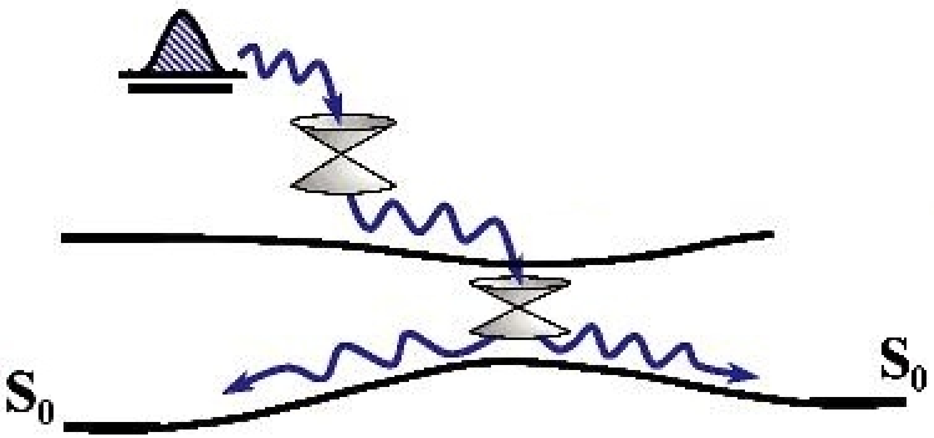
Theoretical Photochemistry WiSe 2016/17

Lecture 8



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http://www.theochem.uni-frankfurt.de/teaching/ ⟶ Theoretical Photochemistry

Topics

1. **Photophysical Processes**
2. **The Born-Oppenheimer approximation**
3. **Wavepackets**
4. **Beyond Born-Oppenheimer – non-adiabatic transitions**
5. **The Franck-Condon picture of electronic transitions**
6. **Interaction with light & what kind of spectroscopies?**
7. **Conical intersections**
8. **Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene**
9. **Some electronic structure aspects**
10. **Dynamics: trajectories or wavefunctions?**
11. **Wavefunction propagation techniques**

12. **Trajectory surface hopping techniques**
13. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
14. **Extended systems: Excitons, light-harvesting, etc.**
15. **Solvent/environmental effects**

What do we need to calculate?

(1) Franck-Condon excitation & beyond:

- Franck-Condon wavepackets
- transition dipole moment, oscillator strength
- absorption spectra, nonlinear optical spectroscopy . . .

(2) PES's from electronic structure calculations:

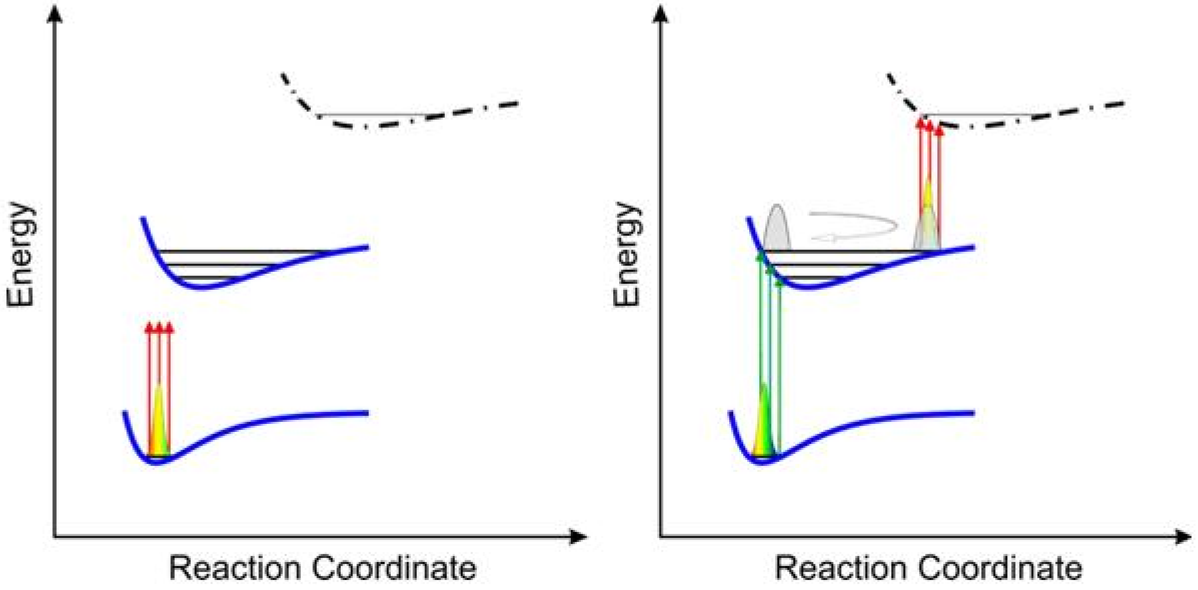
- calculate Potential Energy Surfaces (PES)
- calculate non-adiabatic couplings
- possibly "diabatize" (= transform to a diabatic representation)

