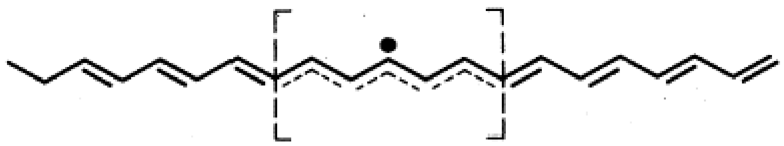


Coherent Control of Charge Transport in Photoexcited *trans*-Polyacetylene

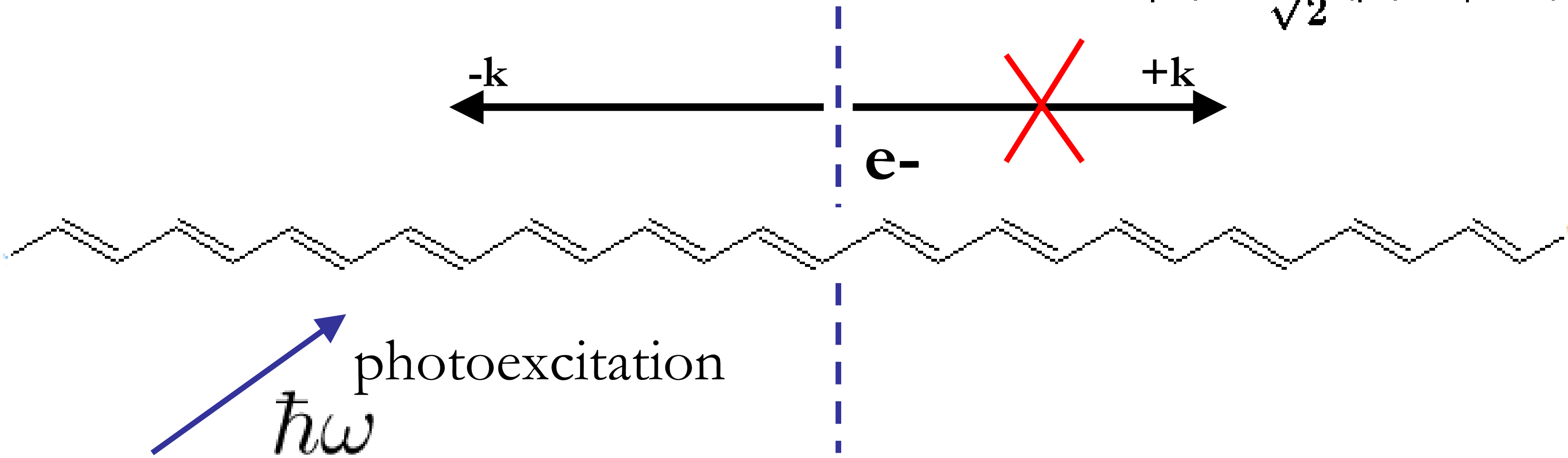
Ignacio Franco and Paul Brumer

July 22, 2004

Quantum Information and Quantum Control Conference

What we want to do

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|\mathbf{k}\rangle \pm |-\mathbf{k}\rangle\right)$$



Left/Right Symmetry

AIM

BREAK the symmetry of a conjugated polymer using lasers and electric dipole interactions (no bias voltage).

HOW?

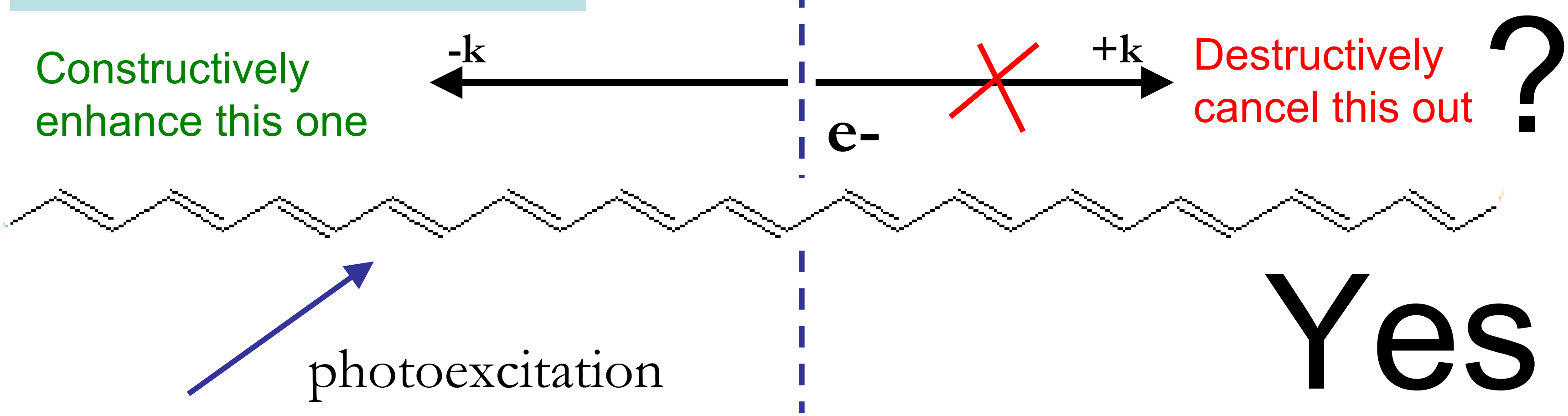
Use the Phase/Coherence of the laser and of matter: Coherent Control

Coherent Control

Laser Control of Physical Processes ⟷ Quantum interference (use coherence of laser + phases physical system)

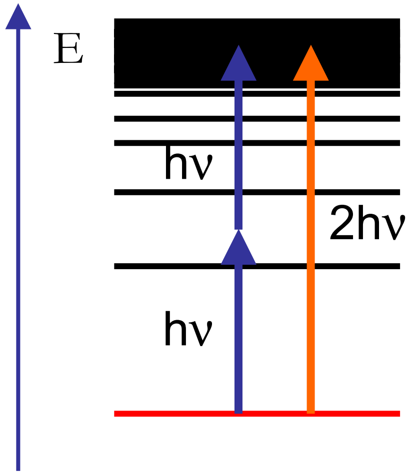
Source of interference: Two or more indistinguishable optical pathways from an initial state to a final state

Can we use this idea for

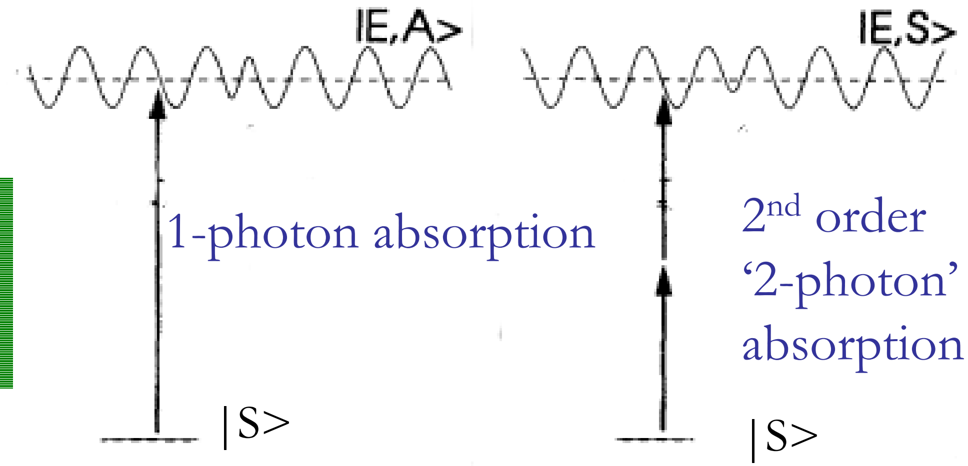


Kurizki + Shapiro + Brumer PRB **39**, 3435 (1989)

This scenario: 1 vs. 2 photon control



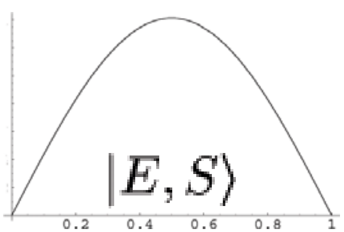
Note two 'routes' to same final state



couples states with opposite parity

couples states with same parity

Final State:



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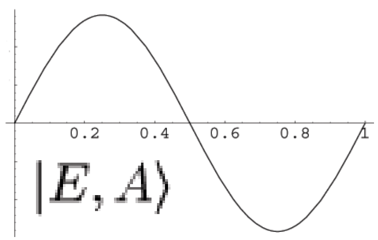

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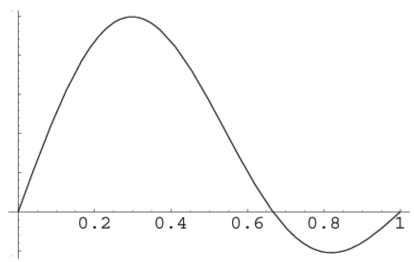


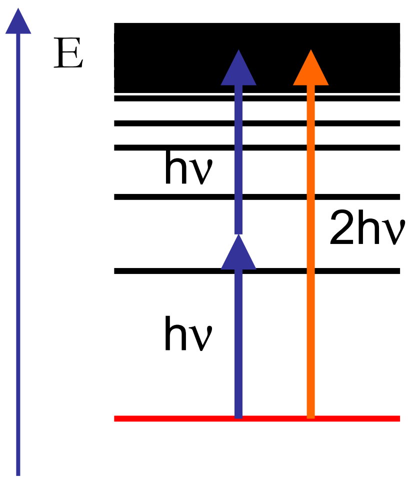
Laser controllable

Not a parity eigenstate

Broken Symmetry

Kurizki + Shapiro + Brumer PRB **39**, 3435 (1989)

This scenario: 1 vs. 2 photon control



Quantum interference between the one- and two-photon processes results in Symmetry Breaking

The selected state will not be of definite parity:

Broken Symmetry

Net dipoles (bound systems)

Currents (infinite systems)

$$E(t) = \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega}) + \epsilon_{\omega} \cos(\omega t + \phi_{\omega})$$

$$P(\mathbf{k}) - P(-\mathbf{k}) \propto (\text{sys. dep. fac.}) \times |\epsilon_{2\omega}||\epsilon_{\omega}|^2 \cos(\phi_{2\omega} - 2\phi_{\omega})$$

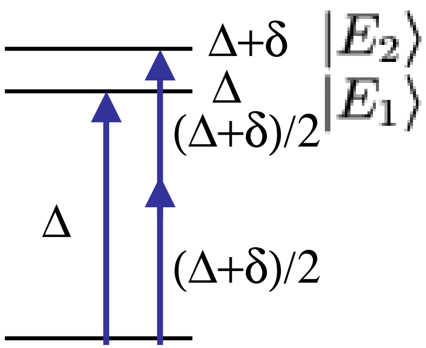
Control:

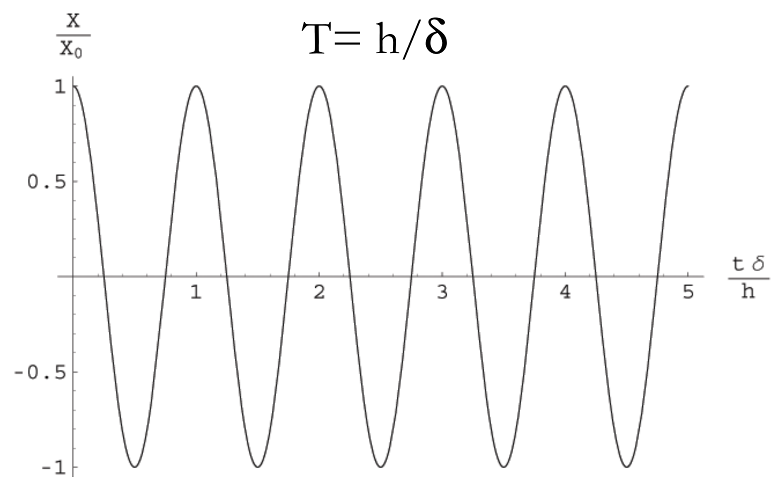
By changing the phase relationship between the two lasers we can control the degree of photoinduced dissymmetry.

