Theory of mixed-field orientation of linear molecules: Loss of adiabaticity

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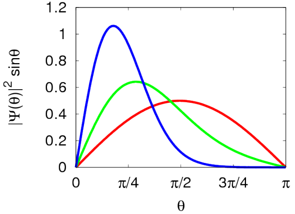
Some basics: Pendular states

- Static field: Orientation
- Laser field: Strong alignment
- Both: Strong alignment and orientation!!

$$H = BJ^2 - \mu E_S \cos\theta_S - \frac{I}{2\epsilon_0 c}\Delta\alpha\cos^2\theta$$

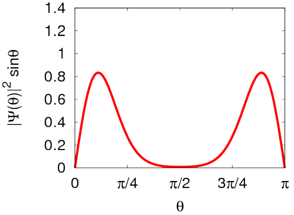


OCS: $\beta = 45^\circ$ ground state

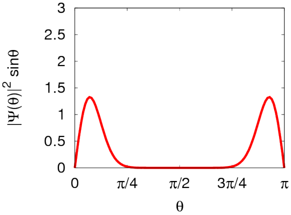
E_S [kVcm^{-1}]	I [Wcm^{-2}]	$\langle\cos\theta\rangle$	$\langle\cos^2\theta\rangle$
0.286	0	$5.6 \cdot 10^{-3}$	0.33
20	0	0.34	0.37
100	0	0.702	0.57
0	10^{11}	0	0.77
0	$5 \cdot 10^{11}$	0	0.90
0.286	10^{11}	0.33	0.77
0.286	$5 \cdot 10^{11}$	0.95	0.90

B. Friedrich and D. R. Herschbach, J. Chem. Phys. 111, 6157 (1999)

$I = 10^{11}$ Wcm^{-1}



$I = 5 \cdot 10^{11}$ Wcm^{-1}



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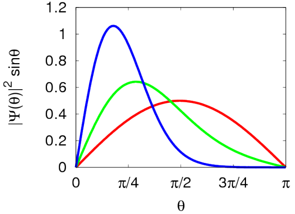

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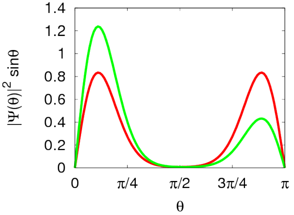

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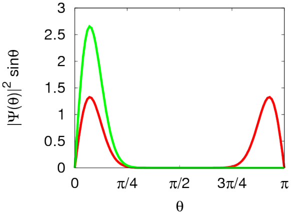
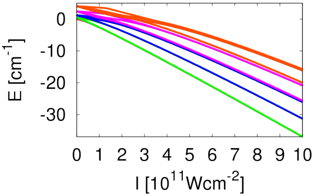
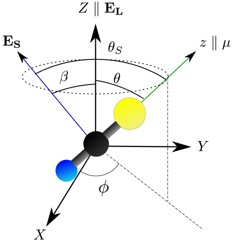
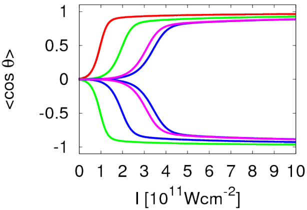


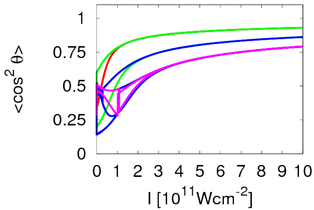
Characteristics of the system

$$H = BJ^2 - \mu E_S \cos\theta_S - \frac{I}{2\epsilon_0 c}\Delta\alpha\cos^2\theta$$









The experiment

2D projection of the density distribution on the screen of (JM) selected states 92%(00) and 8%(11).