(3) Dynamics (once the PES's are known):

- wavepacket simulations on non-adiabatically coupled PES's
- or simplified descriptions of the dynamics: classical trajectories, Gaussian wavepackets

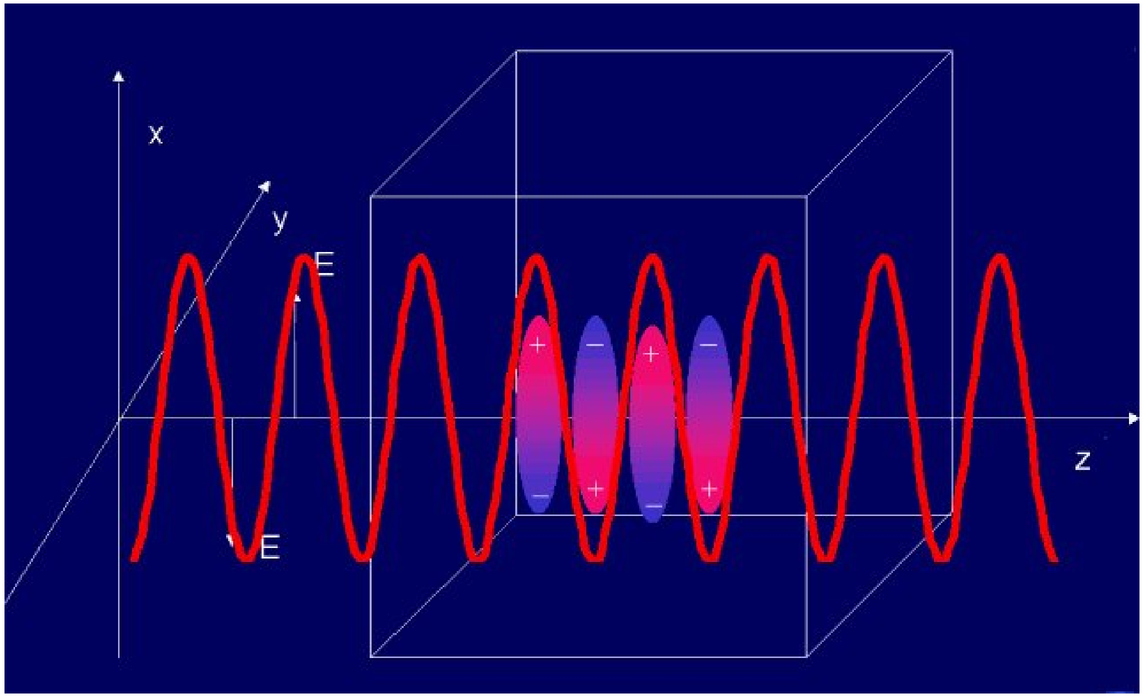
Multiple-Pulse Spectroscopies

E.g., Pump-probe spectroscopy: 2 pulses, 3 states



Monitor the full evolution in the 1st excited state (S_1)

In general: Measure polarisation resulting from the interaction with an electromagnetic field



$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots = \epsilon_0 \Big(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \Big)$$

$\chi^{(n)} =$ nth order susceptibility

We need a quantum mechanical setting . . .