Energy degeneracy of the final states is crucial otherwise the two 'routes' are distinguishable.

Kurizki + Shapiro + Brumer PRB **39**, 3435 (1989)

This scenario: 1 vs. 2 photon control





Symmetry breaking averages out in time if the final states are not degenerate!

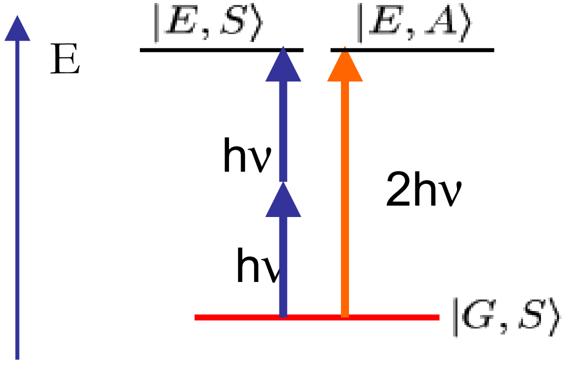
$$|\Psi(t)\rangle = a\exp(-i\Delta t/\hbar)|E_1\rangle + b\exp(-i(\Delta+\delta)t/\hbar)|E_2\rangle$$

$$\langle x\rangle = \langle\Psi(t)|x|\Psi(t)\rangle = 2\Re\{ab^*\langle E_2|x|E_1\rangle\exp(i\delta t/\hbar)\}$$

Energy degeneracy of the final states is crucial otherwise the two 'routes' are distinguishable.

This scenario: 1 vs. 2 photon control

Minimal Structure for the 1+2 photon coherent control scenario



(to be generalized)

Anisotropy in atomic photodissociation

$$E(t) = \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega}) + \epsilon_{\omega} \cos(\omega t + \phi_{\omega})$$

$$P(\mathbf{k}) - P(-\mathbf{k}) \propto (\text{sys. dep. fac.}) \times |\epsilon_{2\omega}||\epsilon_{\omega}|^2 \cos(\phi_{2\omega} - 2\phi_{\omega})$$

Rb atoms

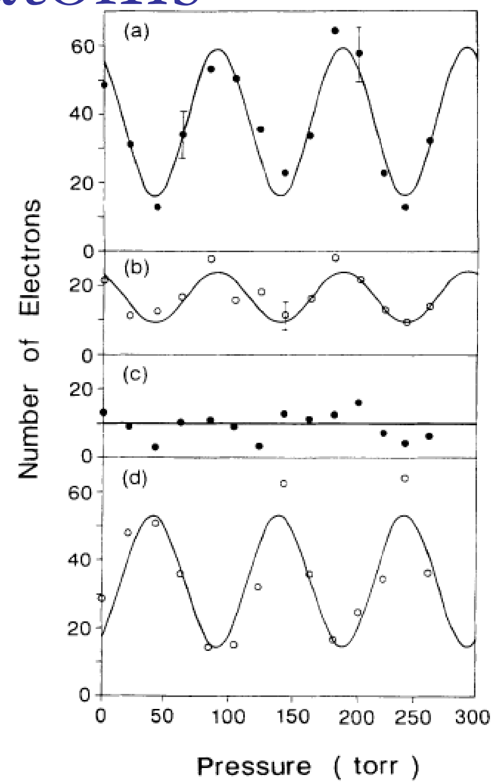


FIG. 3. Experimental data. The total electron count as a function of pressure of N_2 gas in the phase delay cell for the four detectors positioned at (a) 0°, (b) 45°, (c) 90°, and (d) 180°. The solid line is the result of a least-squares fit of a sinusoidally varying curve to the data.

Asymmetric distribution of the photoelectrons ejected from a spherically symmetric atom.

The asymmetry can be reversed through variation of the relative phase of the two field components

Yin et al. PRL **69**, 2353 (1992)

280 nm/560 nm Nd:YAG laser.

Relative phase controlled with a variable pressure cell

Photocurrent in a quantum well

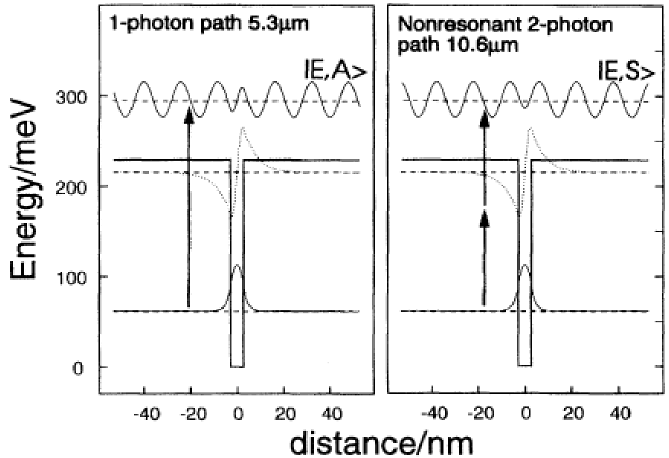


FIG. 1. Energy band diagram of a 55 Å GaAs/$Ga_{0.74}Al_{0.26}As$ QW and wave functions of the states implied in a 5.3 μm single-photon pathway and a 10.6 μm two-photon process. Neither dephasing nor reflections of the electronic waves on the neighbor QWs are considered in this simplified figure.

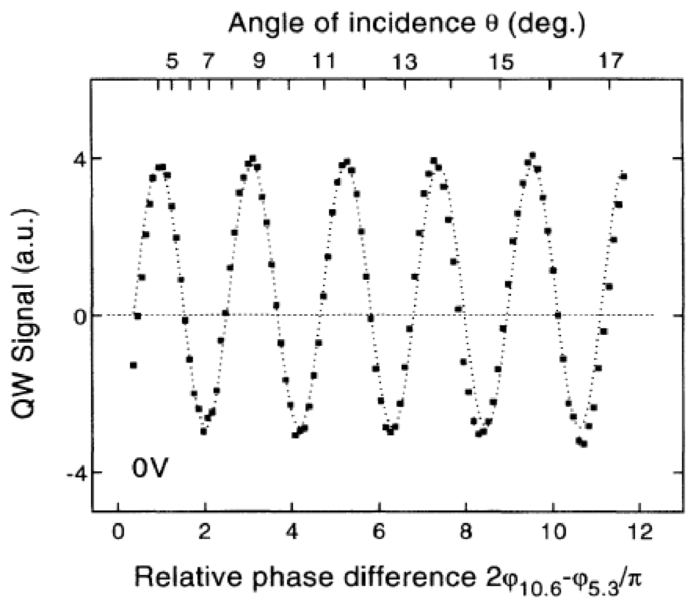


FIG. 4. Integrated QW response versus the angle of incidence. Dashed line: sinusoidal fit.

Dupont et al. PRL **74**, 3596 (1995)

CO_2 pulse laser (100 ns)

… and in a semiconductor

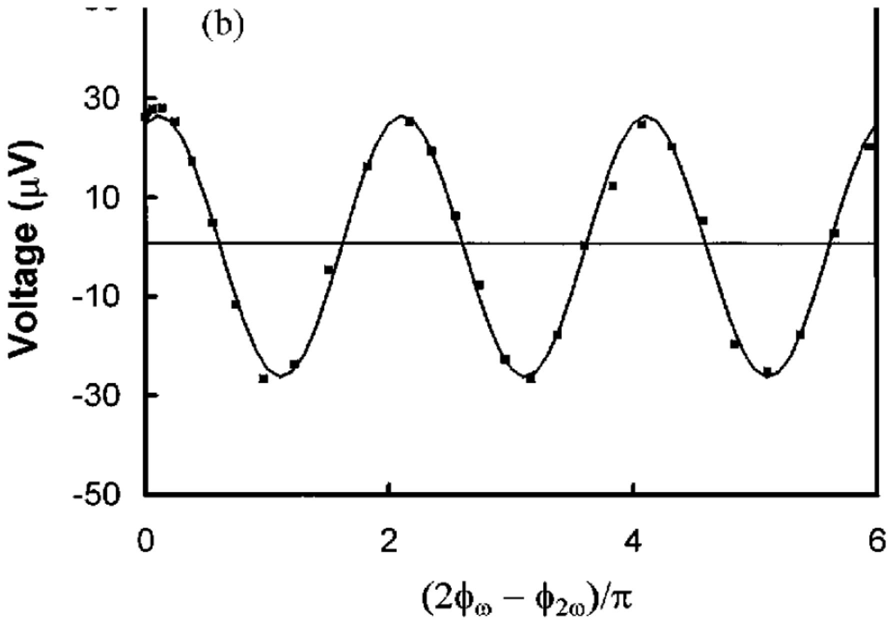
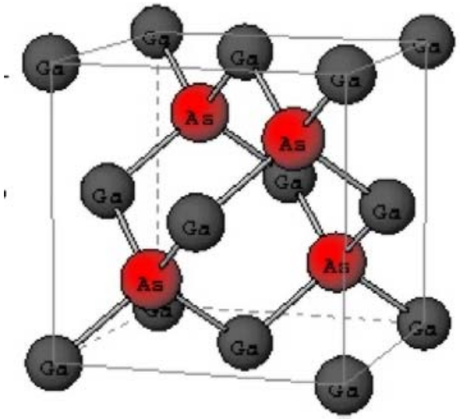
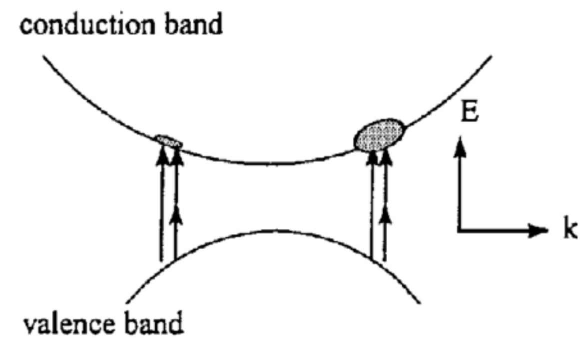


FIG. 2. (a) Induced voltage on a 25 μm gap LT-GaAs MSM detector in the presence of the ω beam (triangles), the 2ω beam (circles), and both beams (squares) from the OPO as a function of glass plate rotation angle θ; the voltage is adjusted to read zero volts when the two beams are simultaneously present on the sample with $\theta = 0$. (b) Induced coherently controlled current signature as a function of $\Delta\phi$ for a 5 μm gap MSM; the solid curve is the best fit for a sine function.





Current without a bias voltage!

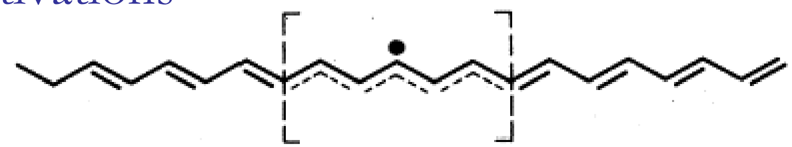
Hache et al. PRL **78**, 306 (1997)

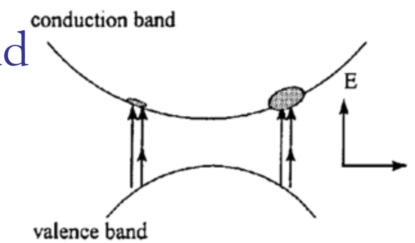
1550/775 nm beams, intense fs pulses.

