Infrared Pump-Probe Spectra of Alpha-Helical Polypeptides: An Application of the MCTDH-Method

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Outline

- IR pump-probe spectroscopy of oligopeptides
- Goals of the study and the model
- Adiabatic vibrational excitons
- Calculation of IR pump-probe spectra applying the multiconfiguration time-dependent Hartree method
- Conclusions

Infrared pump-probe spectroscopy of oligopeptides

- Experiments:

  P. Hamm et al., J. Phys. Chem. B 102, 6123 (1998)

  R.M. Hochstrasser et al., J. Phys. Chem. B 108, 10415 (2004)

  J. Edler et al., Phys. Rev. Lett. 93, 106405 (2004)

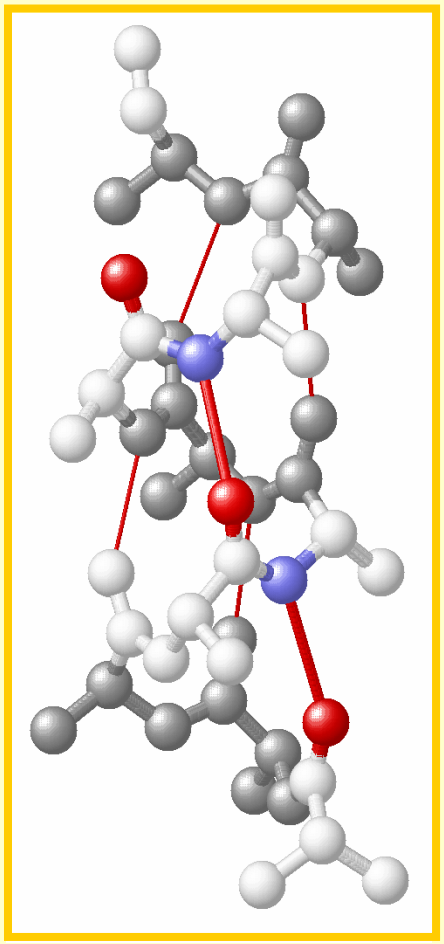
- Theory:

  J. Knoester et al., J. Phys. Chem. B 109, 9787 (2005)

  S. Mukamel et al., J. Chem. Phys. 118, 3651 (2003)

  V. Pouthier et al., J. Chem Phys. 123, 184710 (2005)

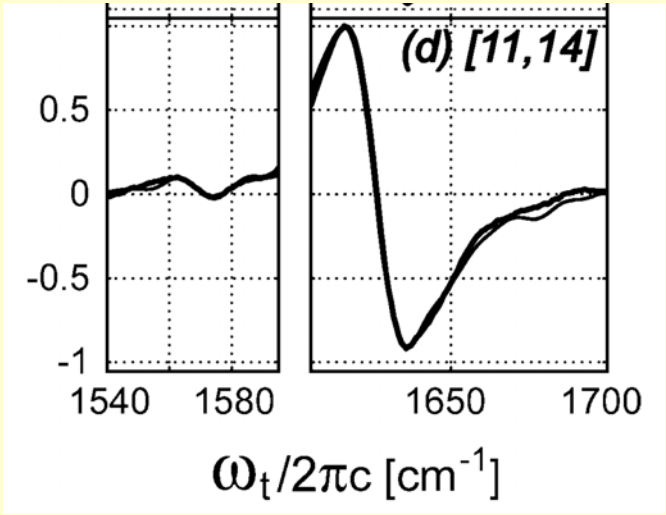
Alpha-helical polypeptides



- a sequence of amide units (-CONH-)
- 3 strands of hydrogen bonds
- IR active local amide vibrations
- longitudinal vibrations (frequency below 100 cm-1)

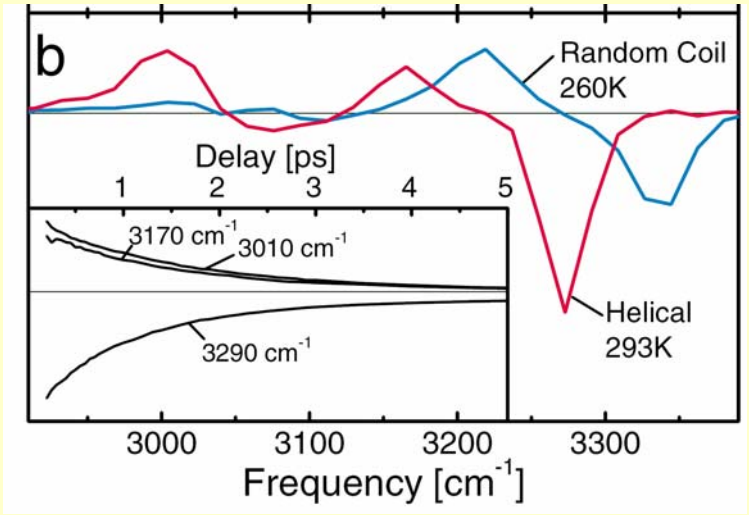
Infrared pump-probe spectra

C=O mode



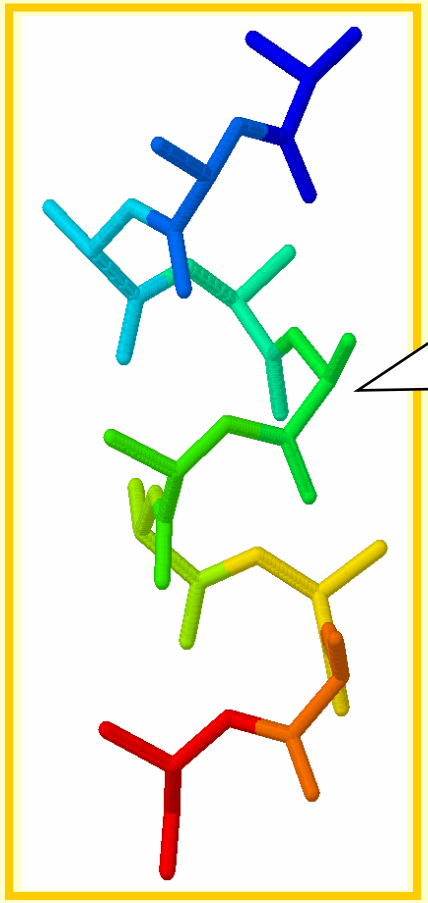
R.M. Hochstrasser *et al.*,
J.Phys.Chem.B **108**, 10415 (2004)

