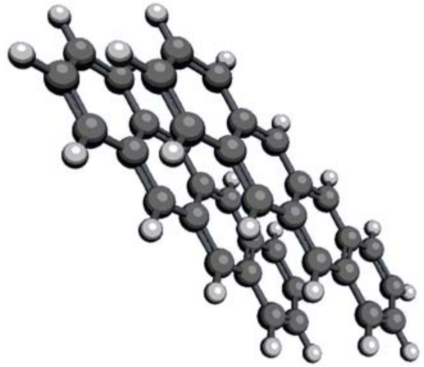
Coulomb explosion imaging

We'll looks at three complex, and explain the technique on the way

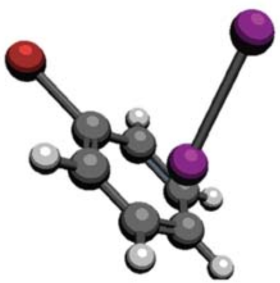
1) CS_2 dimers



2) Tetracene dimers

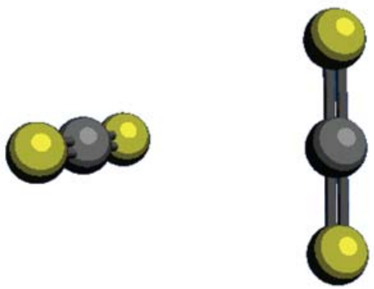


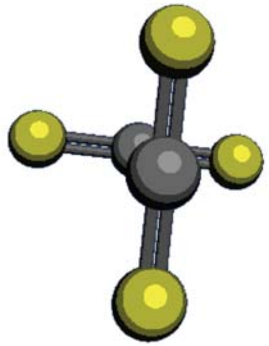
3) Bromobenzene – I_2 complex



CS_2 dimers

In the gas phase, CS2 dimers are a symmetric cross shape





Can we measure the structure in droplets?

THE JOURNAL OF CHEMICAL PHYSICS **149**, 154306 (2018)

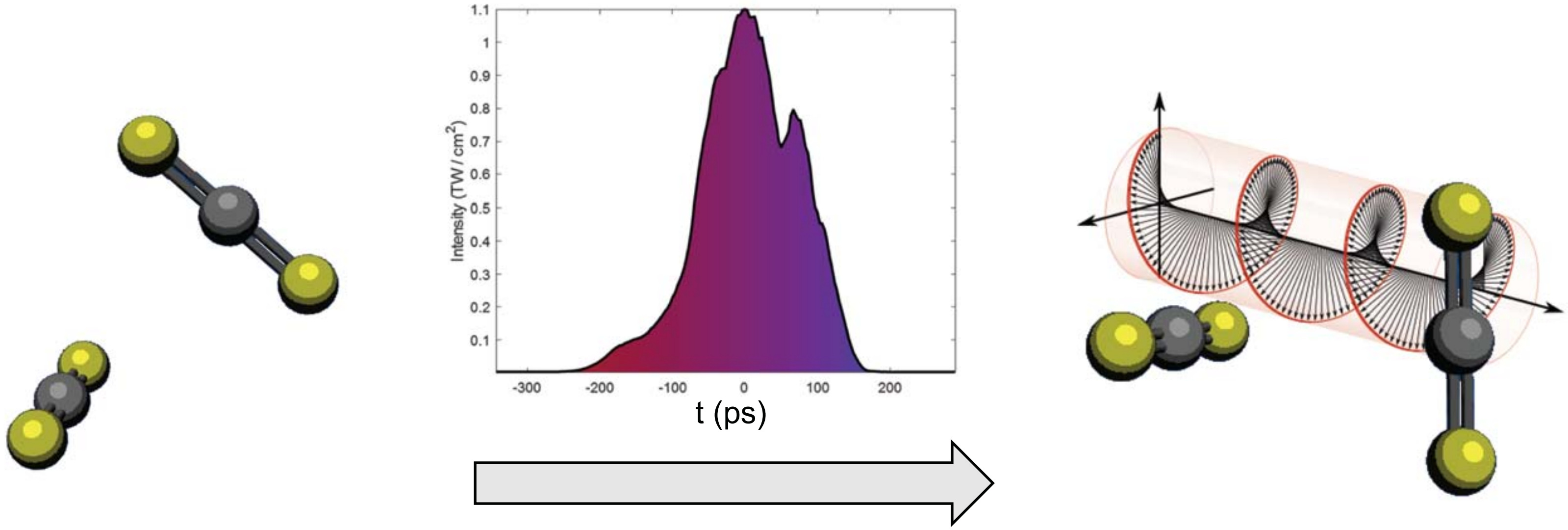
Femtosecond laser induced Coulomb explosion imaging of aligned OCS oligomers inside helium nanodroplets

James D. Pickering, Benjamin Shepperson, Lars Christiansen, and Henrik Stapelfeldt[a]
Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark

CS_2 dimers

Step one: align the dimers in droplets

For CS_2 dimers we use **circular polarized** light to induce alignment



The strong electric field brings both the CS2 molecules into the polarization plane

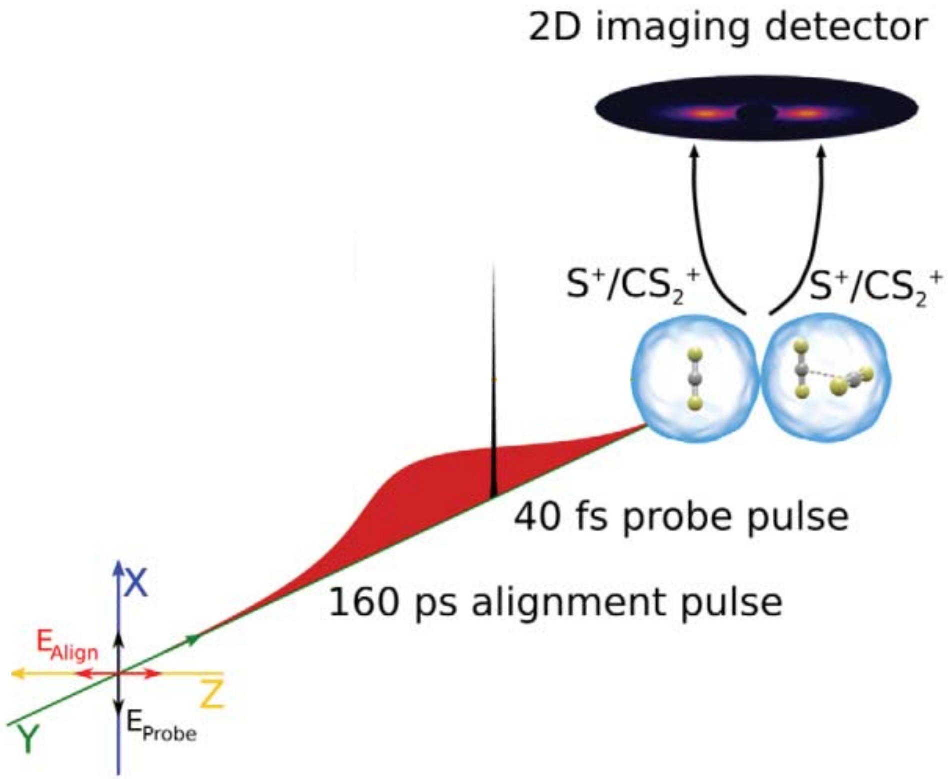
This fixes the internuclear axis to the laser propagation direction

