Towards the transient orientation of linear molecules

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History : alignment and orientation in dilute gases

- **Static fields**
  - Quadrupole field and Hexapole field focusing: Stark effect used to select a rotational state $|J,M_J\rangle$ of a molecule from a thermal mixture of rotational states
    - Diatomic molecules: *Zeitschrift für Physics, 141 : 6 (1955)*
    - Symmetric top molecules: *JCP, 42 : 767 (1965)*
  - Brute Force orientation: strong static electric field to orientate molecules with a big dipole moment
    - *JCP, 93 : 4779 (1990)*

- **Laser fields**
  - Adiabatic alignment: intense laser electric field, pulse whose duration is much longer than the rotational period of the molecule
    - *JCP, 104 : 3 (1996)*
  - Diabatic alignment: femtosecond laser electric field pulse, duration smaller than the rotational period of the molecule, field-free alignment

- **Transient Orientation ?**
Outline

- Orientation with static fields
  - Orientation and alignment with laser fields
    \(\Rightarrow\) femtochemistry, interferometry, quantum information, atosecond pulses...
- Transient Orientation of linear molecules
  - Computations
  - Half-cycle pulses
  - Asymmetric femtosecond pulses
  - Perspectives, status of the AMO experiments
Orientation/Alignment : signification

\[ W_s = W_{el} + W_{vib} + W_{rot} \]

\[ |\Psi_s\rangle = |\Psi_{el}\rangle |\Psi_{vib}\rangle |\Psi_{rot}\rangle \]

For singlet molecules (\(\Lambda=0\))

\[ \Psi_{rot} = \langle \vec{R} | J, M \rangle = Y_J^M(\theta, \phi) \quad W_{rot} = B J(J+1) \]

Orientation :

\[ \vec{R} \cdot \vec{u}_z \quad R_e \cos \theta \]

Alignment :

\[ \left| \vec{R} \cdot \vec{u}_z \right|^2 \quad R_e^2 \cos^2 \theta \]
Graph of the Stark energy change $W_{J,M}(E^2)$

$$\vec{F} = -\text{grad}(W_{J,M})$$

$|J,M\rangle = |20,0\rangle$

$|J,M\rangle = |0,0\rangle$
Hexapole focusing

Used for symmetric top molecules

\[ |\Psi_s\rangle \propto |J,K,M\rangle \]

\[ \vec{F} \propto \frac{KM}{J(J+1)} \vec{r} \]

CH\textsubscript{3}I (iodomethane)
Interaction energy of a polar molecule with a strong static electric field

Brute force orientation

\[
W = -\mu E \cos \theta
\]

Classical picture: torque exerted on the molecule, alignment of the permanent dipole moment on the field

Possibility with symmetric top molecules, but also singlet molecules

Necessity of a very strong static field. Example: KCl, \( \mu_0 = 10.27 \text{ D} \), \( E_s \sim 30 \text{ kV/cm} \)

Also very small temperatures (supersonic molecular beams)

Supersonic jet: rotational cooling

\[
P(\{J,M\}) = e^{-BJ(J+1)/(kT)}
\]
Stereodynamics studies

Studies on the steric effect (modification of reactions depending on the geometry and the presence of different chemical groups in molecules)

Collisionnal studies, head versus tail preferential reactions

\[ K + CH_3I \rightarrow KI + CH_3 \]

Preferential reaction

\[ CH_3I \] (iodomethane)
Laser induced alignment

Strong static field replaced by a strong non-resonant laser field

\[ H_{\text{eff}} = -\frac{1}{2} \sum_{i,j=x,y,z} \alpha_{ij} E_i E_j \]

\[ H_{\text{eff}} = -\frac{1}{4} (\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \theta \, E_0^2 \]

\[ \Delta \alpha = 6 \text{ for } N_2 \]
Adiabatic alignment

**Condition of adiabaticity**

\[ \nu_{\text{rot}} (J) = \frac{BJ(J+1)}{h} \]

\[ T_p \quad T_{\text{rot}} (1) = \frac{1}{\nu_{\text{rot}} (1)} = \frac{\pi \hbar}{B} \]

Pendular states observation for symmetric top molecules


« Adiabatic » orientation : Strong laser field + static field

\[ H_{\text{eff}} = -\mu_0 \cdot E_s - \frac{1}{4} (\alpha_\perp - \alpha_//) \cos^2 \theta E_0^2 - \frac{1}{4} \alpha_// E_0^2 \]

CO ionization


![Diagram of CO ionization](image)

30 ps laser pulse

\[ \text{CO}^+ \rightarrow \text{O}^+ + \text{C}^+ + \text{C}^0 \]

