CENTRE NATIONAL
DE LA RECHERCHE
SCIENTIFIQUE

DYNAMIQUE MOLECULAIRE QUANTIQUE: DE LA SIMULATION AU CONTRÔLE

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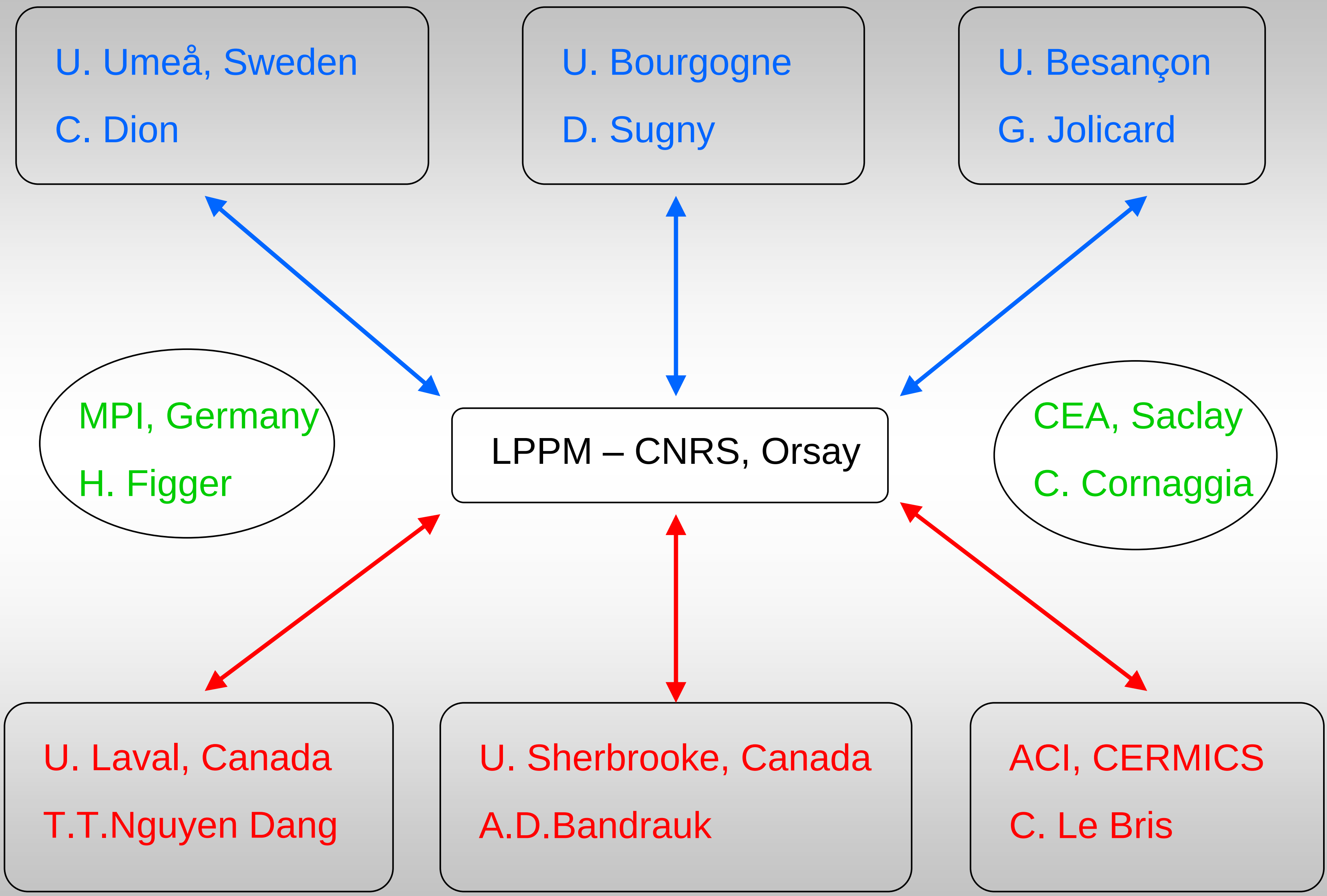
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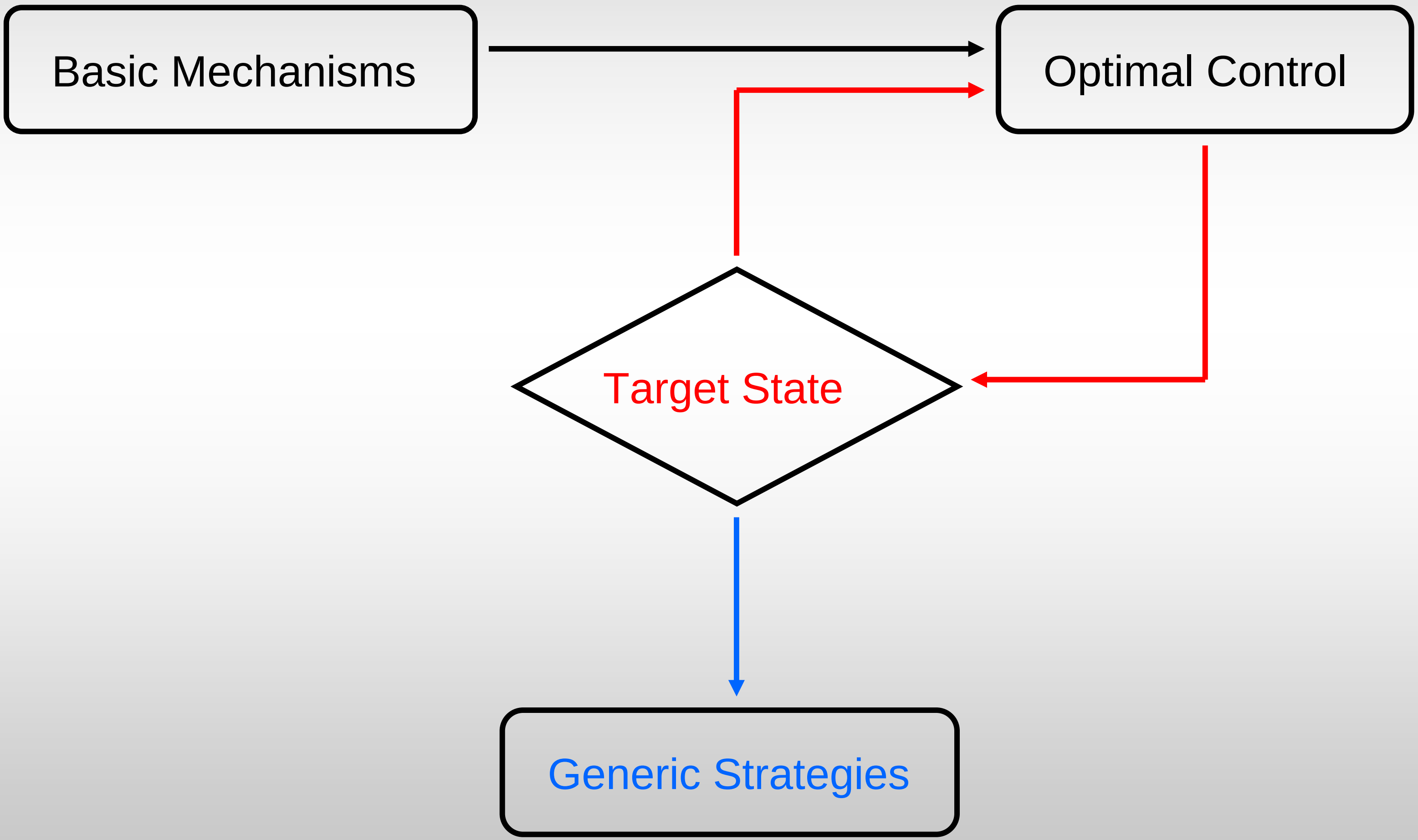
LASER CONTROL STRATEGIES



BASIC MECHANISMS

Internal degrees of freedom: Nuclear vibrational dynamics

High frequency regime: $\omega_{field} >> \omega_{mol}$

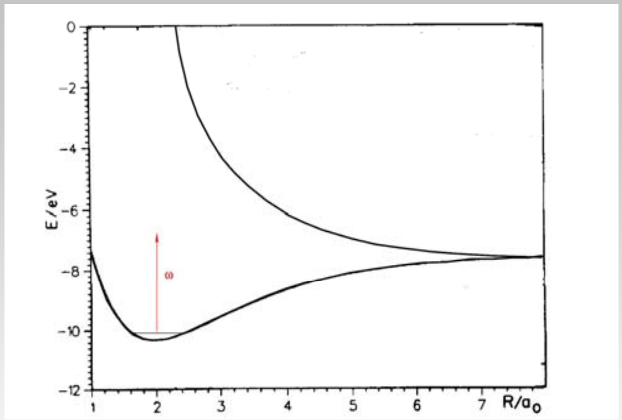
Time independent picture

ATD*, BS*, VT*

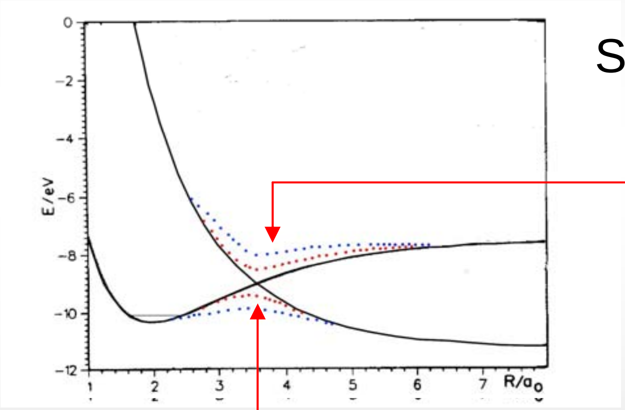
Experimental verification

* Above Threshold Dissociation, Bond Softening, Vibrational Trapping

Field-free potentials



Field-dressed potentials



Strong field mechanisms:

Vibrational Trapping

Bond Softening

Diagonalization of the radiative coupling:

$$\det \begin{vmatrix} V_g + h\omega - V_\pm(R) & \frac{1}{2}\mu E_0 \\ \frac{1}{2}\mu E_0 & V_u - V_\pm(R) \end{vmatrix} = 0$$

COUPLED EQUATIONS IN FLOQUET FORMALISM

$$H_{cl}^L = H_{el}^0 + T_N + eE_0\cos(\omega t)\boldsymbol{\epsilon}\cdot\mathbf{r}$$

$$H_{el}^0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, R) \quad T_N = -\frac{\hbar^2}{2\mathcal{M}}\frac{\partial^2}{\partial R^2}.$$

$$\Omega^L(\mathbf{r}, R, t) = \Psi_1(R,t)\Xi_1(\mathbf{r}, R) + \Psi_2(R,t)\Xi_2(\mathbf{r}, R)$$

$$\begin{aligned}\Xi_1(\mathbf{r}, R) &= 1s\sigma_g(\mathbf{r}, R),\\ \Xi_2(\mathbf{r}, R) &= 2p\sigma_u(\mathbf{r}, R).\end{aligned}$$

Floquet ansatz

$$\begin{pmatrix}\Psi_1(R,t)\\ \Psi_2(R,t)\end{pmatrix} = e^{-i\frac{Et}{\hbar}}\begin{pmatrix}\Phi_1(R,t)\\ \Phi_2(R,t)\end{pmatrix}$$

$$i\hbar\frac{\partial\Phi_1(R,t)}{\partial t} = [T_N + \epsilon_g(R) - E]\Phi_1(R,t) - \frac{E_0}{2}\mu_{gu}(R)\cos(\omega t)\Phi_2(R,t)$$

$$i\hbar\frac{\partial\Phi_2(R,t)}{\partial t} = [T_N + \epsilon_u(R) - E]\Phi_2(R,t) - \frac{E_0}{2}\mu_{ug}(R)\cos\omega t)\Phi_1(R,t)$$

$$\mu_{gu}(R) = \langle\Xi_1(\mathbf{r}, R)| - ez|\Xi_2(\mathbf{r}, R)\rangle_{\mathbf{r}} = \mu_{ug}(R)$$

Integration over r

Time periodicity

$$\Phi_k(R,t) = \sum_{-\infty}^{+\infty} e^{in\omega t}\Psi_{k,n}(R)$$

$$[T_N + \epsilon_g(R) + n\hbar\omega]\Psi_{1,n}(R) - \frac{E_0}{2}\mu_{gu}(R)[\Psi_{2,n-1}(R) + \Psi_{2,n+1}(R)] = E\Psi_{1,n}(R),$$

$$[T_N + \epsilon_u(R) + n\hbar\omega]\Psi_{2,n}(R) - \frac{E_0}{2}\mu_{ug}(R)[\Psi_{1,n-1}(R) + \Psi_{1,n+1}(R)] = E\Psi_{2,n}(R).$$

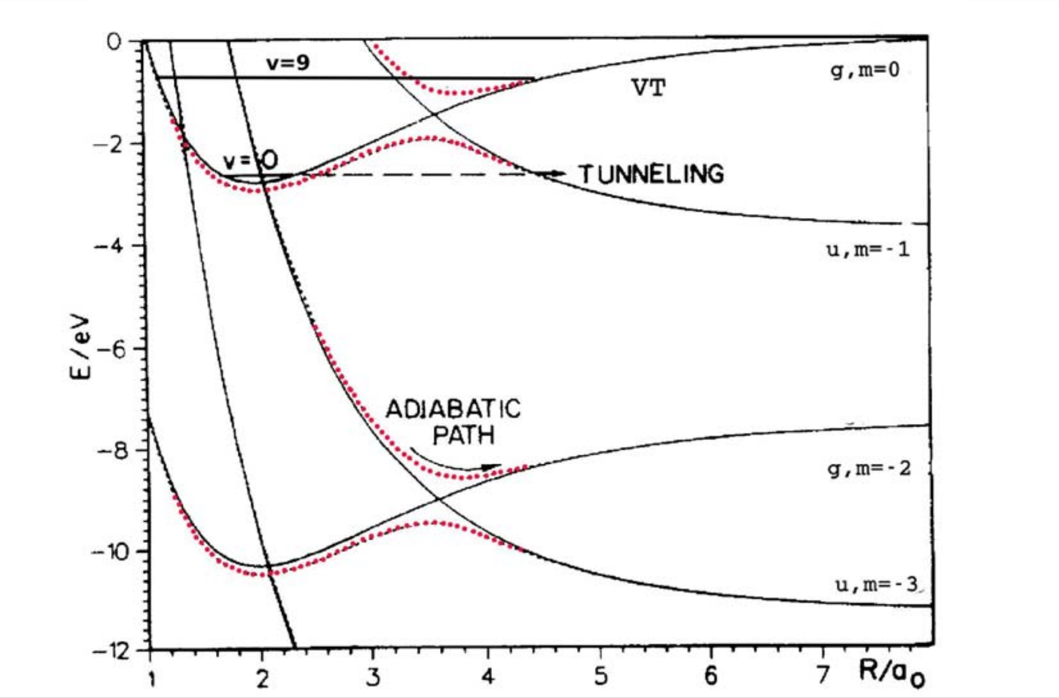
Integration over t

MULTI-PHOTON ABOVE THRESHOLD DISSOCIATION

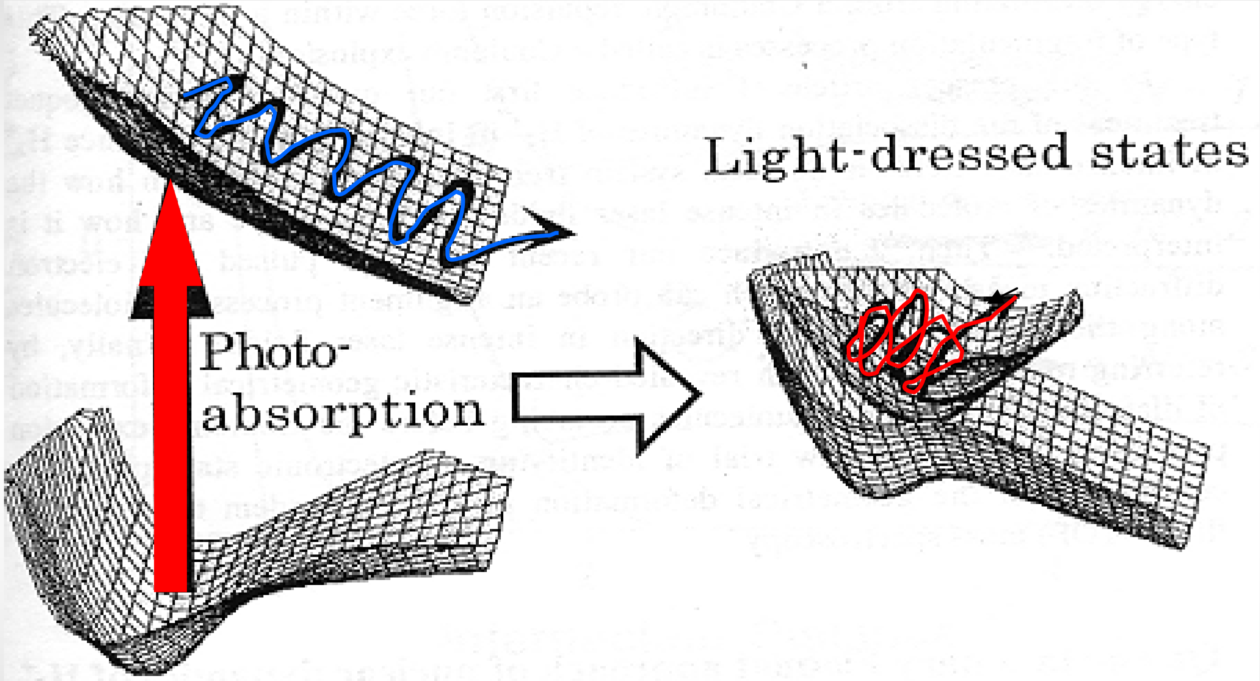
A. Giusti-Suzor, X. He, O. Atabek and F.H. Mies, Phys. Rev. Lett., ***64****, 515 (1990);*

P. Bucksbaum, A. Zavriyev, H.G. Muller and D.W. Schumacher, Phys. Rev. Lett., ***64****, 1883 (1990)*

Multi-photon ATD basic mechanisms

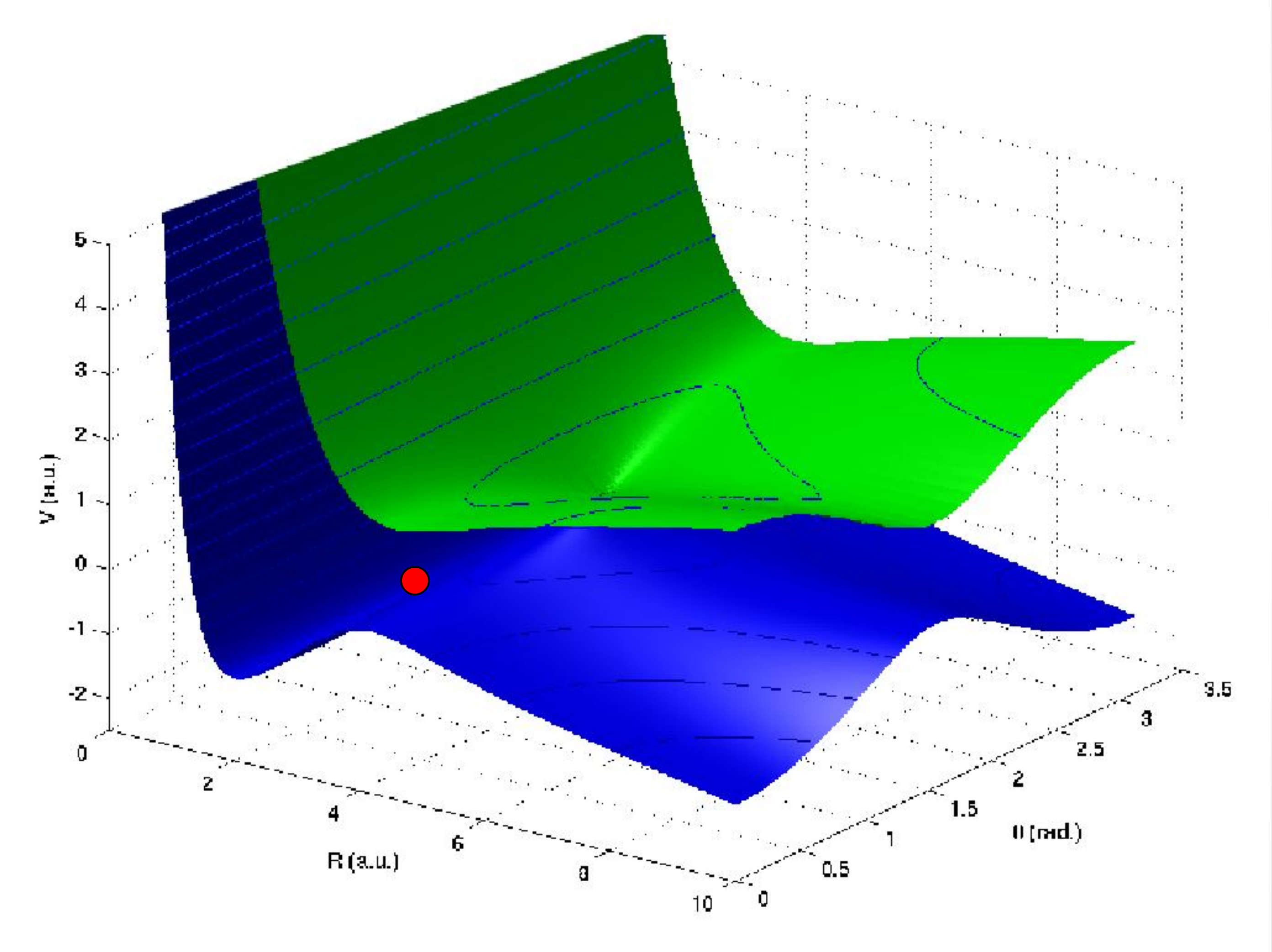


3D LIGHT-DRESSED POTENTIALS
(Schematic view)