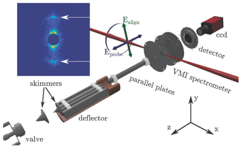
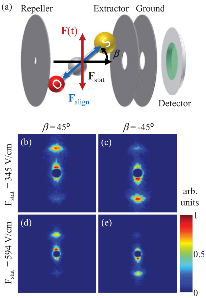


Fig. 1 Schematic of the experimental setup. The inset shows an S^+ ion image recorded when the molecules are aligned along the y-axis (t = 40.6 ps). The arrows indicate the S^+ + CO^+ Coulomb-explosion channel employed to determine the degree of alignment.

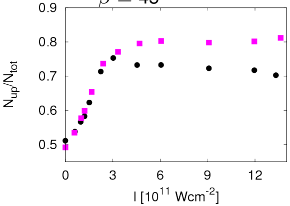


J. H. Nielsen et al, Phys. Chem. Chem. Phys **13**, 18971 (2011)
D. Dimitrovski et al, Phys. Rev. A **83**, 023405 (2011)

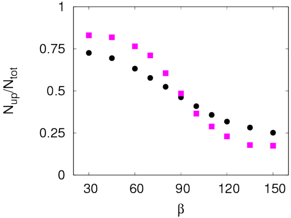
$\frac{N_{up}}{N_{tot}}$ is the ratio of ions detected in the upper half of the screen.

286 (●) and 571 Vcm^{-1} (□)

$\beta = 45°$



$I = 9.1 \cdot 10^{11}\ \mathrm{Wcm}^{-2}$



Reproducing the quantities in the experiment

With volume effect and population distribution

Projection of the density of the wavefunction on the detector.
The 2D screen spatial distribution of a state γ is given by

$$P^i_\gamma(y,z) = \frac{|\psi(\theta(y,z),\phi(y,z))|^2}{\sqrt{1-y^2-z^2}} A_i(y,z),$$

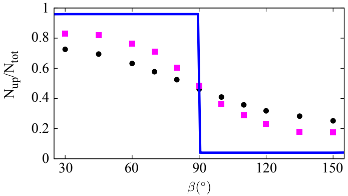
with $A_i(y,z)$ is the selectivity of the laser.

$$\begin{aligned} P^i_T(y,z) &= \sum_\gamma W_\gamma P^i_\gamma(y,z) \\ \frac{N_{\text{up}}}{N_{\text{tot}}} &= \frac{\int_{-\infty}^{\infty}\int_{z\geq 0} P_T(y,z)dydz}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P_T(y,z)dydz} \end{aligned}$$

Adiabatic approach of the experiment

Exp: 286 (•) and 571 Vcm^{-1} (□)

$I = 9.1 \cdot 10^{11}$ Wcm^{-2}



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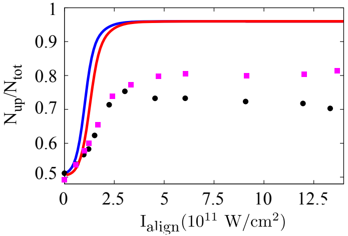

286 Vcm^{-1} and 571 Vcm^{-1}

Experimentally:

- The orientation changes smoothly with β.
- For different E_S the orientation varies.
- For a fixed β, the orientation does not increase monotically with I.

Adiabatically:

- For a fixed I, the orientation jumps abruptly for $\beta = 90°$ and constant for $20 \leq \beta \leq 160$.
- The orientation does not vary for different values of E_S.
- The orientation increases with increasing I.

We can not reproduce the experiment using the adiabatic approach.

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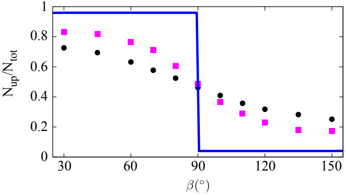
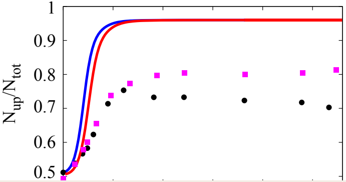


$\beta = 45^\circ$



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We can not reproduce the experiment using

But we knew it! We have proved that for asymmetric molecules is not adiabatic!