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{int}}(t)$$

- **semiclassical equations for the interaction with the field:**

$$\hat{H}_{\text{int}}(t) = -E(r,t)\hat{\mu} = -E\sum_{\alpha} q_{\alpha}(\hat{r}_{\alpha} - R)$$

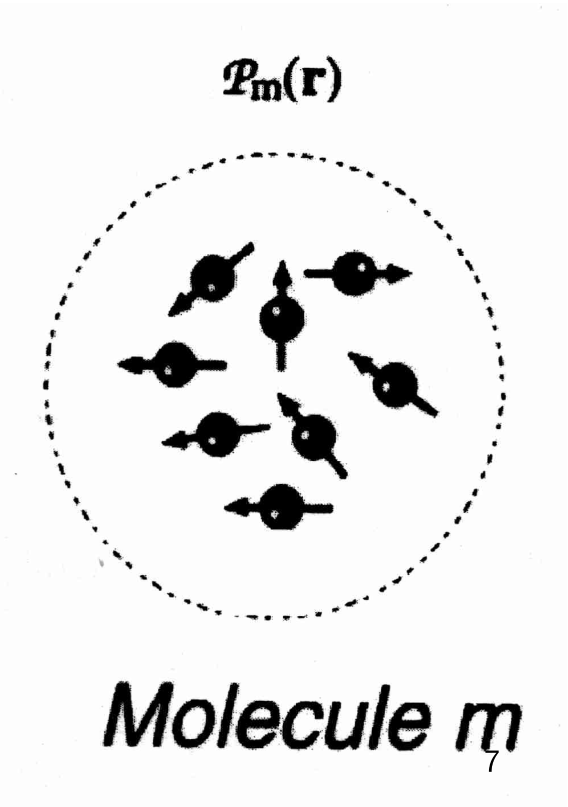
- **macroscopic observable: polarisation of the sample**

$$\hat{P}(r) = \sum_{m} \hat{\mu}_m \delta(r - R_m)$$

i.e., sum over all molecular dipoles. Thus:

$$\hat{H}_{\text{int}}(t) = -\int dr \hat{P}(r) E(r,t)$$

- **observable polarisation:** $P(r,t) = \langle \psi(t) | \hat{P}(r) | \psi(t) \rangle$



Solve the Schrödinger equation perturbatively

$$i\hbar\frac{\partial\psi}{\partial t} = \left(\hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{int}}(t)\right)\psi$$

- solve in terms of a perturbation series:

$$\psi(t) = \sum_{n=0}^{\infty} \psi^{(n)}(t)$$

- obtain the corresponding series for the polarisation:

$$P(r,t) = \langle\psi(t)|\hat{P}(r)|\psi(t)\rangle = \sum_{n=0}^{\infty} P^{(n)}(r,t)$$

- where $P^{(n)}(r,t) = \sum_{m=0}^{n}\langle\psi^{(n-m)}(t)|\hat{P}|\psi^{(m)}(t)\rangle$
- $n = 1$: linear response; $n > 1$: nonlinear response

How to obtain $\psi^{(n)}$?

- we'll use a perturbation series for the propagator $\hat{U}(t,t_0)$ which generates the wavefunction at time t,

$$\psi(t) = \hat{U}(t,t_0)\psi(t_0)$$

- for a time-independent Hamiltonian $\hat{H}$, e.g., for the molecule by itself, we have

$$\hat{U}_0(t,t_0) = \exp\Big(-\frac{i}{\hbar}\hat{H}_{\mathrm{mol}}(t-t_0)\Big)$$

- but if we include the time-dependent field, we have a time-dependent $\hat{H}(t)$, resulting in a time-ordered series:

$$\hat{U}(t,t_0) \quad = \quad \exp_+\Big(-\frac{i}{\hbar}\int_{t_0}^{t} d\tau\,\hat{H}(\tau)\Big) = \sum_{n=0}^{\infty}\hat{U}^{(n)}(t,t_0)$$

. . . $\psi^{(n)}$, cont'd . . .

