Theoretical studies on field-induced orientation of molecules

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Outlook

- General remarks

- Adiabatic regime \(^a\)
  - Orientation by Combined static and nonresonant fields
  - Orientation through two-color laser field (hyperpolarizability)

- Nonadiabatic regime (∆ field-free conditions)
  - Combined static and nonresonant fields
  - Multicolor laser fields (µ0 and α-contributions)

\(^a\)adiabatic: field turned on/off slowly compared with rotational periods
General remarks

Definitions

- **Alignment** (last talk):
  - angular distribution (for prolate) peaks at $\theta = 0$ and $\theta = \pi$
  - axial anisotropy like double-headed arrow $\uparrow \downarrow$ (symmetric potential)
  - quantity: $\langle \cos^2 \theta \rangle$

- **Orientation**:
  - distribution peaks at $\theta = 0$ or $\theta = \pi$
  - axial anisotropy like single-headed arrow $\uparrow$ (asymmetric potential)
  - quantity: $\langle \cos \theta \rangle$

Nonadiabatic regime

- $\tau \lesssim \hbar / B$
- same theoretical methods as for nonadiabatic alignment (Time-dependent Schrödinger equation)
Orientation by combined static and nonresonant fields

B. Friedrich, D. Herschbach, JCP 111, 6157 (1999); JPC A 103, 10280 (1999)

- polar molecules in strong uniform fields $\Rightarrow$ oriented pendular states
- nonresonant plane-polarized laser field $\Rightarrow$ aligned pendular states

$\rightarrow$ Combination: enhanced orientation

- time averaged Hamiltonian:
  \[ \hat{H} = B \hat{J}^2 + V_{\mu_0}(\theta_s) + V_\alpha(\theta_L) \]
  \[ \theta_s = \angle(z\text{-axis, static field}) \]
  \[ \theta_L = \angle(z\text{-axis, laser-field}) \]
Static and nonresonant fields – cont.

• if $\vec{\varepsilon}_s \parallel \vec{\varepsilon}_L$:
  
  – enhanced hybridization of $J$-states
  
  – aligned pendular states: nearly degenerated tunneling pairs in prolate case
    
    $\rightarrow$ pseudo-first-order Stark-Effect for combined fields

• if $\vec{\varepsilon}_s$ not $\parallel \vec{\varepsilon}_L$:
  
  $M$-states are also hybridized $\Rightarrow$ no good quantum number

• example: ICl ($B = 0.114\text{cm}^{-1}, \mu_0 = 1.24\text{D}, \ \Delta \alpha = 9\text{Å}^3$), $\varepsilon_s = 30\ \text{kV/cm}, \ I_L = 10^{12}\text{W/cm}^2$
  
  ($\omega \propto \mu_0 \varepsilon_s / B$, $\Delta \omega = c^2$)

energy splitting and orientation for $\tilde{J}, \tilde{M} = 0, 0(1, 0)$

(solid,(dashed))
Adiabatic orientation through hyperpolarizability

T. Kanai, H. Sakai, JCP 115, 5492 (2001)

• asymmetric potential through nonresonant, two-color laser field \( (\delta = 0) \):
\[
\varepsilon(t) = \varepsilon_0(t) [\cos \omega t + \gamma \cos (2\omega t + \phi)]
\]

• combine \( \alpha \)- and \( \beta \)-interaction

• averaging over \( \tau_{\text{pulse}} \): \( \hat{H}_{\text{hyp}} \) survives if exactly \( \omega \) and \( 2\omega \) were chosen (becomes maximal for \( \gamma = 1, \phi = 0 \)):
\[
\overline{\hat{H}_{\text{hyp}}} = -\frac{3}{8} \beta_{\perp} \varepsilon_0^3 \cos \theta - \frac{1}{8} (\beta_{\parallel} - 3\beta_{\perp}) \varepsilon_0^3 \cos^3 \theta
\]

• Schrödinger equation with time averaged Hamiltonian:
\[
\left[ \frac{d}{dz} \left[ (1 - z^2) \frac{d}{dz} \right] - \frac{M^2}{(1-z^2)} + \lambda \hat{j},M + a_1 z + c^2 z^2 + a_3 z^3 \right] S_{\hat{j},M} = 0
\]

“generalized spheroidal WF”

\[
z = \cos \theta \quad a_1 = \frac{3\beta_{\perp} \varepsilon_0^3}{8B}, \quad a_3 = \frac{(\beta_{\parallel} - 3\beta_{\perp}) \varepsilon_0^3}{8B}
\]
Another point of view