Outline

Induce directed electronic transport in PA:
centrosymmetric molecule with strong e-ph interactions

1. 1 vs. 2 photon control in soft materials: challenges and motivations

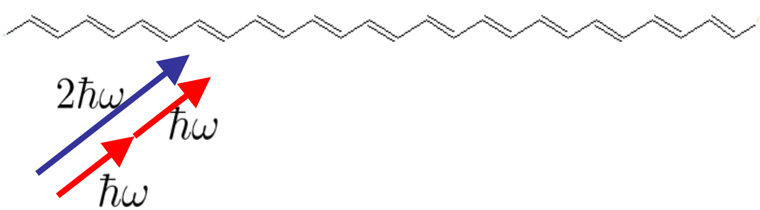




2. Phenomenology of trans-PA and the SSH Hamiltonian

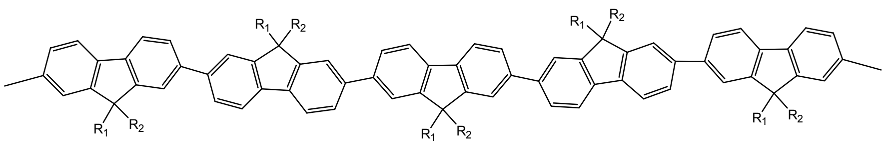
$$H_{\mathrm{SSH}} = H_{\pi} + H_{\pi-\mathrm{ph}} + H_{\mathrm{ph}}$$

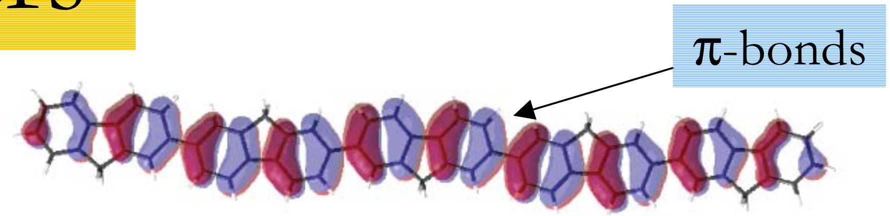
3. Photoinduced dynamics in the presence of a two-color laser



A) Rigid Chain
B) Flexible Polymer

Conjugated Polymers





Delocalized, mobile and highly polarizable π-electronic cloud

<u>Principal excitation:</u>
Electron-hole pair coupled with a local distortion in the molecule (Excitons, Polarons, …)

Band-Gap Energy ~ 1 eV
Electronic Correlations ~ 0.2-1 eV

Electron-phonon couplings ~ 0.2-1 eV

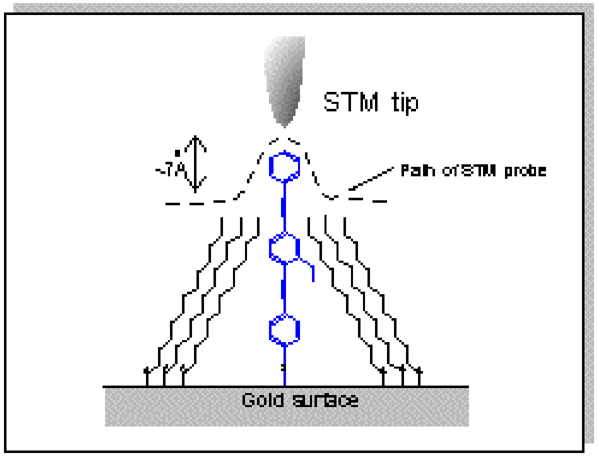
Chemical Structure is Important

1 vs 2 in a conjugated polymer: Motivations

Really interesting systems:

Applicability of Coherent Control in soft condensed matter

Our reward:
Ultrafast Currents in Molecular Wires



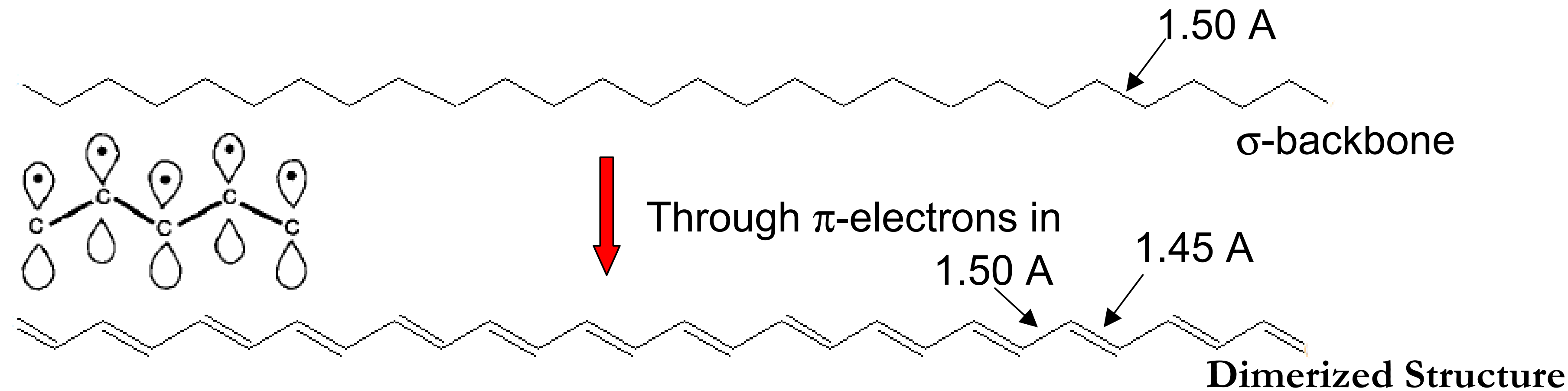
Challenges:

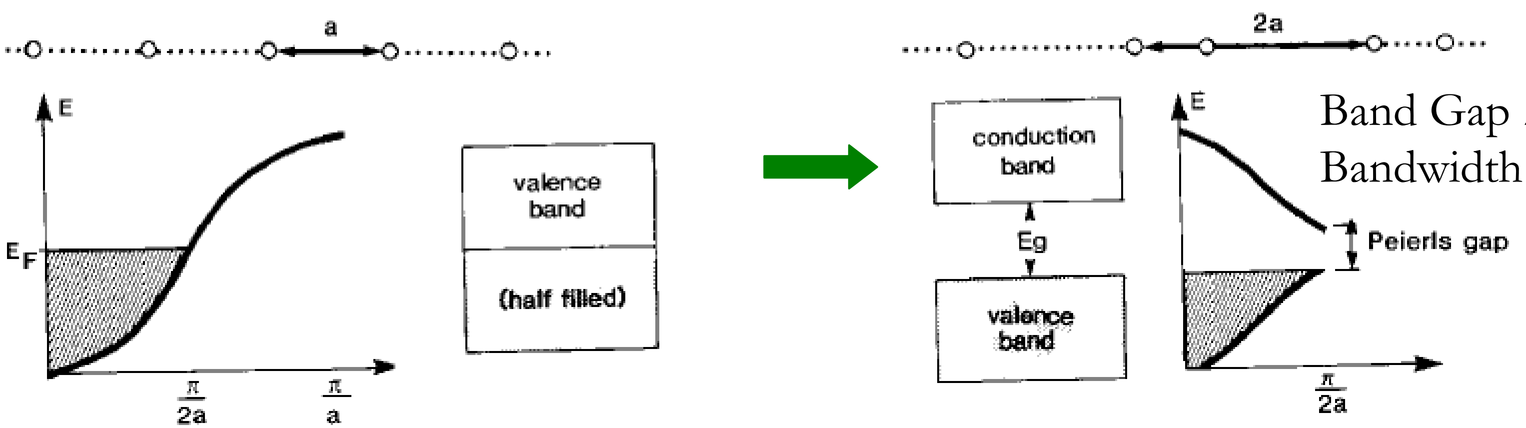
No degeneracies in the final states (for finite molecules)

Decoherence time ~40 fs due to strong e-ph coupling.

trans-polyacetylene: Phenomenology

Ground state PA is like a direct band gap intrinsic semiconductor …





Band Gap $2\Delta_0$ ~ 1.3 eV

Bandwidth $2t_0$ ~ 5 eV

1D metals are unstable w.r.t. a periodic structural deformation which opens a gap at the Fermi level (Peierls Distortion)

trans-polyacetylene: Phenomenology

Strong electron-ion coupling

Great Review: Heeger, Kivelson, Schrieffer, Su.
Rev. Mod. Phys. **60**, 781 (1988)

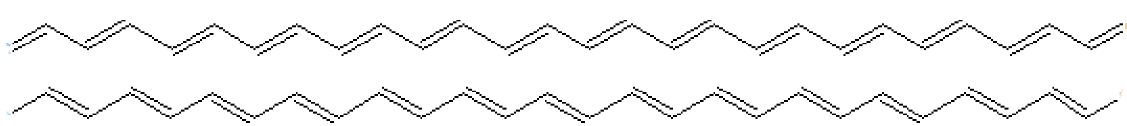
electrons ⟷ nuclei

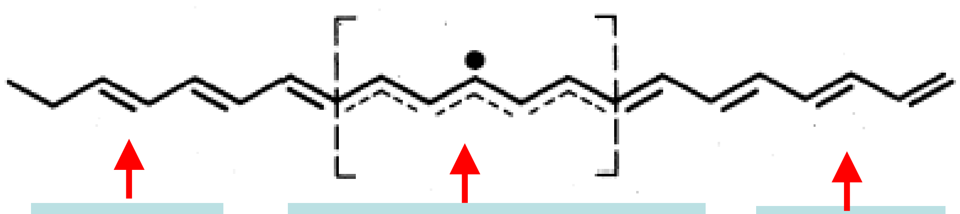
Electronic excitations ⟷ Lattice distortions

Polarons | **Excitons** | **Soliton Pairs**

Self-localized nonlinear excitations associated with a lattice distortion

Two-fold degenerate ground state



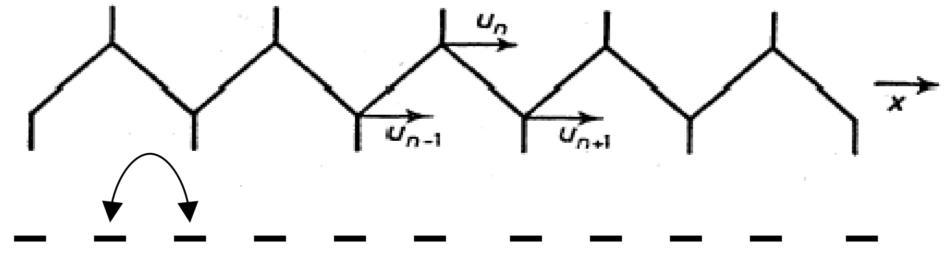


SSH Hamiltonian: a minimum model for PA

Tight-binding Fermionic Hamiltonian

$$\{c_{n,s}, c^\dagger_{m,s'}\} = \delta_{n,m}\delta_{s,s'}$$

$$H_{\rm SSH} = H_\pi + H_{\pi-{\rm ph}} + H_{\rm ph}$$



Hopping of π-electrons

$$H_\pi = -t_0 \sum_{n,s} \left(c^\dagger_{n+1,s} c_{n,s} + c^\dagger_{n,s} c_{n+1,s} \right)$$

π-electron-ion coupling

$$H_{\pi-{\rm ph}} = \alpha \sum_{n,s} (u_{n+1} - u_n) \left(c^\dagger_{n+1,s} c_{n,s} + c^\dagger_{n,s} c_{n+1,s} \right)$$

Nuclear Hamiltonian

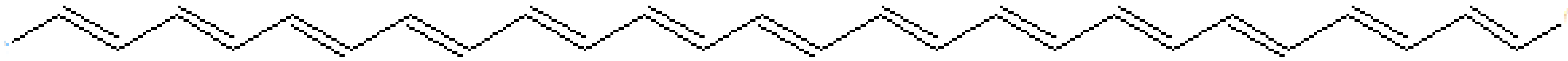
$$H_{\rm ph} = \sum_n \frac{p_n^2}{2M} + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2$$