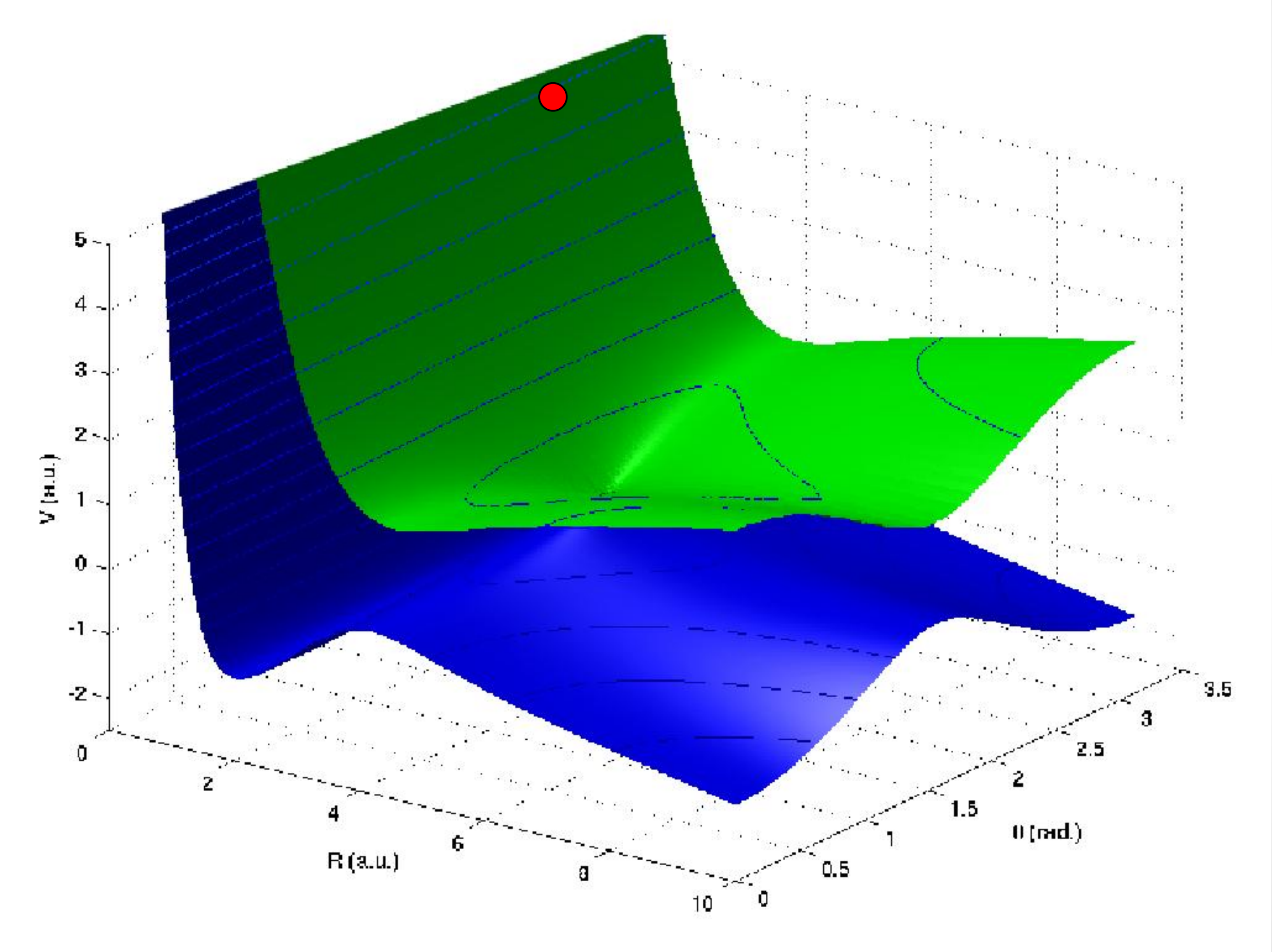
K. Yamanouchi, Science, **295**, 1659 (2002)

BARRIER LOWERING – BOND SOFTENING



Aligned fragments

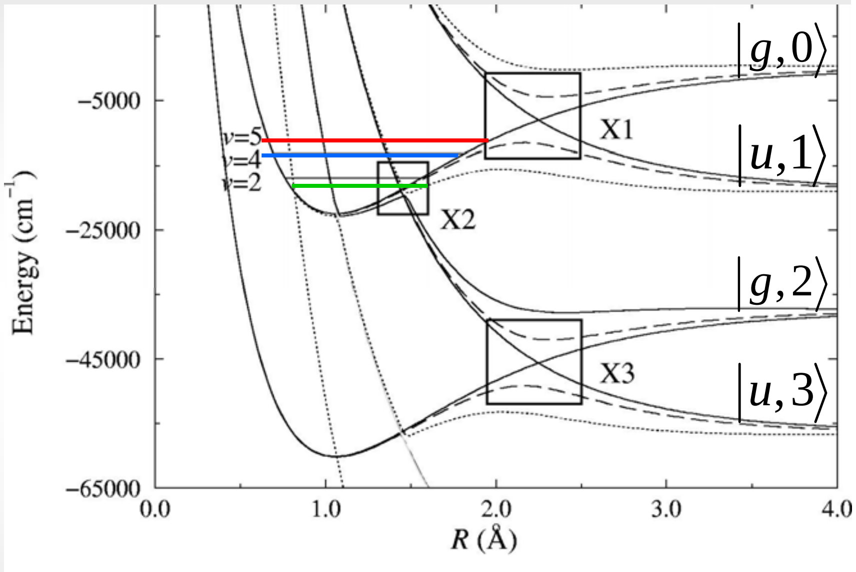
VIBRATIONAL TRAPPING

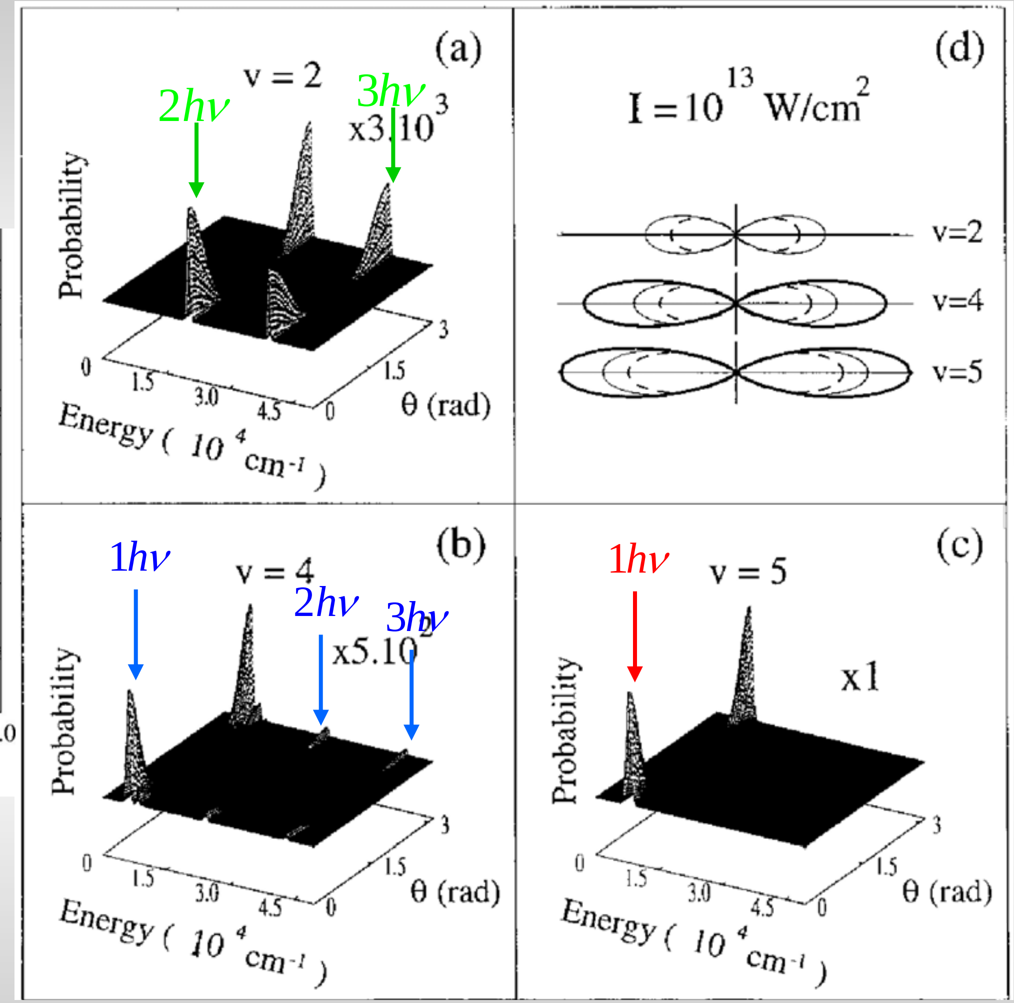


Misaligned fragments

ANGULAR RESOLVED KINETIC ENERGY DISTRIBUTIONS

$$H_2^+({}^2\Sigma_g^+, v) \xrightarrow[\lambda=532nm]{} H_2^+({}^2\Sigma_u^+, v) \longrightarrow H(1s) + H^+$$





R. Numico, A. Keller and O. Atabek, *Phys. Rev.* A , **60**, 406 (1999)

EXPERIMENT vs THEORY

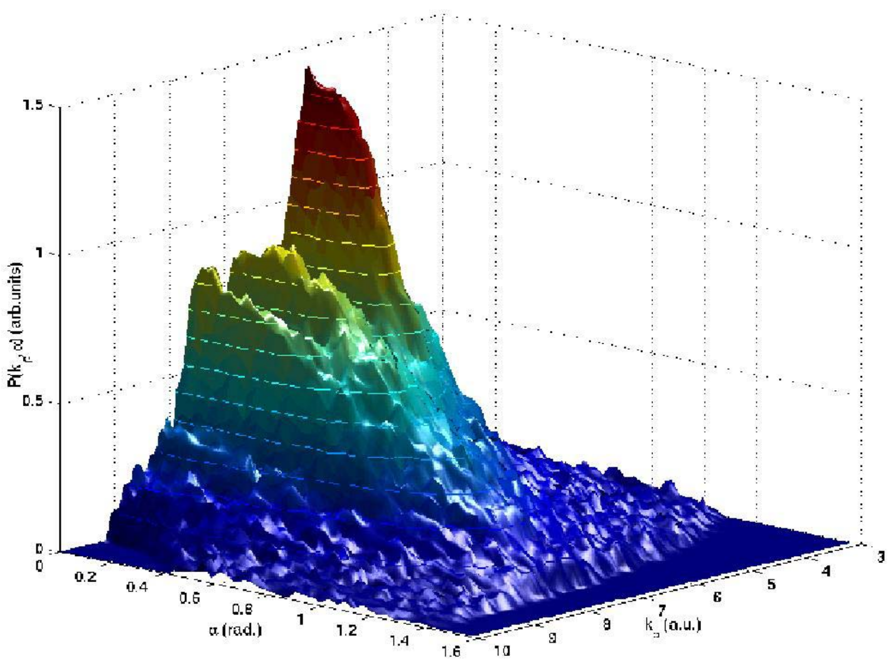
$$H_2^+ \quad \lambda = 785nm \quad I_0 = 16TW/cm^2$$

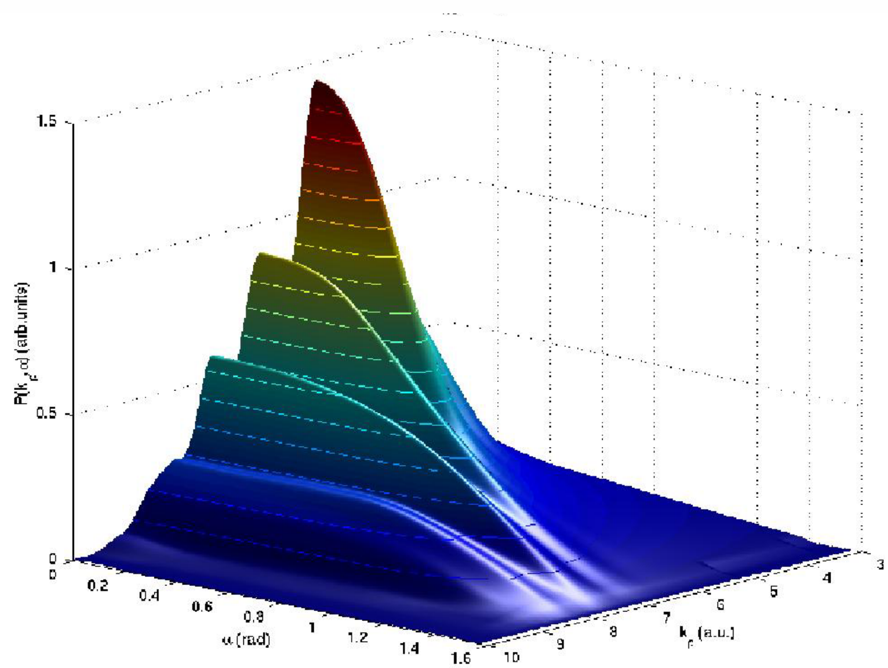
- Electric discharge producing well defined rovibrational populations of H_2^+

- Spatial intensity distribution;
- Initial rovibrational distribution;
- Abel transformation

*K. Sandig, H. Figger, T.W. Hänsch, Phys. Rev. Lett., **85**, 4876 (2000)*

*V.N. Serov, A. Keller, O. Atabek, N. Billy, Phys. Rev. A**68**, 053401 (2003)*





BASIC MECHANISMS

Internal degrees of freedom: Nuclear vibrational dynamics

Low frequency regime: $\omega_{field} \approx \omega_{mol}$

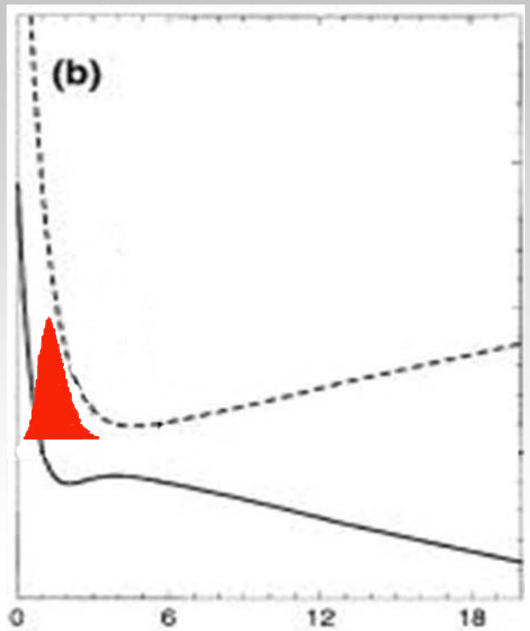
Time dependent picture

DDQ*, BL*

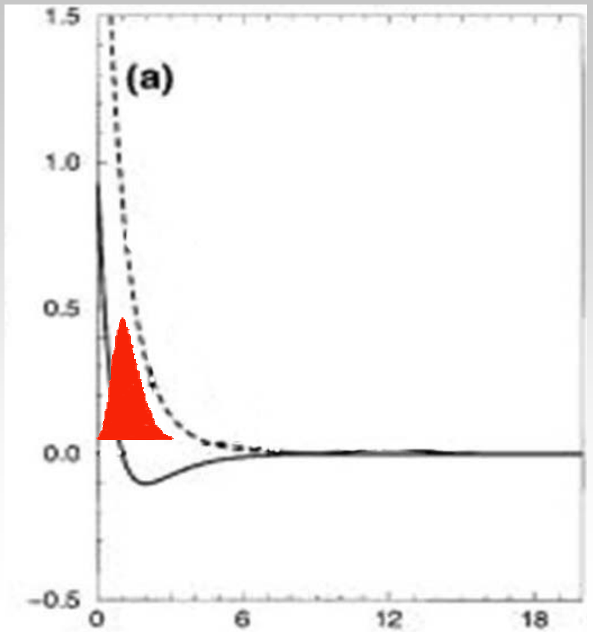
Experimental verification

* Dynamical Dissociation Quenching, Barrier Lowering

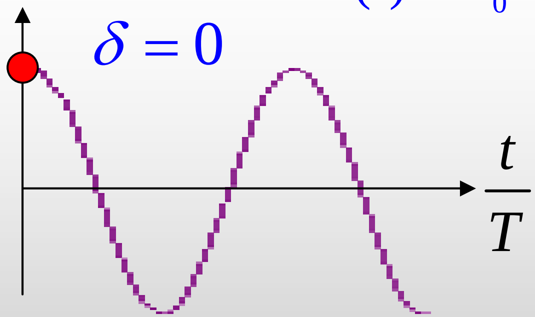
DYNAMICAL DISSOCIATION QUENCHING

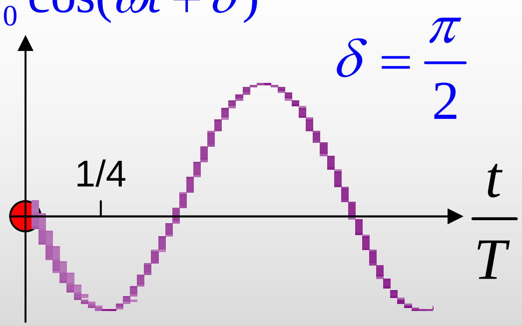


t=0



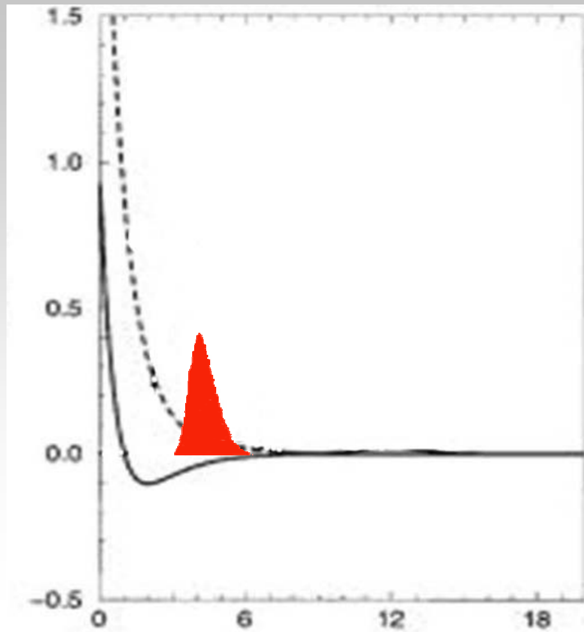
$$E(t) = E_0 \cos\left[\omega(t - t_0)\right] = E_0 \cos(\omega t + \delta)$$