Coulomb explosion

<table>
<thead>
<tr>
<th>Decay path</th>
<th>Energy released (eV)</th>
<th>Branching ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) (\text{CO}^+ \rightarrow \text{C}^+ + \text{O}^+)</td>
<td>1.2</td>
<td>11</td>
</tr>
<tr>
<td>(2) (\text{CO}^+ \rightarrow \text{C} + \text{O}^+)</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>(3) (\text{CO}^2+ \rightarrow \text{C}^+ + \text{O}^+)</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>(4) (\text{CO}^3+ \rightarrow \text{C}^2+ + \text{O}^+)</td>
<td>10</td>
<td>39</td>
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<tr>
<td>(5) (\text{CO}^3+ \rightarrow \text{C}^+ + \text{O}^{2+})</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>(6) (\text{CO}^4+ \rightarrow \text{C}^2+ + \text{O}^{2+})</td>
<td>20</td>
<td>3</td>
</tr>
</tbody>
</table>
Experimental observation: TOF spectroscopy

30 ps laser pulse

$E(t)$

Alignment?

Ion signal

Ion yield

$C^+$

$O^+$

$C^+$

$O^{++}$

$C^+$

$H_2O^+$
Detection ($N_2$)

- Laser pulse (fs)
- $E_C(t)$
- $E_y(t)$
- $E_x(t)$

Graph showing ion yield vs. time (ns) with aligned molecules and randomly aligned molecules.
Adiabatic alignment of Diiodine (I\textsubscript{2})

*JCP, 110 : 10235 (1999)*
Diabatic alignment

\[ H_{\text{eff}} = \frac{1}{4} (\alpha_\perp - \alpha_\parallel) \cos^2 \theta E_0^2 - \frac{1}{4} \alpha_\perp E_0^2 \]

Short Pulse → Impulsive Angular Kick

\[ \frac{dp}{dt} \propto - \sin 2\theta E_0^2 \hat{u}_\theta \]

Wavepacket excitation: revivals

\[ W_J = B J(J+1) \]

\[ \left| J_0, M_0 \right> \Rightarrow \Psi(t) = \sum_{J,M} c_J e^{\frac{W_J t}{\hbar}} \left| J, M \right> \]

Raman excitation of rotationnal states

<\hat{J}>
Diabatic alignment


Enhanced ionization
Half-Revival
Revival

Ratio = \frac{A_2 - A_1}{A_1 + A_2}
Non-Zero Temperature: \( P_{\{J,M\}} \sim \exp \left[ -J(J+1)B/k_B T \right] \)

At high \( T \), high Bohr frequencies, Centrifugal distortion

\[ \rightarrow \text{Reduced Net Alignment} \]
Applications

- Preferential dissociation, Fragments selection
- Control: pulse shaping
- 3D alignment
- Lithography: Focusing and orienting molecules
- Orientation of molecules and quantum information processing
- Rotational temperature measurement
- Attosecond pulses, rescattering experiments
- Tomographic imaging of molecular orbitals
Orientation of molecules and quantum information processing

Stark addressing of individual trapped polar oriented molecules (qubit), interaction between the qubits driven by the dipole–dipole interaction

D. DeMille, PRL 88, 067901
Rotational temperature analysis


Fourier analysis

Amplitude of the states after excitation

\[ P(J, M) = S(J) e^{-BJ(J+1)/(\hbar T)} \]
Attosecond pulses, rescattering experiments

Attosecond pulses from High Harmonic generation

*Science, 292: 1689 (2001)*

Symmetry properties ⇒ odd harmonics for atoms

Even harmonics for non centrosymmetric molecules
Tomographic imaging of molecular orbitals

Reconstructed of N2 in its ground state HOMO (highest occupied molecular orbital)
Experimental HHG (High Harmonic generation) spectrum (dependence with alignment)
Intermediate conclusion

- Orientation in a static field
- Adiabatic alignment
- Diabatic (field-free) alignment
- Field-free orientation
Theory

Interaction energy of a molecule with an electric field

\[ H = H^{(0)} + V \]

\[ = H^{(0)} - \vec{\mu} \cdot \vec{E} - \sum_{\alpha, \beta = x, y, z} \frac{1}{3} \Theta_{\alpha\beta} \frac{\partial E^\beta}{\partial \alpha} - \vec{m} \cdot \vec{H} - ... \]

Dipolar moment operator

\[ \vec{\mu} = \sum_i e_i \vec{r}_i = \sum_{\alpha = x, y, z} \mu_\alpha = \sum_{\alpha} \sum_i e_i r_{i\alpha} \]

Quadrupolar moment operator

\[ \Theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i \left( 3r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta} \right) \]