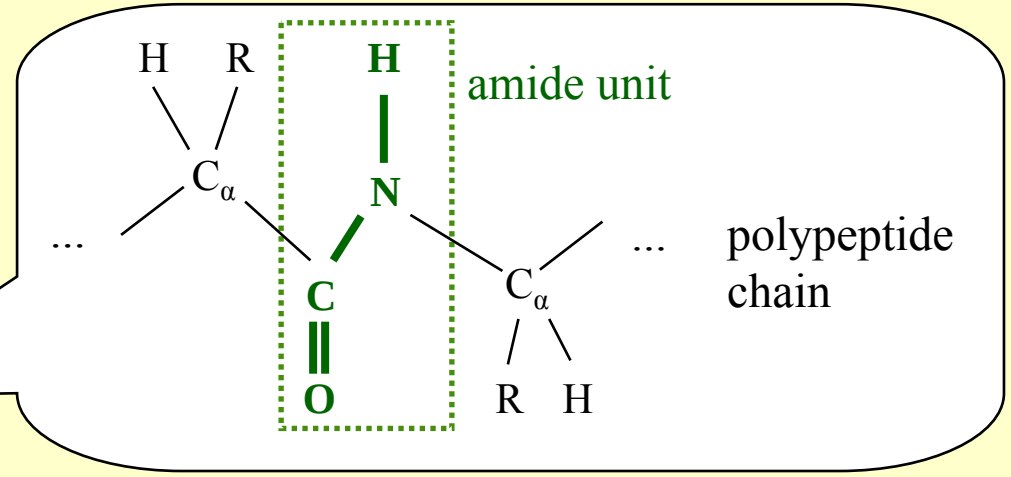
N-H mode



J. Edler *et al.*,
Phys. Rev. Lett. **93**, 106405 (2004)

Normal modes of the amide unit

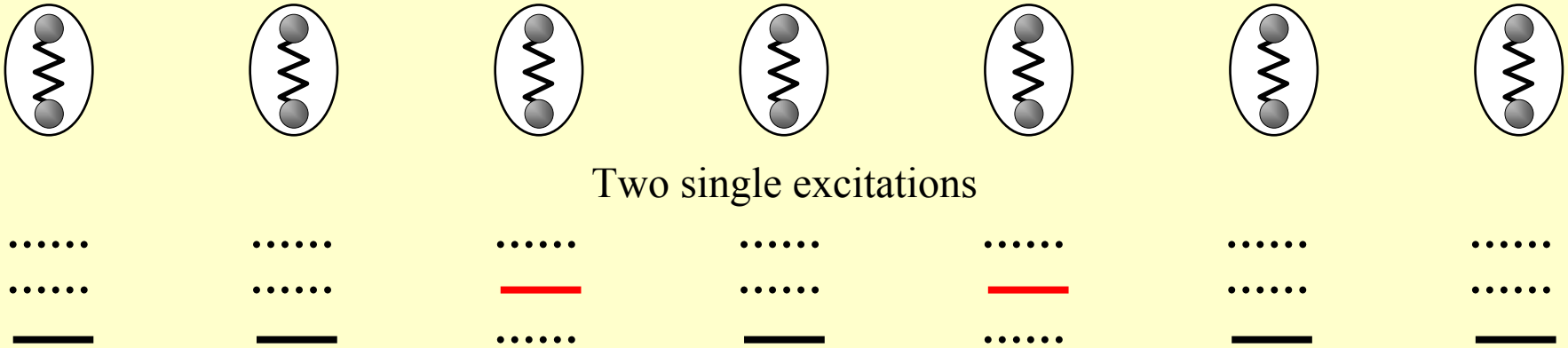




Studied local vibrational modes:

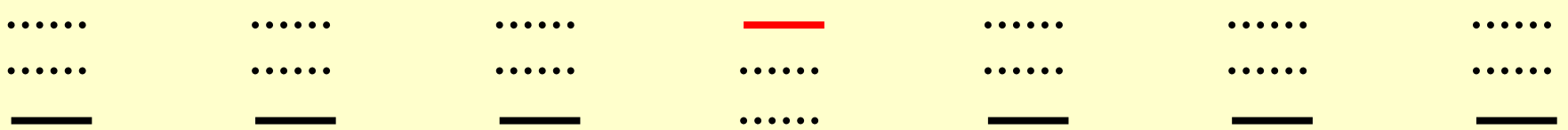
- Amide I (mostly C=O stretching)
- Amide A (mostly N-H stretching)