- General state of diatomic molecule excited by laser field given by superposition of different $v$'s and $J$'s:
  \[
  \Psi(Q, \theta) = \sum_{v,J} c_{v,J} \chi_v(Q) Y_J(\theta)
  \]

- Angular distribution by integrating over nuclear coordinate $Q$ taking into account orthogonality of vibrational functions $\chi_v(Q)$:
  \[
  w(\theta) = \int |\Psi(Q, \theta)|^2 dQ = \sum_v \sum_{J,J'} c^*_{v,J} c_{v,J'} Y^*_J(\theta) Y_{J'}(\theta)
  \]

  → if for given $v$: $J, J'$ with same parity ⇒ no asymmetry ⇒ no orientation

  → necessary for orientation: $J, J'$ with different parity for given $v$ (even and odd)

\[ \varepsilon(t) = \varepsilon_0(t) [\cos \omega t + \gamma \cos (2\omega t + \phi)] \]

For given \( v \): \( J \) even and odd => symmetry breaking orientation possible.
• **Example**: FCN \((B = 0.4 \text{cm}^{-1})\), Gaussian pulse \((5 \text{ ns}, \leq 1.4 \cdot 10^{12} \text{W/cm}^2)\)

• \(a_1 = c^2 = a_3 = 0\) (low-field limit): spherical harmonics

• \(a_1 = a_3 = 0, c^2 \neq 0\): “spheroidal WF”

\[\langle\langle \cos^2 \theta \rangle\rangle \text{ and } \langle\langle \cos \theta \rangle\rangle \text{ from Hellman-Feynman theorem}\]
Nonadiabatic orientation of molecules

Time dependent alignment in combined fields (static + nonres. laser)

- important: envelope function $g(t)$ of $\varepsilon_L(t)$
- example: KCl, $\varepsilon_s = 730$ V/cm, $I_L = 10^{12}$ W/cm²
- result: wave packet behavior for $\sigma < \hbar/B$

orientation: solid line; alignment: dotted line

$\tau = 2(\ln 2)^{1/2}\sigma$
**Multifrequency IR laser orientation**

### Numerical simulations for HCN

Dion, Bandrauk, Atabek, Keller, Umeda, Fujimura, CPL 302, 215 (1999)

- similar approach as for Hyperpolarizability
- resonant, two-color laser field ($\delta = 0$):
  \[
  \varepsilon(t) = \varepsilon_0(t) \left[ \cos \omega t + \gamma \cos (2\omega t + \phi) \right]
  \]
- combine $\mu_0$- and $\alpha$-interaction:

  \[
  J_{init} = 0 \xrightarrow{\mu_0} \text{odd } J's \\
  J_{init} = 0 \xrightarrow{\alpha} \text{even } J's
  \]

  $\Rightarrow$ symmetry breaking $\Rightarrow$ orientation

- $\tau_p = 1.7$ ps, $2\omega = \omega_{CH}$, $I_L \approx 10^{13}$ W/cm$^2$
  
  (IP(HCN)=13.6 eV)
IR laser orientation — schematic view

\[ \mu_0 \]

\[ \mu_0 + \alpha \]

\[ \Delta J = \pm 1 \]

\[ \Delta J = 0, (\pm 2) \]

for given \( v \): J even or odd

\( \Rightarrow \) no asymmetry

for given \( v \): J even and odd

\( \Rightarrow \) symmetry breaking orientation possible
Multifrequency orientation – cont.

Results for HCN

- Quantity for orientation: $P_0^0 - P_\pi^\pi$
  \[= \left[ \int_0^{\pi/2} - \int_{\pi/2}^{\pi} \right] |\Psi(\theta, t)|^2 \sin \theta d\theta\]
- Starting from $v = 0, J = M = 0$
- No orientation during the pulse $(0 < t < 1.7 \text{ps})$
- Maximum around 3 ps
- Half angles $\theta_{1/2}^{(0)}$ and $\theta_{1/2}^{(\pi)}$ for upper and lower halfspace out of phase
Rovibrational distribution for HCN after pulse is turned off

Disentangling of $\mu_0$ and $\alpha$-contributions:

- a) $\mu_0$-interaction only
- b) $\alpha$-interaction only
- c) both
Optimal control

K. Hoki, Y. Fujimura, CPL 267, 187 (2001)

- idea: designing laser pulse to obtain optimal alignment and orientation
- applied to CO ($\omega_{res} = 1700\text{cm}^{-1}$)

\[ \rightarrow \text{optimal field consists of 2 sequences of odd and even numbers of } \omega = 850\text{cm}^{-1} = \omega_{res}/2 \]

\[ \Rightarrow \text{parity condition fulfilled (one- and two-photon processes)} \]