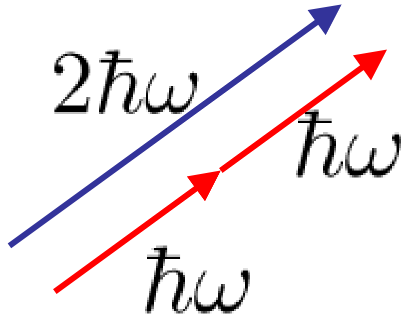
Effective empirical model for non-interacting quasiparticles in PA

$$t_0 = 2.5 \text{ eV} \quad K = 21 \text{ eV/Å}^2$$
$$M = 1349.14 \text{ eV fs}^2\text{/Å}^2$$
$$a = 1.22 \text{ Å} \quad \alpha = 4.1 \text{ eV/Å}$$

So our problem:

Coupled nonlinear dynamics of electronic and vibrational degrees of freedom in the presence of a (symmetry-breaking) radiation field





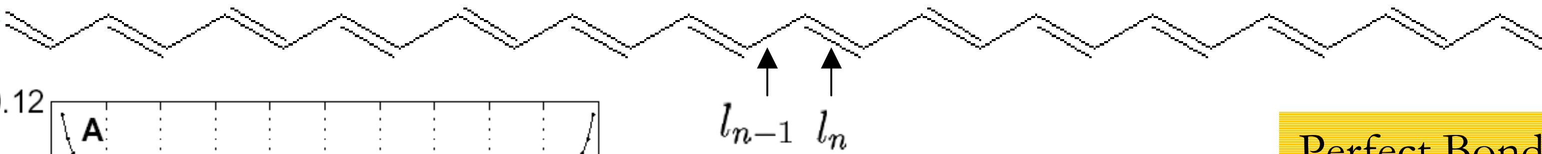
Dynamics during and after the pulse

Influence of e-ph coupling

Effect of quasidegeneracies in the scenario

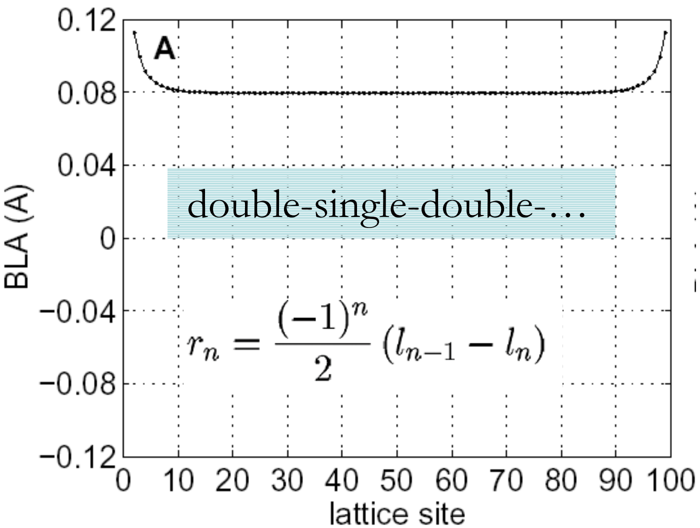
4N degrees of freedom (4*100=800!)

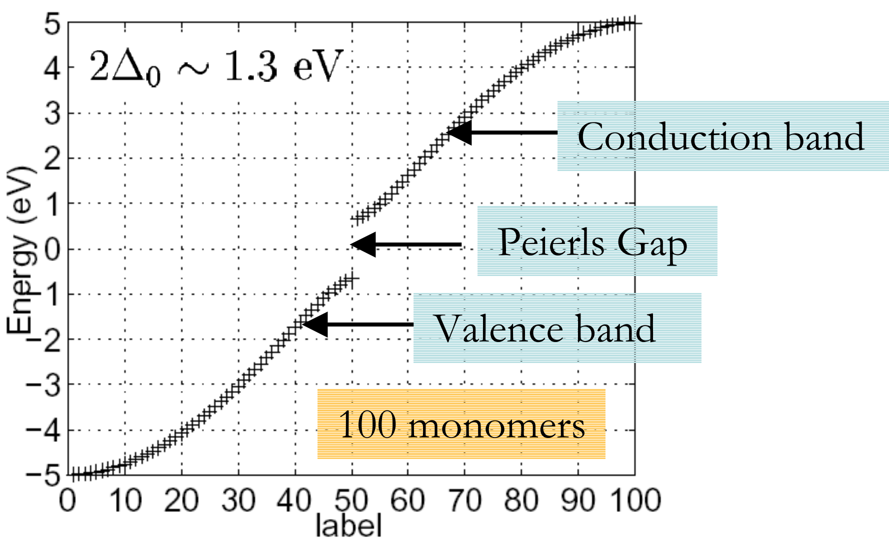
Selection of Chain Size

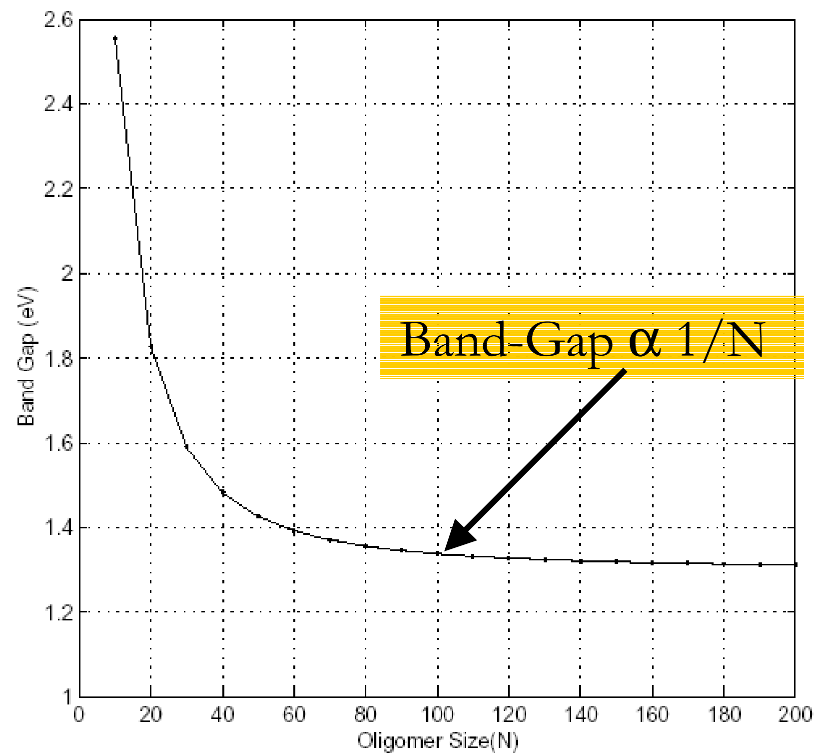


$$r_n = \frac{(-1)^n}{2}(l_{n-1} - l_n) = \frac{(-1)^n}{2}(2u_n - u_{n-1} - u_{n+1})$$

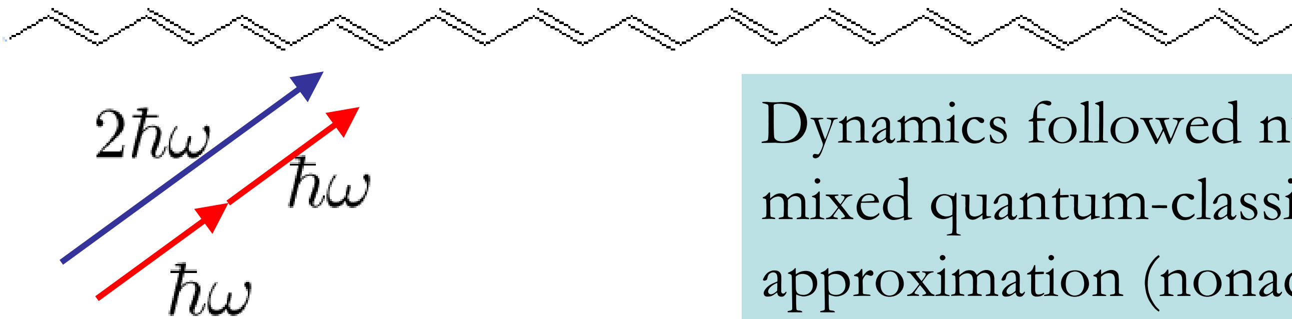
Perfect Bond Length Alternation (double-single-…)







Photoinduced Dynamics



Dynamics followed numerically in mixed quantum-classical mean-field approximation (nonadiabatic)

$$|\Phi(\mathbf{r},\mathbf{R},t)\rangle = |\Psi(\mathbf{r},t)\rangle \otimes |\Omega(\mathbf{R},t)\rangle$$

Mean-field ansatz

$$\frac{d\mathbf{p}_n}{dt} = -\langle\Psi(\mathbf{r},\mathbf{R},t)|\nabla_{\mathbf{R}_n} H_e(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r},\mathbf{R},t)\rangle$$

Classical nuclei moving in a mean-field potential

$$i\hbar\frac{\partial}{\partial t}|\Psi(\mathbf{r},\mathbf{R},t)\rangle = H_e(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r},\mathbf{R},t)\rangle$$

Electrons respond to the classical (“average”) trajectory of the nuclei

$$H_E(t) = -(\mu_e + \mu_i)E(t)$$

Radiation-Matter interaction in dipole approximation

Photoinduced Dynamics

My coupled highly non-linear equations of motion …

The nuclei

$$\dot{u}_n = \frac{p_n}{M}$$

$$\dot{p}_n = -K\left(2u_n(t) - u_{n+1}(t) - u_{n-1}(t)\right) + 2\alpha \mathrm{Re}\left\{\rho_{n,n+1} - \rho_{n,n-1}\right\} - |e|E(t)\left(\rho_{n,n} - 1\right)$$

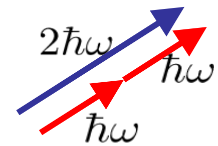
The orbitals

$$i\hbar\dot{\psi}_{n\epsilon} = \left[-t_0 + \alpha(u_{n+1} - u_n)\right]\psi_{n+1,\epsilon} + \left[-t_0 + \alpha(u_n - u_{n-1})\right]\psi_{n-1,\epsilon} + |e|E(t)\left((na + u_n) - a\frac{N(N+1)}{2}\right)\psi_{n,\epsilon},$$

$$\rho_{n,m} = \sum_s \langle\Psi(t)|c^\dagger_{m,s}c_{n,s}|\Psi(t)\rangle$$

Closed set of 2N(N+1) coupled first-order differential eqns.
Integrated using RK order 8 with step size control (time-step ~ 1as)

Photoinduced Dynamics



1) Rigid Chain (Frozen Nuclei)

Initial state: Ground state (minimum energy) geometry

2) Flexible Chain

100 monomer long

Ensemble of trajectories with initial conditions determined by the nuclear ground state wave-function

The laser

fs gaussian pulse

$$E(t) = E_0 \exp\left[-(t-T_C)^2/T_W^2\right]\left(\cos(2\Delta_0 t/\hbar) + \cos(\Delta_0 t/\hbar + 2\pi\phi/360)\right)$$