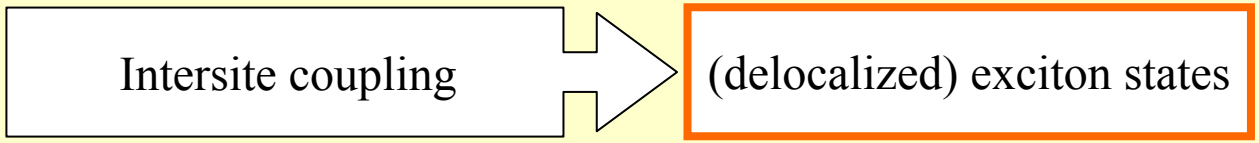
The two-exciton states



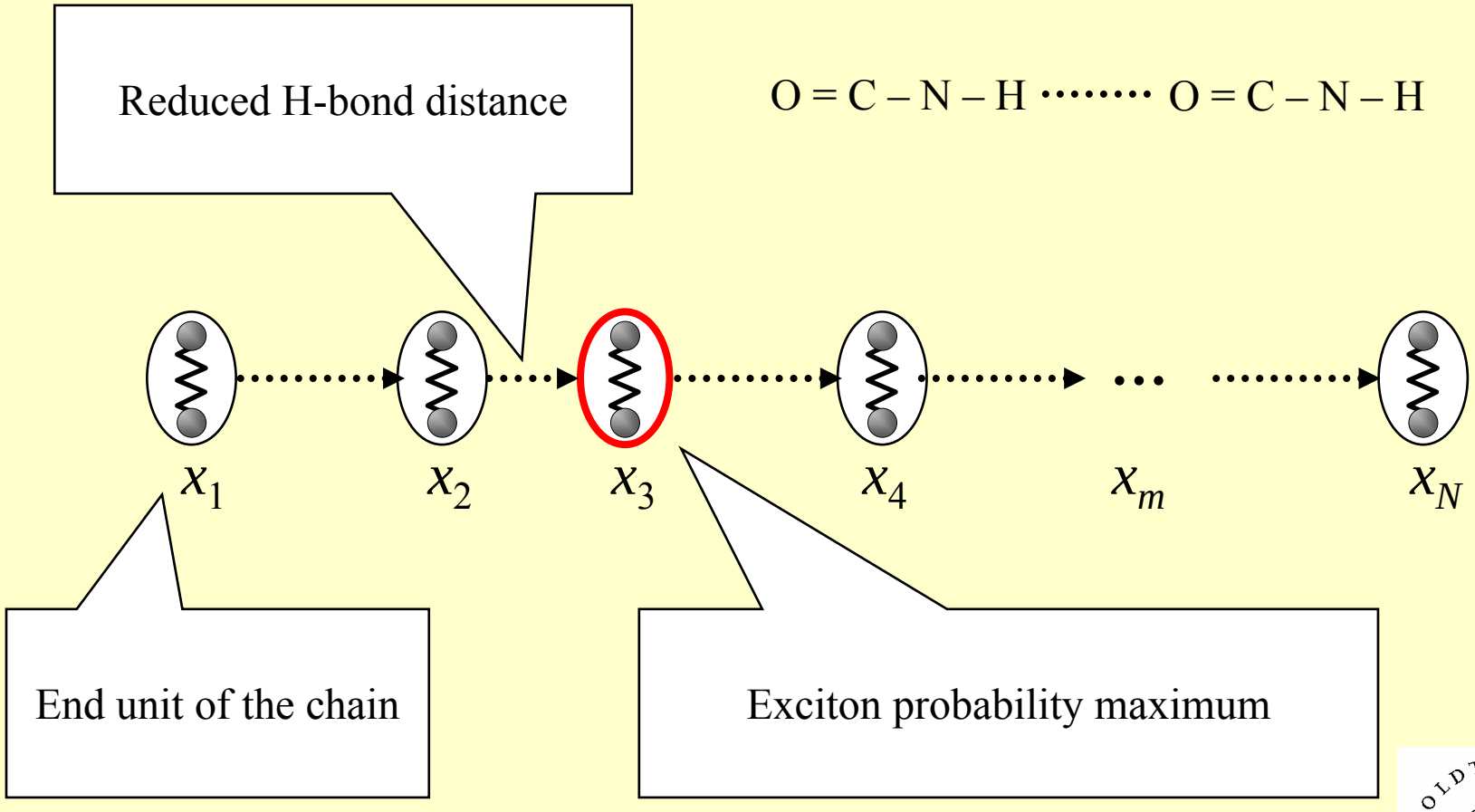
Two single excitations

Excitation of an overtone





Self-trapping of excitons



Theory of exciton self-trapping

Originally: Davydov model of exciton self-trapping in α-helices (1973)

Recent publications:

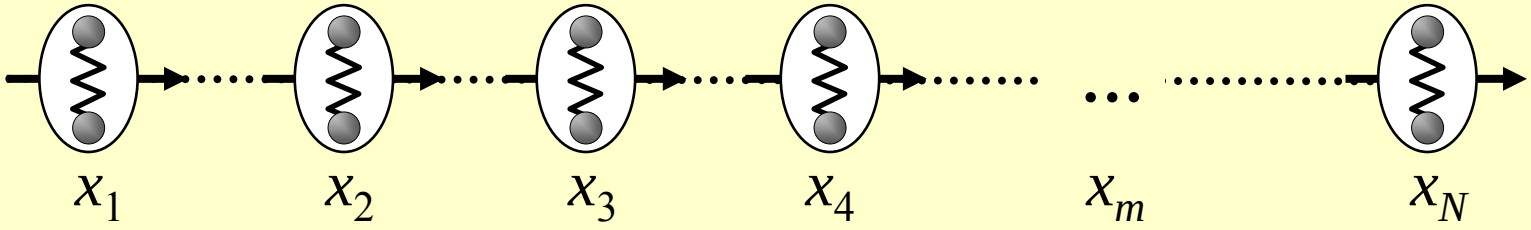
- Pouthier, Phys. Rev. E 68, 021909 (2003)
  - Self-trapped two-exciton states in the lenear chain model of α-helix

- Falvo and Pouthier, J. Chem Phys. 123, 184710 (2005)
  - Calculation of the pump-probe spectrum for amide C=O mode
  - Effect of the longitudinal chain vibrations on the spectrum is not considered

Goals

- ✓ Use mapping of the α-helix on one strand of hydrogen bonds (1D model)
- ✓ Represent the full exciton-chain vibrational wavefunction in the basis of local amide excitations
- ✓ Obtain a numerically exact solution of coupled time-dependent Schrödinger equations for 55 two-exciton states and 9 vibrational DOF
- ✓ Calculate the sequential infrared pump-probe spectrum at T=0 K

The model Hamiltonian



$$H(t) = H_{\text{amide}} + H_{\text{chain}} + H_{\text{coup}} - \sum_m \boldsymbol{\mu}_m \boldsymbol{E}(t)$$

$$H_{\text{amide}} = \sum_{m=1}^{N} \left(-\hbar\omega_0 \frac{\partial^2}{\partial q_m^2} + V(q_m) \right) - J \sum_{m=2}^{N} q_m q_{m-1}$$

amide excitons

$$H_{\text{chain}} = \sum_{m=1}^{N} \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_m^2} \right) + \frac{W}{2} \sum_{m=2}^{N} (x_m - x_{m-1})^2$$

chain vibrations

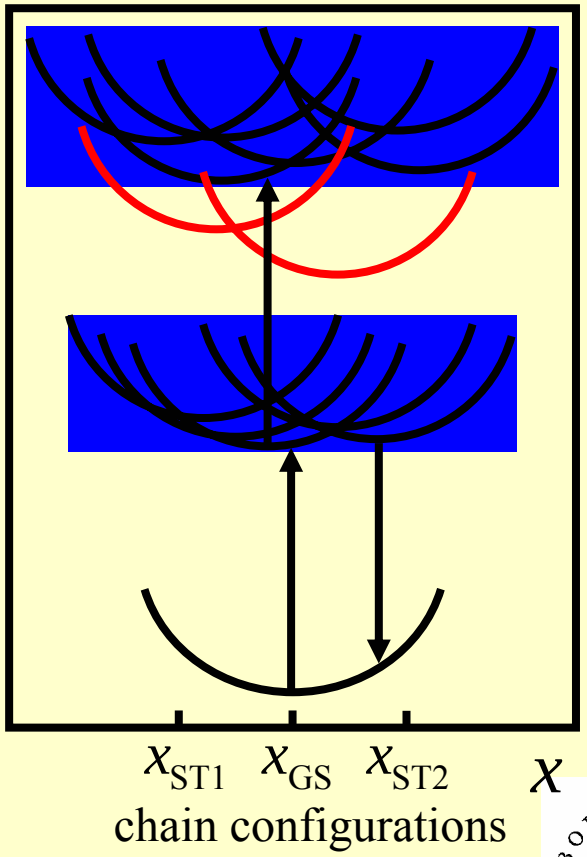
$$H_{\text{coup}} = \frac{\chi}{2} \sum_{m=2}^{N} q_m^2 \, (x_m - x_{m-1})$$