Explicitly, this series reads:

$$\hat{U}(t,t_0) = 1 + \sum_{n=1}^{\infty}\left(\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1}\ldots\int_{t_0}^{\tau_2} d\tau_1 \hat{H}(\tau_n)\ldots\hat{H}(\tau_1)$$

$$= 1 + \sum_{n=1}^{\infty} \hat{U}^{(n)}(t,t_0)$$

If we have a partitioning of the Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{H}_1$, we'll use an interaction representation:

$$\hat{U}(t,t_0) = \hat{U}_0(t,t_0)\hat{U}_1(t,t_0) = \hat{U}_0(t,t_0)\Big(1 + \sum_{n=1}^{\infty}\hat{U}_1^{(n)}(t,t_0)\Big)$$

The wavefunction is then given as

$$\psi(t) = \hat{U}(t,t_0)\psi(t_0) = \hat{U}_0(t,t_0)\Big(1 + \sum_{n=1}^{\infty}\hat{U}_1^{(n)}(t,t_0)\Big)\psi(t_0) \equiv \sum_{n=0}^{\infty}\psi^{(n)}(t)$$

General concept of perturbation treatment

Count the number of interactions with the electric field

e.g., first order:

$$t \xleftarrow{U_0(t,\tau)} \tau \xleftarrow{U_0(\tau,t_0)} t_0$$

- if we have an instantaneous (delta function) pulse:

interaction with the field only at one specific time τ

- if the field acts over longer times: integrate over τ

$$\psi^{(1)}(t) = \left(-\frac{i}{\hbar}\right) \int_{t_0}^{t} d\tau \hat{U}_0(t,\tau) \Big(\hat{\mu} E(\tau)\Big) \hat{U}_0(\tau,t_0)\psi(t_0)$$

Perturbation theory, cont'd: second order

$$t \xleftarrow{U_0(t,\tau)} \tau \xleftarrow{U_0(\tau,\tau')} \tau' \xleftarrow{U_0(\tau',t_0)} t_0$$

- again, for two δ-function pulses, account for interaction at τ and τ'
- for general fields, integrate over τ and τ':

$$\psi^{(2)}(t) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' \hat{U}_0(t,\tau)\Big(-\hat{\mu}E(\tau)\Big)\hat{U}_0(\tau,\tau')\Big(-\mu E(\tau')\Big)\hat{U}_0(\tau',t_0)\psi(t_0)$$

. . . and so on for higher orders!

Linear response – absorption spectroscopy

$$\psi^{(1)}(t) = \left(-\frac{i}{\hbar}\right) \int_{t_0}^{t} d\tau \hat{U}_0^X(t,\tau)\Big(\hat{\mu}_{XG} E(\tau)\Big)\hat{U}_0^G(\tau,t_0)\psi_G(t_0)$$

Here, we assumed

- a CW field
- a wavefunction that has been prepared in the ground state (G)
- the dipole moment operator is given as $\hat{\mu}_{XG} = \mu_{XG}(|X\rangle\langle G| + |G\rangle\langle X|)$

The associated 1st-order polarisation is

$$\begin{aligned} P^{(1)}(t) &= \langle\psi^{(0)}|\hat{\mu}|\psi^{(1)}\rangle + \langle\psi^{(1)}|\hat{\mu}|\psi^{(0)}\rangle \\ &= \left(\frac{i}{\hbar}\right)\int_{-\infty}^{\infty} d\tau C(t-\tau)E(\tau) = \left(\frac{i}{\hbar}\right) C(t) \otimes E(t) \end{aligned}$$

with $C(t) = \langle\Phi_X(t)|\Phi_X(0)\rangle$ = excited-state wavepacket autocorrelation function