The pulse is long, so the alignment is **adiabatic**

CS_2 dimers

Step two: Coulomb explode it

At the peak of alignment, we use a strong field to ionize both CS_2 molecules



Velocity map imaging shows which way the fragments go

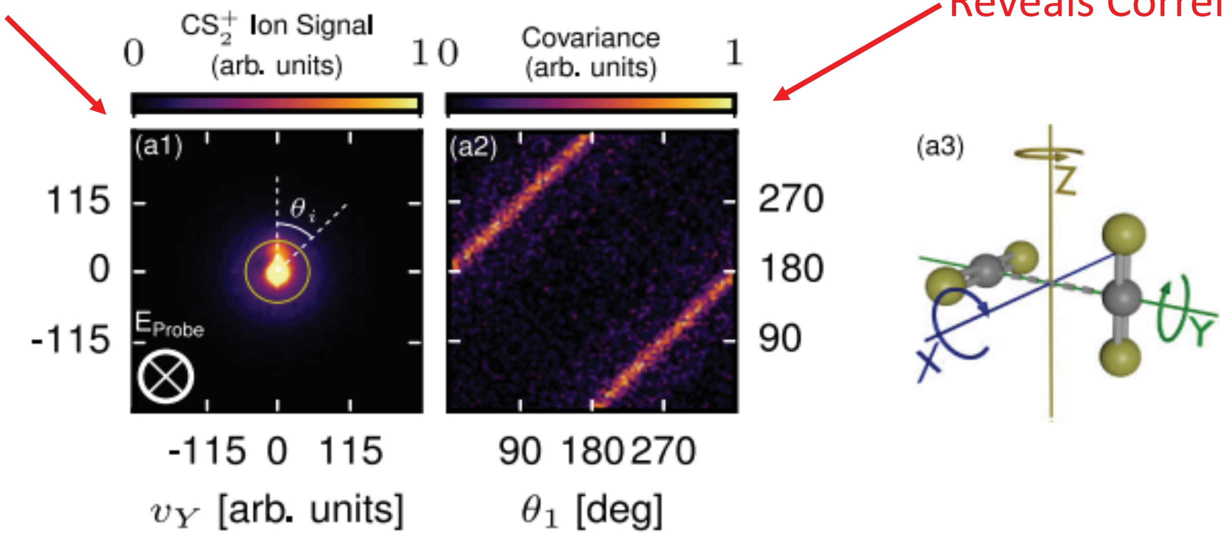
CS_2 dimers

Step three: Analyze coincident events

Ion image

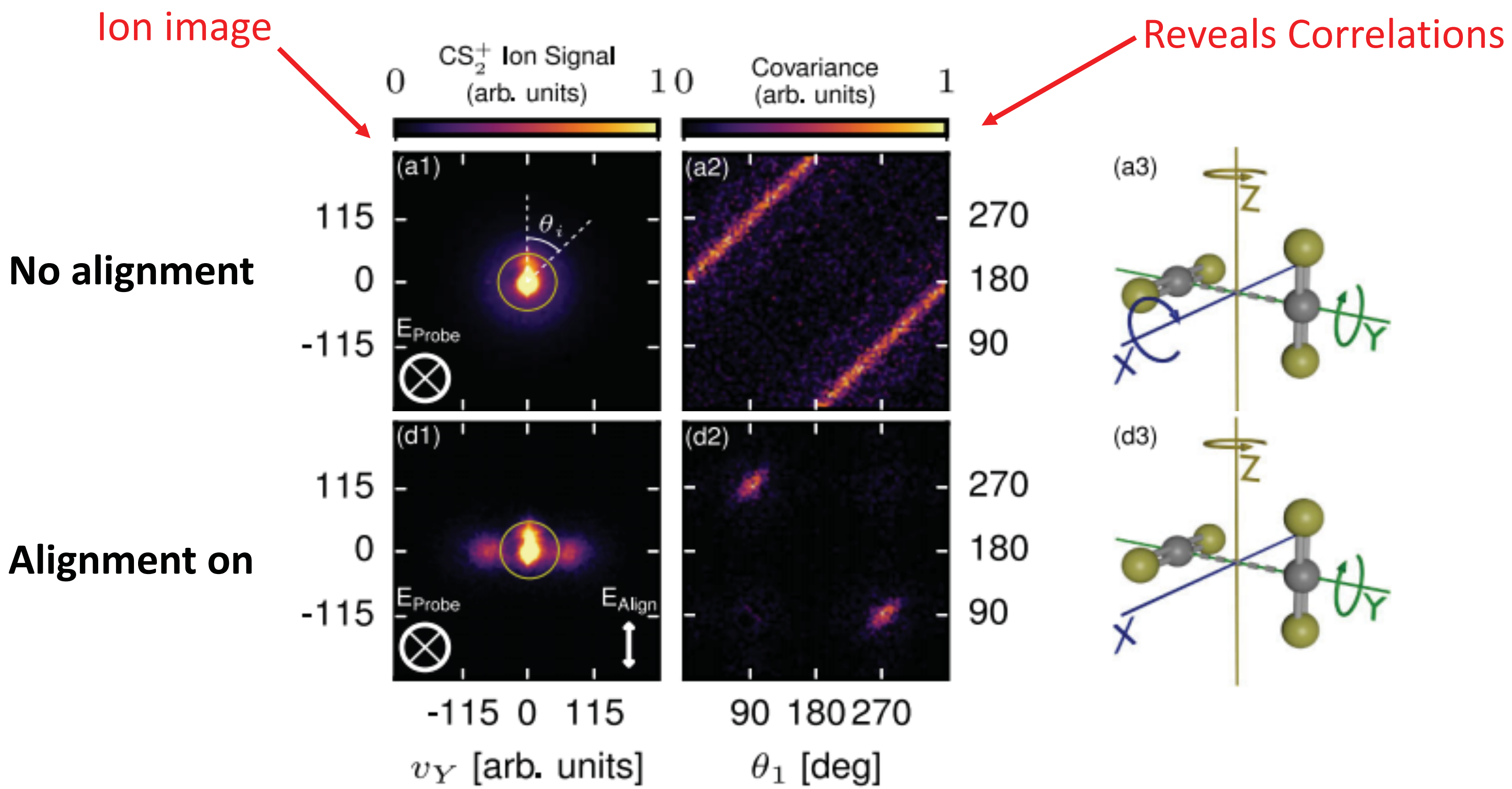
Reveals Correlations

No alignment



CS_2 dimers

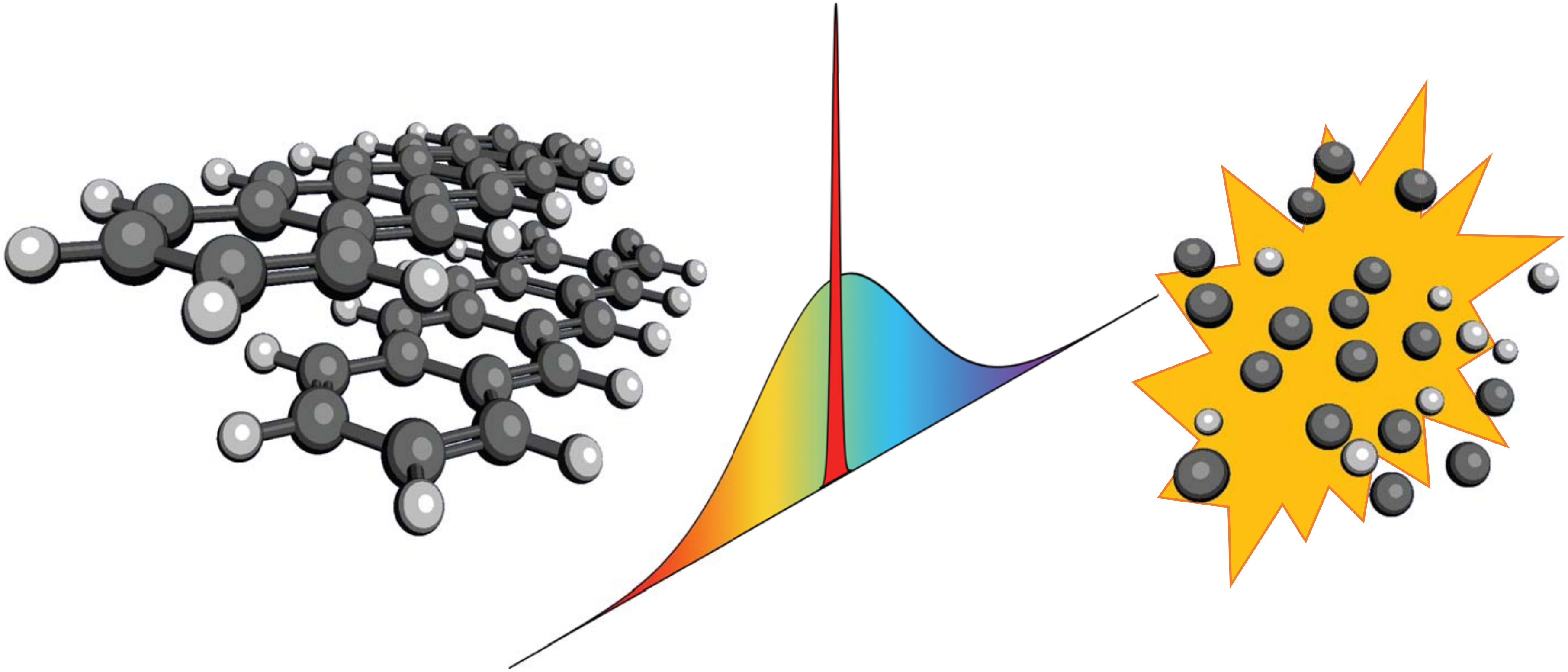
Step three: Analyze coincident events