exciton-chain coupling

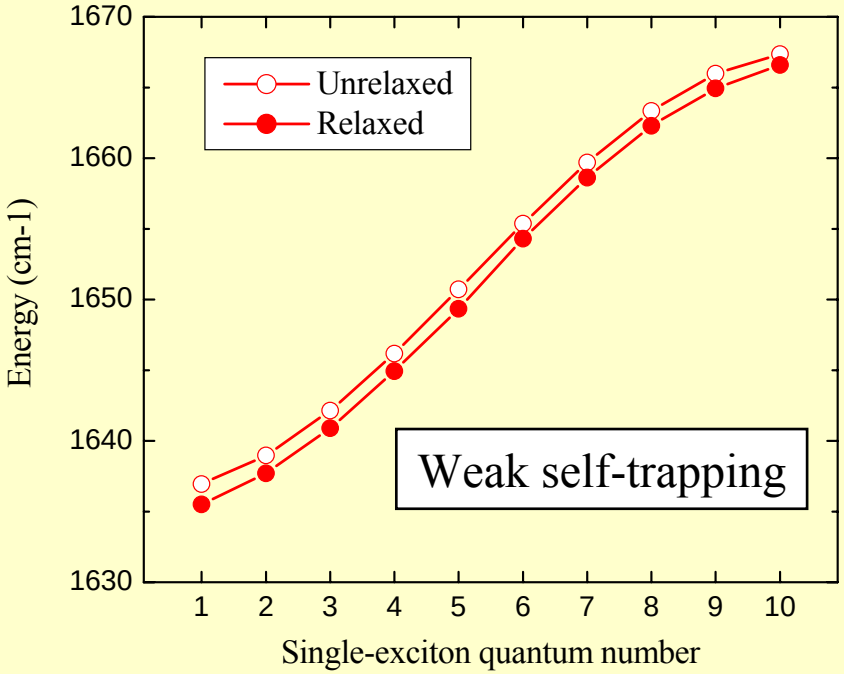
Parameters of the model: J – amide exciton coupling,
χ – exciton-chain coupling

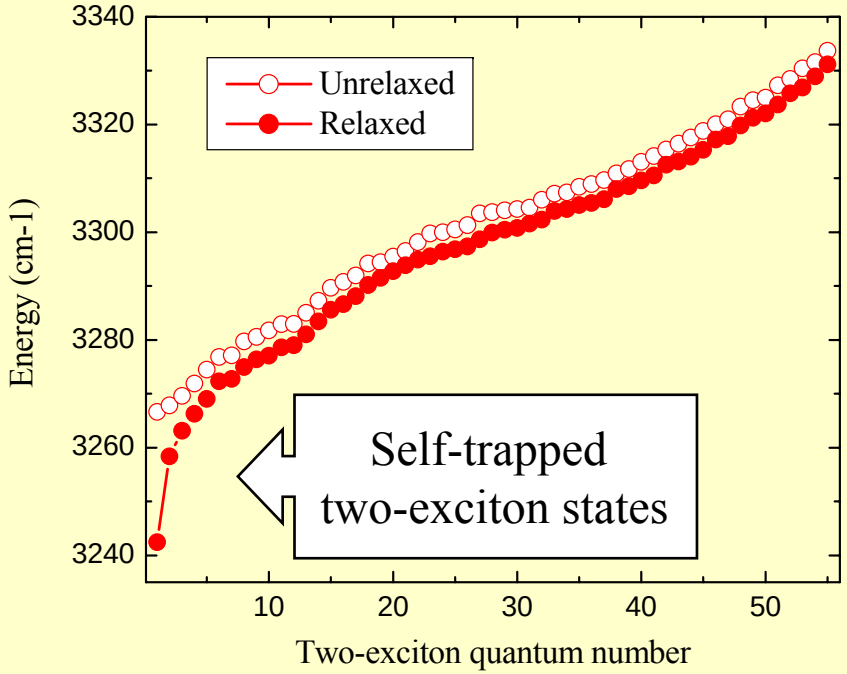
Adiabatic exciton potential energy surfaces (PES)

- Treat chain coordinates *x* as parameters
- Diagonalize the excitonic part of *H*, obtain the adiabatic exciton energy levels
- Vary the parameters *x* to obtain the (*N*-dimensional) adiabatic PES