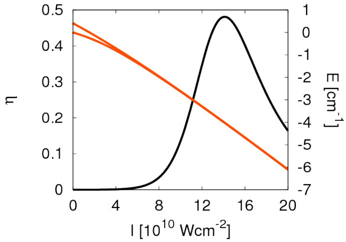
J.J. Omiste et al. Phys. Chem. Chem. Phys., 2011, **13**, 18815-18824

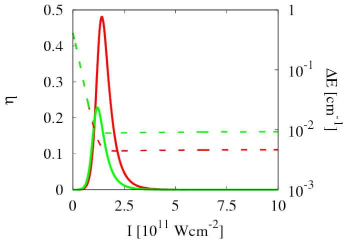
Why is the process not adiabatic?

Adiabaticity criteria:

$$\eta = \frac{\left| \left\langle i \left| \frac{\partial H}{\partial t} \right| j \right\rangle \right|}{|E_i - E_j|^2} = \begin{cases} \ll 1, & \text{adiabatic} \\ \gg 1, & \text{diabatic} \end{cases}$$

Formation of the doublets: First doublet. 286 Vcm^{-1} and 571 Vcm^{-1}





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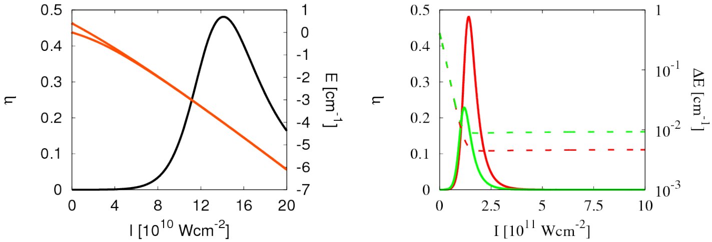


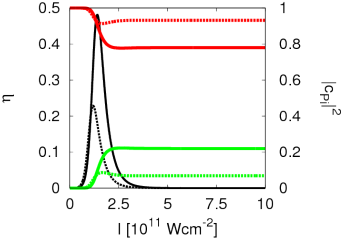
We need a time dependent treatment!!

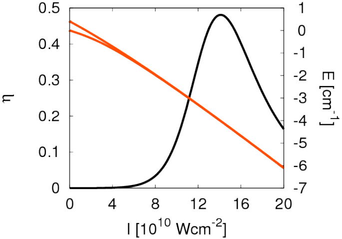
Transfer of population

Pulse: $I_0 = 10^{12}$ Wcm^{-2} and FWHM=10ns

η, Ground, First pendular states

Formation of the doublets: First doublet. 286 Vcm^{-1} (solid) and 571 Vcm^{-1} (dash)





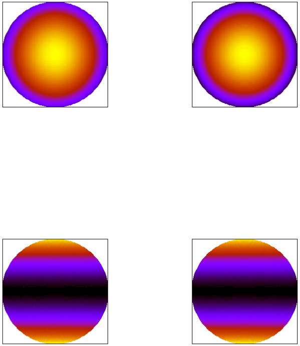
$$\Psi(\theta,\phi,t) = \sum_{i=0} c_{Pi}(t)\psi_{Pi,I}(\theta,\phi)$$

$\psi_{Pi,I}(\theta,\phi)$ is the i-th pendular state for an intensity I

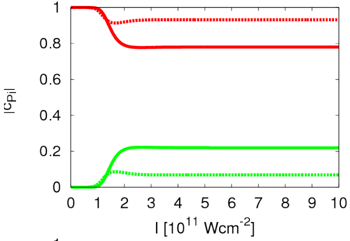
Evolution of the states

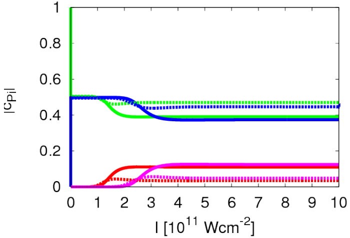
Pulse: $I_0 = 10^{12}$ Wcm^{-2} and FWHM=10ns