Dipolar approximation: size of the molecule \( << \lambda \)
**Interaction energy of a molecule with a static electric field**

\[ H = H^{(0)} - \vec{\mu} \cdot \vec{E} \]

\[ \vec{\mu} = \sum_{i=x,y,z} \mu_i = \sum_i \sum_n e_n r_{ni} \]

Result from the perturbation theory, for a given state \( \Psi \):

\[ W = \langle \Psi | H | \Psi \rangle = W^{(0)} - \mu_i^{(0)} E_i - \frac{1}{2} \alpha_{ij} E_i E_j - \frac{1}{6} \beta_{ijk} E_i E_j E_k - \ldots \]

**Linear Polarisability** : \( \alpha_{ij} \)

**Diatominc molecules** :

\[ -\frac{1}{2} \alpha_{\parallel} E_{\parallel}^2 - \frac{1}{2} \alpha_{\perp} E_{\perp}^2 \]

**First Hyperpolarisability** : \( \beta_{ijk} \)
Interaction energy of a molecule with a periodic electric field

\[ H = H^{(0)} - \mu \cdot \vec{E}(t) \]

\[ \mu = \sum_{i=x,y,z} \mu_i = \sum_{i} \sum_{n} e_n r_{ni} \]

\[ W = \langle \Psi | H | \Psi \rangle = W^{(0)} - \mu^{(0)} E_i - \frac{1}{2} \alpha_{ij} E_i E_j - \frac{1}{6} \beta_{ijk} E_i E_j E_k - \ldots \]

“Explanation” : Floquet theorem \(\Rightarrow\) wavefunction expanded in Fourier series

\[ \Psi_s = e^{-iW_s t/\hbar} \sum_{n=\infty}^{\infty} C_n e^{-i\alpha t} \]

sum of wavefunctions \( C_n e^{-i(W_s /\hbar + n\omega) t} \)

with \( W_s = \langle \Psi_s | - \mu \cdot \vec{E} | \Psi_s \rangle \)

Very weak interaction \(\Rightarrow\) \( C_0 \) only non negligible term \(\Rightarrow\) Possibility to define one energy

\[ W'_{s} = W_s \quad \Psi_s = e^{-iW_s t/\hbar} \Phi_s = e^{-iW_s t/\hbar} C_0 \]

Time independent Schrodinger equation, possibility to apply time independent perturbation theory to these wavefunctions
Field–free orientation of molecules

Interaction energy of a molecule with one periodic electric field

\[
H_{\text{eff}} = H^{(0)} - \mu_0 E_i \left(1 + \frac{1}{2} \alpha_j E_i E_j - \frac{1}{6} \beta_{ijk} E_i E_j E_k \right) + \ldots
\]

⇒ Asymmetric electric field necessary, 2 possibilities:

- "Half-Cycle Pulse" (HCP)

\[\text{Cos}(\omega t) + \text{Cos}(2\omega t)\]
Computations

1) Semi-analytical solutions: impulsive limit
2) Numerical solutions of the TDSE (Time dependent Schrödinger equation)

\[ i\hbar \frac{\partial \Psi(t)}{\partial t} = H(t)\Psi(t) \]

Resolution in the basis of the rotational states

Initially \[ |J, M\rangle \]

\[ P(|J,M\rangle) = e^{-BJ(J+1)/(kT)} \]

\[ \Psi(t) = \sum c_{J',M'}(t)|J', M'\rangle \]

\[ i\hbar \dot{c}_{J',M'} = \sum_{J'',M''} c_{J',M'} \langle J', M'|H(t)|J'', M''\rangle \]
Impulsive limit

\[ \Psi(t) = U(t_0, t)\Psi(t_0) \]

\[ H = H_0 \implies U(t, t_0) = e^{-i \frac{H_0 (t-t_0)}{\hbar}} \]

\[ U(t, t_0) = e^{-i \frac{1}{\hbar} \int_{t_0}^{t} H_0 dt'} \]

Impulsive limit approximation : case of a time-dependent Hamiltonian

\[ U(t, t_0) \approx e^{-i \frac{1}{\hbar} \int_{t_0}^{t} H(t') dt'} \]

Our case : \( T_p \gg T_{rot} = \frac{\pi \hbar}{B} \)

Our case : equivalent to neglect the rotation of the molecules during the interaction

Momentum kick

\[ U(t, t_0) \approx e^{-i \frac{1}{\hbar} \left( -\mu_0 \cos \theta \int_{t_0}^{t} E(t') dt' - \frac{\Delta \alpha}{2} \cos^2 \theta \int_{t_0}^{t} E^2(t') dt' + \ldots \right)} \]
Transient Field-Free Orientation of Polar Molecules