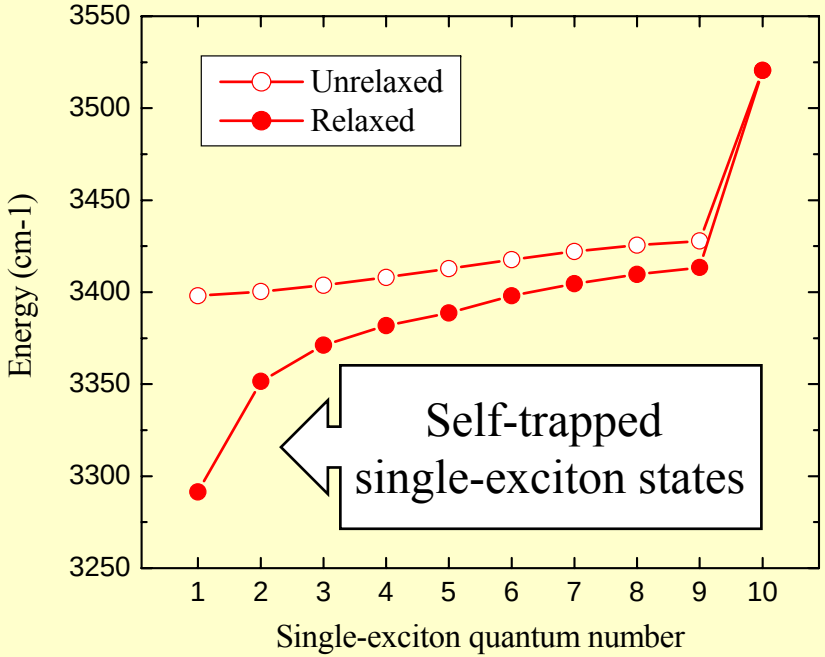
Exciton energy minimization: C=O mode

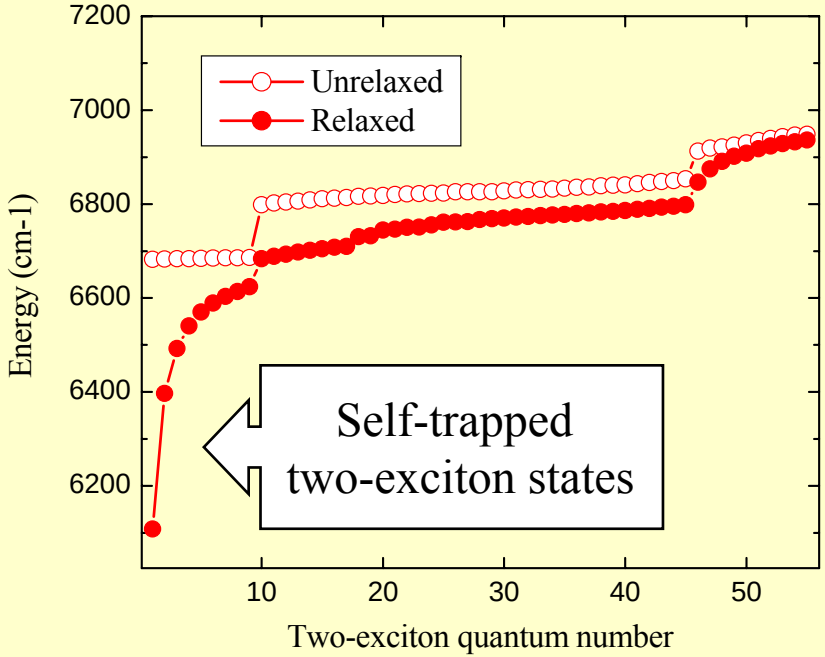




D.T., V. May, CPL **408**, 360 (2005)

Exciton energy minimization: N-H mode





Quantum-dynamical description of amide excitons

Full wavefunction $|\Psi(t)\rangle =$

$$\sum_{m\leq n} \tilde{\psi}_{m,n}(x_1, x_2, \ldots, x_N, t)|\tilde{\phi}_{m,n}\rangle$$

$$+\sum_{m} \psi_m(x_1, x_2, \ldots, x_N, t)|\phi_m\rangle$$

$$+ \quad \psi_0(x_1, x_2, \ldots, x_N, t)|0\rangle$$

Chain of 10 units:

double excitations (55)

single excitations (10)

amide ground state (1)

The MCTDH representation for the wavefunction

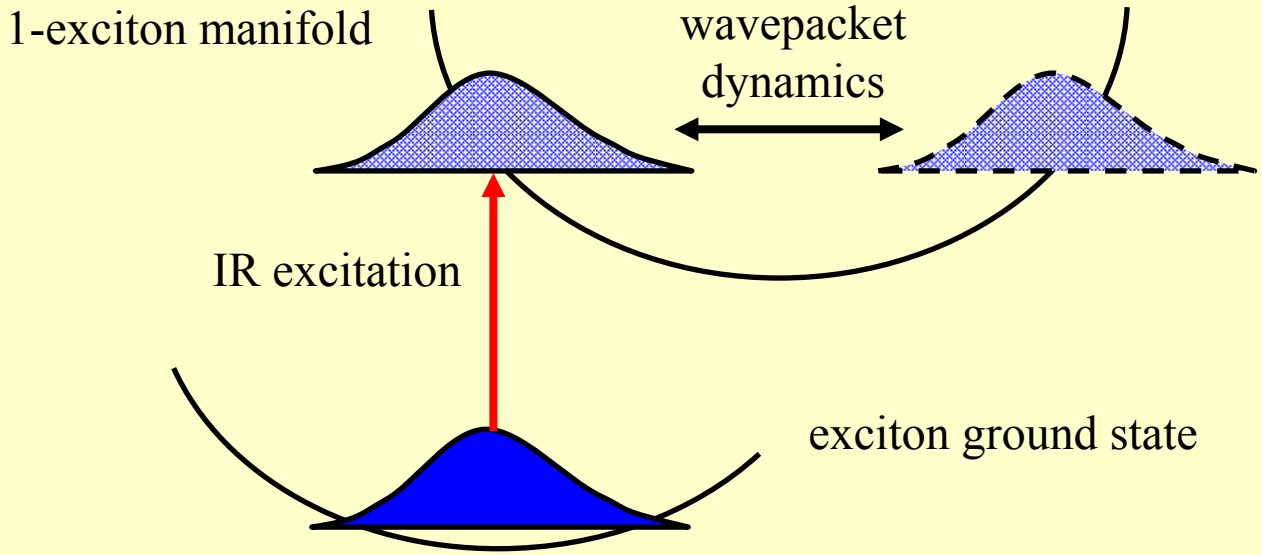
Expansion of the chain-vibrational wavefunctions of two-exciton states in the basis of time-dependent Hartree products:

$$\tilde{\psi}_{m,n}(x,t) = \sum_{j_1=1}^{M_1} \sum_{j_2=1}^{M_2} \cdots \sum_{j_N=1}^{M_N} A^{(m,n)}_{j_1 j_2 \ldots j_N}(t) \prod_{\kappa=1}^{N} \varphi^{(m,n)}_{j_\kappa}(x_\kappa, t)$$

Time-integration of 55 coupled differential equations for the wavefunctions using the multiconfiguration time-dependent Hartree method

G.A. Worth, M.H. Beck, A. Jäckle, and H.-D. Meyer. The MCTDH Package, Version 8.3 (2002), University of Heidelberg, Heidelberg, Germany