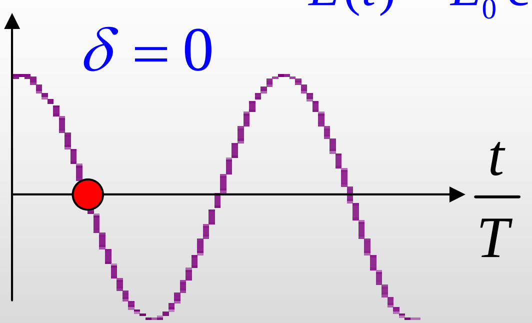
$$\det\begin{bmatrix} V_g - W_\pm(R,t) & \mu E_0 \cos(\omega t + \delta) \\ \mu E_0 \cos(\omega t + \delta) & V_g - W_\pm(R,t) \end{bmatrix} = 0$$

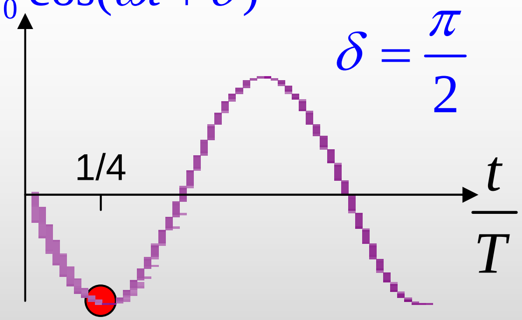
DYNAMICAL DISSOCIATION QUENCHING



t=T/4

$$E(t) = E_0 \cos\left[\omega(t - t_0)\right] = E_0 \cos(\omega t + \delta)$$



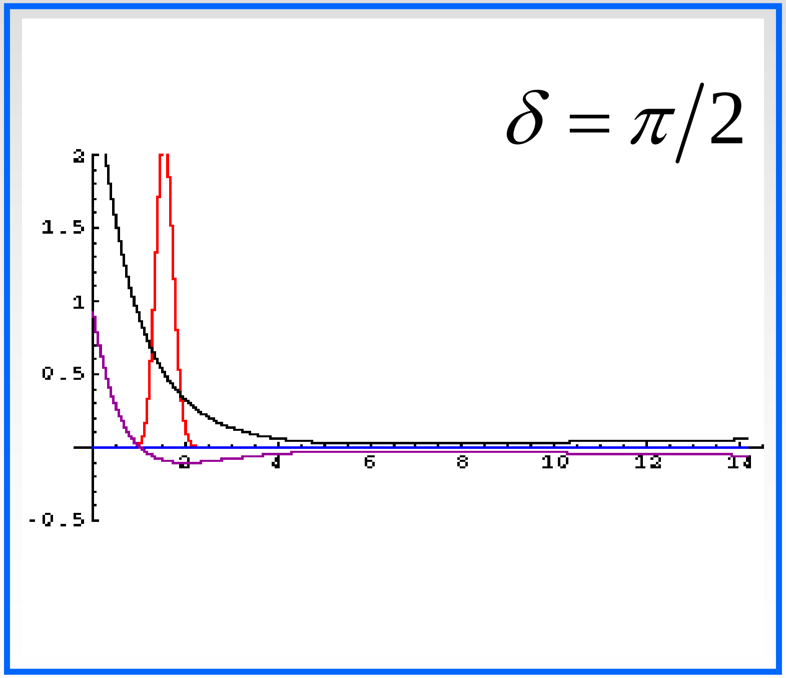


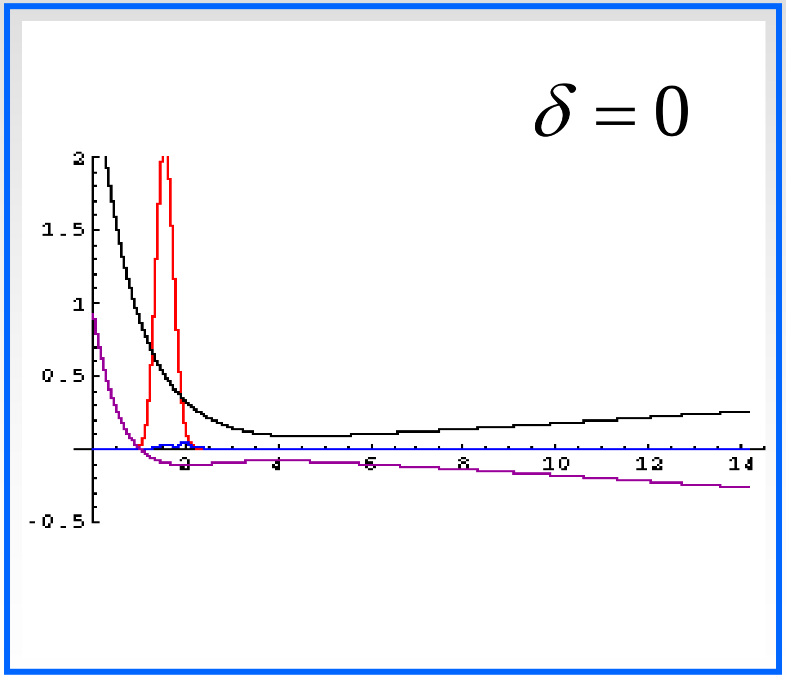
$$\det\begin{bmatrix} V_g - W_{\pm}(R,t) & \mu E_0 \cos(\omega t + \delta) \\ \mu E_0 \cos(\omega t + \delta) & V_g - W_{\pm}(R,t) \end{bmatrix} = 0$$

WAVE PACKET PROPAGATION

Time t=0

$$E(t) = E_0 \cos\left[\omega(t - t_0)\right] = E_0 \cos(\omega t + \delta)$$

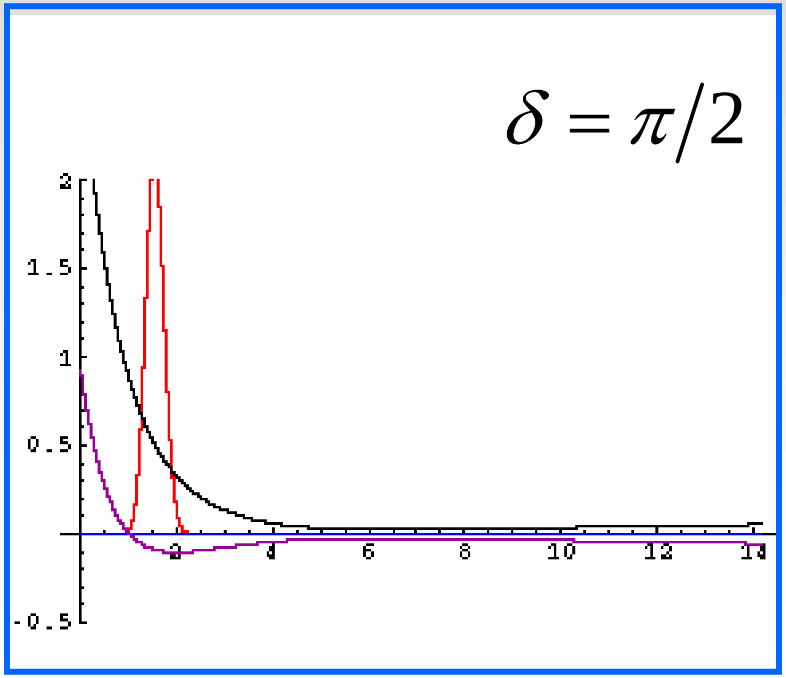


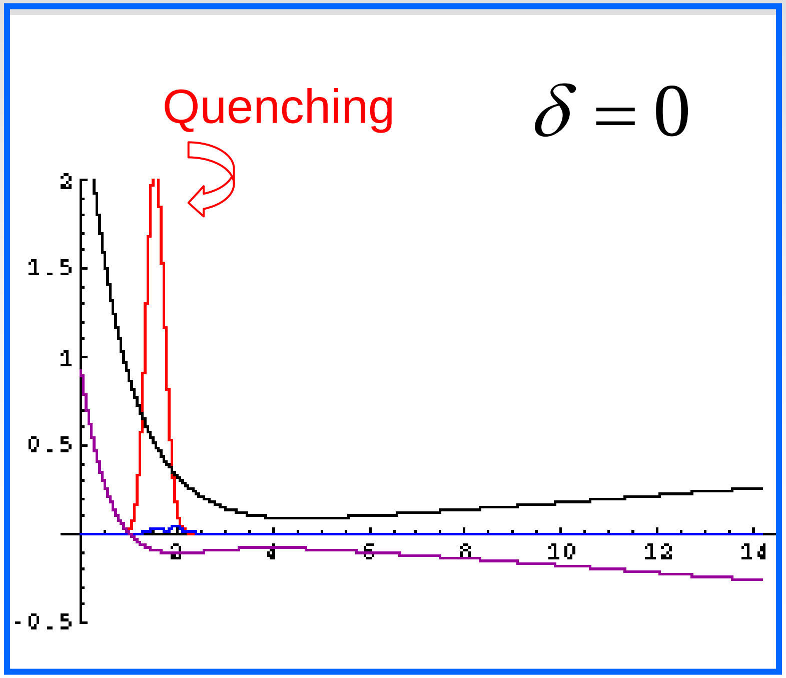


WAVE PACKET PROPAGATION

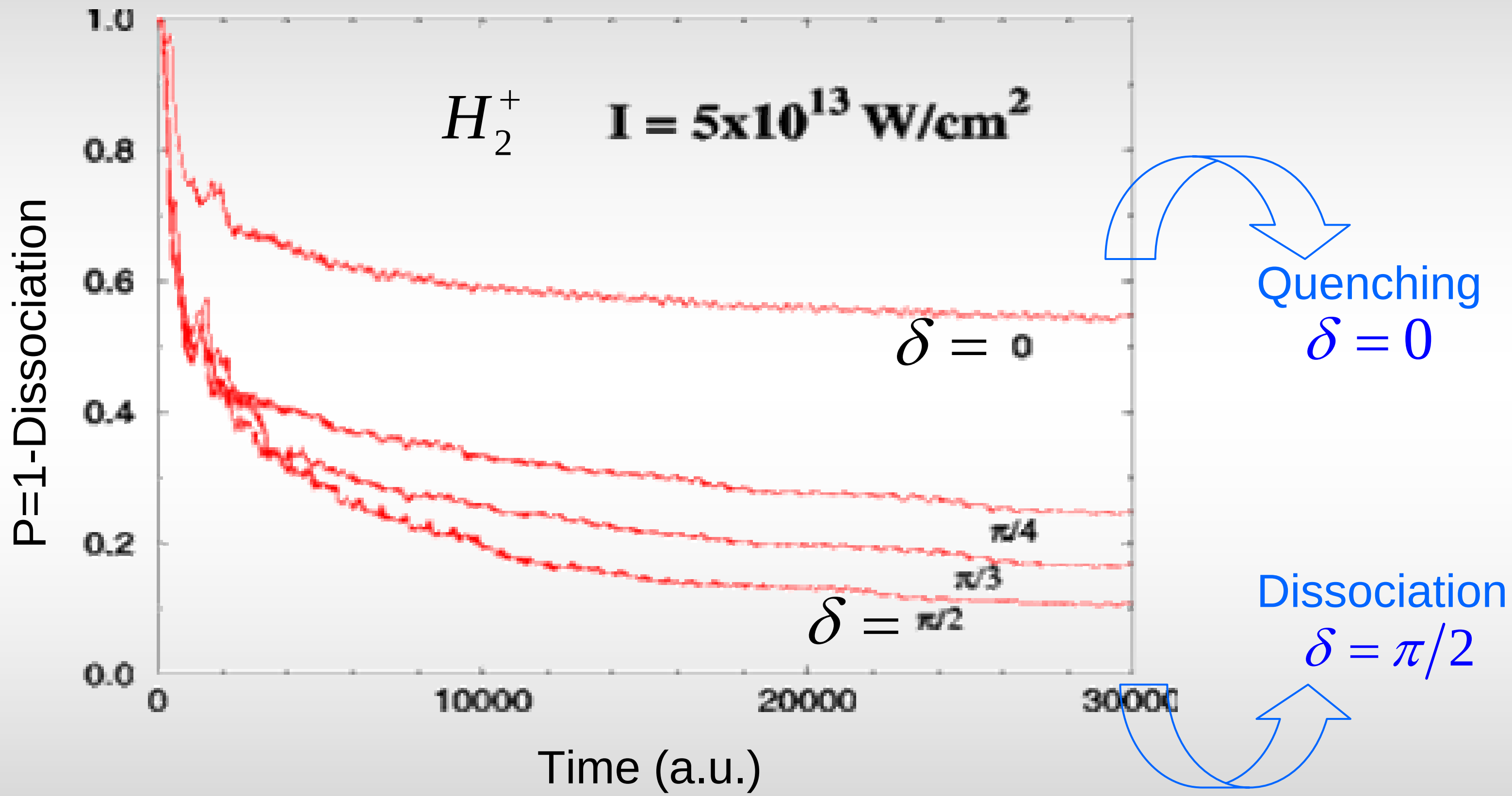
Time t=4T

$$E(t) = E_0 \cos\left[\omega(t - t_0)\right] = E_0 \cos(\omega t + \delta)$$





Dynamical Dissociation Quenching



F. Châteauneuf, T.T. Nguyen Dang, N Ouellet and O. Atabek,
J. Chem. Phys. **108**, 3974 (1998)

EXPERIMENTAL VERIFICATION

Two-colour field

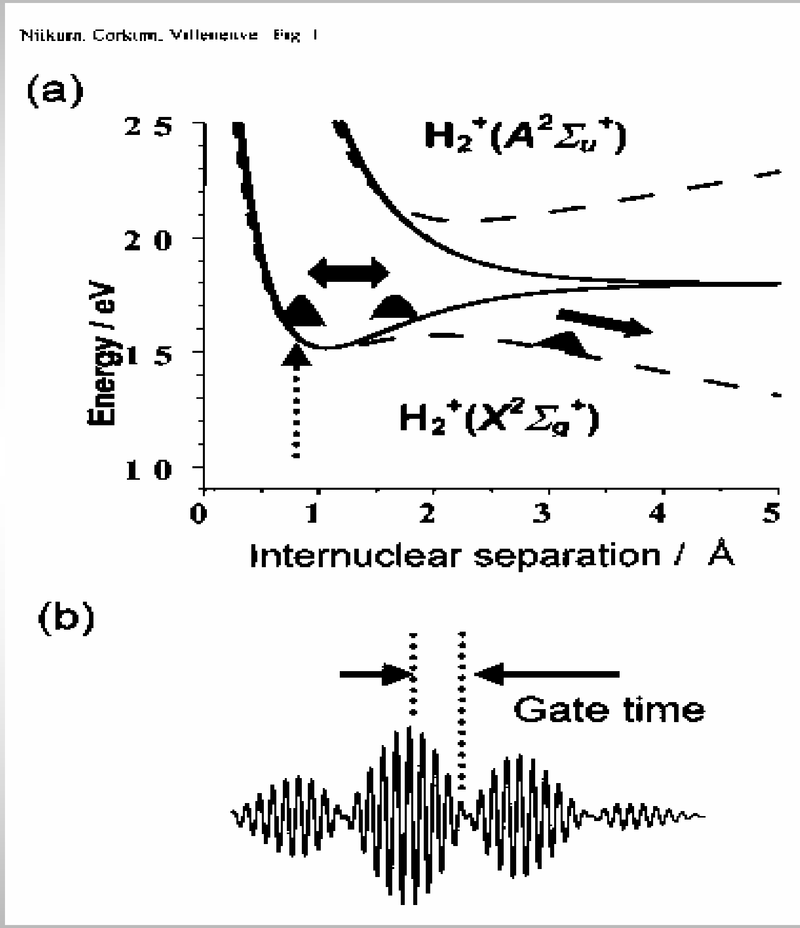
$E(t) = E_0 \cos(\omega_1 t) + E_0 \cos(\omega_2 t)$

$\quad = E_0 \cos[(\omega_1+\omega_2)t/2] \cos[(\omega_1-\omega_2)t/2]$

with c/ω_1 =1280-1550 nm

c/ω_2 =2180-1700 nm

OPA- Ti Sapphire

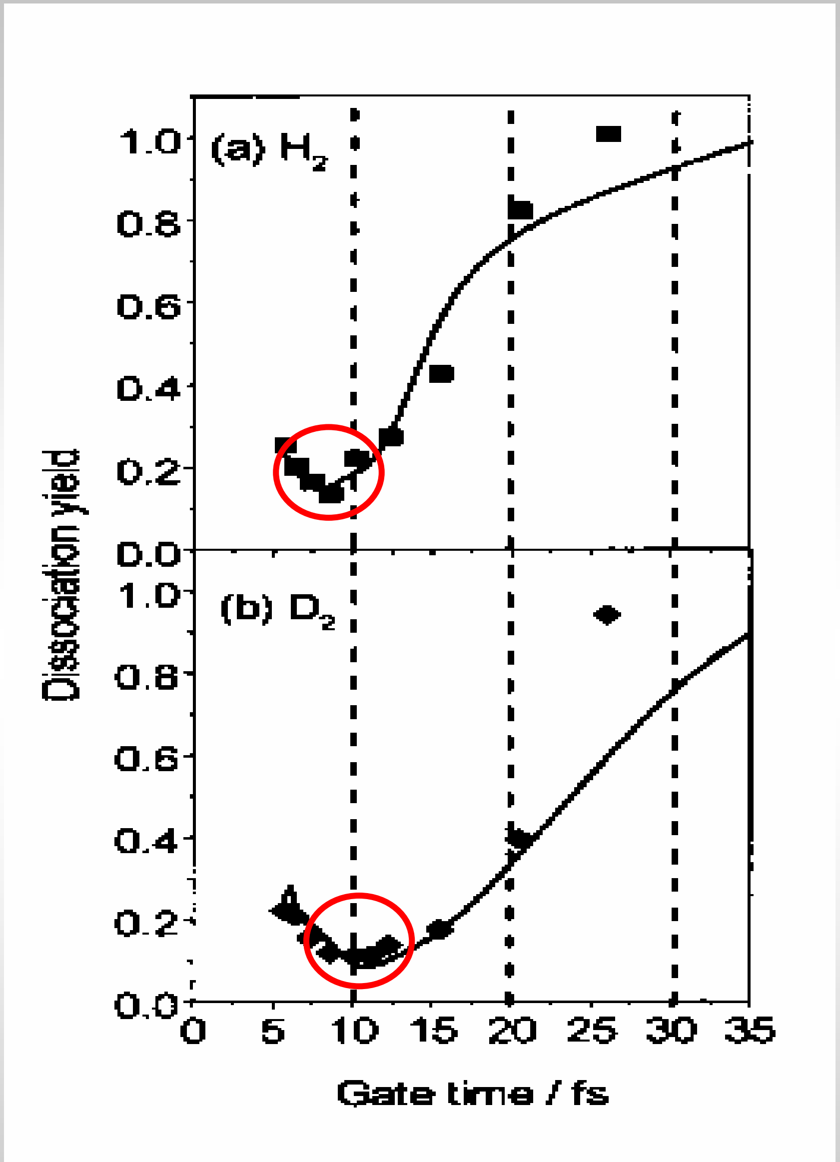


H. Niikura, P. B. Corkum, D. M. Villeneuve, *Phys.Rev.Lett,* **90**, 203601 (2003)

Vibrational periods

$T_{H_2^+(v=2)}$: 16 fs

$T_{D_2^+(v=2)}$: 22 fs



Optimal gate times

t_{gate} : $T/2$

t_{gate} : 8 fs

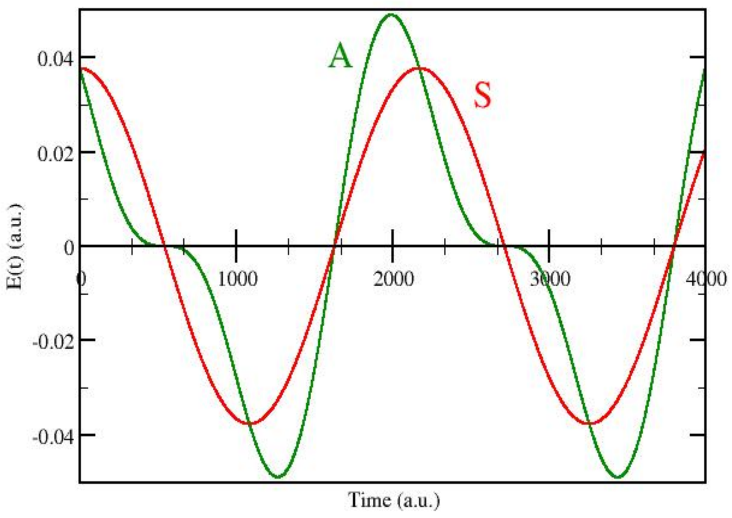
t_{gate} : 11 fs

H. Niikura, P. B. Corkum, D. M. Villeneuve, *Phys.Rev.Lett.*, **90**, 203601 (2003)

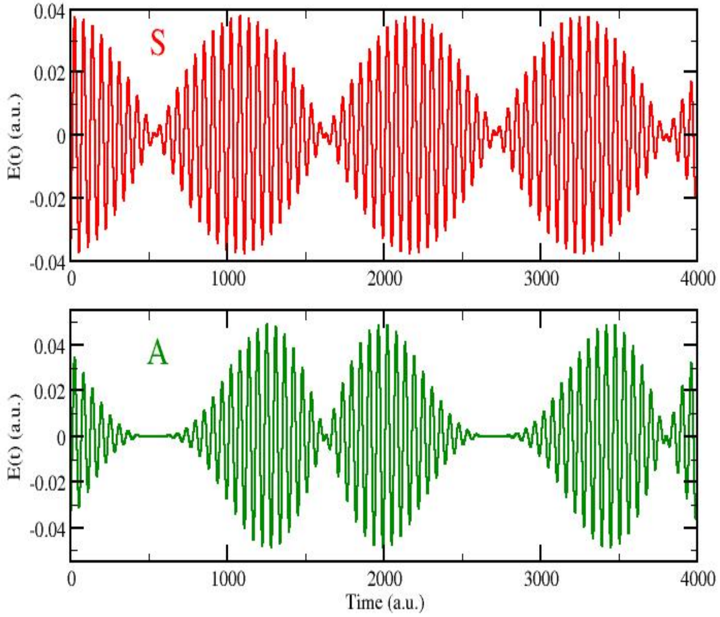
$$E(t) = E_0 \cos(\omega t + \delta)\left[\cos(\Omega t + \theta) + \gamma \cos(2\Omega t + 2\theta + \phi)\right]$$