Nonlinear response functions

$$P(r,t) = \langle \psi(t)|\hat{P}(r)|\psi(t)\rangle = \sum_{n=0}^{\infty} P^{(n)}(r,t)$$

$$\begin{aligned} P^{(n)}(r,t) \quad = \quad & \int_0^{\infty} d\tau_n \int_0^{\infty} d\tau_{n-1} \ldots \int_0^{\infty} d\tau_1 \; S^{(n)}(t_n, t_{n-1}, \ldots, t_1) \\ & E(r, t-t_n) E(r, t-t_n-t_{n-1}) \ldots E(r, t-t_n-t_{n-1} \ldots - t_1) \end{aligned}$$

- the $S^{(n)}$'s are nth order non-linear response functions
- in isotropic media, only the odd-order response functions are non-vanishing
- femtosecond pump-probe spectroscopy is associated with the 3rd order response

What do the fields look like?

- **incoming fields:**

$$E(r,t) = \sum_{j=1}^{n} E_j(r,t)\exp\Big(ik_j r - i\omega_j t\Big) + E_j^*(r,t)\exp\Big(-ik_j r + i\omega_j t\Big)$$

- **induced polarisation – source for the observed field**

$$\begin{aligned} P_{NL}(r,t) &= \sum_{n=2,3,\ldots} \sum_{s} P_s^{(n)}(t)\exp\Big(ik_s r - i\omega_s t\Big) \\ k_s &= \pm k_1 \pm k_2 \pm k_3 \ldots \pm k_n; \omega_s = \pm\omega_1 \pm \omega_2 \pm \omega_3 \ldots \pm \omega_n \end{aligned}$$

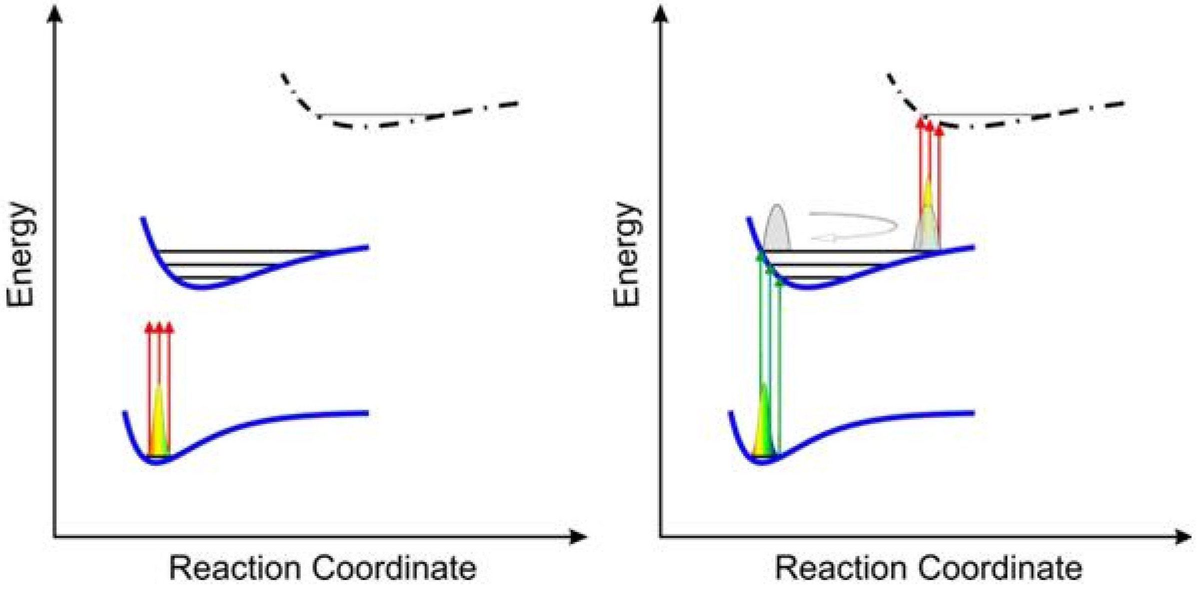
i.e., "wave mixing"!