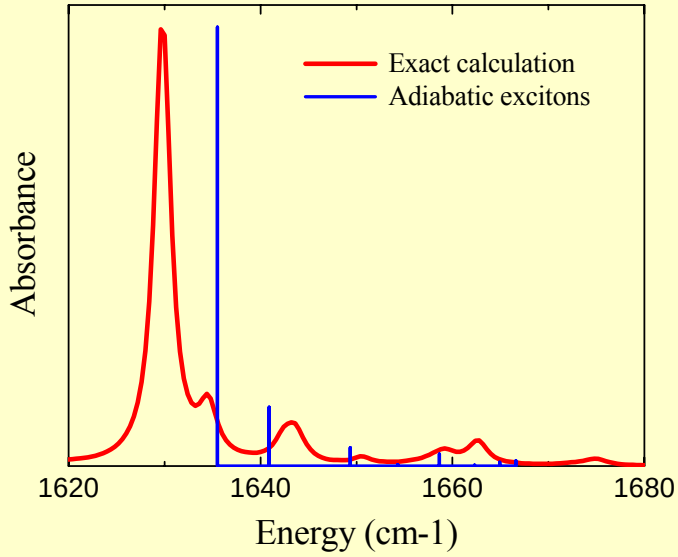
The infrared linear absorption



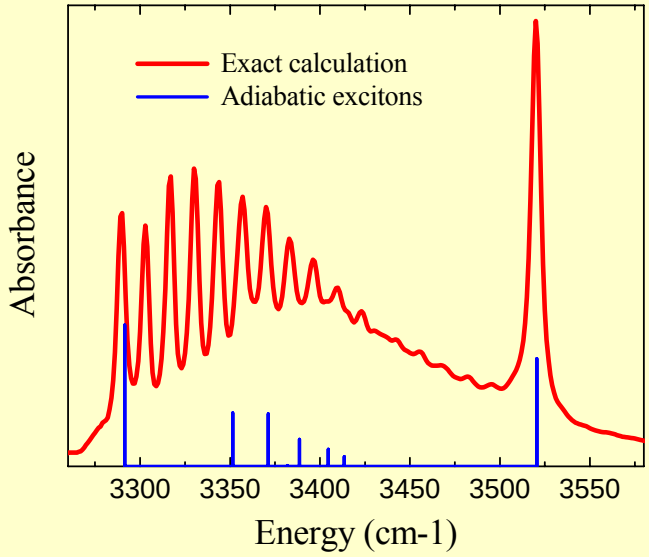
$$A(\omega) \sim \omega \,\mathrm{Re} \int_{t_0}^{\infty} dt\, e^{i\omega t} \,\langle \Psi(t_0)|\; \hat{\mu}\, U(t,t_0)\, \hat{\mu}\; |\Psi(t_0)\rangle$$

Spectrum of linear absorption

C=O mode



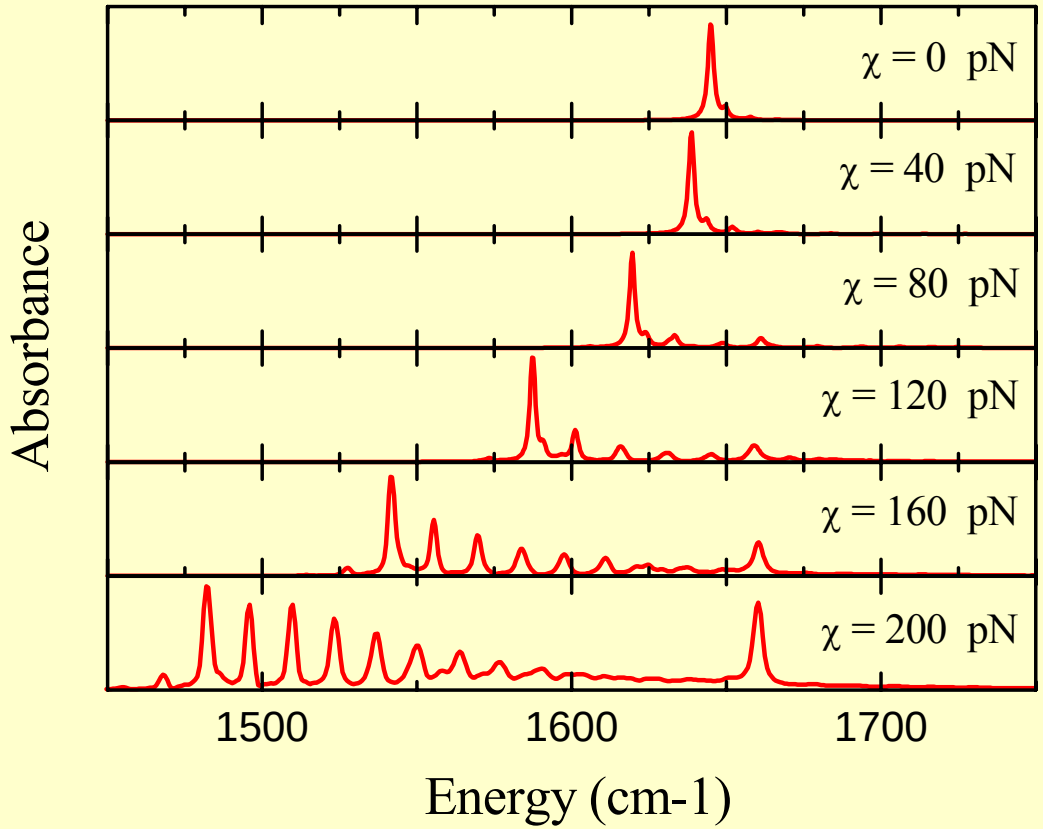
N-H mode



- Nonadiabatic couplings are important
- Weak self-trapping
- Weak vibrational progression

- Adiabatic picture is nearly valid
- Strong self-trapping
- Large vibrational progression

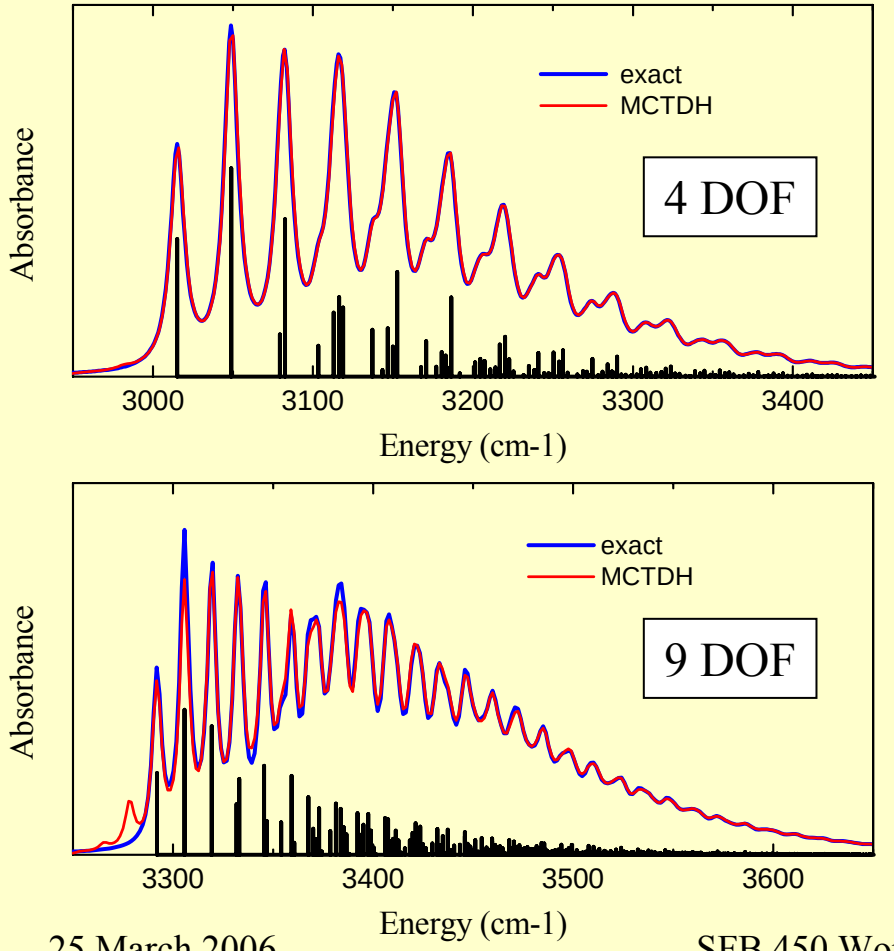
Exciton coupling to chain vibrations: Spectral response of self-trapped states