The Coulomb explosion is consistent with the cross structure

Tetracene dimers

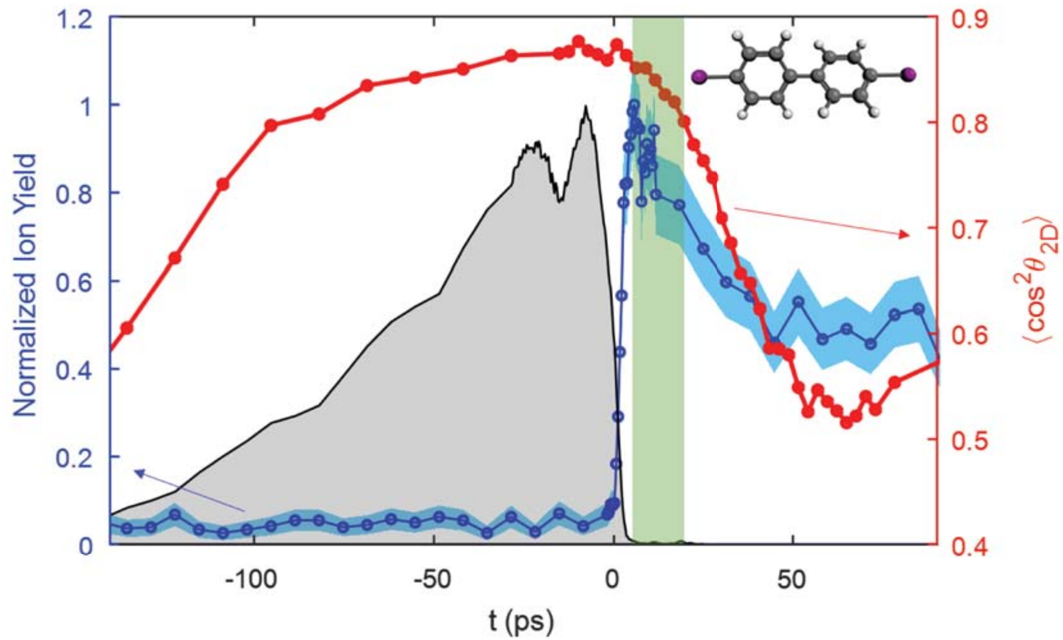
We would like to do the same for more complex systems



But ionizing large molecules in the presence of the alignment field destroys it

Tetracene dimers

We need a way to align the system **field-free**



If we cut the field fast enough, (in a droplet) the alignment lingers little after

We think this is to do with shifted rotational levels…

ARTICLE

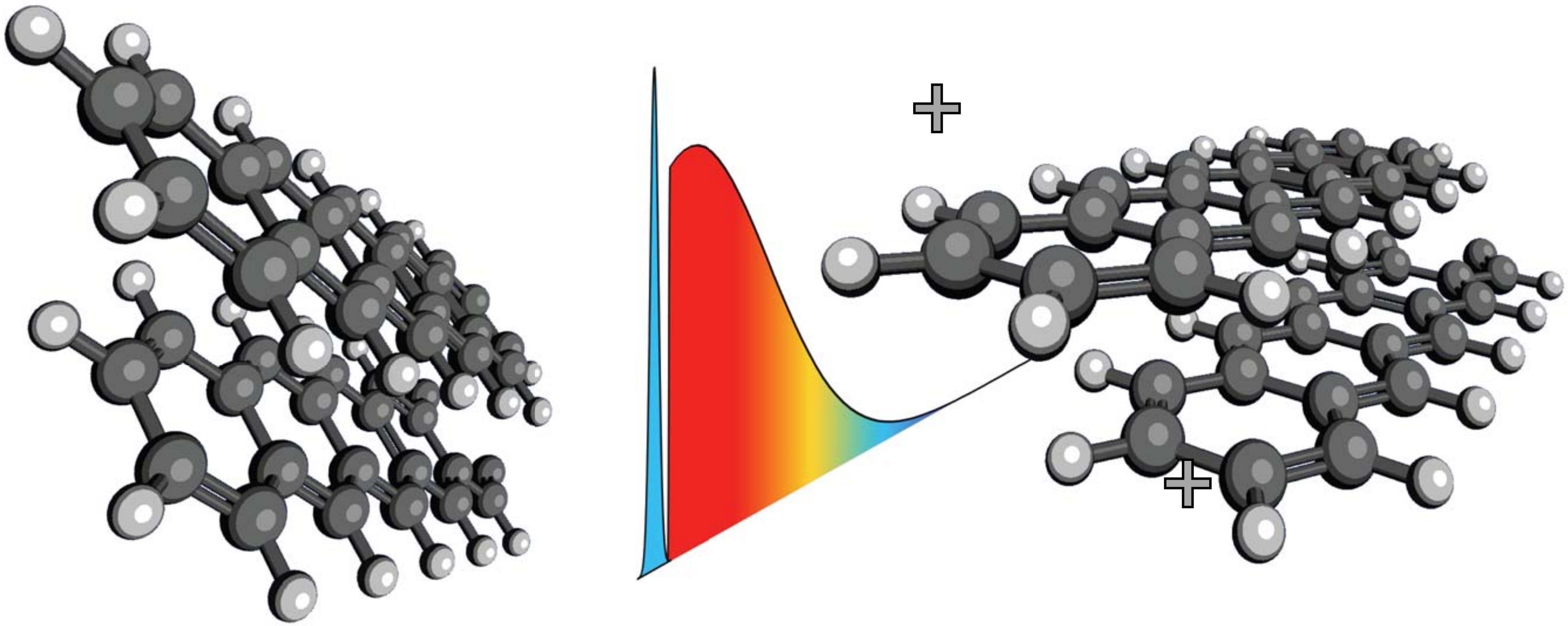
https://doi.org/10.1038/s41467-018-07995-0 OPEN