ω_{UV}=400nm, Ω_{IR}=635cm^{-1} (1.6x10^4 nm), I=5x10^{13} W/cm^2

- IR envelope



- Field



BASIC MECHANISMS

External degrees of freedom: Nuclear rotational dynamics

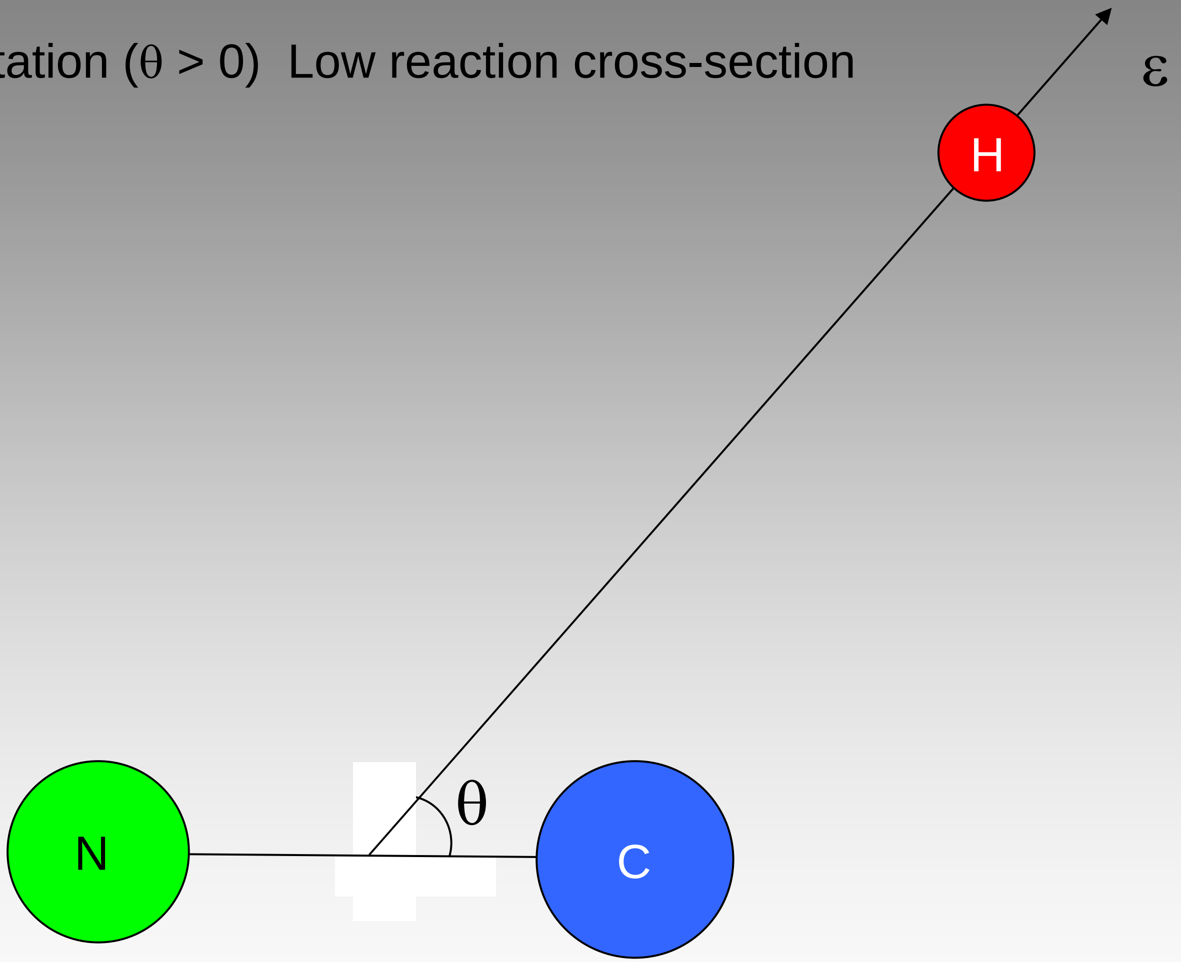
Alignment and orientation

Time dependent picture

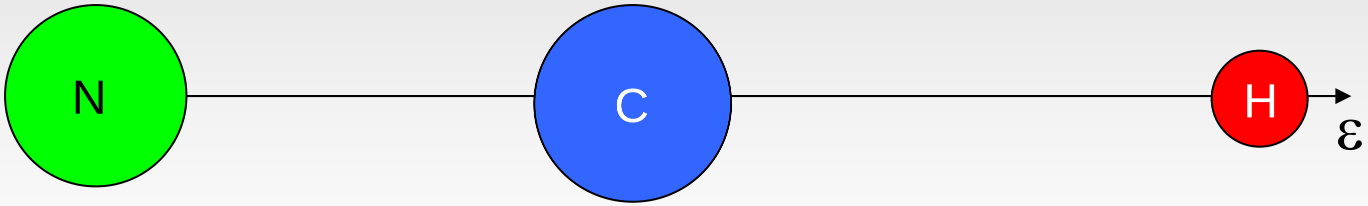
Pendular states, ω+2ω, Kick

Experimental verification

No Orientation (θ > 0) Low reaction cross-section



Orientation (θ = 0) High reaction cross-section



MOTIVATION

- Reaction cross sections *Brooks (1976)*;
- Laser induced isomerisation, isotope separation *Charron, Giuisti-Suzor (1994)*;
- Molecular trapping *Seideman (1997)*;
- High order harmonic generation *Hay (2002)*;
- Surface processing, catalysis *Tenner (1991)*;
- Nanotechnologies *Sakai (1998)*.

EXPERIMENTAL MEASUREMENT

- Breaking the molecule by MEDI (Multielectron Dissociative Ionization) measure the angular distributions of the ionized fragments, *Rosca-Pruna and Vrakking, Phys. Rev. Lett.* ***87****, 153902 (2001);*

- RIPS (Raman Induced Polarization Spectroscopy): non-intrusive observation of a signal proportional to $< \cos^2\theta > -1/3$

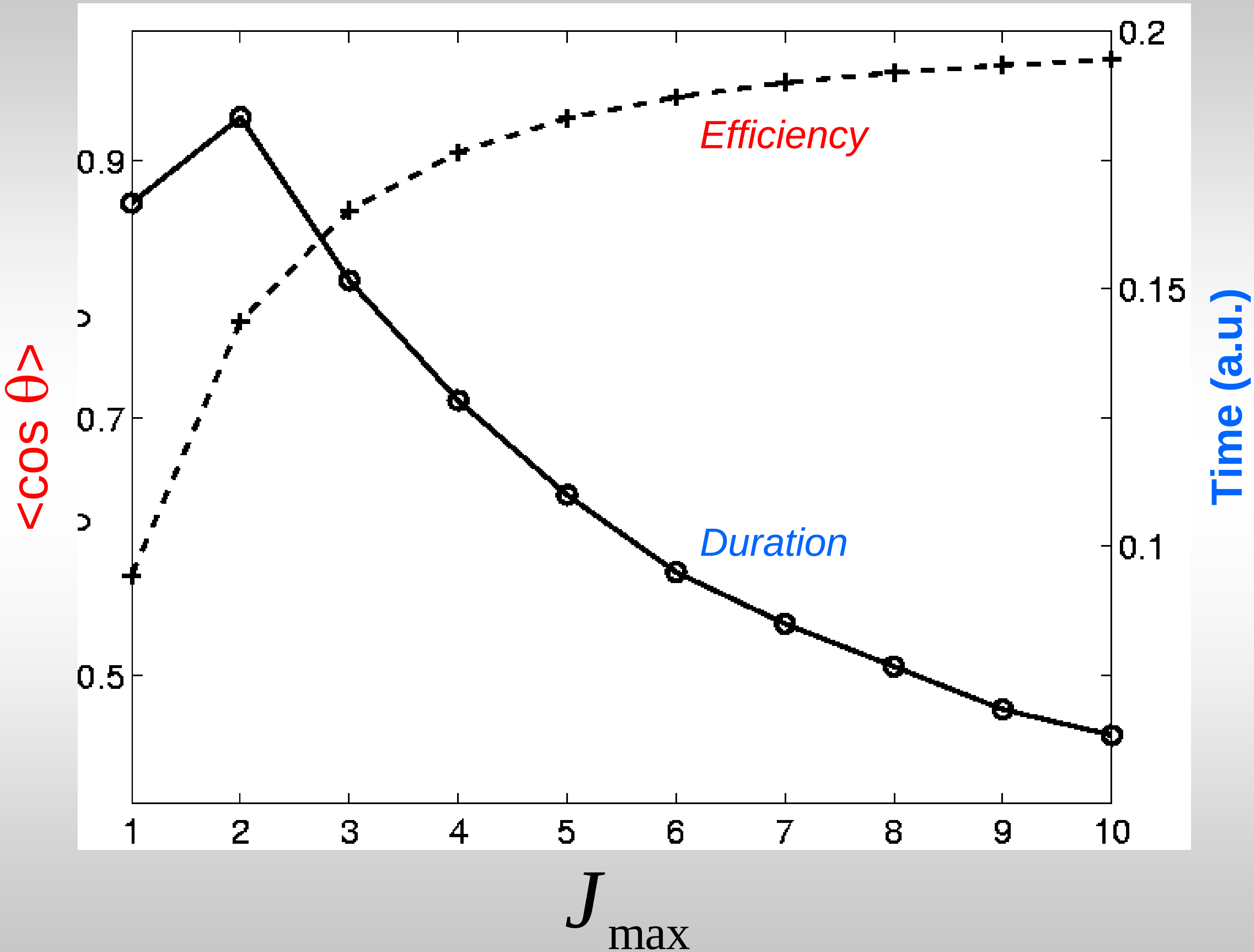
Renard et.al. Phys. Rev.Lett. ***90****, 153601 (2003).*

TECHNIQUES

- ❑Brute force, DC electric field (combined with lasers), *Friedrich, Herchbach (1991);*
- ❑Microwave pulses in optimal control schemes, *Judson, Lehmann, Rabitz, Warren (1990)*;
- ❑Picosecond two-color phase-locked lasers in coherent control, *Vrakking, Stolte (1997)*;
- ❑Two IR lasers ($\omega+2\omega$) resonant with a vibrational transition of a polar molecule, *Dion, Keller, Bandrauk, Atabek (1998)*;
- ❑Half-cycle pulses HCP, *Dion, Keller, Atabek (2001)*;
- ❑Train of short pulses, *Rabitz, Keller, Atabek (2004)*.

*H. Stapelfeldt and T. Seideman, Rev. Mod. Phys., **75**, 543 (2003)*

$$\Delta J . \Delta \theta \sim \hbar$$



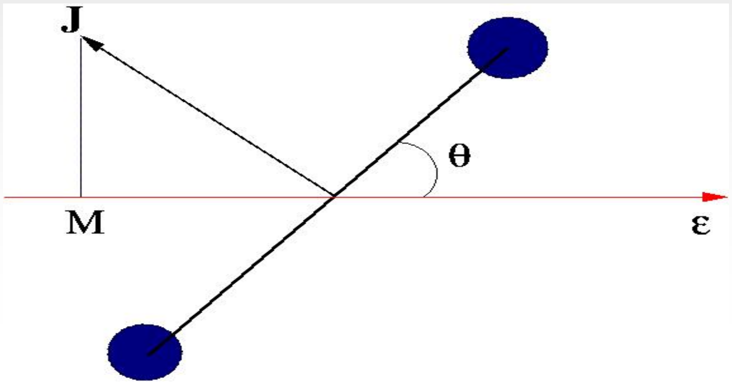
0.2
0.15
0.1
0.9
0.7
0.5
1
2
3
4
5
6
7
8
9
10
Efficiency
Duration
<cos θ>
Time (a.u.)
J max

The Model

Rigid rotor Hamiltonian:

$$H = BJ^2 - \mu_0 E(t)\cos\theta - \frac{1}{2}E^2(t)(\Delta\alpha\cos^2\theta + \alpha_\perp)$$

$$\Delta\alpha = \alpha_{//} - \alpha_\perp$$



Time dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\psi(\theta,\phi,t) = H(t)\psi(\theta,\phi,t)$$

Measure of alignment / orientation

$$\left\langle\cos^2\theta\right\rangle(t) = \int_0^{2\pi}\int_0^{\pi}\left|\psi(\theta,\phi,t)\right|^2\cos^2\theta\sin\theta d\theta d\phi$$

$$\left\langle\cos\theta\right\rangle(t) = \int_0^{2\pi}\int_0^{\pi}\left|\psi(\theta,\phi,t)\right|^2\cos\theta\sin\theta d\theta d\phi$$

Basis set method

Basis set of spherical harmonics

$$\psi(\theta,\phi,t) = \sum_{J=0}^{N} c_J(t) Y_{J,M}(\theta,\phi)$$

Coupled equations for $c_J(t)$

$$i\hbar \dot{c}_J(t) = \left[BJ(J+1) - \tfrac{1}{2}\alpha_\perp E^2(t) \right] c_J(t)$$

$$-\mu_0 E(t) \sum_{J'=0}^{N} c_{J'}(t) \langle J,M | \cos\theta | J',M \rangle$$

$$-\tfrac{1}{2}\Delta\alpha E^2(t) \sum_{J'=0}^{N} c_{J'}(t) \langle J,M | \cos^2\theta | J',M \rangle$$

with $c_J(t=0)$ known

Split-operator method

Wave packet propagation

$$\psi(t+\delta t) = \exp\left[-\tfrac{i}{\hbar} \int_t^{t+\delta t} H(t')dt' \right] \psi(t)$$

For small time steps

$$\psi(t+\delta t) \approx \exp\left[-\tfrac{i}{\hbar} \delta t H(t+\delta t/2) \right] \psi(t)$$

$$\approx \exp\left[-\frac{i}{\hbar}\frac{\delta t}{2} V \right] \exp\left[-\frac{i}{\hbar} \delta t T \right] \exp\left[-\frac{i}{\hbar}\frac{\delta t}{2} V \right]$$

with $H = T + V$

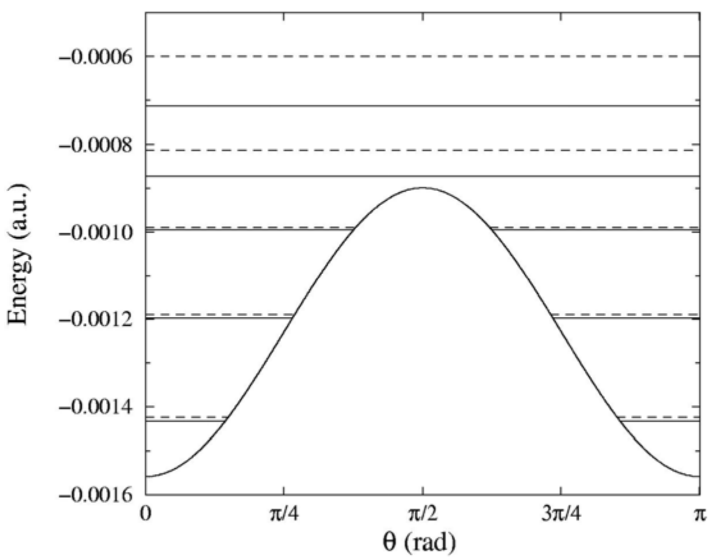
Solved using Fast Fourier Transforms

PENDULAR STATES

$\partial / \partial\theta$

Quantum Model

$$\left[\frac{\hbar^2}{2I}\hat{J}^2 + \frac{\hbar^2}{2I}\frac{M^2}{\sin^2\theta} + \left(\Delta\alpha + \frac{\mu_0^2}{I\omega^2}\right)\frac{\mathcal{E}_0}{4}\sin^2\theta + \frac{\Delta\alpha^2\mathcal{E}_0^4}{256 I\omega^2}\sin^2 2\theta\right]\xi_{nJ}(\theta) = \left(\lambda_n - J\hbar\omega + \frac{\alpha_\parallel\mathcal{E}_0^2}{4}\right)\xi_{nJ}(\theta),$$



Classical Model

$$I\ddot{\theta} \simeq \frac{M^2}{I}\frac{\cos\theta}{\sin^3\theta} - \left(\Delta\alpha + \frac{\mu_0^2}{I\omega^2}\right)\frac{\mathcal{E}_0^2}{4}\sin 2\theta - \frac{\Delta\alpha^2\mathcal{E}_0^4}{128 I\omega^2}\sin 4\theta,$$