Increase of the coupling χ (= stronger self-trapping):

- Redshift of the main peak
- Emerging vibrational progression
- Absorption at the end unit of the chain

A reference case: Single amide-unit absorption spectrum



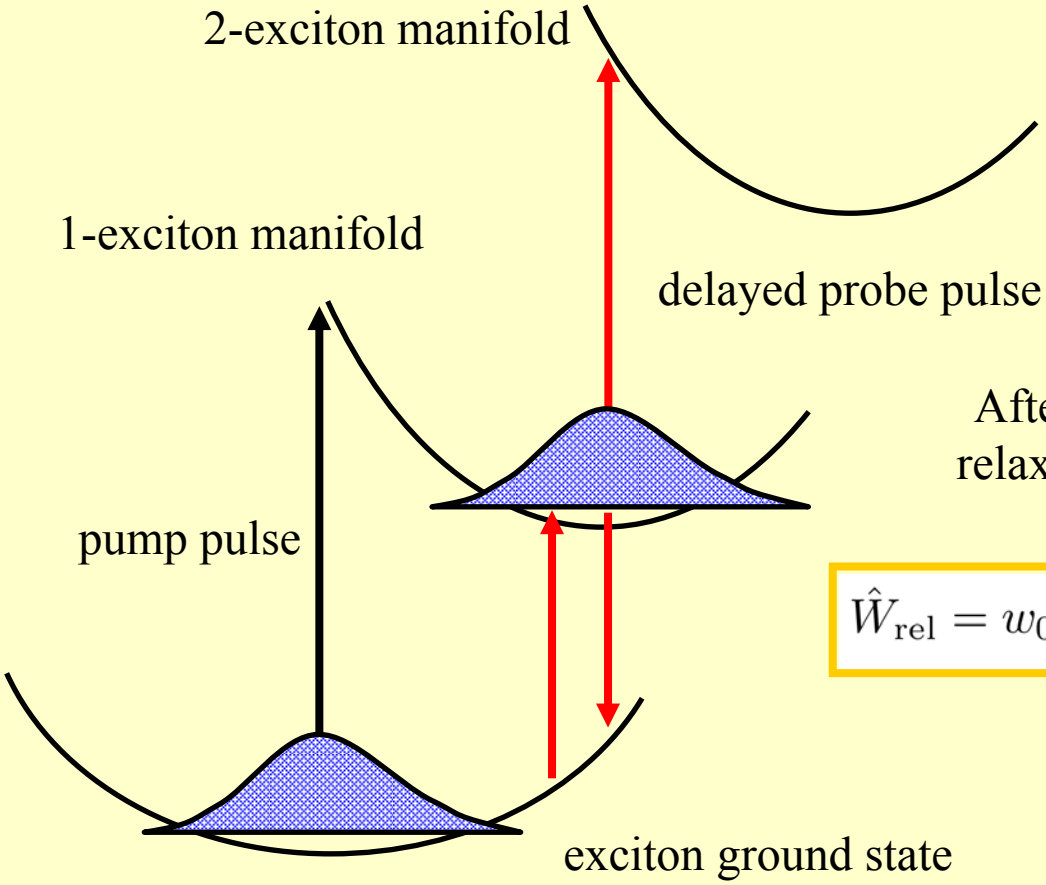
Exact absorption spectrum
- no exciton coupling (J=0)
- excitation of single amide unit
- T=0 K

$$\alpha(\omega) \sim \omega \int_0^\infty dt\; e^{i(\omega-\omega_{1,0})t+G(t)-G(0)}$$

$$G(t) = \sum_\xi \Delta g_{1,0}^2(\xi) e^{-i\omega_\xi t}$$

Normal modes of the chain vibrations:
$\Delta g_{1,0}(\xi)$ - normal mode displacements
ω_ξ - normal mode frequencies

Sequential pump-probe absorption



After the action of the pump-pulse – relaxation into a mixed stationary state

$$\hat{W}_{\mathrm{rel}} = w_0 |\Psi_0^{(\mathrm{rel})}\rangle\langle\Psi_0^{(\mathrm{rel})}| + w_1 |\Psi_1^{(\mathrm{rel})}\rangle\langle\Psi_1^{(\mathrm{rel})}|$$

Transient absorption signal

Differential TAS

$$\Delta A_{\mathrm{pr}}(\omega) \sim \mathrm{Im}\left(R_{\mathrm{pr}}^{(\mathrm{ESA})}(\omega) - R_{\mathrm{pr}}^{(\mathrm{LA})}(\omega) - R_{\mathrm{pr}}^{(\mathrm{SE})}(\omega)\right)$$

Linear absorption

$$R_{\mathrm{pr}}^{(\mathrm{LA})}(t) \sim \int dx \sum_m \left[d_m^* \psi_0^{(\mathrm{rel})*}(x)\right] \psi_m(x,t)$$

Stimulated emission

$$R_{\mathrm{pr}}^{(\mathrm{SE})}(t) \sim \int dx \left[\sum_m d_m \psi_m^{(\mathrm{rel})}(x)\right] \psi_0^*(x,t)$$

Excited state absorption

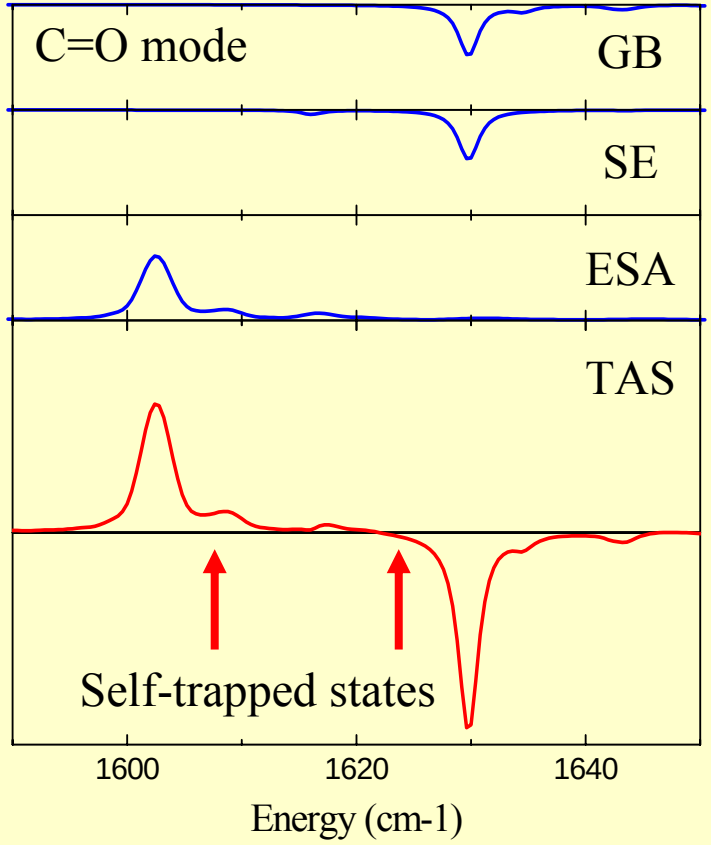
$$R_{\mathrm{pr}}^{(\mathrm{ESA})}(t) \sim \int dx \left(\sum_m \left[\tilde{d}_m^* \psi_m^{(\mathrm{rel})*}(x)\right] \psi_{m,m}(x,t) + \sum_{m<n} \left[d_m^* \psi_n^{(\mathrm{rel})*}(x) + d_n^* \psi_m^{(\mathrm{rel})*}(x)\right] \psi_{m,n}(x,t) \right)$$