- **heterodyne detection:**

add "local oscillator" field that has the same wavevector as the signal field

Pump-Probe Spectroscopy

Pump-probe spectroscopy: 2 pulses, 3 states



Monitor the full evolution in the 1st excited state (S_1)

Pump-probe spectroscopy: step by step

$|\psi_{S0}\rangle = |\psi_{S0}(0)\rangle$ – ground state wavefunction (time $t = 0$)

$|\psi^{(1)}_{S1}(0)\rangle = \hat{\mu}|\psi_{S0}(0)\rangle$ – wavepacket created “instantaneously” in S_1

$|\psi^{(1)}_{S1}(t')\rangle = \hat{U}_{S1}(t', 0)|\psi^{(1)}_{S1}(0)\rangle$ – wavepacket evolves in S_1

$\hat{U}(t', 0) = \exp\left(-i\hat{H}_{S1}t'/\hbar\right)$ = propagator

$|\psi^{(2)}_{S2}(t')\rangle = \hat{\mu}|\psi^{(2)}_{S1}(t')\rangle$ – 2nd pulse acts to transport wavepacket to S_2

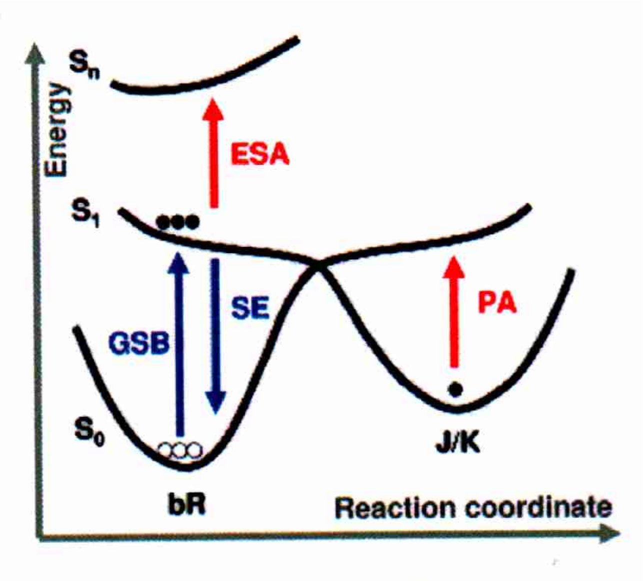
$|\psi^{(2)}_{S2}(t)\rangle = \hat{U}_{S2}(t, t')|\psi^{(2)}_{S2}(t')\rangle$ – wavepacket evolves in S_2

$$\begin{aligned} \text{signal} &= \langle\psi^{(1)}(t)|\hat{\mu}|\psi^{(2)}(t)\rangle + c.c. \\ &= \int_{\infty}^{\infty} \langle\psi^{(2)}_{S2}(t')|\psi^{(2)}_{S2}(t)\rangle E(t')dt' \end{aligned}$$

Again, with a different notation . . .