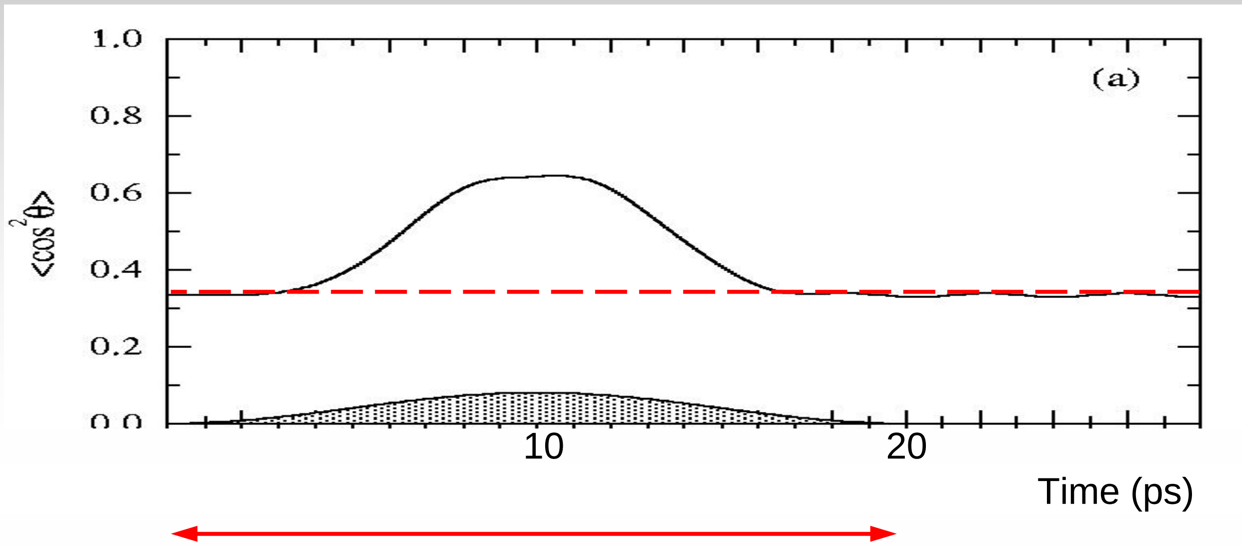
$$\Theta = 2\theta$$

$$\ddot{\Theta} + \Omega^2 \sin\Theta = 0$$

$$\Omega = \frac{1}{\sqrt{I}}\left(\frac{1}{2}\frac{\mu_0^2\mathcal{E}_0^2}{I\omega^2} + \frac{1}{2}\Delta\alpha\mathcal{E}_0^2\right)^{1/2}$$

B. Friedrich and D. Herschbach, Phys. Rev. Lett., 74, 4623 (1995)

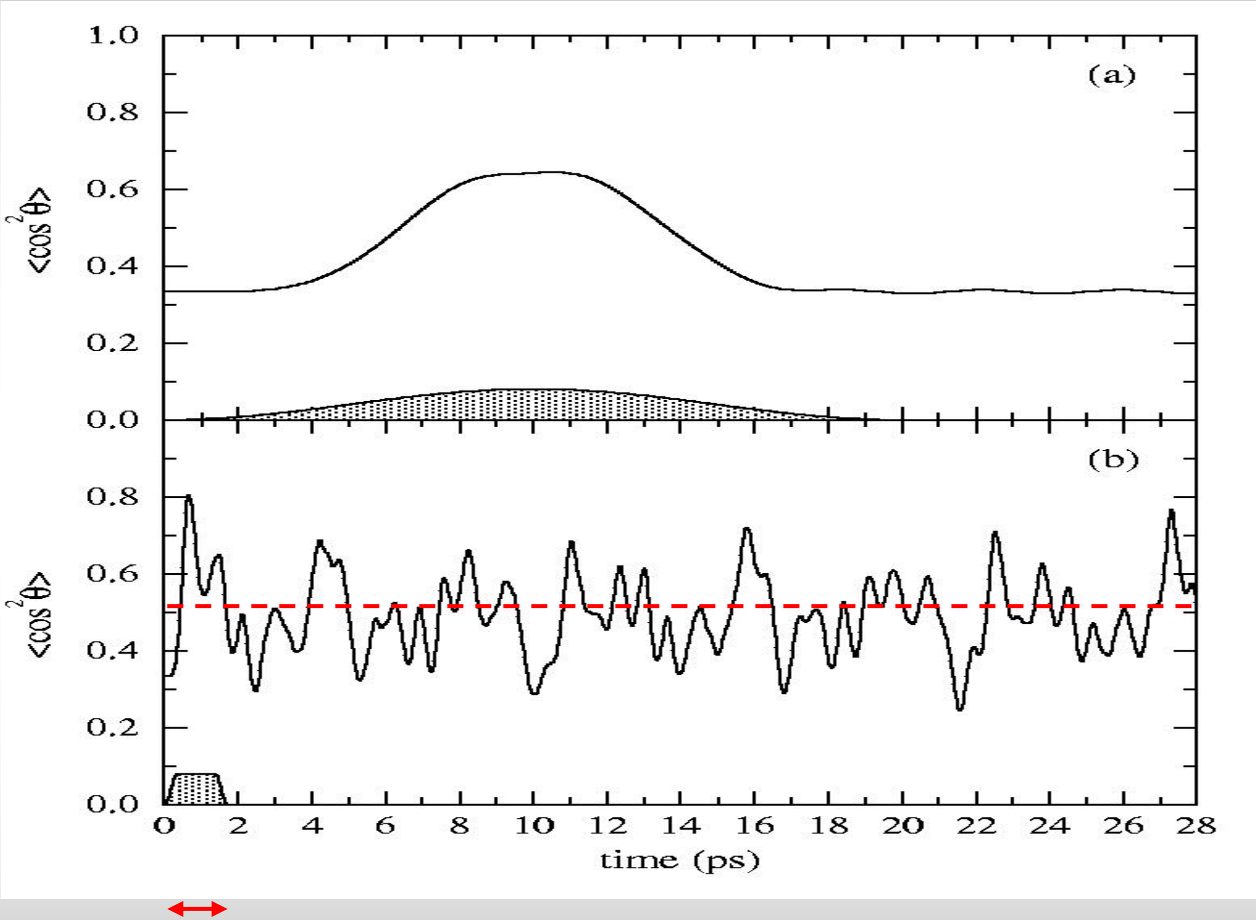
ADIABATIC vs SUDDEN PULSES



Pulse duration 20 ps

Adiabatic excitation of a single pendular state; isotropic distribution at the end of the pulse.

ADIABATIC vs SUDDEN PULSES

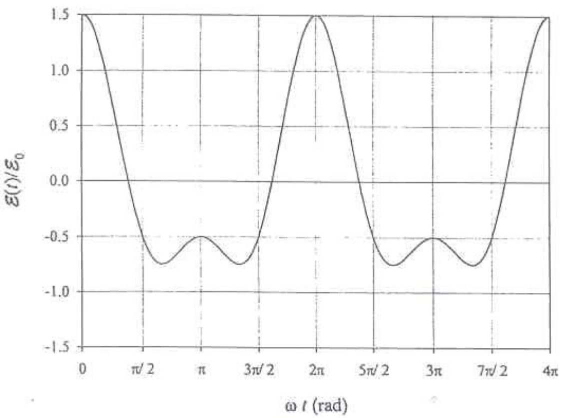


Pulse duration 1.7 ps

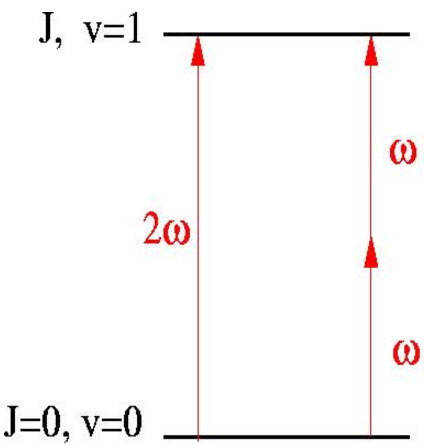
Sudden excitation; post-pulse alignment

A. Keller, C. Dion and O. Atabek, Phys. Rev. A ***61****, 023409 (2000)*

(ω+2ω) Mechanism

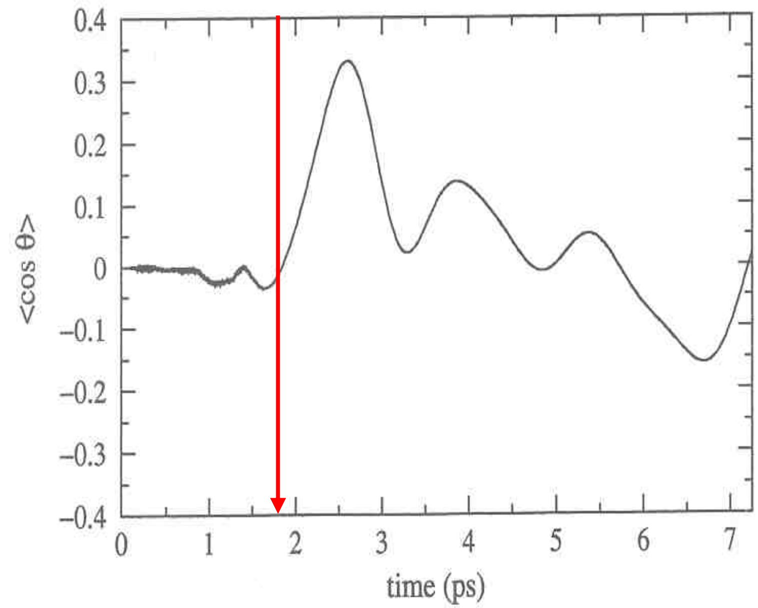


$$E(t) = E_0\left[\cos(\omega t) + \gamma\cos(2\omega t)\right]; \gamma = 0.5$$



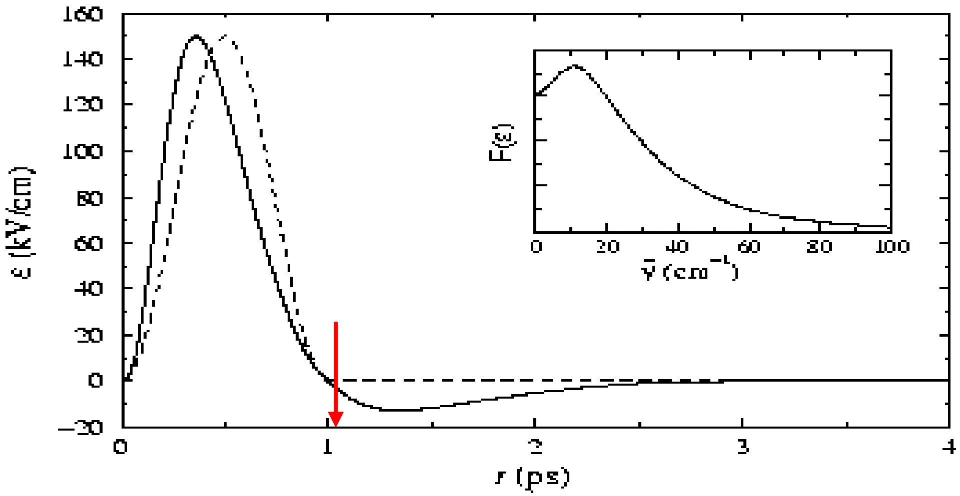
$2\omega = \omega_{CH}$ odd J (via $\mu \boldsymbol{E}$)

ω even J (via $\alpha \boldsymbol{E}^2$)



*C.Dion,et.al, Chem. Phys.Lett.**302**,215 (1999)*

The Kick Mechanism: Half Cycle Pulses



- ε~150kV/cm (~$10^8 W/cm^2$), no risk of ionization damage;
- Non-negligible field components at rotational transition;
- Sudden excitation $(t_p \sim 1ps) << (T_{rot} \sim 20ps)$
- Marked asymmetry (12:1) between max and min.

*D.You, R.Jones, P.Bucksbaum, D.Dykaar, Opt. Lett.**18**,290 (1993)*

Impulsive limit: sudden approximation

$$\tilde{\psi}(\theta,\phi,t) = \exp\left(\tfrac{i}{\hbar} BJ^2 t\right)\psi(\theta,\phi,t)$$

$$i\hbar\frac{\partial}{\partial t}\tilde{\psi}(\theta,\phi,t) = -\left[\exp\left({}^{i}\!/_{\hbar}\, BJ^2 t\right)\mu_0 E(t)\cos\theta\, \exp\left(-{}^{i}\!/_{\hbar}\, BJ^2 t\right)\right]\tilde{\psi}(\theta,\phi,t)$$

$$\tilde{\psi}(\theta,\phi,t_p) =$$

$$\frac{i\mu_0}{\hbar}\int_0^{t_p}\left[\exp\left({}^{i}\!/_{\hbar}\, BJ^2 t\right)E(t)\cos\theta\, \exp\left(-{}^{i}\!/_{\hbar}\, BJ^2 t\right)\right]\tilde{\psi}(\theta,\phi,t)\,dt + \tilde{\psi}(\theta,\phi,0)$$

$$t_p \ll \frac{\hbar}{BJ^2} \Rightarrow \exp\left({}^{i}\!/_{\hbar}\, BJ^2 t\right) \sim 1$$

$$\tilde{\psi}(\theta,\phi,t_p) = \exp(iA\cos\theta)\tilde{\psi}(\theta,\phi,0)$$

$$A = \frac{\mu_0}{\hbar}\int_0^{t_p} E(t)\,dt$$

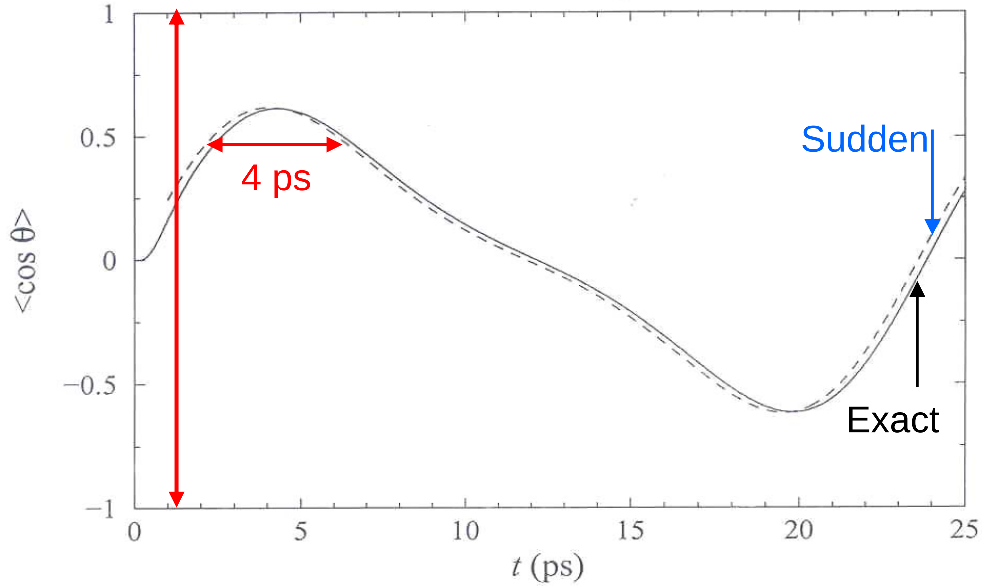
$$\psi(\theta,\phi,t \geq t_p) = \exp\left(-{}^{i}\!/_{\hbar}\, BJ^2 t\right)\exp(iA\cos\theta)\psi(\theta,\phi,0)$$

The Kick Mechanism: Half Cycle Pulses

Validity of the sudden limit

$$(t_p \sim 1ps) << (T_{rot} \sim 20\,ps)$$

$$\frac{BJ^2 t_p}{\hbar} \sim 0.13J(J+1) << 1$$



Final rotational distribution

$$\underset{J}{Max}\left|P_J^{exact}(t=25ps) - P_J^{sudden}(t=25ps)\right| \leq 0.015$$

Root mean-square η = *0.03*

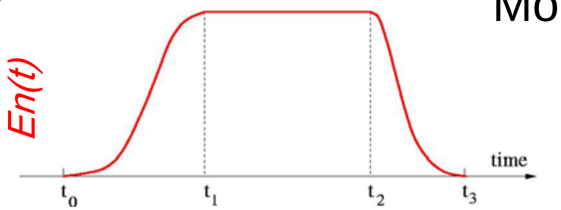
*C.Dion, A.Keller, O.Atabek, Eur. Phy. J. D**14**,249 (2001)*

OPTIMAL CONTROL

- Molecular Orientation dynamics
- Attosecond pulse synthesis

Optimal Control

Model



$$E(t) = \sum_{n=1}^{N} E_n(t)\sin(\omega_n t + \phi_n)$$

$$H(t) = BJ^2 - \mu_0 E(t)\cos\theta - \tfrac{1}{2}(\Delta\alpha\cos^2\theta + \alpha_\perp)E^2(t)$$

$$i\hbar\frac{\partial}{\partial t}\psi(\theta,\phi,t) = H(t)\psi(\theta,\phi,t)$$

Optimization loop

Evaluation function

$$\langle\cos\theta\rangle(t) = \langle\psi|\cos\theta|\psi\rangle$$

Target(s)

$$j_1 = \langle\cos\theta\rangle(t_f)$$

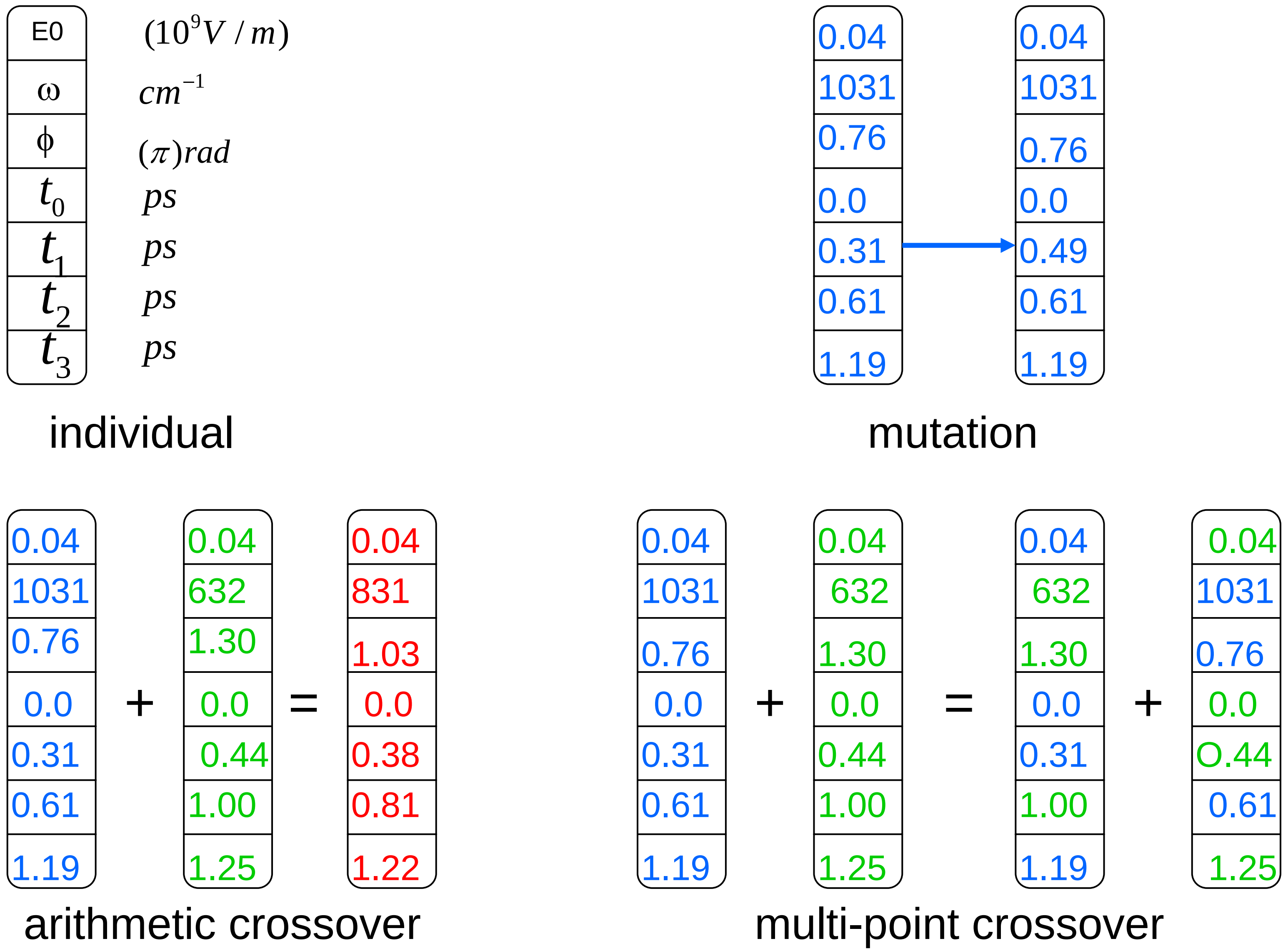
$$j_2 = \frac{1}{T_{rot}}\int_{t_f}^{t_f+T_{rot}}\langle\cos\theta\rangle^2(t)\,dt$$