D.T., H.-D. Meyer, V. May, JCP (accepted, 2006).

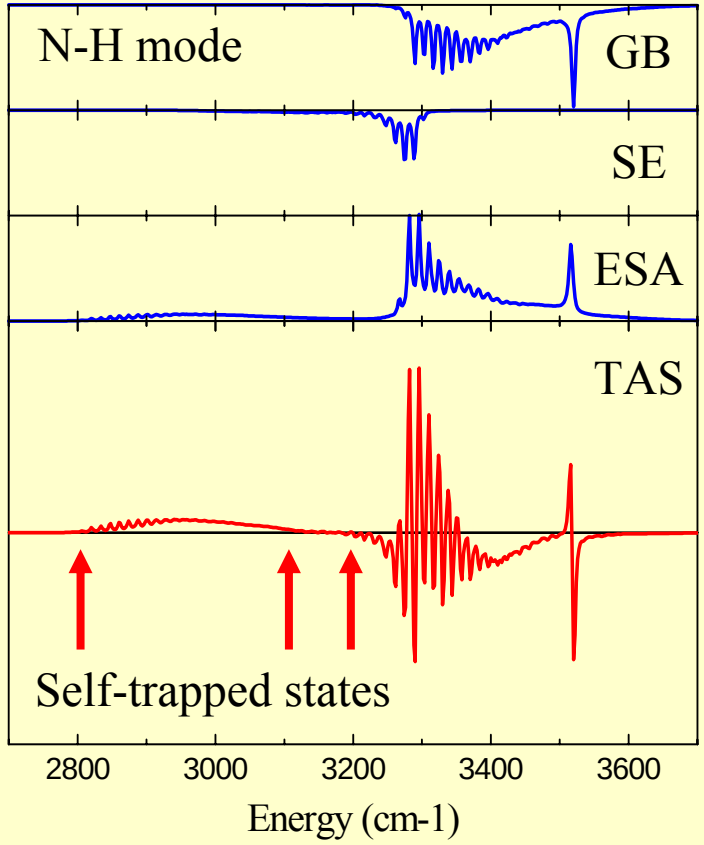
d_m - local 0→1 transition dipole moment

$\tilde{d}_m$ - local 1→2 transition dipole moment

TAS calculation (C=O, N-H modes)

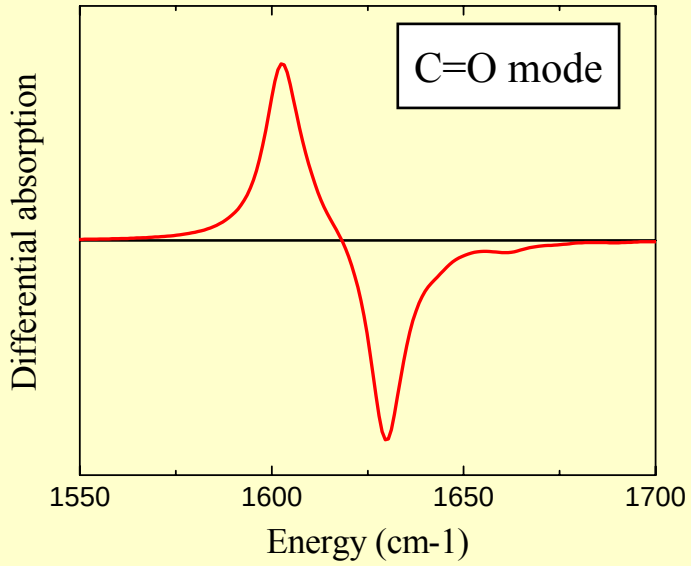


(dephasing time 5 ps)

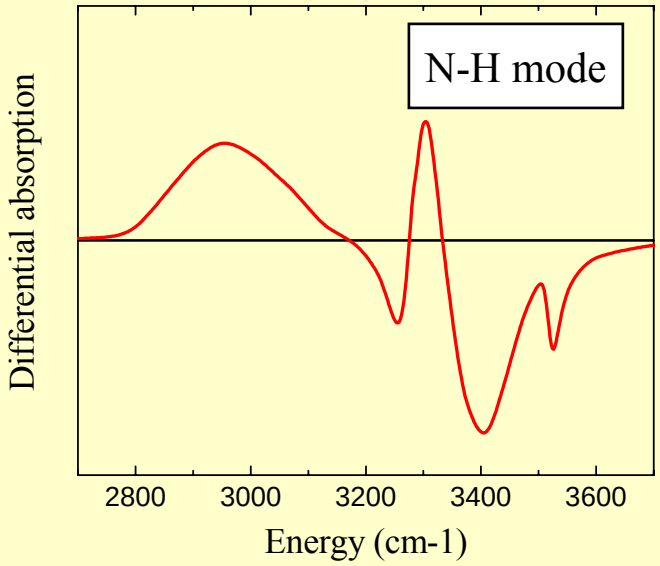


(dephasing time 2 ps)

Reproduced experimental features



(dephasing time 1 ps)



(dephasing time 0.3 ps)

Qualitative agreement with the experiment:
Negative band (bleach+stimulated emission)
Positive redshifted band (excited state absorption)

But for the N– H mode:
Only one band of
two-exciton self-trapped states

Summary

- first numerically exact calculation of the pump-probe spectrum for the linear chain model of an alpha-helix
- quantum description of the longitudinal chain vibrations based on the MCTDH method
- consideration of up to 55 two-exciton states and 9 degrees of freedom for the longitudinal chain vibrations
- interpretation of the spectra using the adiabatic exciton model

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