1-photon excitation across the Peierls gap

2-photon excitation

Relative phase: source of control

Photoinduced asymmetry characterized through molecular dipoles

$$\langle X(t)\rangle = \mathrm{Tr}(\rho(t)\hat{x}) - a\frac{N(N+1)}{2}$$

$$\hat{x} = \sum_n (na+u_n) \sum_s c^\dagger_{ns} c_{ns}$$

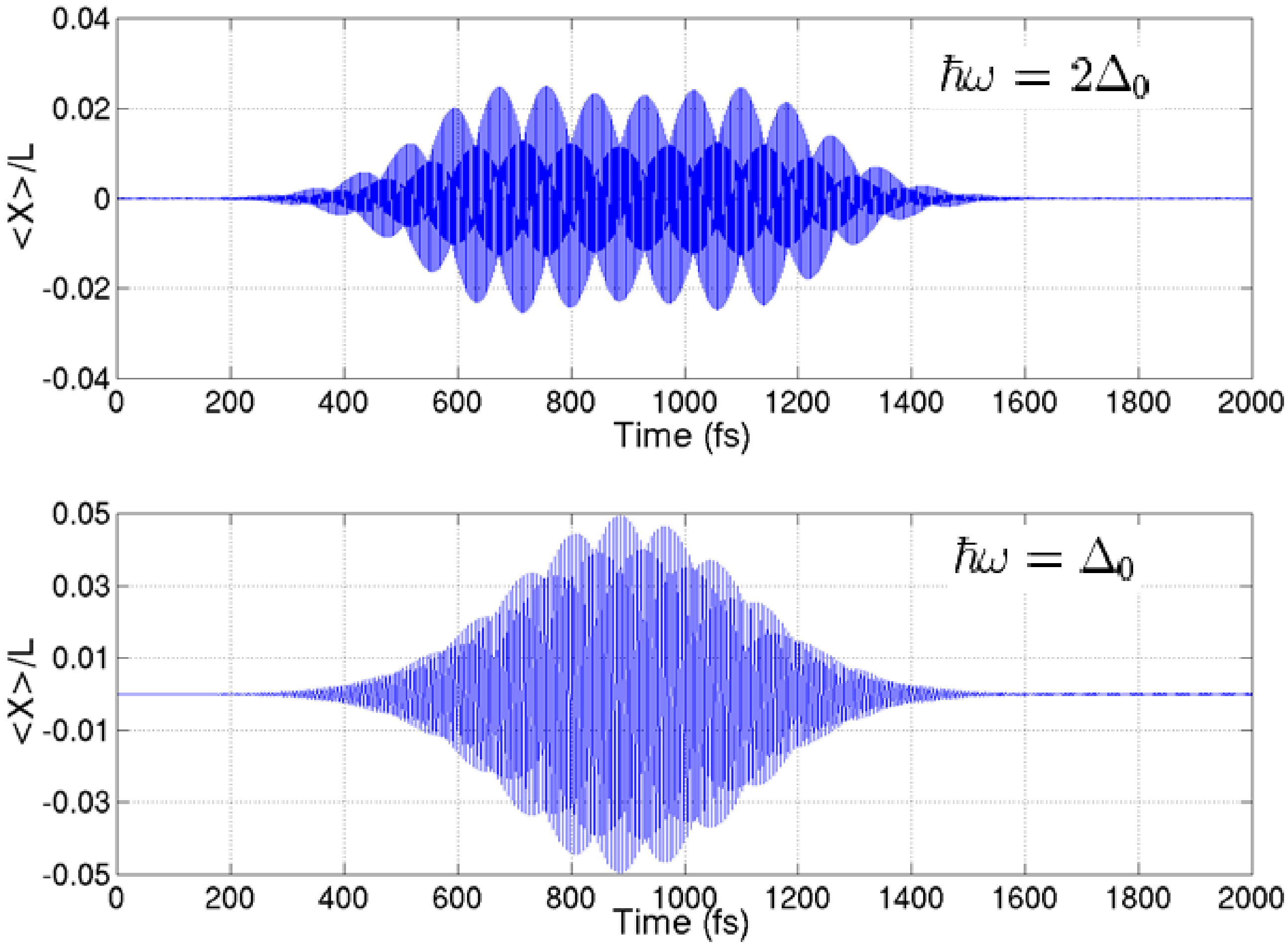
Photoinduced Dynamics : **Rigid Chain**

Dynamics in the presence of a **single** laser pulse

300 fs pulse

Frozen Nuclei

$\langle X(t) \rangle$ *vs.* t

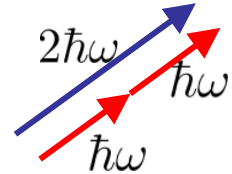


$$\int dt \langle X(t) \rangle = 0$$

Photoinduced dipoles are small + not symmetry breaking

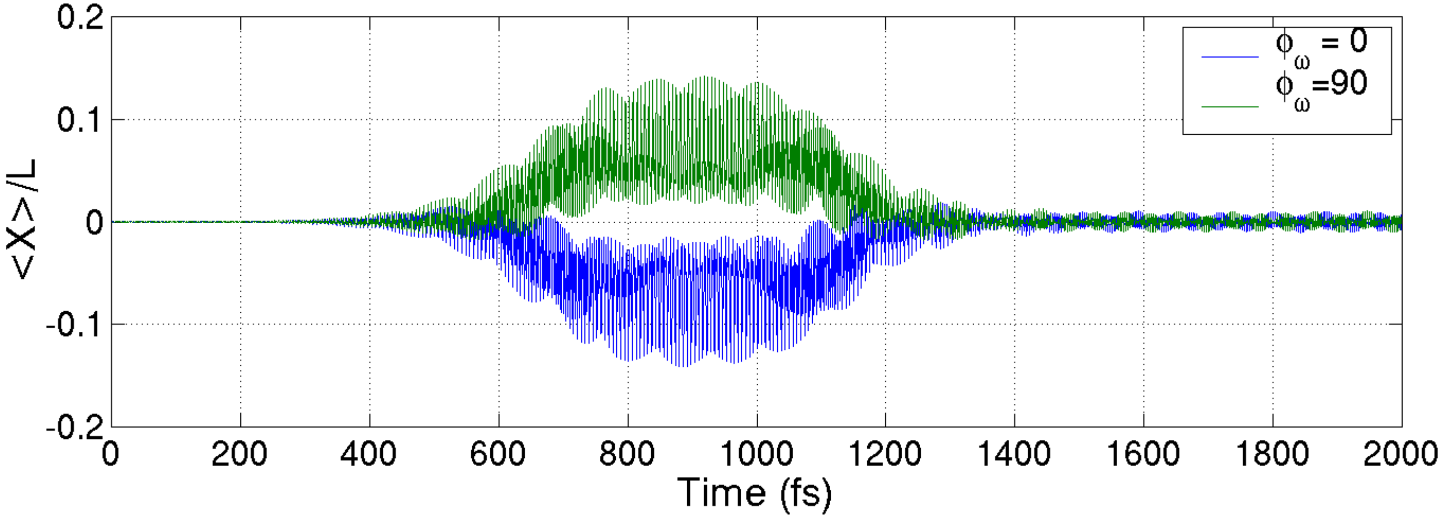
300 fs pulses centered at 900 fs of $I \sim 10^9$ W cm^{-2}

1 vs 2 : Rigid Chain

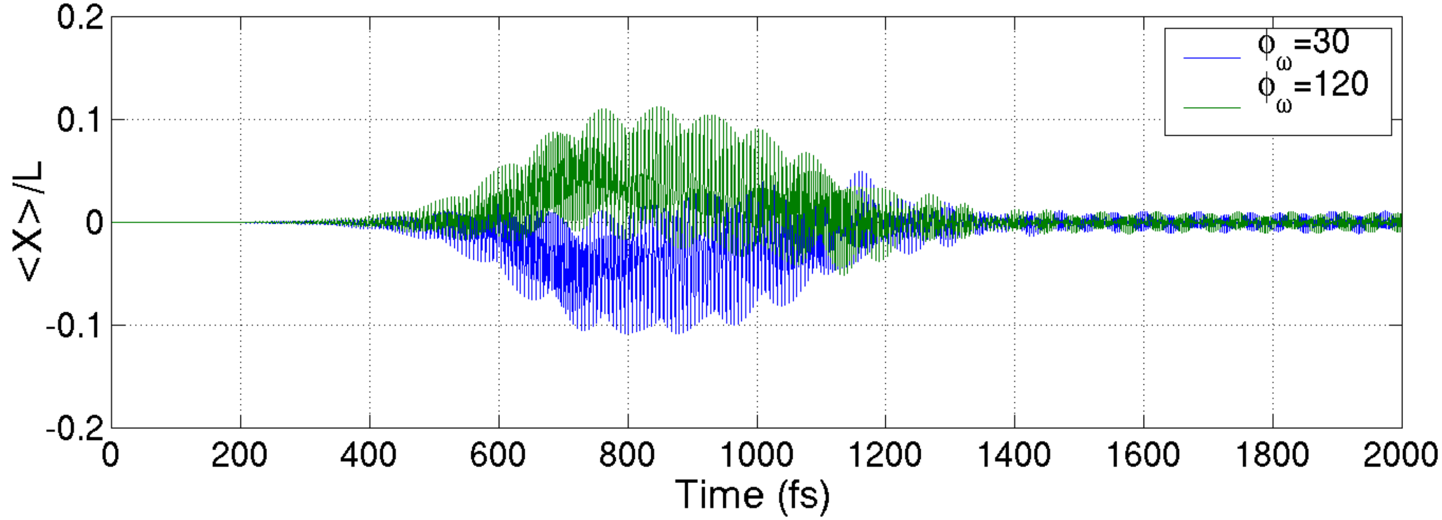


300 fs pulse

$$\int dt\langle X(t)\rangle \neq 0$$



Phase controllable symmetry breaking while the pulse is on!

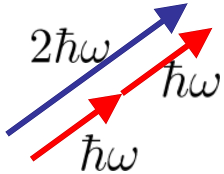


300 fs pulses centered at 900 fs of I~10^9 W cm^{-2}

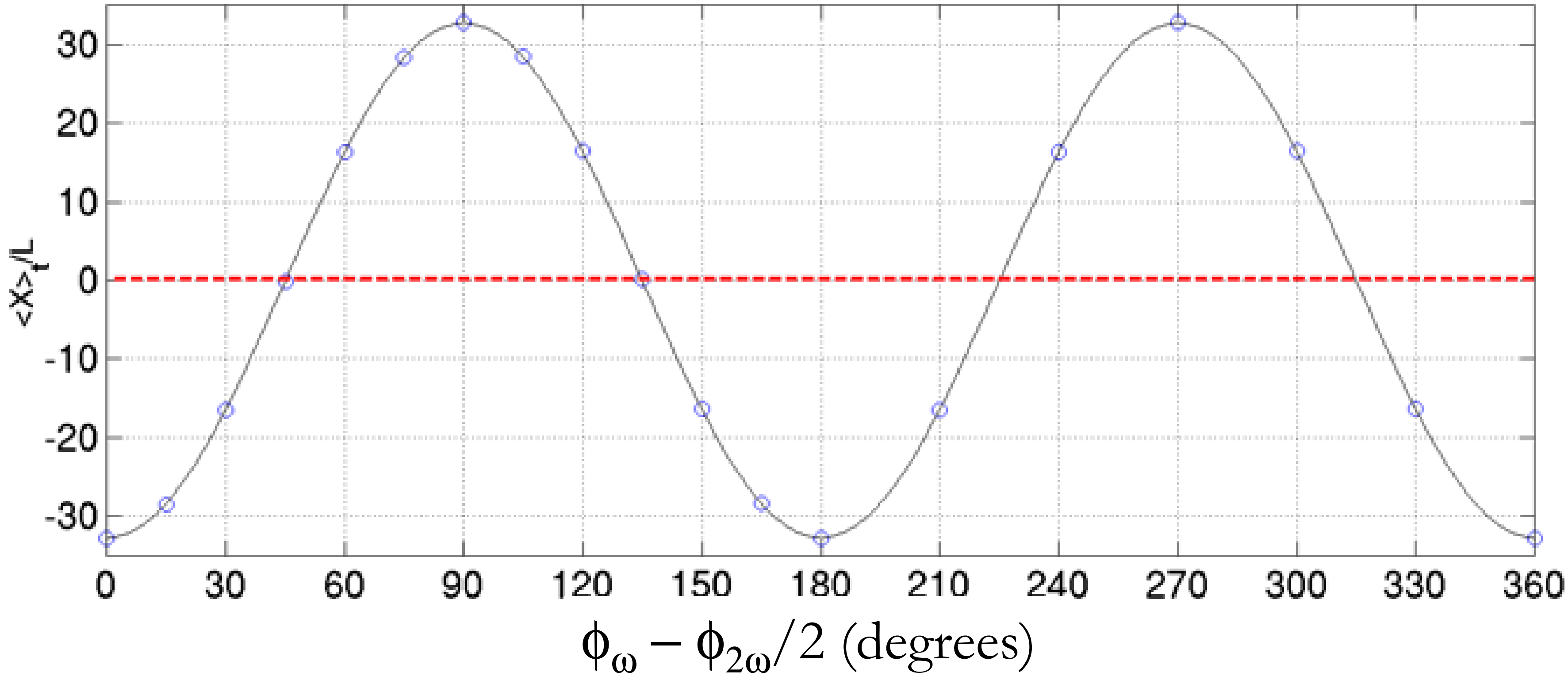
1 vs 2 : **Rigid Chain – Control**

300 fs pulse

$$\overline{\langle X(t)\rangle} = \frac{1}{L}\sum_{t=0}^{t_f}\langle X(t)\rangle$$