Parameters

$$E, \omega, \phi,$$

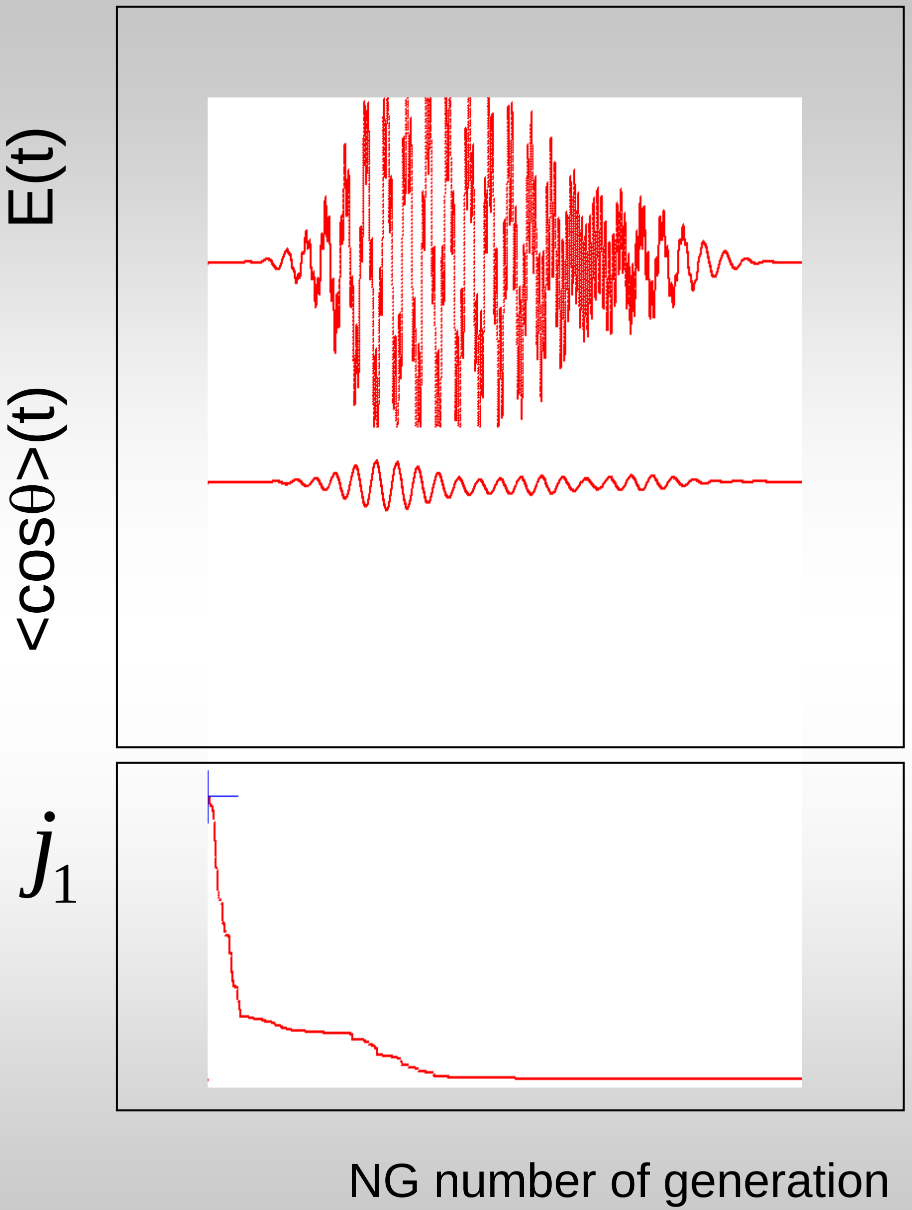
$$t_0, t_1, t_2, t_3$$

Generating offspring



HCN

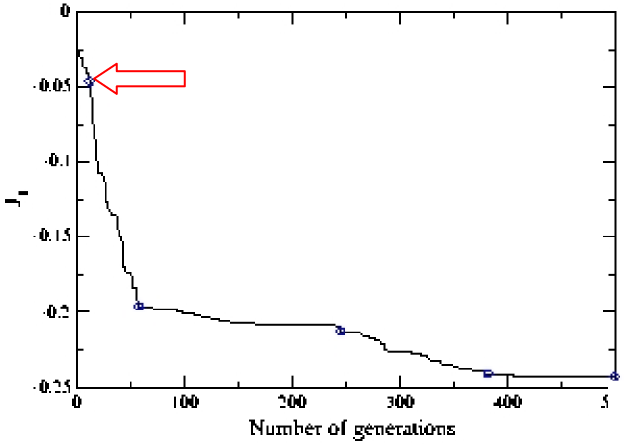
$$j_1 = \langle \cos\theta \rangle (t_f)$$



*O.Atabek, C.Dion,A.B.H.Yedder, J.Phys.B **36**,4667(2003)*

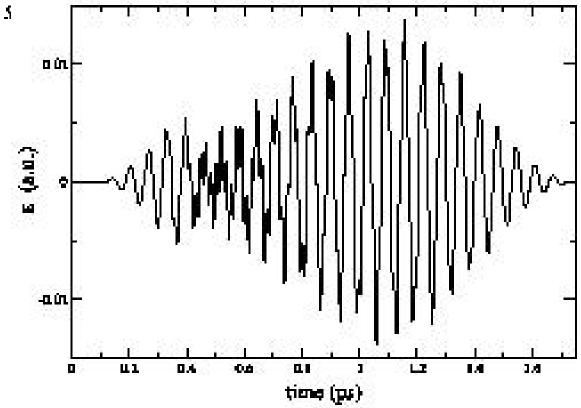
HCN

*O.Atabek, C.Dion,A.B.H.Yedder, J.Phys.B **36**,4667(2003)*

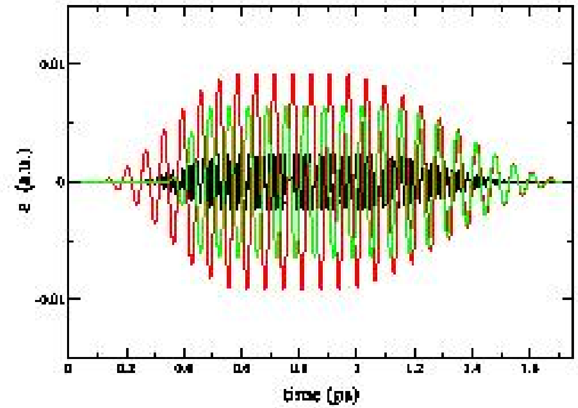


$$j_1 = \langle \cos\theta \rangle (t_f)$$

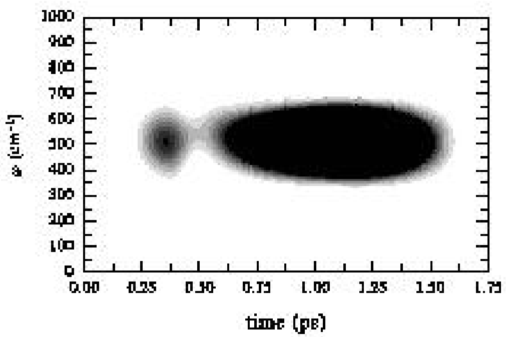
NG=11 ⇦



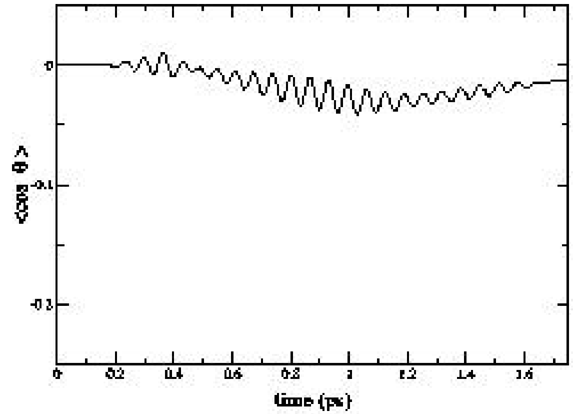
(a)



(b)



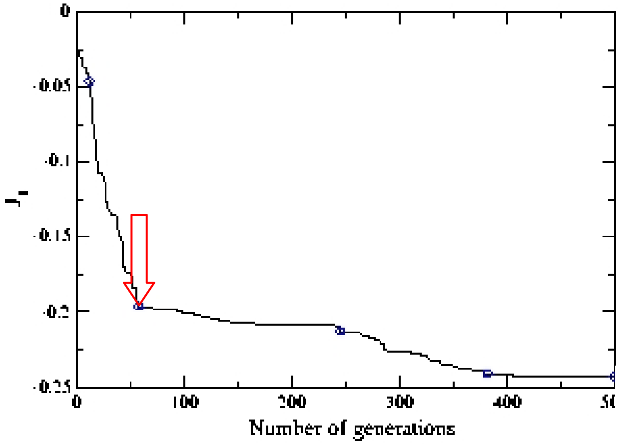
(c)

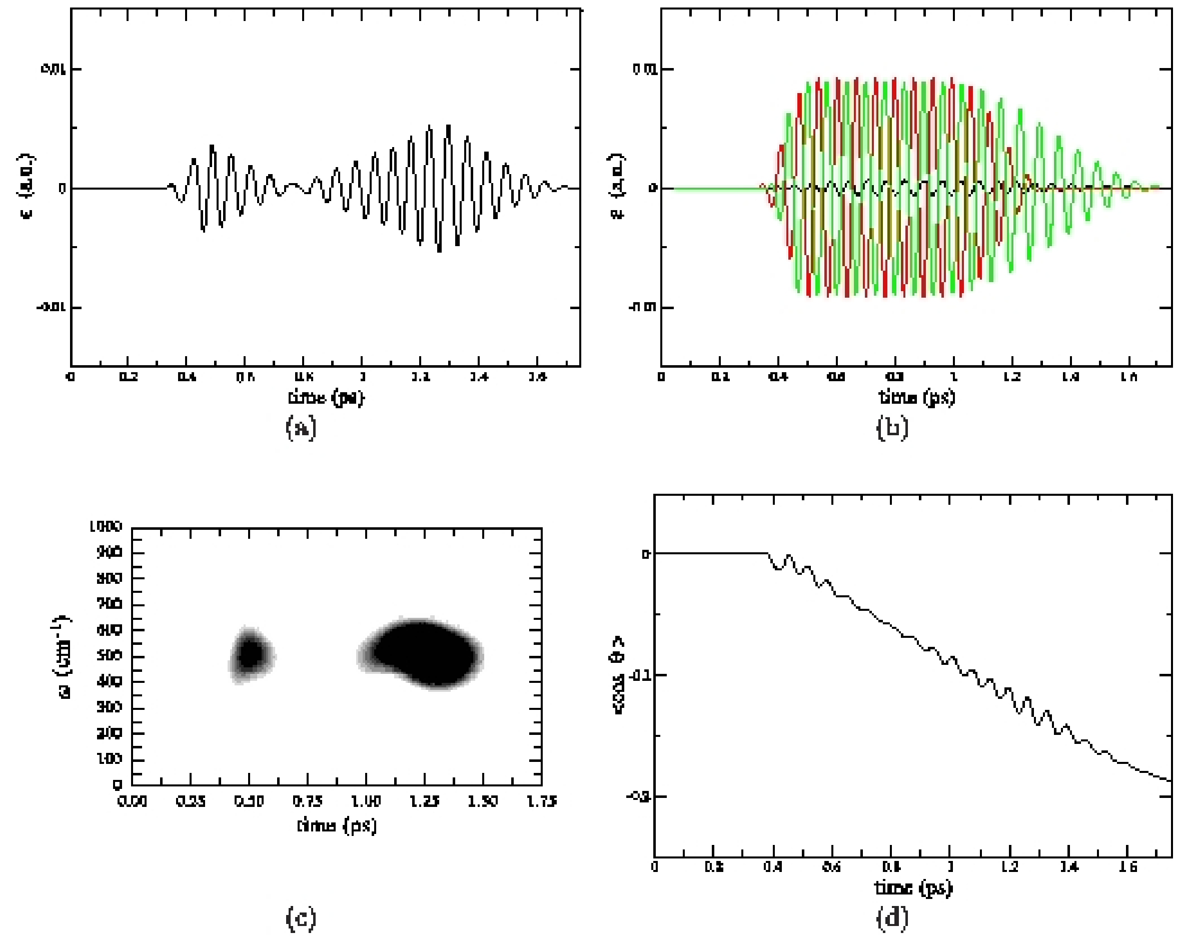


(d)

HCN

*O.Atabek, C.Dion,A.B.H.Yedder, J.Phys.B **36**,4667(2003)*



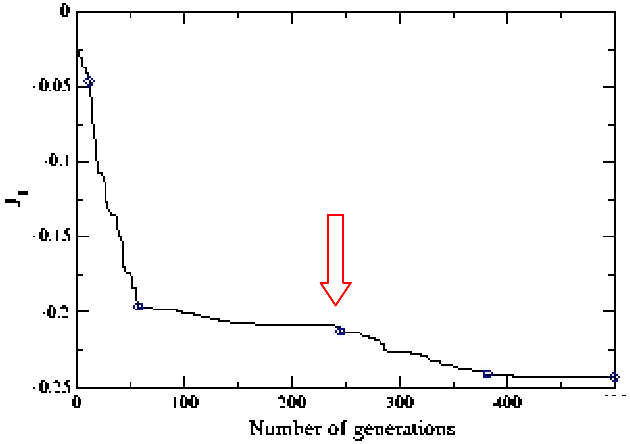


$$j_1 = \langle \cos\theta \rangle (t_f)$$

NG=57

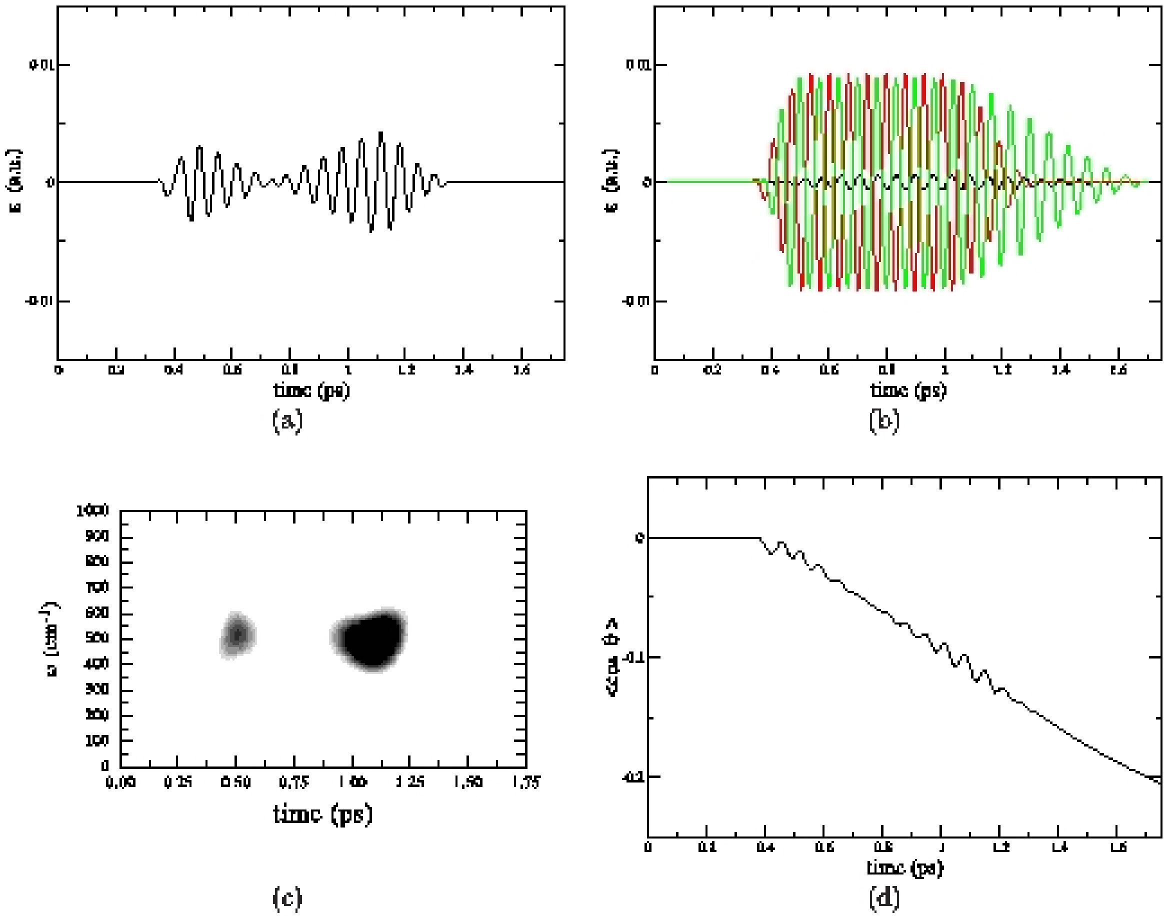
HCN

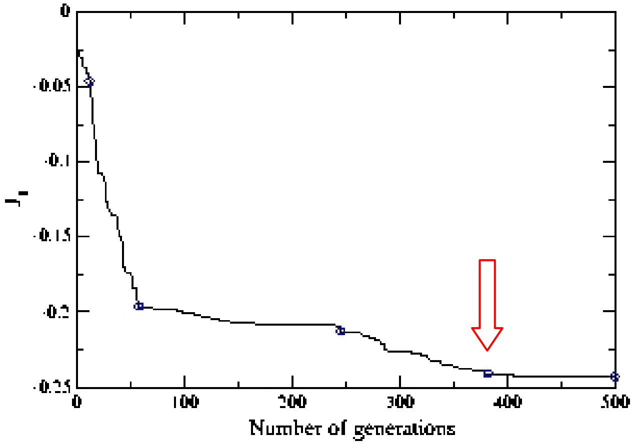
O.Atabek, C.Dion,A.B.H.Yedder, J.Phys.B ***36****,4667(2003)*