$E_S = 286$	571 Vcm^{-1}
Solid	Dash



Ground, First, Second, Third pendular states





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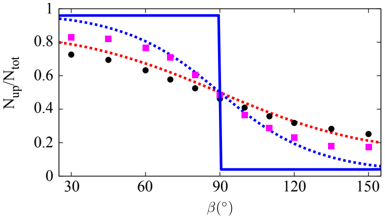

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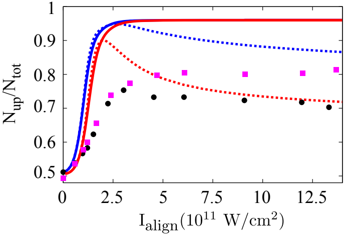

286 Vcm^{-1} and 571 Vcm^{-1}

- Smooth behavior of the orientation as a function of β
- For different values of E_S different values of the orientation.
- For a fixed value of β and certain E_S the orientation decreases as a function of I.

I [Wcm^{-2}]	E_S [Vcm^{-1}]	Exp.	Adiab.	Time
$6 \cdot 10^{11}$	286	0.73	0.96	0.83
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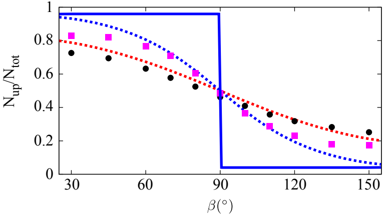

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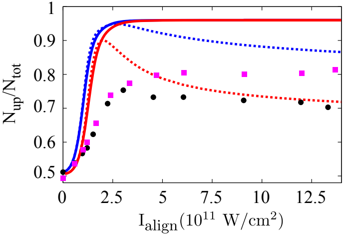

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Quantitative disagreement?!

Possible reasons for the disagreement

Spatial distribution and alignment profile of the alignment laser

Selectivity of the probe laser

Recoil approximation

Initial population

Influence of rovibrational states

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Is it possible to get an adiabatic orientation?

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- **Increasing the static field $\Rightarrow$ We increase the gap in energy in the doublets.**
- Increasing the FWHM of the alignment pulse.

$\sigma = 4.25$ ns and $I = 10^{12}$ Wcm^{-2}

Static field strength	$\langle\cos\theta\rangle$	$\langle\cos^2\theta\rangle$
Time: $E_S = 345$ V/cm	0.712	0.931
Adiabatic:	0.964	0.931
Time: $E_S = 594$ V/cm	0.901	0.931
Time: $E_S = 1000$ V/cm	0.959	0.931
Time: $E_S = 1500$ V/cm	0.964	0.931
Time: $E_S = 2000$ V/cm	0.964	0.931

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$E_S = 345$ Vcm^{-1} and $I = 10^{12}$ Wcm^{-2}

Pulse	$\langle \cos\theta \rangle$	$\langle \cos^2\theta \rangle$
$\sigma = 4.25$ ns	0.712	0.931
2σ	0.921	0.931
3σ	0.958	0.931
Adiabatic	0.964	0.931

Conclusions

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- Mixed fields orientation can not be described, in general, by adiabaticity approach.
- Time dependent approach is mandatory.
- A weak static field combined with a laser field is able to produce a strong orientation and aligment.
- We reproduce the smooth behavior of the orientation with β.
- The orientation depends on the static field applied.
- An adiabatic treatment is enough to describe alignment.

And now...

- Application to asymmetric tops.

Conclusions and outline

Done in colaboration with

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J. Küpper	Center for Free-Electron Laser Science, DESY, Hamburg
J. H. Nielsen	University of Aarhus
H. Stapelfeldt	University of Aarhus

Paper in preparation

THANKS FOR YOUR ATTENTION