$$\int dt \langle X(t)\rangle \neq 0$$

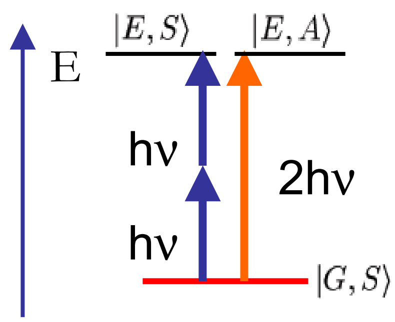


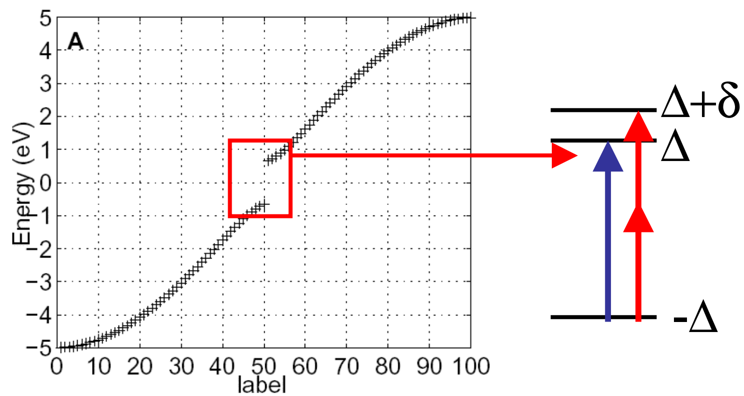
Photoinduced asymmetry controllable by varying the relative phase between the two lasers

300 fs pulses of $I \sim 10^9$ W cm^{-2}

1 vs 2 : **Rigid Chain**

The lack of degeneracy in the final states does not kill the scenario





Usual structure for the scenario

The asymmetry is generated while the pulse is on!

Harmonic Mixing $\langle X(t)\rangle \sim \alpha E(t) + \gamma E(t)^3 + \cdots$

zero-harmonic generation $\overline{\langle X(t)\rangle} \sim \gamma \overline{E(t)^3} + \cdots$

$$\sim \gamma |\epsilon_\omega|^2 |\epsilon_{2\omega}| \cos(\phi_{2\omega} - 2\phi_\omega) + \cdots$$

Due to harmonic mixing we can break the symmetry of ANY nonlinear quantum symmetric system with a 1+2 zero-mean AC source *while the laser is on!*

Usual scenario produces asymmetry that survives after the laser is turned off

So far… Rigid Chain

Flexible (Real) Chain:
electron-phonon interactions

Large exchange of energy between electronic and vibrational degrees of freedom (+ chaotic)

Energy levels change fast (~10fs), lasers get detuned

Decoherence in a ~40 fs time scale

Non adiabatic transitions occur

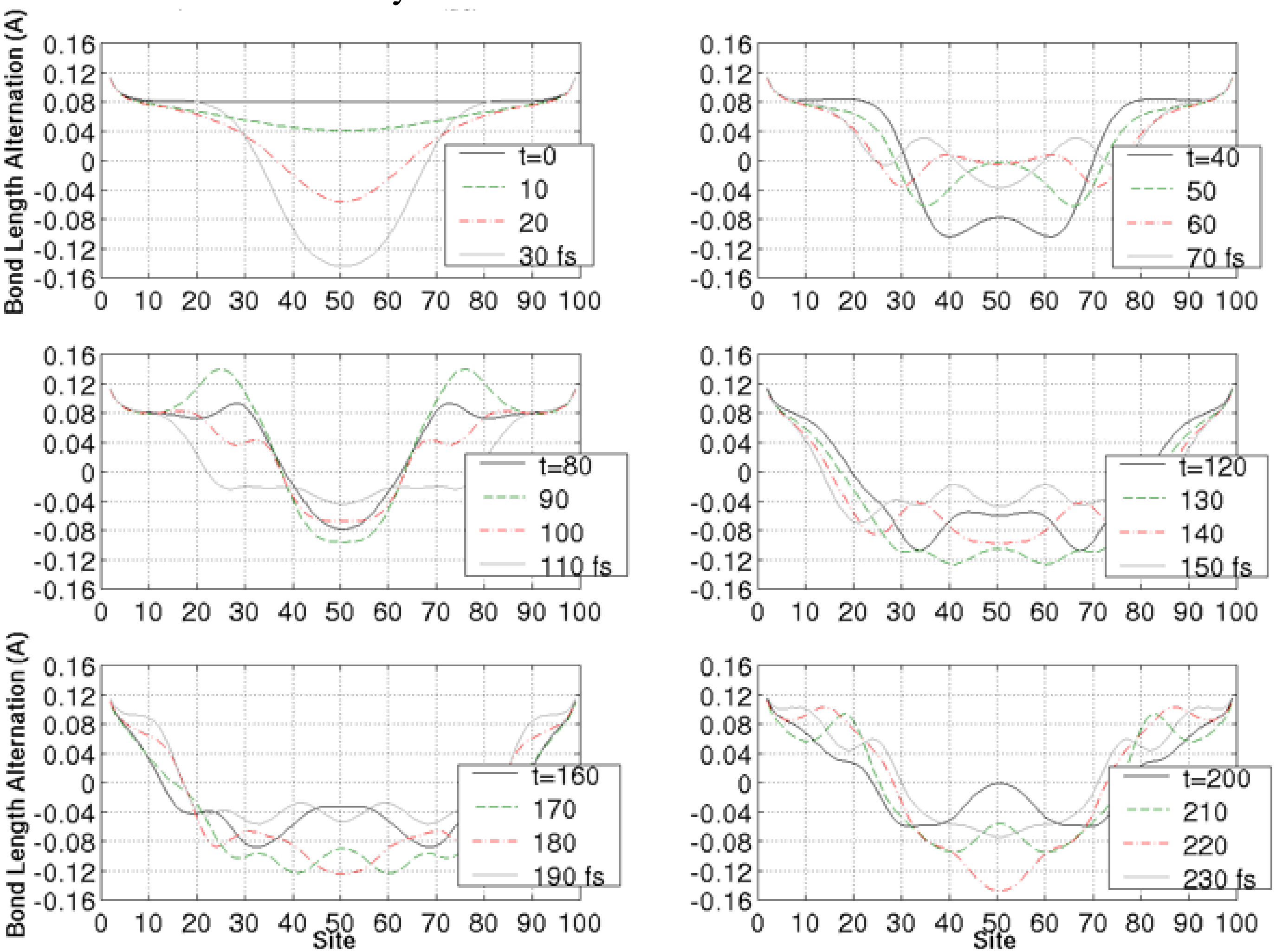
!

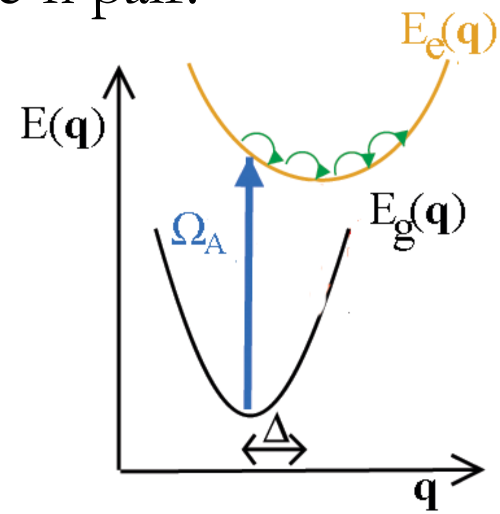
Much harder…

Flexible Chain: manual excitation (no laser)

Example:

Photoexcited dynamics after manual excitation of an e-h pair.

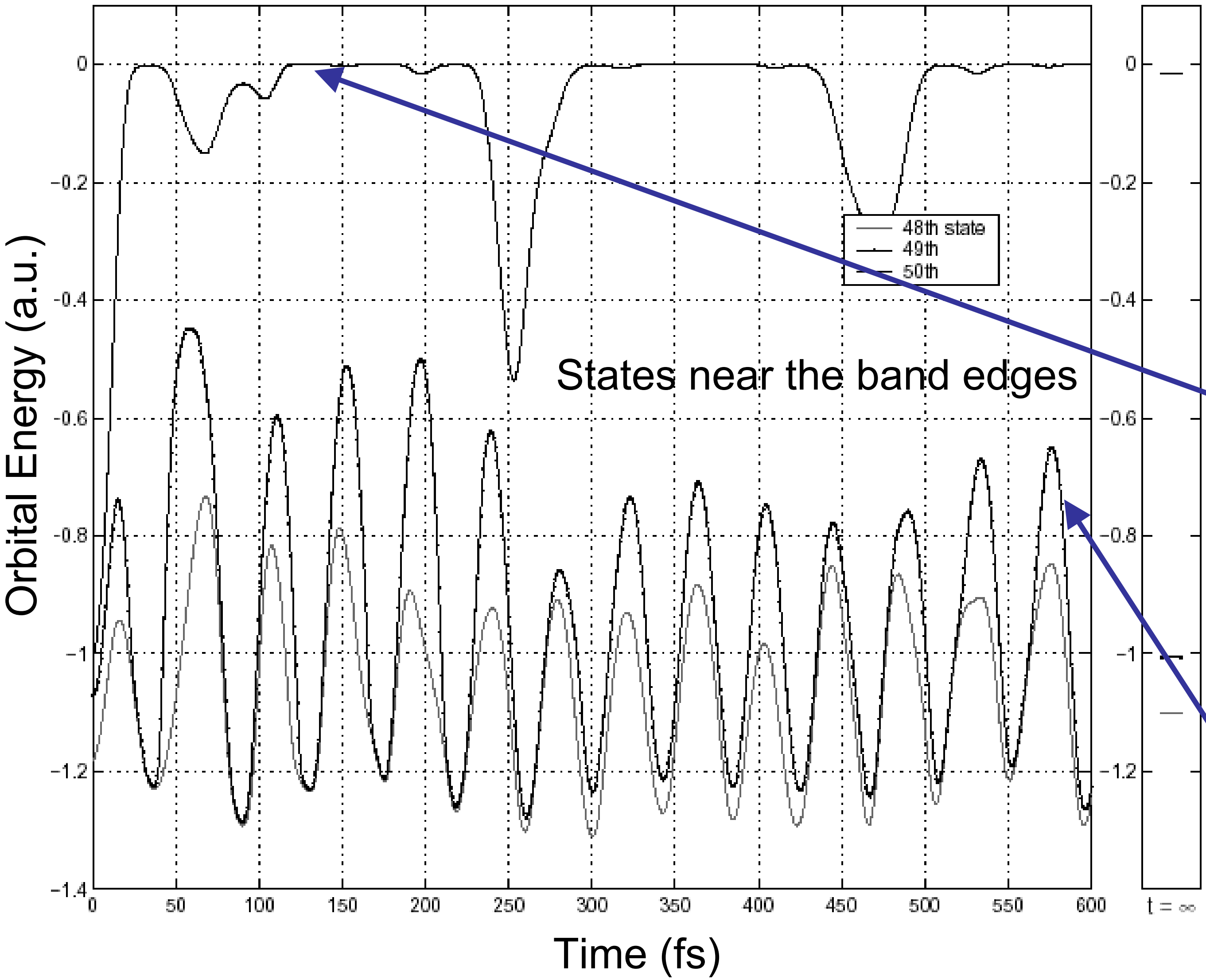


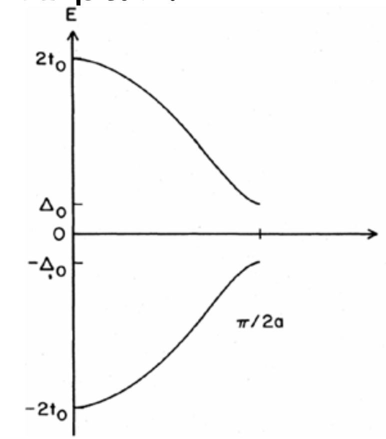


The lattice is set to vibrate in a ~30 fs scale due to the electronic excitation

Example:

Photoexcited dynamics after manual excitation of an e-h pair.