Long-lasting field-free alignment of large molecules inside helium nanodroplets

Adam S. Chatterley[1], Constant Schouder[2], Lars Christiansen[1], Benjamin Shepperson[1], Mette Heidemann Rasmussen[1] & Henrik Stapelfeldt[1]

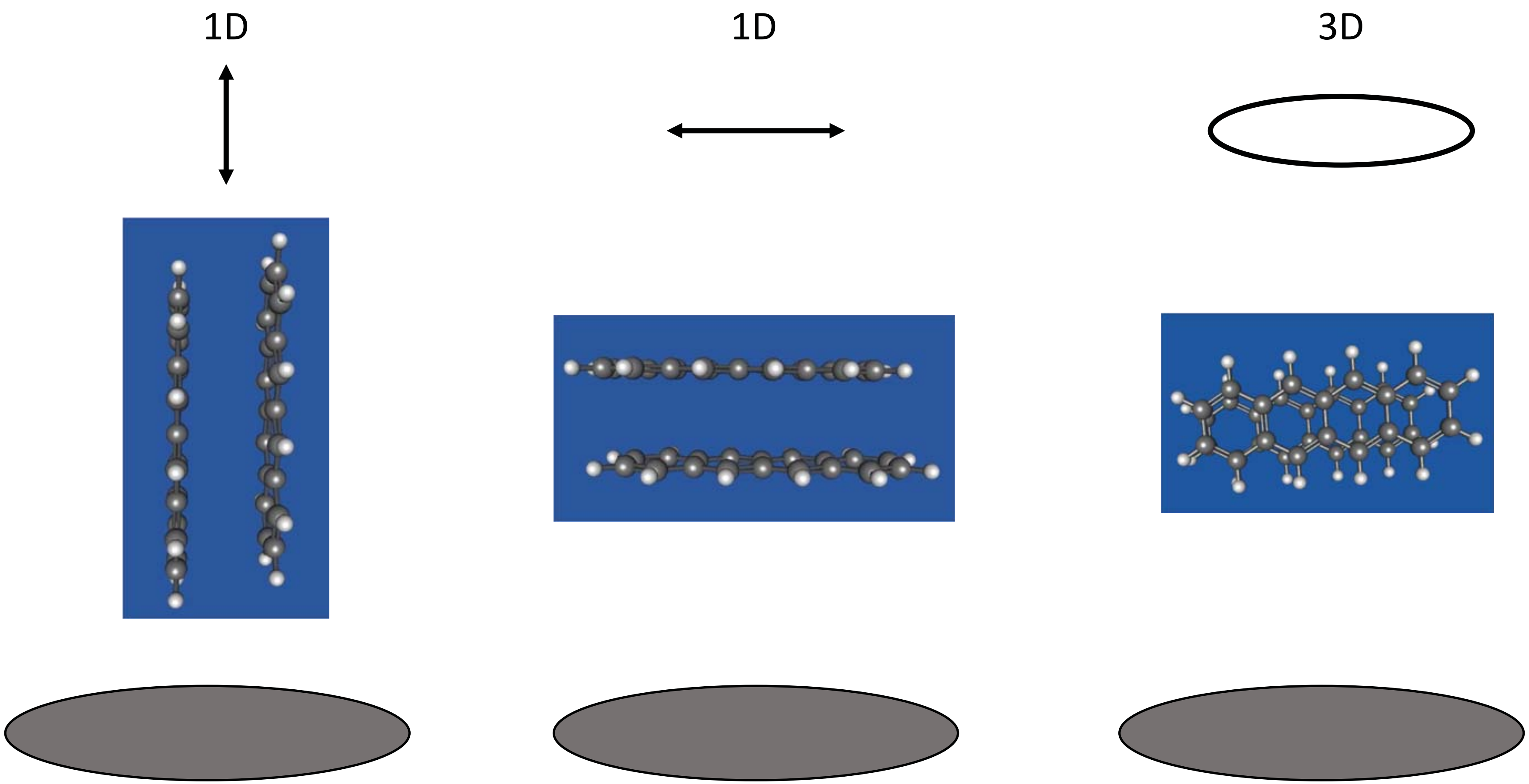
Tetracene dimers

Using truncated pulses, we can Coulomb explode big, aligned complexes



Tetracene dimers

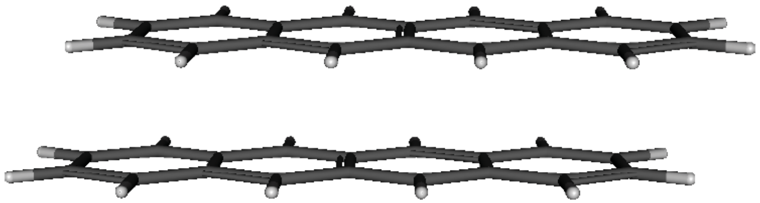
Different alignment polarizations hold the complex differently



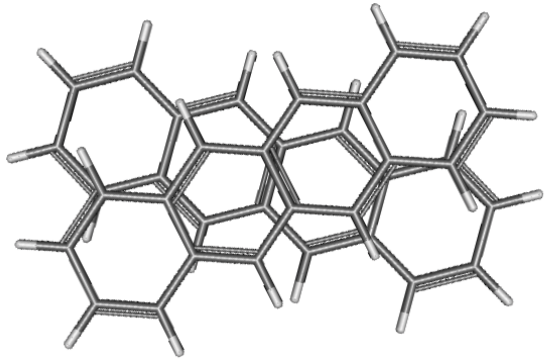
Different configurations will give different images