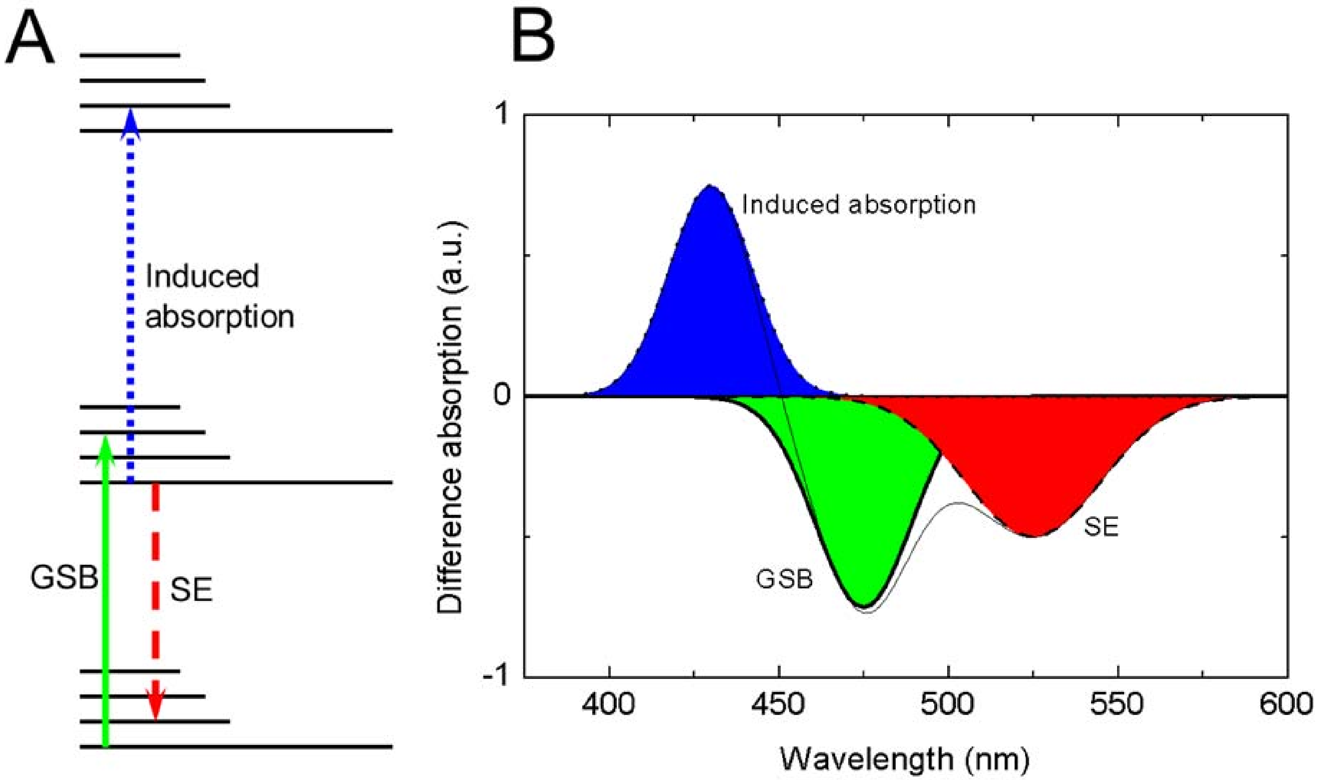
pump-probe spectrum

$$\begin{aligned} P^{(3)}(t) &= \langle\psi^{(1)}(t)|\hat{\mu}|\psi^{(2)}(t)\rangle + c.c. \\ &= \int_{-\infty}^{\infty} \langle\psi_{S1}^{(1)}(t';\tau)|\hat{\mu}\,\exp\Big(-i\hat{H}_{S2}(t-t')\Big)\,\hat{\mu}|\psi_{S1}^{(1)}(t';\tau)\rangle E(t')dt' \end{aligned}$$



- two pulses (pump/probe) with a delay t'
- The experiment probes the excited-state population $|\psi_{S1}(t';\tau)|^2$ as a function of the de time t' between the pump/probe pulse