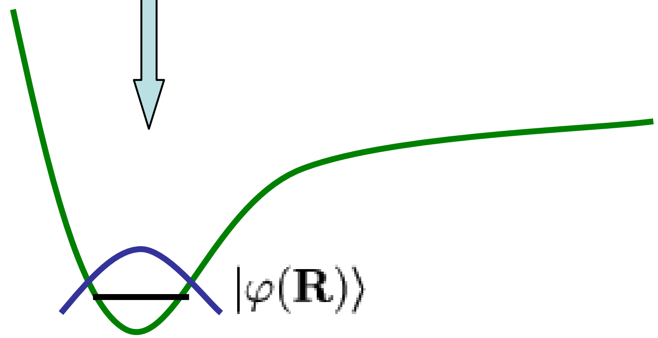
Introduction of soliton states at midgap

The band-structure changes due to the vibrational motion

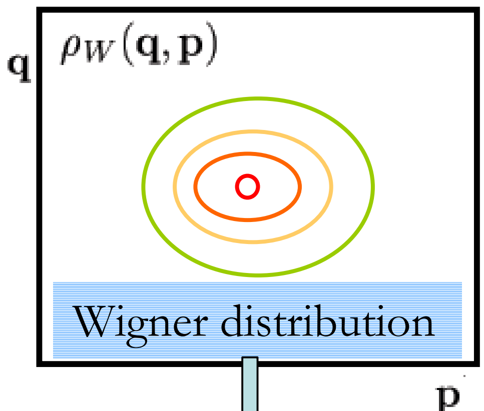
Photoinduced dynamics: Flexible Chain
Ensemble average

The dynamics has to reflect the initial quantum nuclear state

$$H_{\rm SSH} = H_\pi + H_{\pi-{\rm ph}} + H_{\rm ph}$$



Nuclear ground state wavefunction



Wigner distribution

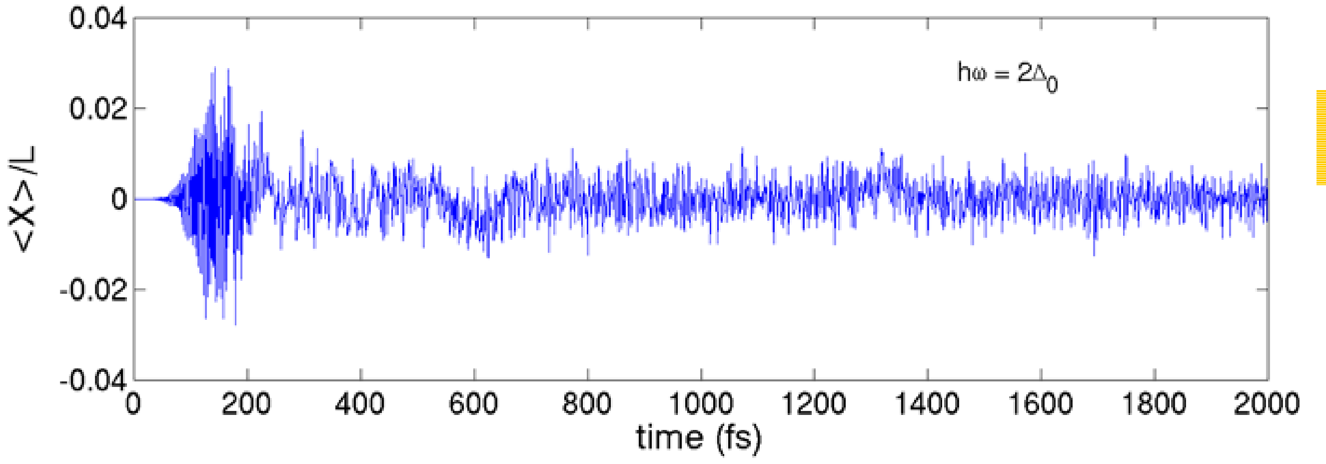
Importance sampling: lattice initial conditions

$$\{\mathbf{q}_i, \mathbf{p}_i\}$$

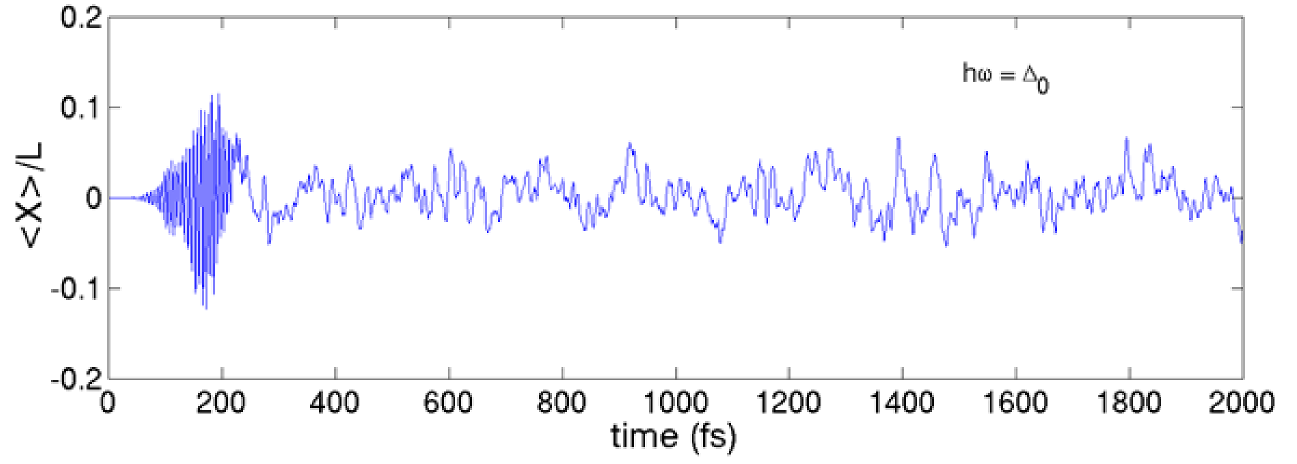
To dynamics + ensemble average

Photoexcited dynamics: Flexible Chain

No photoinduced asymmetry with a single laser (ensemble average over 100 trajectories)

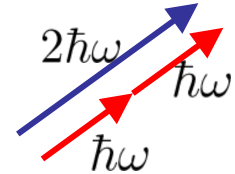


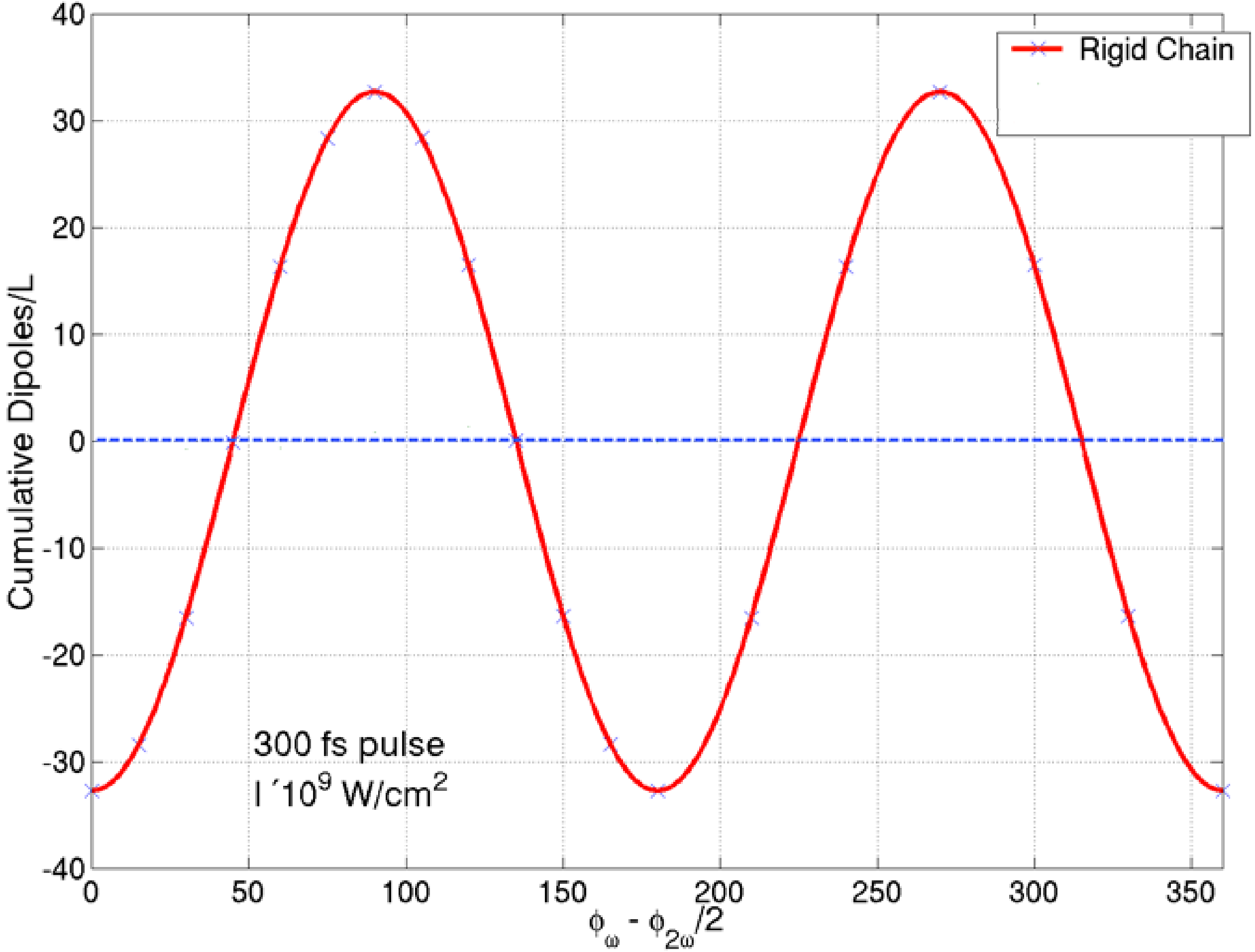
'1-photon' laser



'2-photon' laser

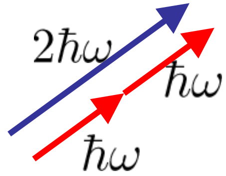
50 fs pulses centered at 150 fs of $I \sim 10^9$ W cm^{-2}