Tetracene dimers

Gas-phase calculations by Florent Calvo



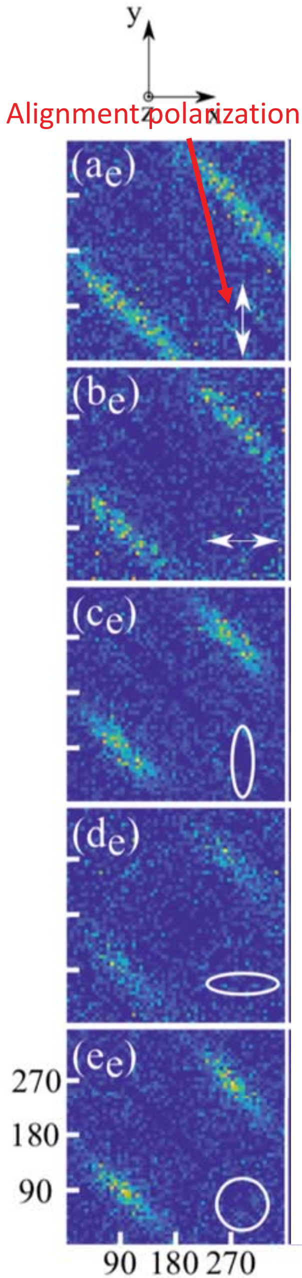
slipped parallel



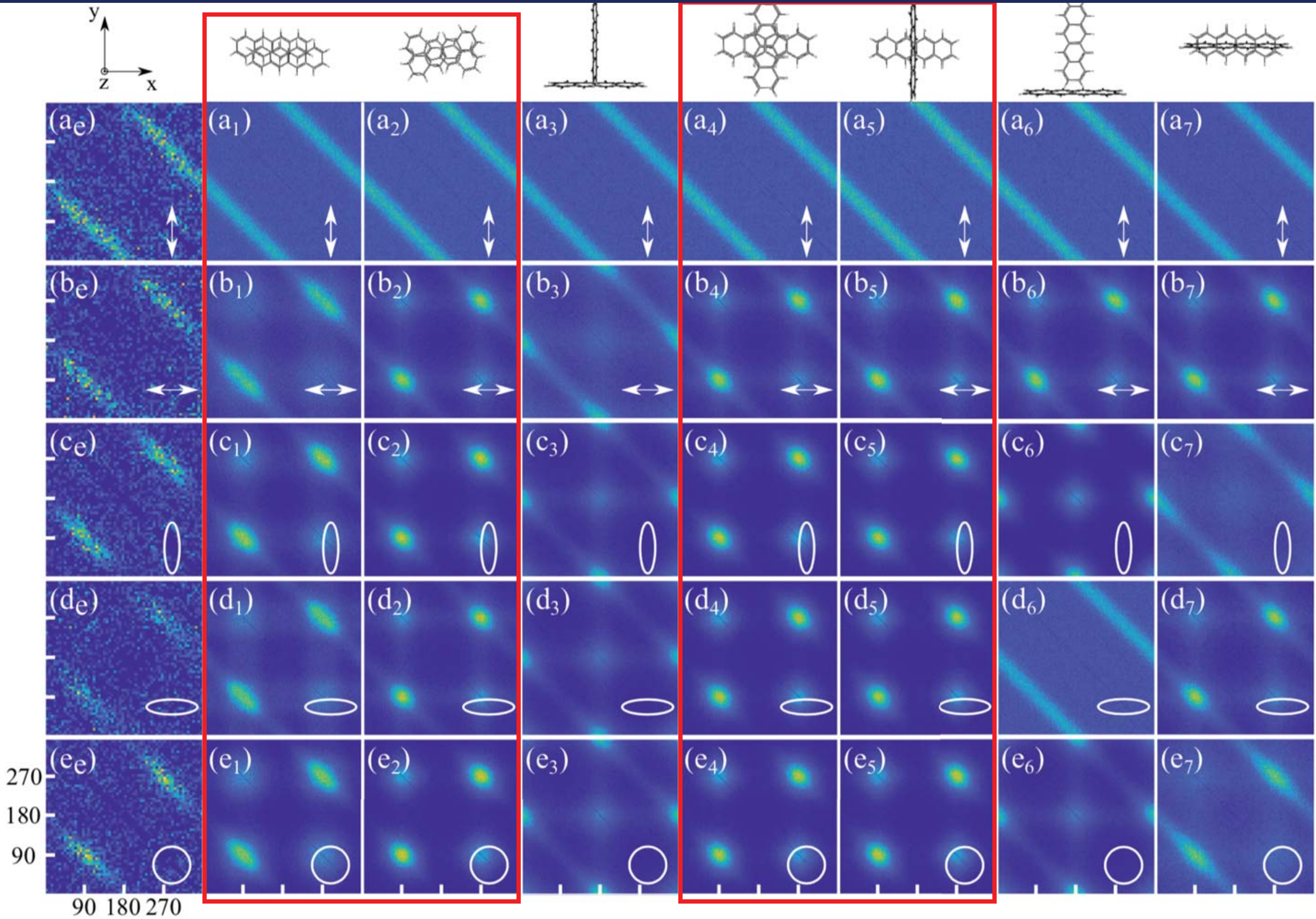
rotated

Do we see these inside the droplets?