$$j_1 = \langle \cos\theta \rangle (t_f)$$

NG=245



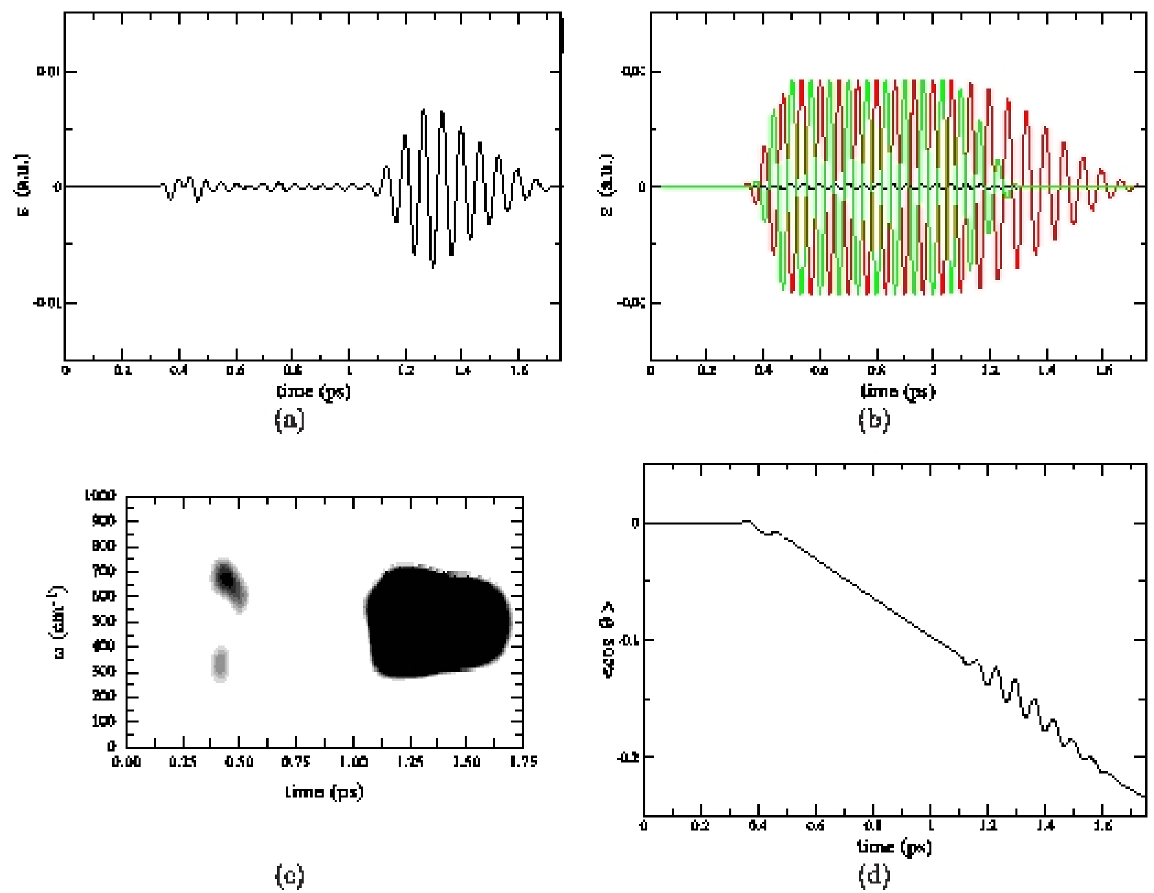


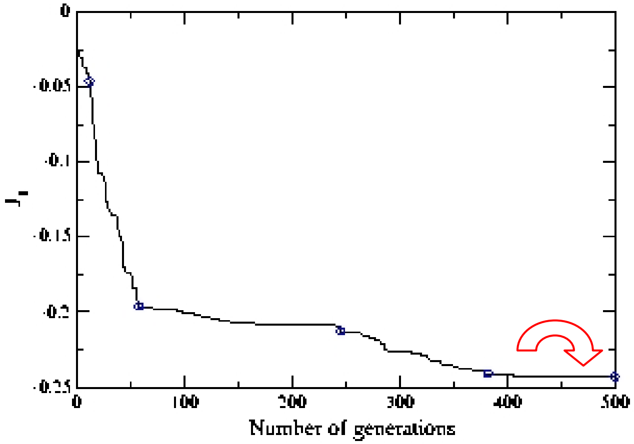
HCN

O.Atabek, C.Dion,A.B.H.Yedder, J.Phys.B ***36****,4667(2003)*

$$j_1 = \langle \cos\theta \rangle (t_f)$$

NG=383



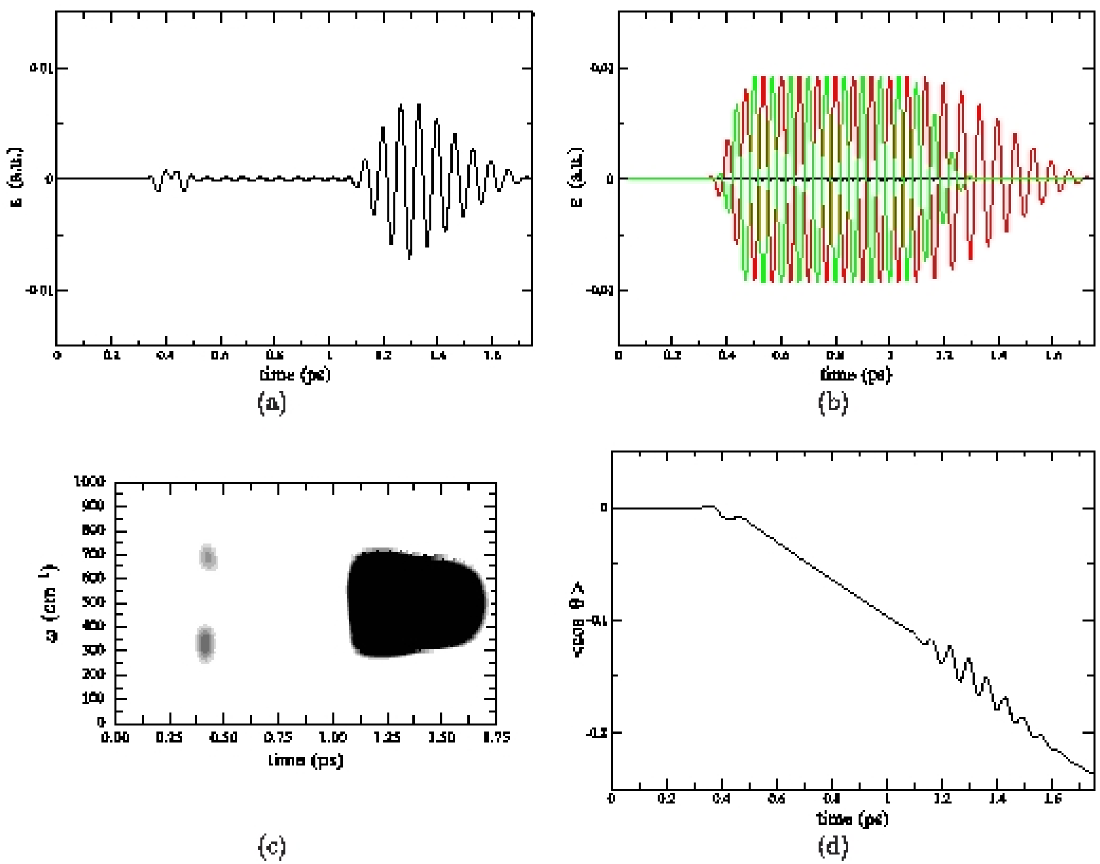


HCN

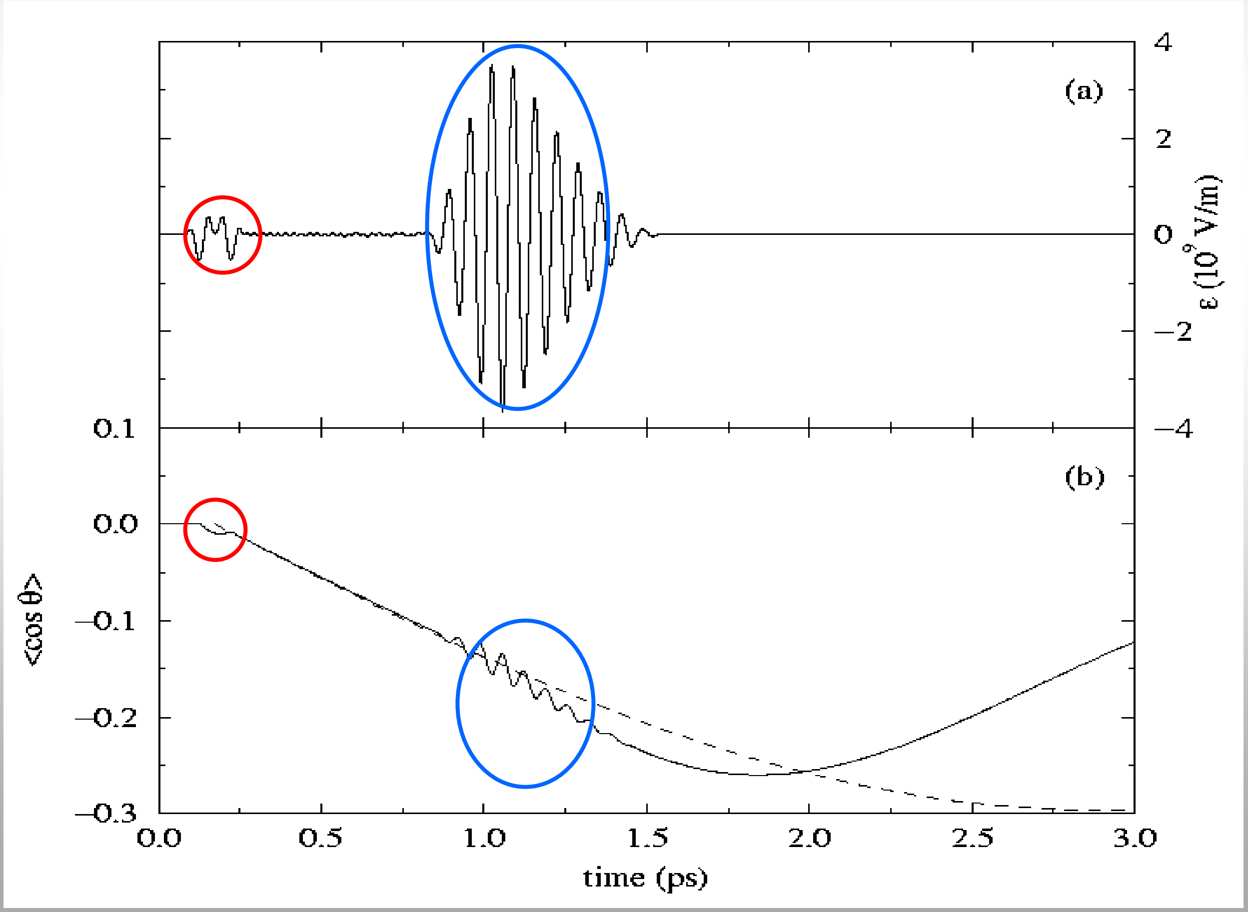
O.Atabek, C.Dion,A.B.H.Yedder, J.Phys.B ***36****,4667(2003)*

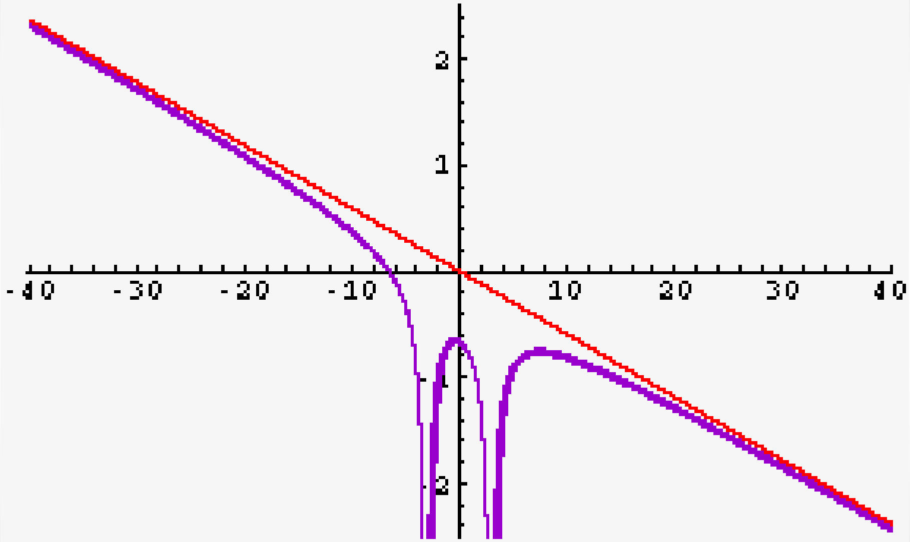
$$j_1 = \langle \cos\theta \rangle (t_f)$$

NG=500



n	E_n (W/cm2)	ω (cm-1)	ϕ (π rad.)
1	1.01364E08	1389.541	1.12406
2	2.99976E12	500.051	0.31723
3	2.99989E12	500.000	1.31887





2
1
-1
-2
-40
-30
-20
-10
10
20
30
40

ATTOSECOND PULSE SYNTHESIS

A. Ben-Haj Yedder, O. Atabek, C. Le Bris, S. Chelkowski, A. Bandrauk,
*Phys. Rev. A**69**, 041802R (2004)*

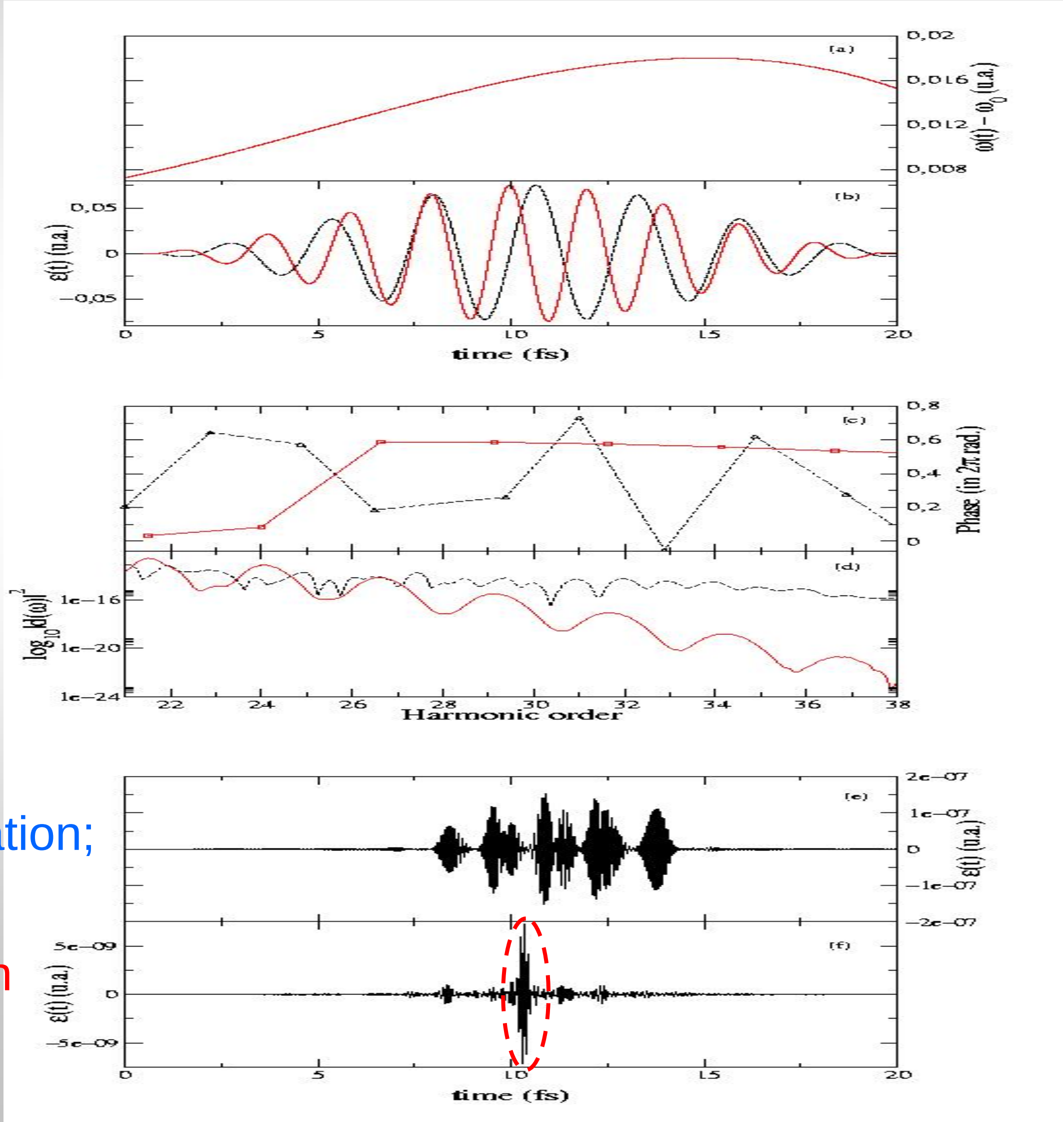
Chirped field

HHG: phases and amplitudes

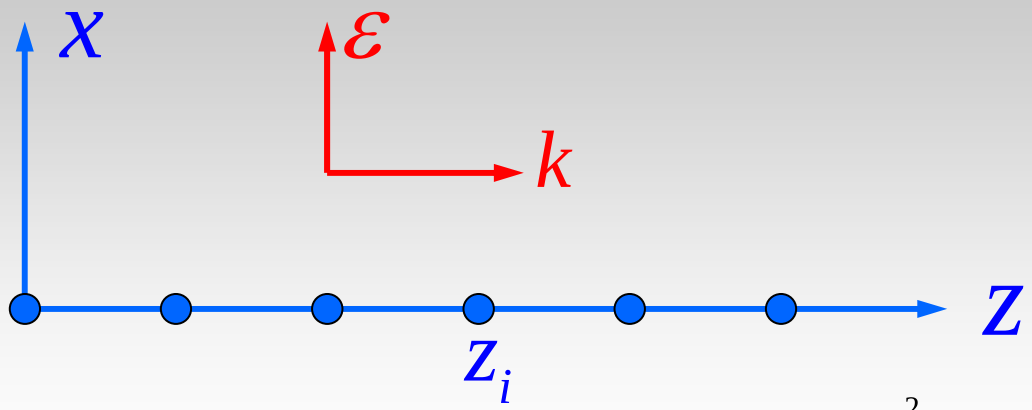
Emitted field:

• without optimization;

•after optimization



HHG FOR 1D OPTICAL LATTICES



$$H(x_1,\dots x_N,t;z_1,\dots z_N)=\sum_{i=1}^{N}H_i(x_i,t;z_i)$$

$$H_i(x_i,t;z_i)=\frac{p_{x_i}^2}{2m}+V(x_i)-ex_i.E(z_i,t)$$

Schrödinger Equation

$$H_i(x_i,t;z_i)\psi_i(x_i,t;z_i)=i\hbar\frac{\partial}{\partial t}\psi_i(x_i,t;z_i)$$

Maxwell Equation

$$\frac{\partial^2E(z,t)}{\partial z^2}-\frac{\mu}{c^2}\frac{\partial^2E(z,t)}{\partial t^2}=\frac{4\pi\mu}{c^2}\frac{\partial^2P(z,t)}{\partial t^2}$$

Polarization

$$P(z,t)=\sum_{i=1}^{N}\left\langle\psi_i(x_i,t;z_i)\middle|ex_i\middle|\psi_i(x_i,t;z_i)\right\rangle.\delta(z-z_i)$$

TARGET STATE

- Projection of the observable into a finite dimensional Hilbert subspace.
- Eigenstate of the projected observable corresponding to its lowest eigenvalue (variational principle).