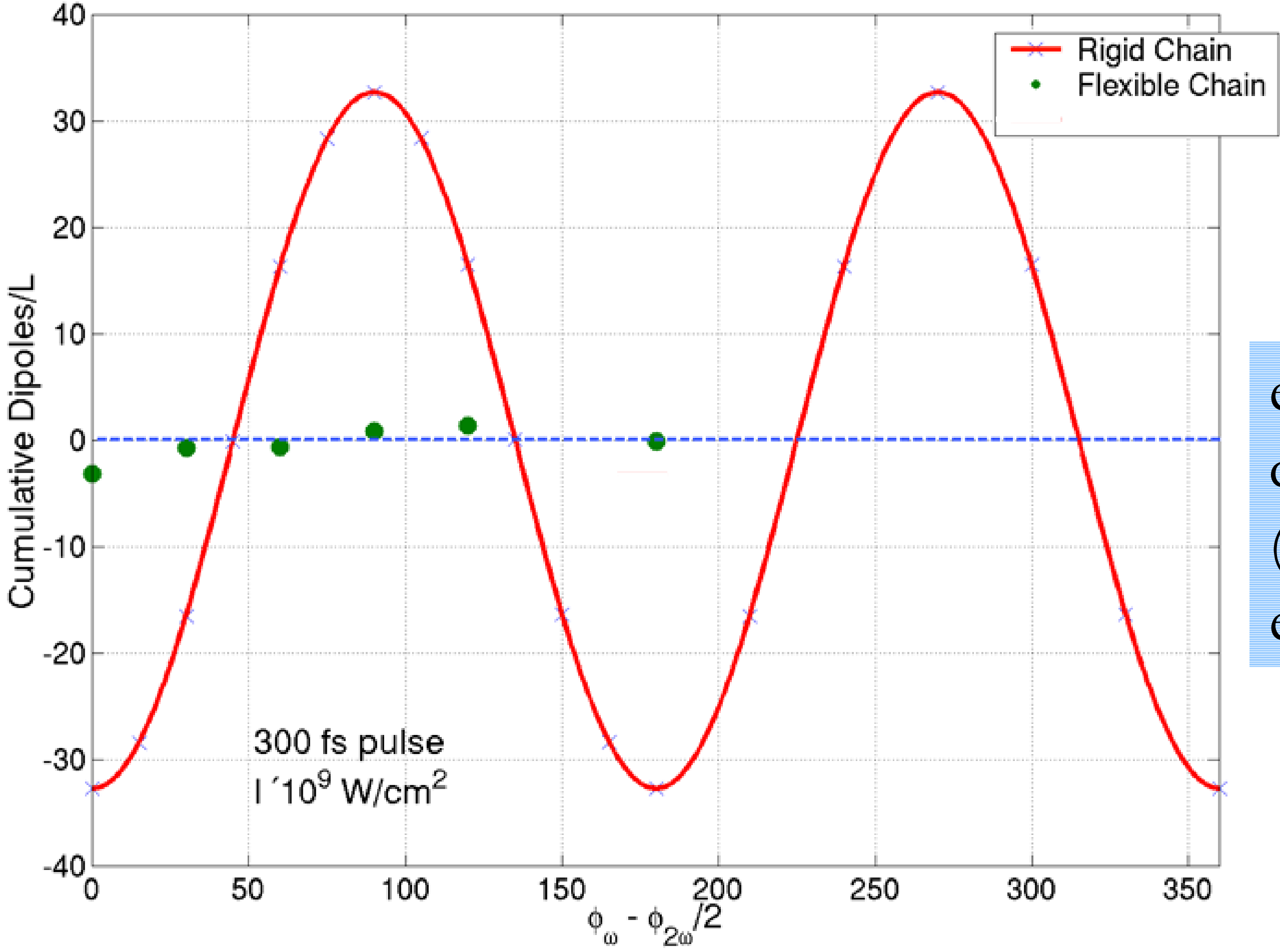


300 fs pulses of I~10^9 W cm^{-2}

1 vs 2 : **Flexible Chain**



Average over 200 trajectories

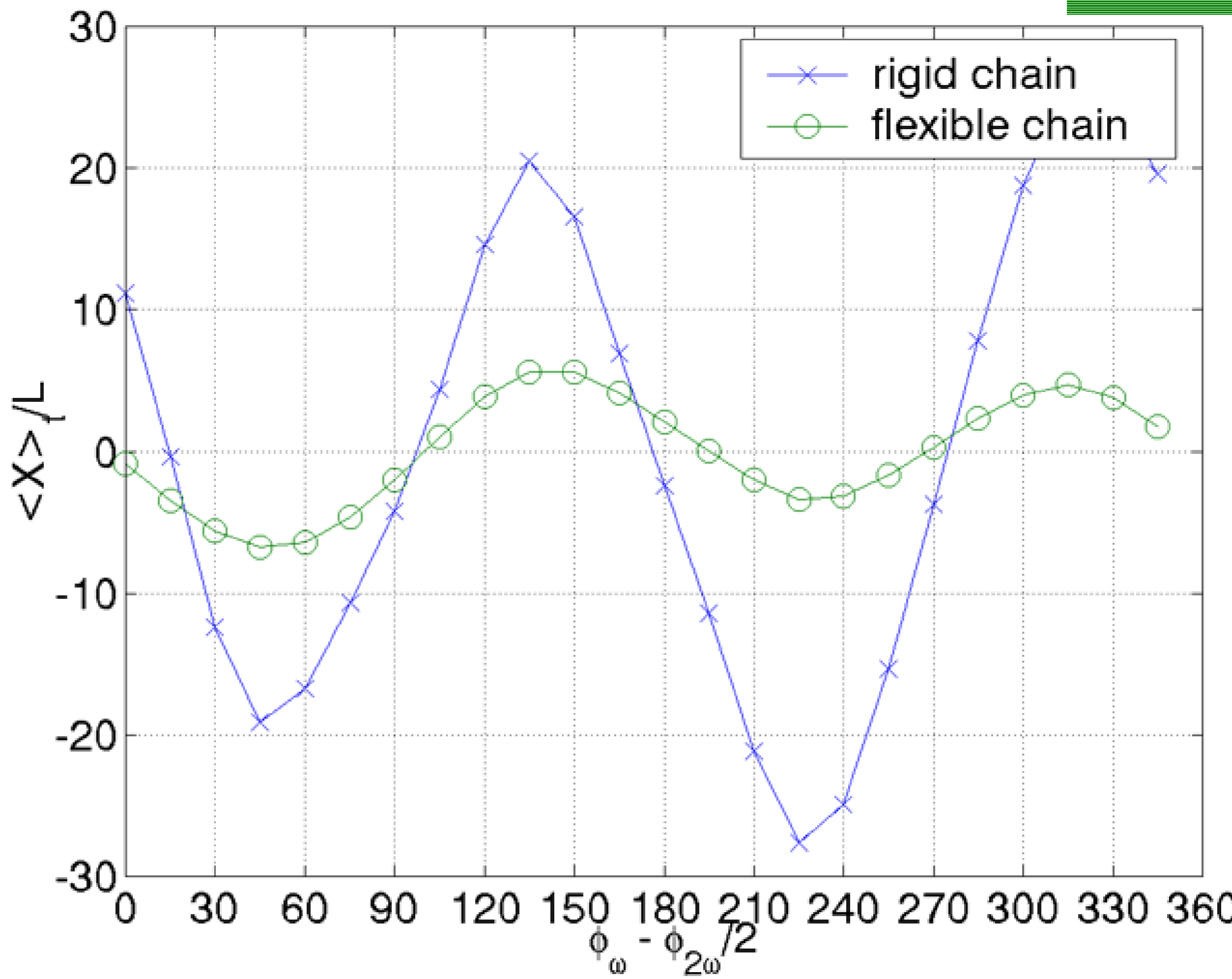


e-ph induced decoherence kills (almost) all of the effect !!

300 fs pulses of $I \sim 10^9$ W cm^{-2}

1 vs 2 : Flexible Chain

There is HOPE…
use pulses shorter than the decoherence time



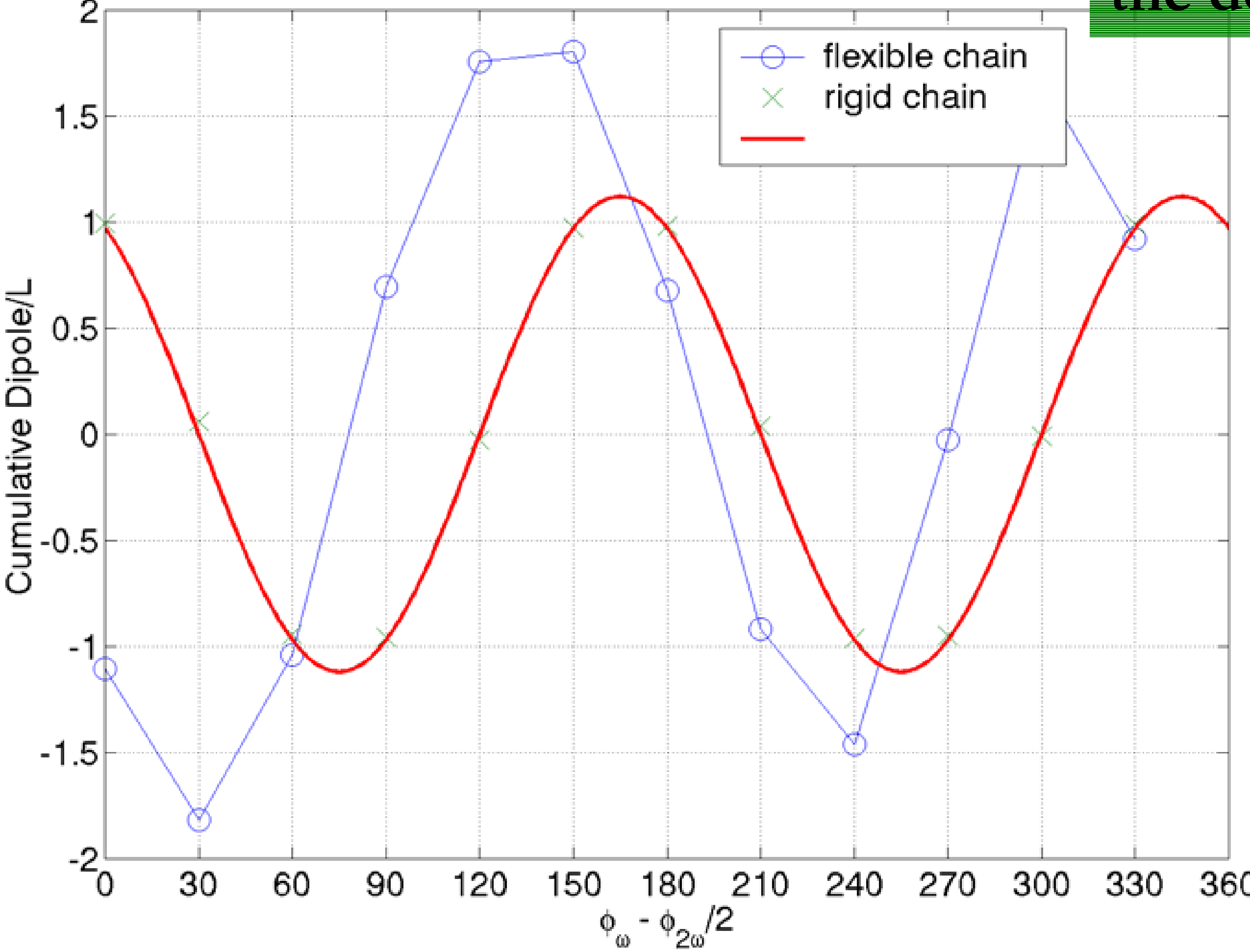
Phase controllable Symmetry Breaking

Average over a 200 trajectories

10 fs pulses of $I \sim 10^{10}$-10^{11} W cm^{-2}

1 vs 2 : **Flexible Chain**

There is HOPE… use pulses shorter than the decoherence time



Phase controllable Symmetry Breaking

Ensemble Average over 200 trajectories

50 fs pulses of $I \sim 10^9$ W cm^{-2}

Summary

Induce directed electronic transport in trans-polyacetylene using coherent control

Motivation:
Coherent Control in soft materials
Ultrafast currents in molecular wires

Follow numerically (mean field) the highly nonlinear coupled dynamics of electronic and vibrational d.o.f. in PA under the influence of a 1+2 radiation field

Rigid Chain: Easy
Flexible chain: more interesting due to strong e-ph coupling. Use lasers shorter than ~50 fs

1+2 photon scenario can be used to break the symmetry of any quantum nonlinear system: Zero-harmonic generation

Thanks…

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Daniel Gruner

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