Tetracene dimers

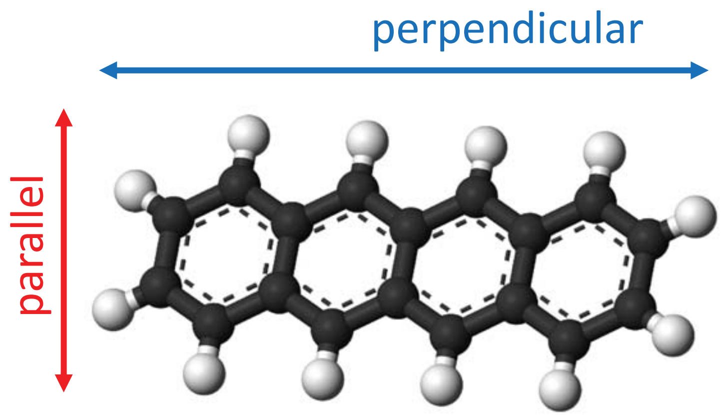


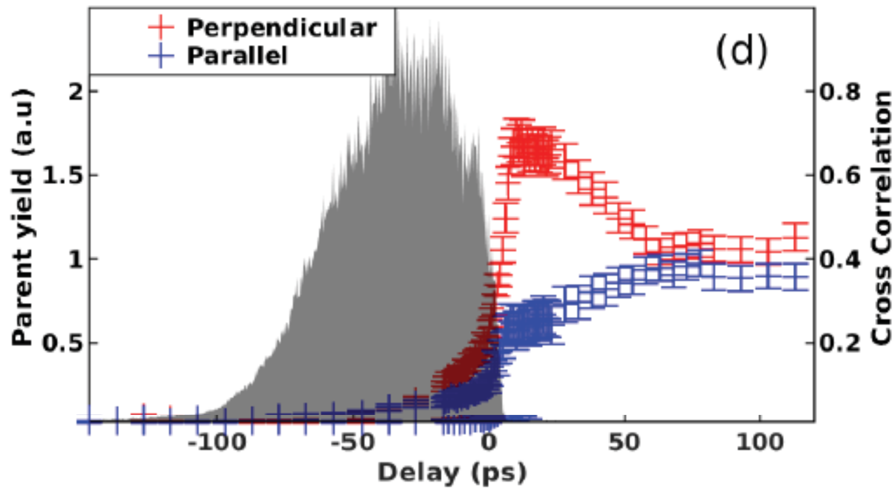
Tetracene dimers



Tetracene dimers

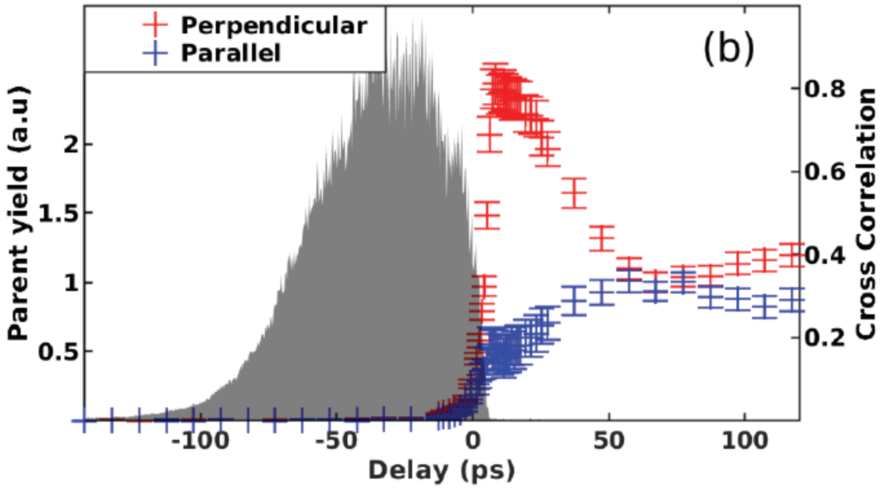
We can tell the symmetry using linear dichroism





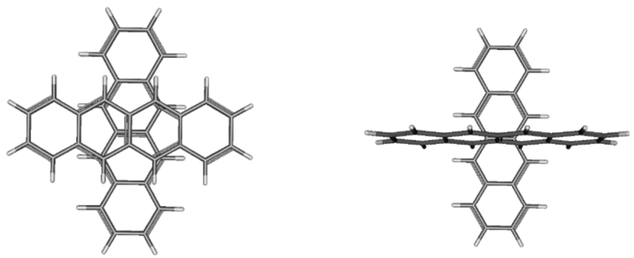
Asymmetric molecules care which way they point when you ionize them with linear polarized light

Tetracene dimers



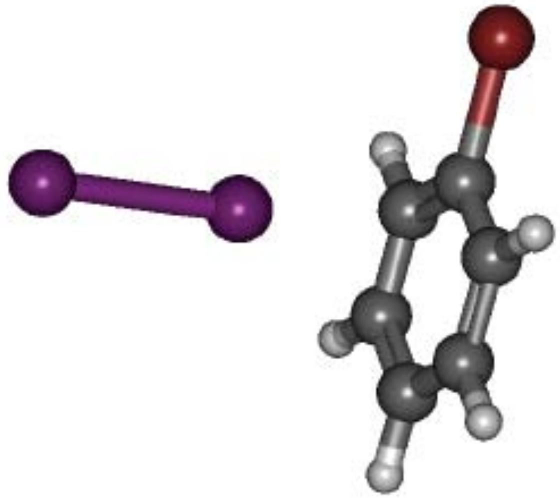
Asymmetric

Symmetric



Heterodimers

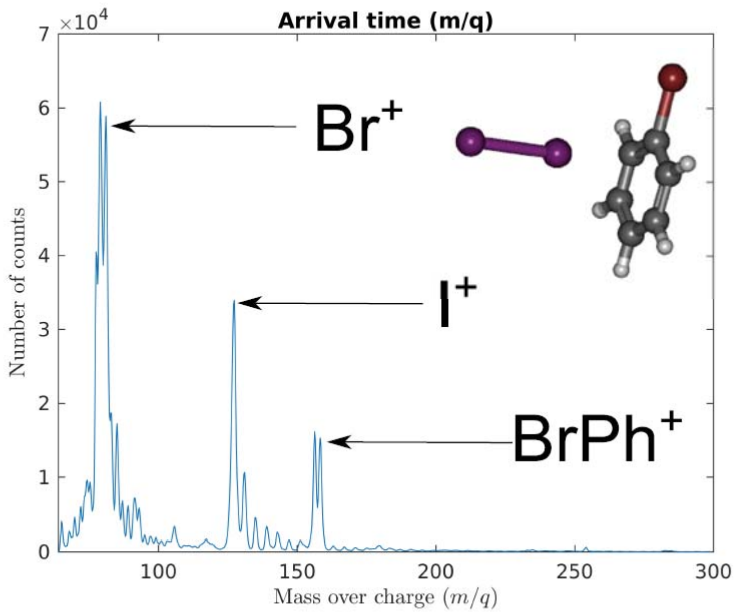
Moving beyond homodimers – can we measure the structure of a complex made of two different molecules?