Train of kicks: the target state

Individual kick

$$U_A = e^{iA\cos\theta} \qquad U_J = e^{-iBJ^2 t}$$

Finite subspace

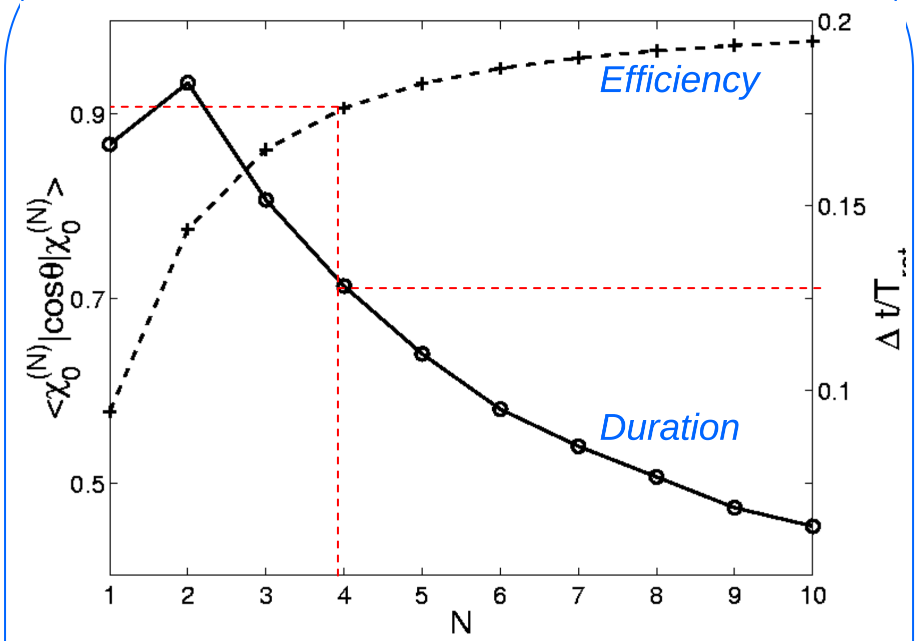
$$H_m^{(N)} : |j,m\rangle \; (j = |m|, |m|+1, \ldots |m|+N)$$

<cos θ> replaced by

$$C_m^{(N)} = P_m^{(N)} \cos\theta P_m^{(N)} \;\; ; P_m^{(N)} = \sum_{j=|m|}^{|m|+N} |j,m\rangle\langle j,m|$$

Target state (eigenfunction of $C_m^{(N)}$)

$$|\chi_m^{(N)}\rangle \approx \left(\frac{2}{N+2}\right)^2 \sum_{j=|m|}^{|m|+N} \sin\left(\pi \frac{j+1-|m|}{N+2}\right) |j,m\rangle$$

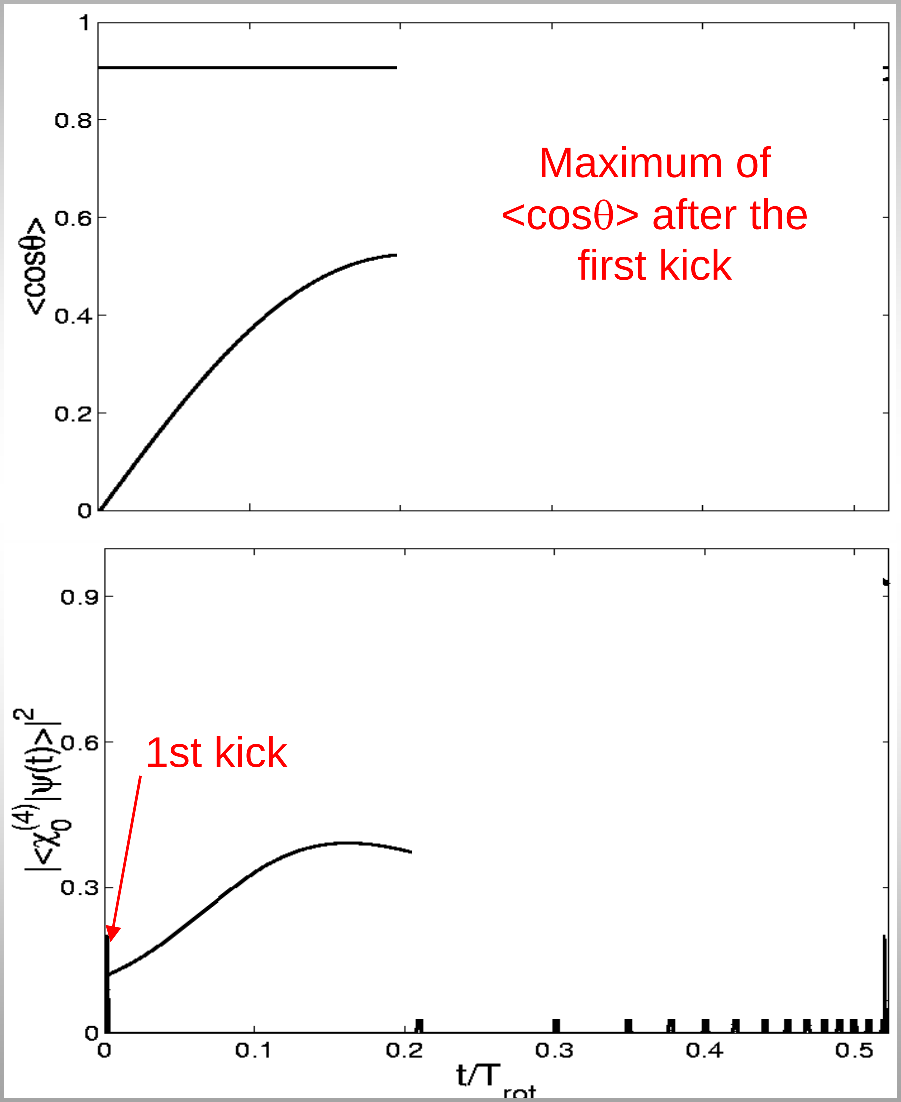


$$\langle \chi_0^{(N)} | \cos\theta | \chi_0^{(N)} \rangle \approx \cos\left(\frac{\pi}{N+2}\right)$$

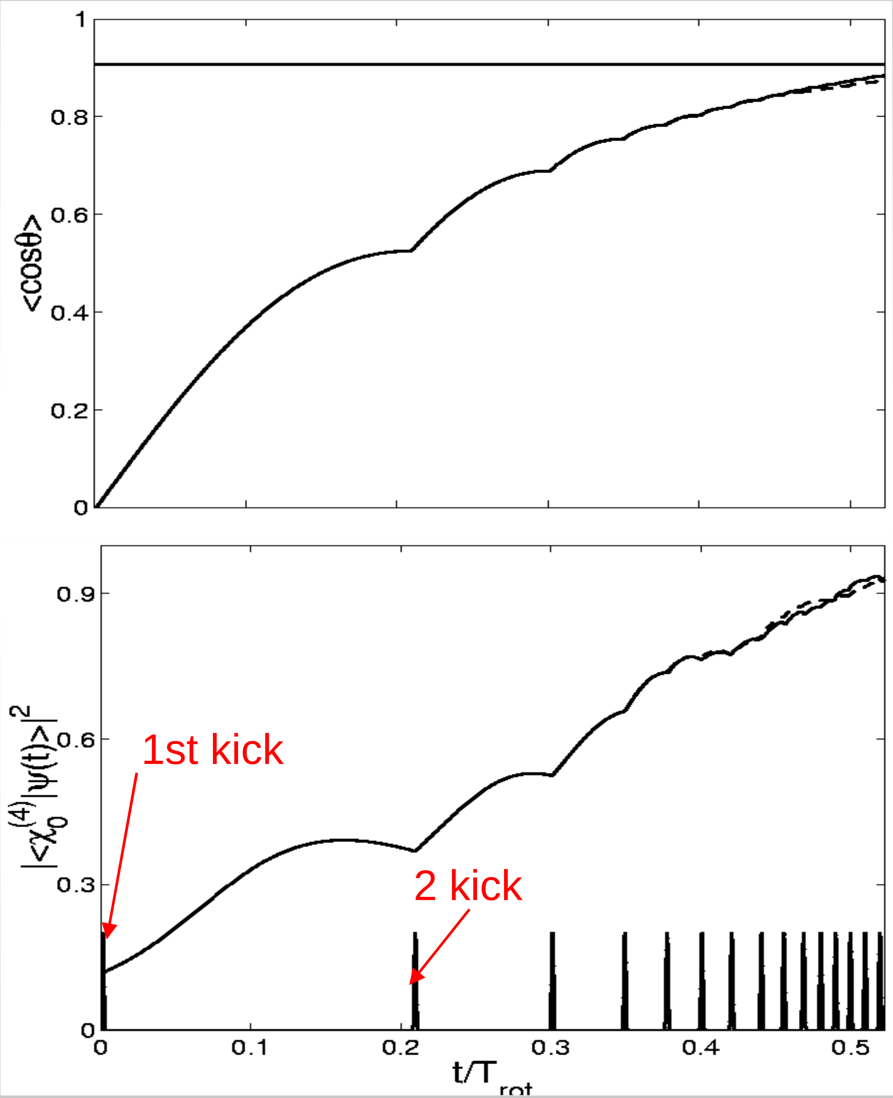
Choice of parameters to remain in $H_m^{(N)}$ $\qquad \left\| \left(e^{iA\cos\theta} - P_0^{(N)} e^{iA\cos\theta} P_0^{(N)}\right) |\chi_0^{(N)}\rangle \right\|^2 \approx \eta$

which, for small A, amounts to $\eta \approx [A\pi]^2 / [2(N+2)^3]$ $\qquad (A=1,\ N=4) \Rightarrow \eta \approx 0.02$

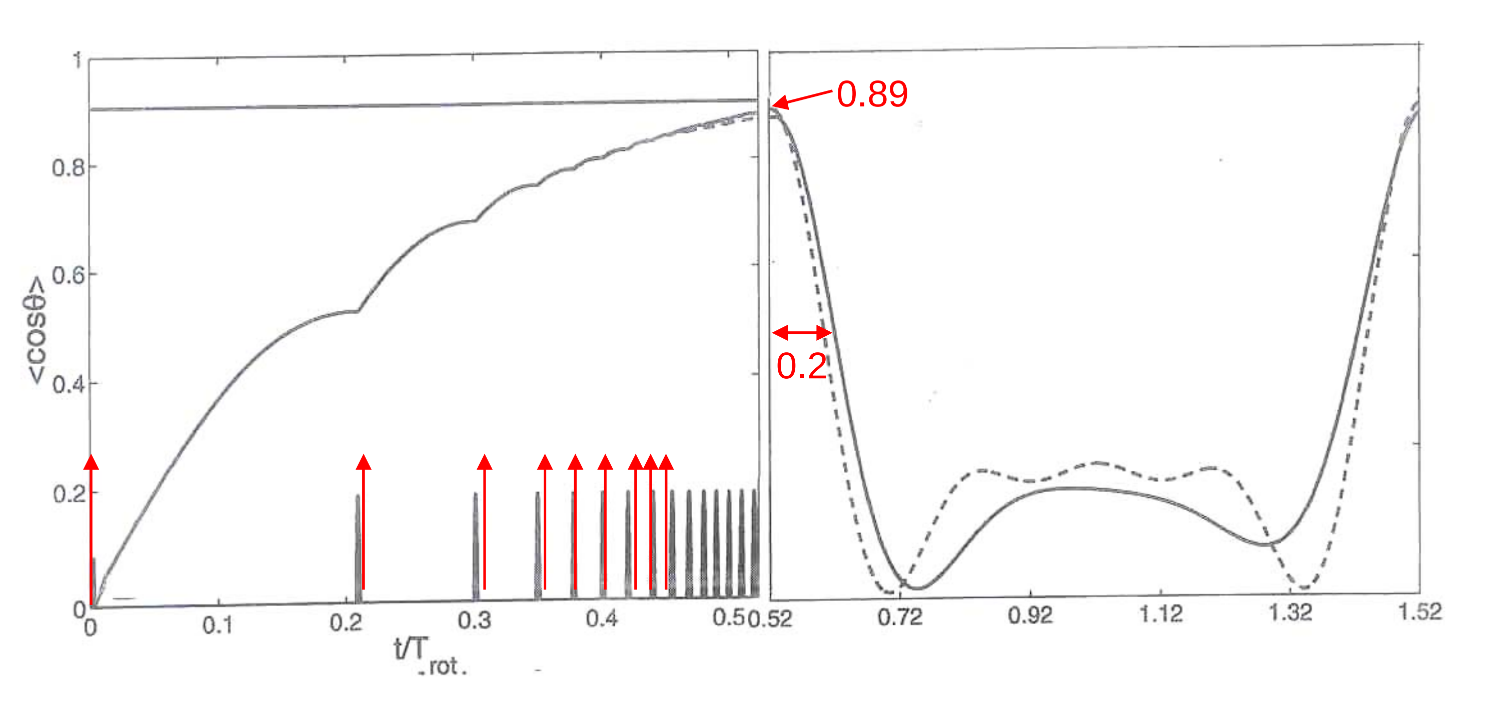
Train of kicks: the strategy



Train of kicks: the strategy



Train of kicks: the result

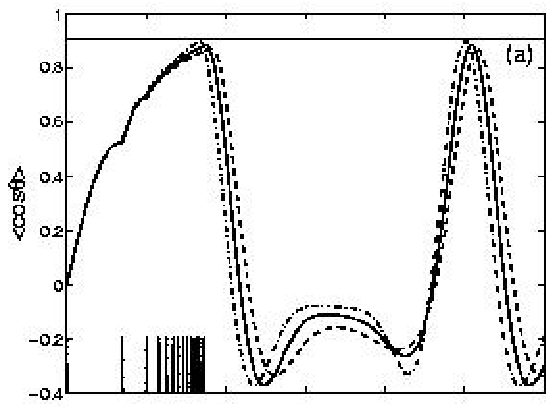


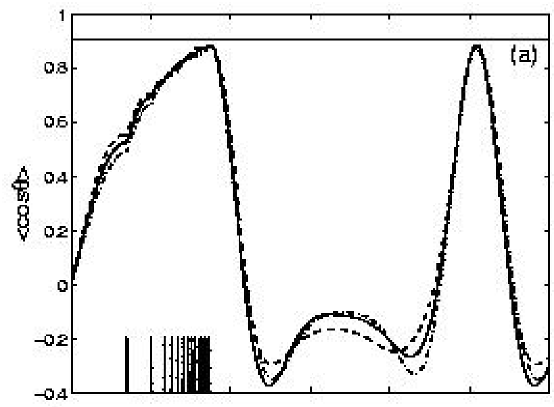
Efficiency = 0.89   Duration = 0.2 T_{rot}

for LiCl 2 ps, for NaI 20 ps

D. Sugny, A.Keller, O.Atabek, D.Daems, C.Dion, S.Guérin, H.Jauslin, *Phys. Rev. A* **69**, 033402 (2004)

Robustness





Robustness shifting time delays by ±1% of the rotational period

Robustness varying the pulse energy by ±10%

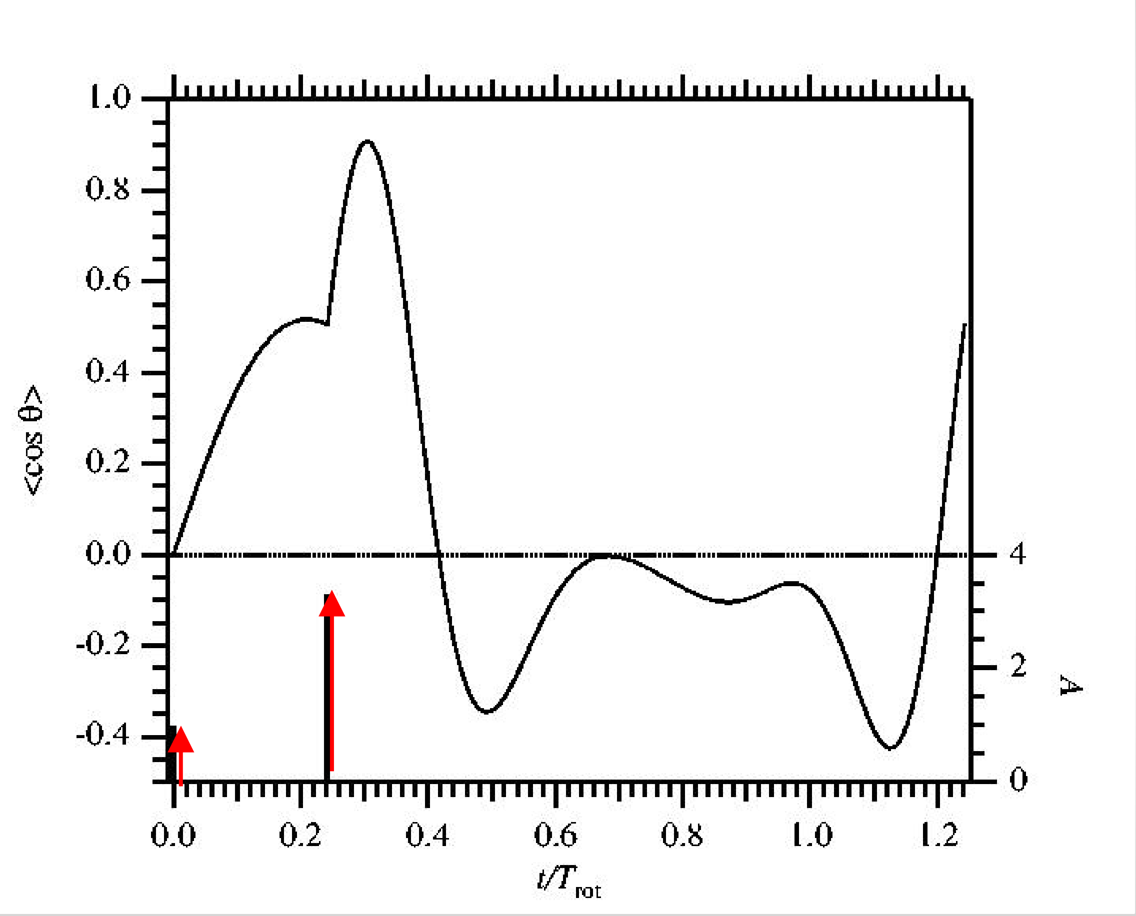
Geometrical accuracy: 0.2 μ, corresponding to 0.6 fsec, as compared to Trot of the order of 10 psec.

BACK TO OPTIMIZATION

- Well defined target state

- Optimize the amplitudes and delays between the HCP’s to reach the target state

Efficient, long-duration orientation with only 2 pulses



C. Dion, A. Keller and O. Atabek, Phys. Rev. Lett. (submitted)

Conclusions

- No single solution arising from optimal control schemes (criteria, parameters,…)
- Investigate basic mechanisms of laser-molecule dynamics ($\omega+2\omega$, kick,…)
- Restricting the parameters sampling space, force optimal control to take advantage of these mechanisms
- From the knowledge of the most relevant basic mechanisms, appropriately shape the laser pulse (train of kicks)

Perspectives: transposition to a generic system

Control objectives

- Free dynamics under H_0 $(e.g.\ BJ^2)$
- Control of an observable O $(e.g.\ \cos\theta)$

($\left[H_0, O\right] \neq 0,\ O$ upper or lower bounded, target: maximize or minimize $\left\langle O \right\rangle(t)$)

Control strategy

- Perturb the system with unitary U $(e.g.\ U_A = e^{iA\cos\theta})$

with: $\left[O, U\right] = 0 \Rightarrow \left\langle O \right\rangle = \left\langle U^{-1} O U \right\rangle$

the optimal target state is an eigenfunction of both $O\ and\ U$

- The optimum corresponds to a fixed point of the sequence $O_i = O(t_i)$

t_i times where $\left\langle O \right\rangle(t)$ reaches its maximum under free evolution

GENERIC STRATEGIES

$$H(t) = H_0 + v(t) H_1$$

Pure state

$$|\psi_\alpha(t=0)\rangle = |\alpha\rangle \;;\; H_0|\alpha\rangle = \alpha|\alpha\rangle$$

Example: $|\alpha\rangle = |j = m = 0\rangle$

$$|\alpha\rangle \xrightarrow[\text{unitary}]{U} |\chi^{(N)}\rangle$$

Strategy : fixed point of convergent series

a) Robustness, experimental feasibility;

b) Optimal control with well-defined targets;

c) Other control objectives : logical gates;

d) Mathematical study of the fixed points

GENERIC STRATEGIES

$$H(t) = H_0 + v(t) H_1$$

Mixed state

$$\rho(t) = \sum_k w_k \left|\psi_k(t)\right\rangle \left\langle \psi_k(t)\right| \qquad \frac{\partial}{\partial t}\rho(t) = -i\hbar^{-1}\left[H,\rho\right]$$

Example $\rho(0) = \frac{1}{Z}\sum_j \sum_m \left| j,m \right\rangle e^{-Bj(j+1)/kT} \left\langle j,m \right|$

$$\left|\rho(t=0)\right\rangle \xrightarrow[unitary]{U} \left|\rho^{(N)}(t)\right\rangle$$

Strategy : $\langle\langle O(t)\rangle\rangle = Tr\left[O\rho(t)\right]$; $\left[O,\rho\right] = 0$

specific ordering of the common eigenvectors of ρ and O

Use of different polarization schemes (elliptical); application to polyatomics

GENERIC STRATEGIES

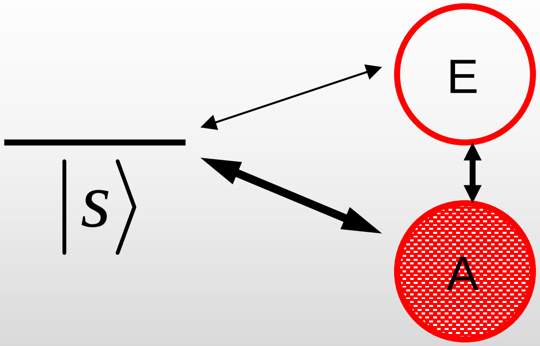
$$H(t) = H_0 + v(t) H_1$$

Molecular system interacting with an environment

Examples : collisions in a gas, frictions in a liquid

$$\left|\rho(t=0)\right\rangle \xrightarrow[non-unitary]{U} \left|\rho^{(N)}(t)\right\rangle$$

Strategy : Artificial reservoir against decoherence



What are the targets? Are they attainable?