**Half-Cycle Pulse**

\[ H(t) = -\mu_0 E(t) \cos\theta \]

- **E(t)**
- **J=0**
- **J=1**
- **J=2**
- **J=3**
- **J=4**
- **J=5**

**HCP**

- 150kV/cm
- \( \Delta t = 0.5 \text{ ps} \)

**Half Cycle Pulse**

- **Dephasing**
- **Rephasing**
HBr  $T = 2K$

$\text{Cos}(\theta)$

-1 0 1 2 3 4 5

Delay (psec)

150kV/cm

300kV/cm

150kV/cm + 800 nm
HCP generation

$E(t) + HV (50 \text{ kV})$

$100 \text{ fs pulse}$

$150 \text{kV/cm}$

$\Delta t = 0.5 \text{ ps}$
Experiment

Ex: Hydrogen Bromide (HBr)  
$\mu_0 \approx 0.8 \text{ D}$

Lasers (780 nm)  
HCP
Difficulties

- Synchronization (delay stage)
- Space overlap
- Stabilization (intensities, chirp)
- Calibration of an intense HCP
- Temperature
Alignment : $N_2$

**Linear pump pulse**  |  **Circular probe pulse**

**Enhanced ionization**

**Revival**

**Ratio**

\[
\text{Ratio} = \frac{N_2 - N_1}{N_1 + N_2}
\]
\[ \Delta \alpha \approx 1.5 \text{ (a. u.)} \] and \[ T_r \approx 15 \text{ K} \]

Strong dependence of the degree of orientation with the temperature: we hope to get better!
Orientation with two overlapping femtosecond pulses

\[ E(t) \propto \cos(\omega t) + \cos(2\omega t) \]

Promising: possibility to orientate molecules without the need of any dipole moment

Carbon monoxide (CO) \[ \mu_0 \approx 0.12 \text{ D} \]

Parity of a \( |J,M\rangle \) state is \((-1)^J\)

\[ \Rightarrow \text{Even and odd } J \text{ states population necessary} \]

\[ |\Psi(-\vec{R})|^2 \neq |\Psi(\vec{R})|^2 \]

Excitation of even rotational states

\[ \langle J \rangle \]
Orientation with two overlapping femtosecond pulses

\[ H_{\text{eff}} = \frac{1}{2} \alpha_{ij} E_i E_j - \frac{1}{6} \beta_{ijk} E_i E_j E_k \]

\[ H_{\text{eff}} = -\frac{1}{4} (E_{\omega}^2 + E_{2\omega}^2) (\Delta \alpha \cos^2 \theta) - \frac{1}{12} E_{\omega}^2 E_{2\omega} (\Delta \beta \cos^3 \theta + \beta_{\perp} \cos \theta) \]

\[ \Delta \beta = \beta_{\parallel} - \beta_{\perp} \]

\[ \frac{\beta_{\perp}}{3} = \beta_{xx} = \beta_{xx} = \beta_{yy} = \beta_{yy} = \beta_{yy} \]

\[ \beta_{\parallel} = \beta_{zz} \]

Experimental difficulty: Problems of ionization

Other problem:
Strong alignment of the molecules (orientation messed up by the alignment)

Possibility to try HBr (polarisability anisotropy 3 times smaller than for CO)
I = 2.2 \times 10^{14} \text{ W/cm}^2 \text{ in both pump beams}
Computations

CO

HBr

Very low temperatures necessary!
Conclusion

- Orientation of molecules with electric fields
  
  Stereodynamics studies, fragments selection...
  
  but not yet field-free oriented molecules
  
  Important for recollision experiments, tomographic imaging

- Experimental difficulties with the two overlapping femtosecond pulses (temperature, alignment…)

- Half-cycle pulse?
Ultrafast Laser / Atomic Physics group

Pr. Robert R. Jones
Dan Pinkham
Xiangdong Zhang
Mary Kutteruf
Brett Sickmiller
Kelsie Betsch
Three-dimensional molecular orientation with combined electrostatic and elliptically polarized laser fields

PHYSICAL REVIEW A 72, 063401 2005
Haruka Tanji, Shinichirou Minemoto, and Hirofumi Sakai*

Experimental Observation of Revival Structures in Picosecond Laser Induced Alignment of I₂
F. Rosca-Pruna and M. J. J. Vrakking

Controlling the Orientation of Polar Molecules with Combined Electrostatic and Pulsed, Nonresonant Laser Fields
Hirofumi Sakai, * Shinichirou Minemoto, Hiroshi Nanjo, Haruka Tanji, and Takayuki Suzuki

Photodissociation of oriented HXeI molecules in the gas phase