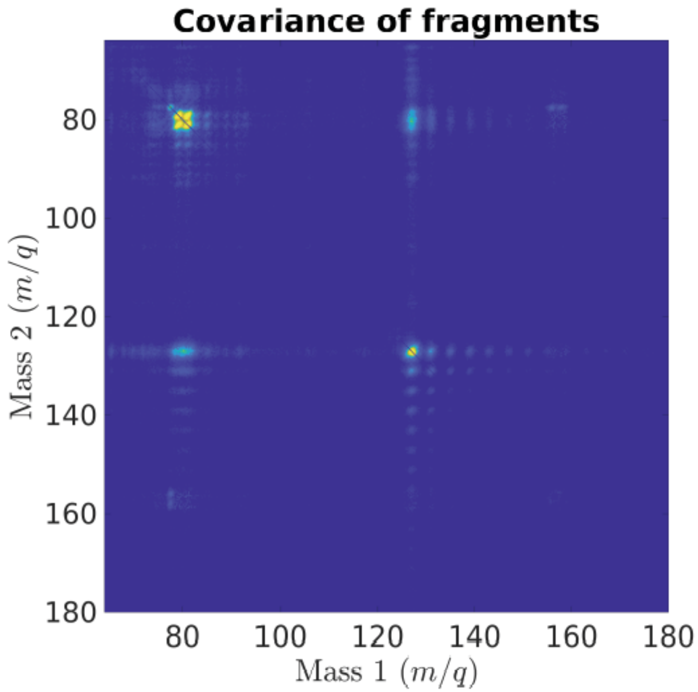


To do this we need to correlate different ion species with each other

Heterodimers

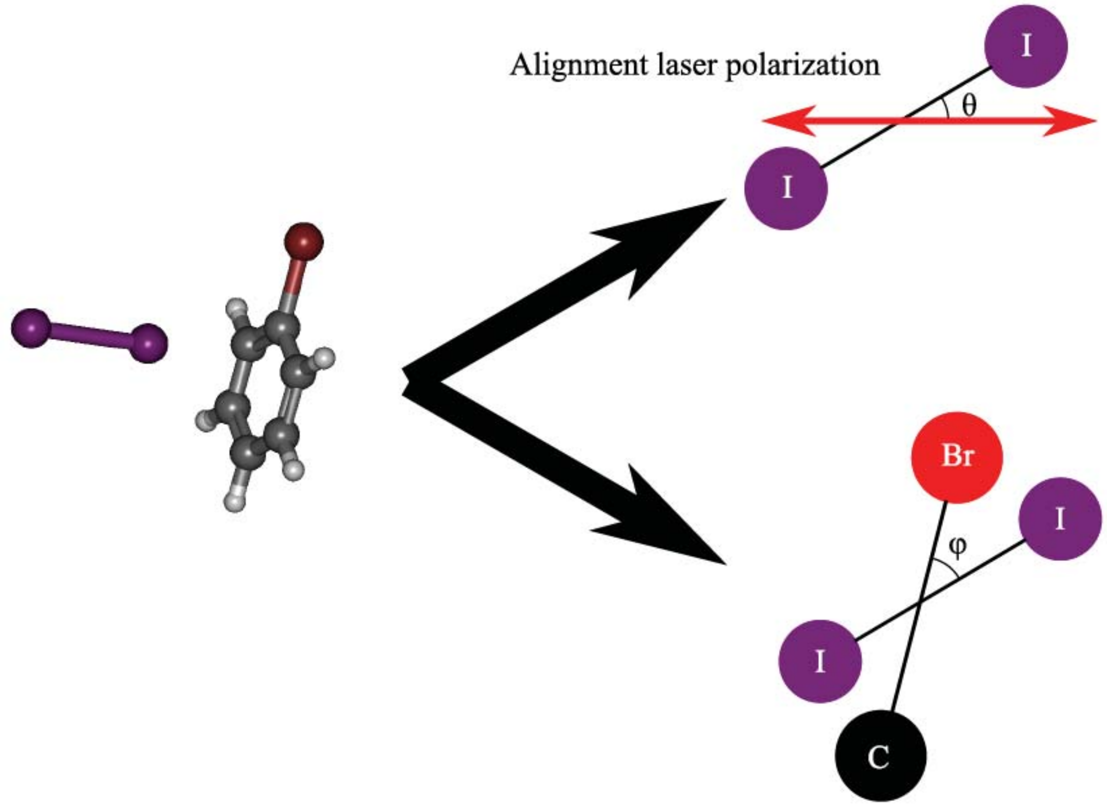
We used a Timepix3 camera, which measures both position and time of flight for every ion in the Coulomb explosion





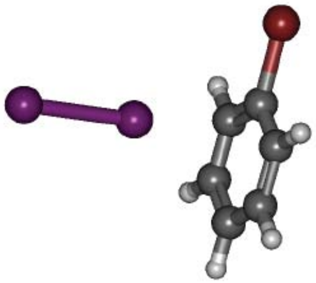
Heterodimers

We align the bromobenzene – I_2 complex, and then look at the correlations between Br and I atoms

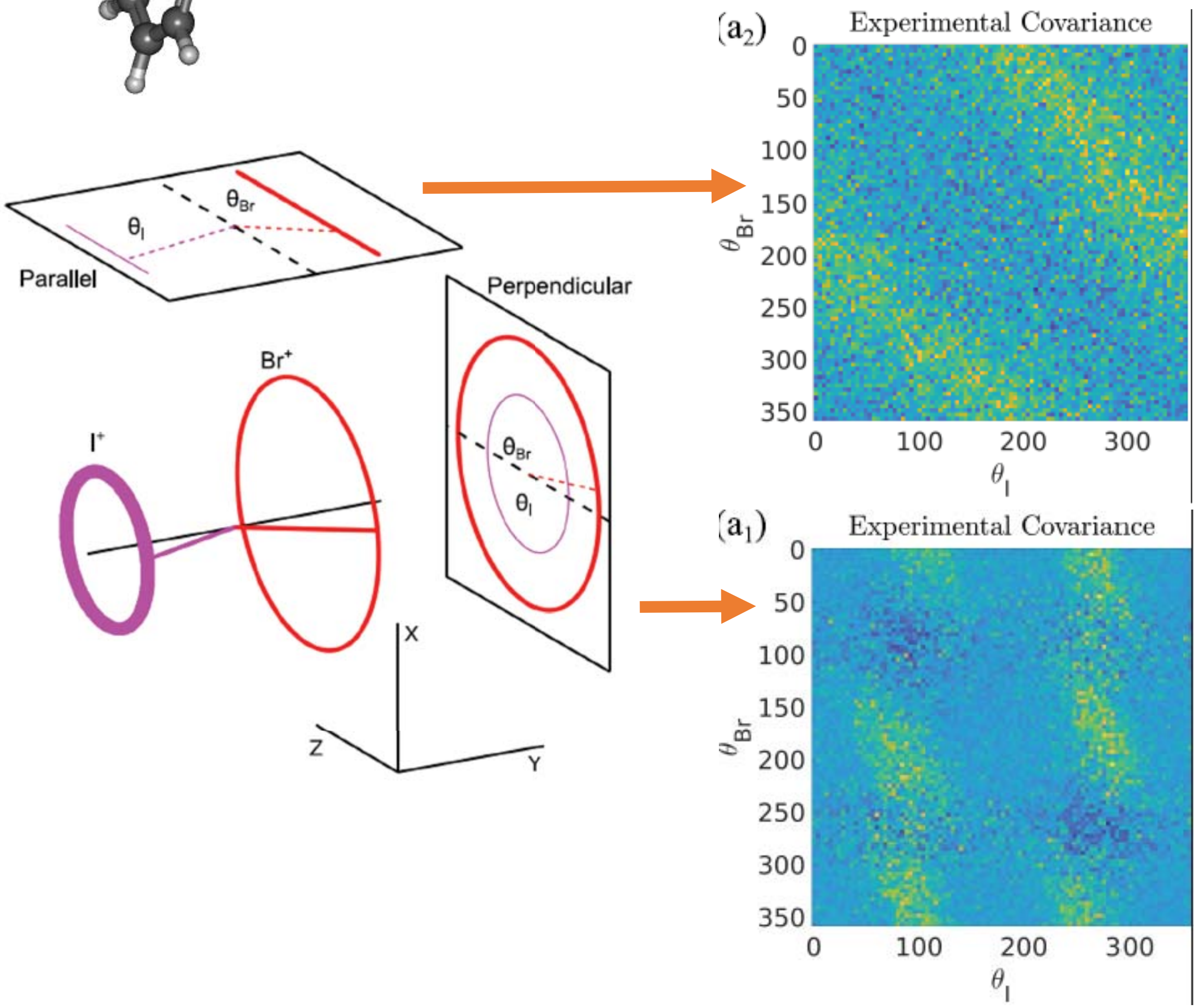


Model the complex as ‘two sticks’

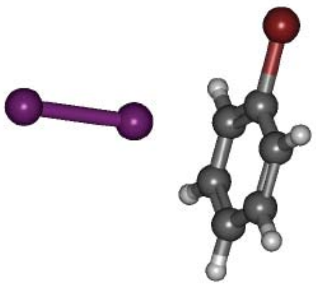
Heterodimers



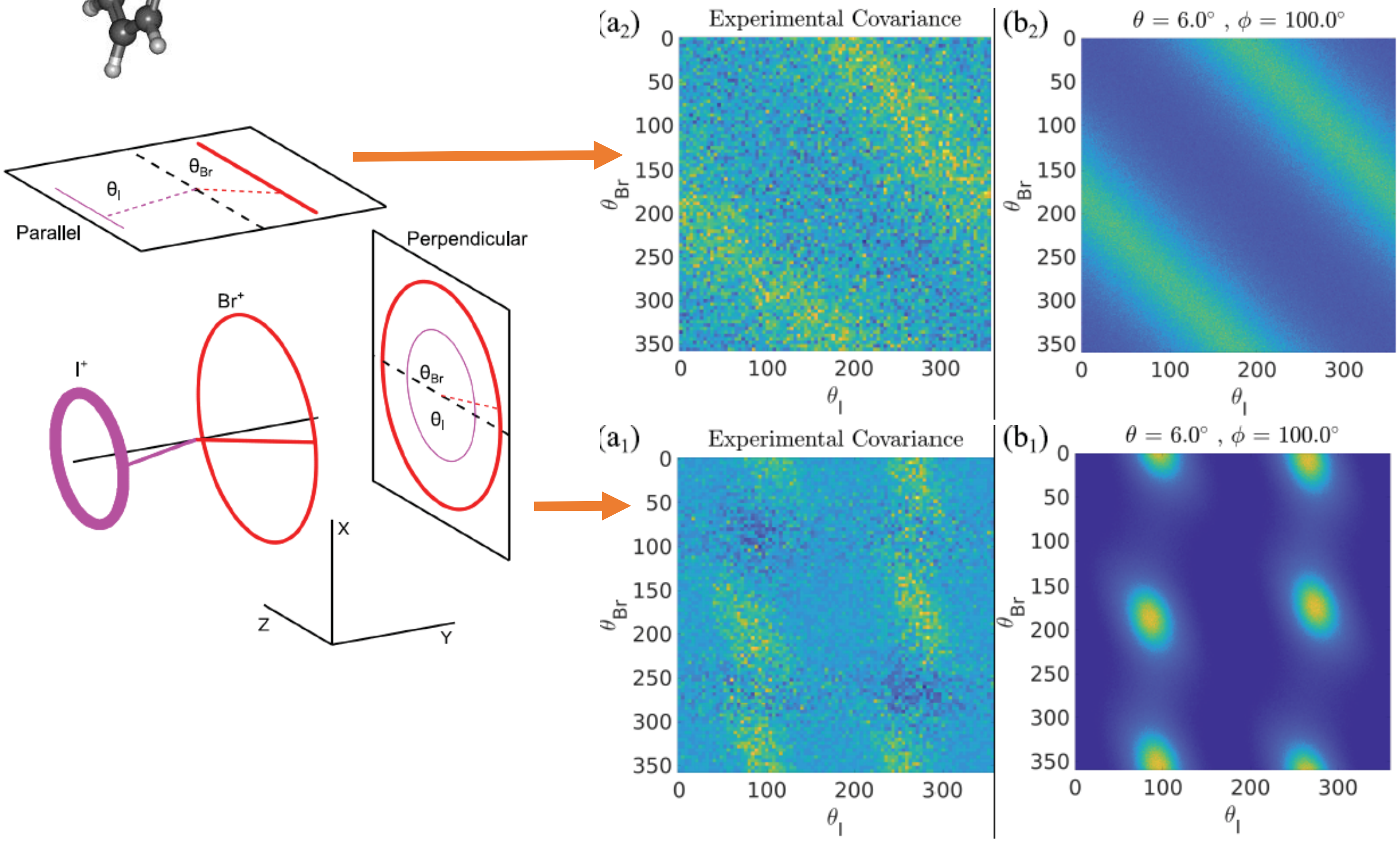
Different alignments give different projections



Heterodimers

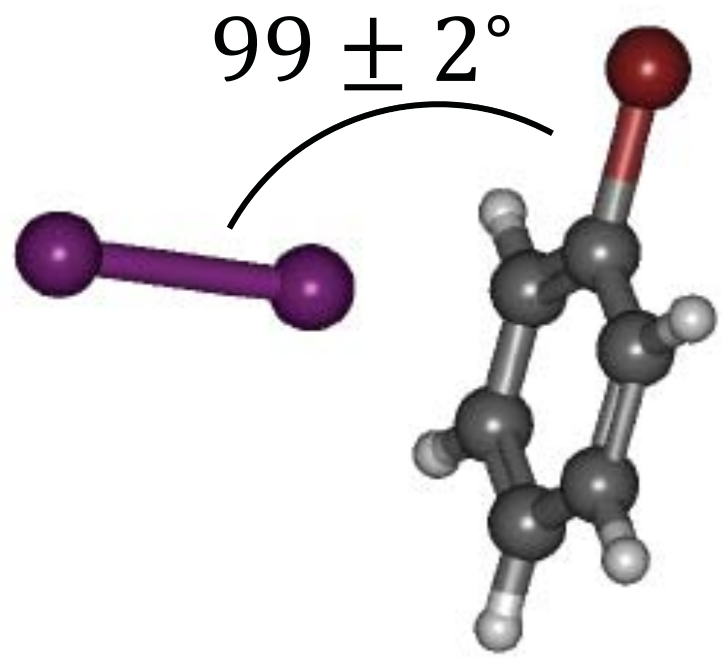


Simulations find the structure



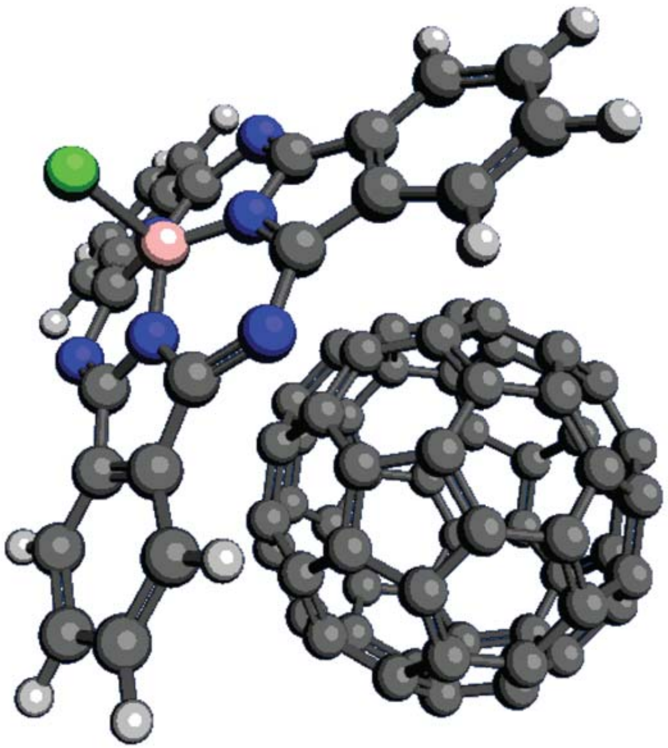
Heterodimers

We retrieve the angle of the I_2 molecule relative to the C – Br axis

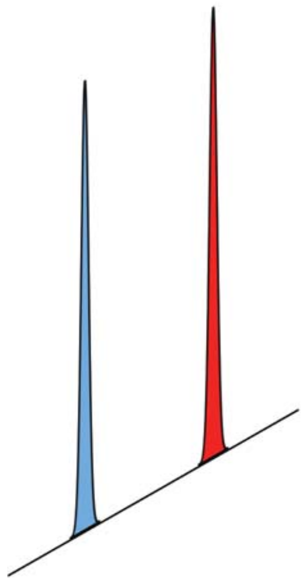


What next?

Go bigger



Measure dynamics



Acknowledgments

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