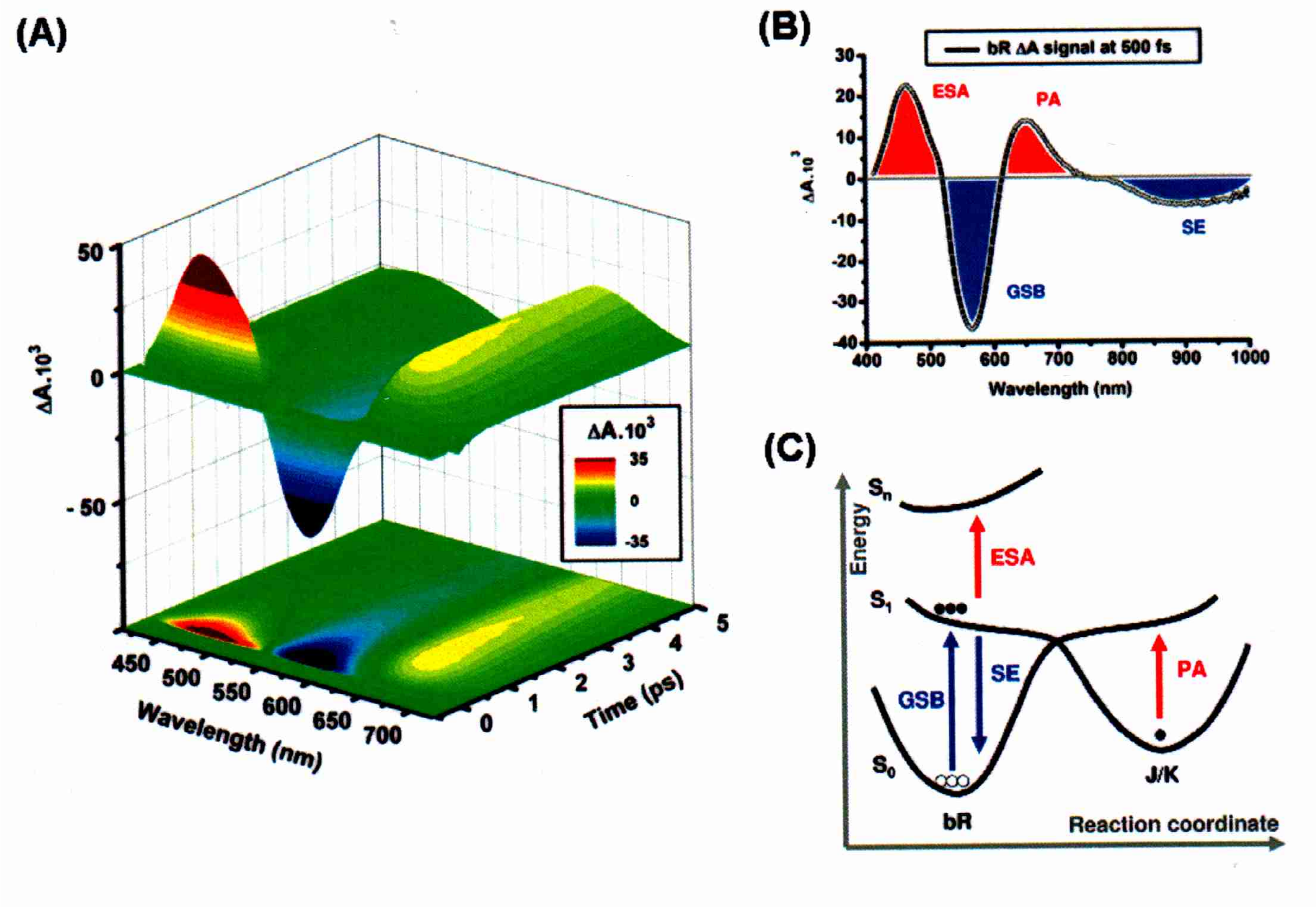
Transient absorption



web.vu.lt/ff/m.vengris/images/TRspectroscopy02.pdf

- **time-resolved two-pulse (pump-probe) spectroscopy**

Transient absorption for a photochemical switch



from: "Ultrafast isomerization and vibrational coherence of biomimetic photoswitches: Experimental investigation by femtosecond transient absorption spectroscopy", by Julien Briand, Ph.D. thesis Université de Strasbourg (2009).

NaI: one of the first fs pump-probe experiments

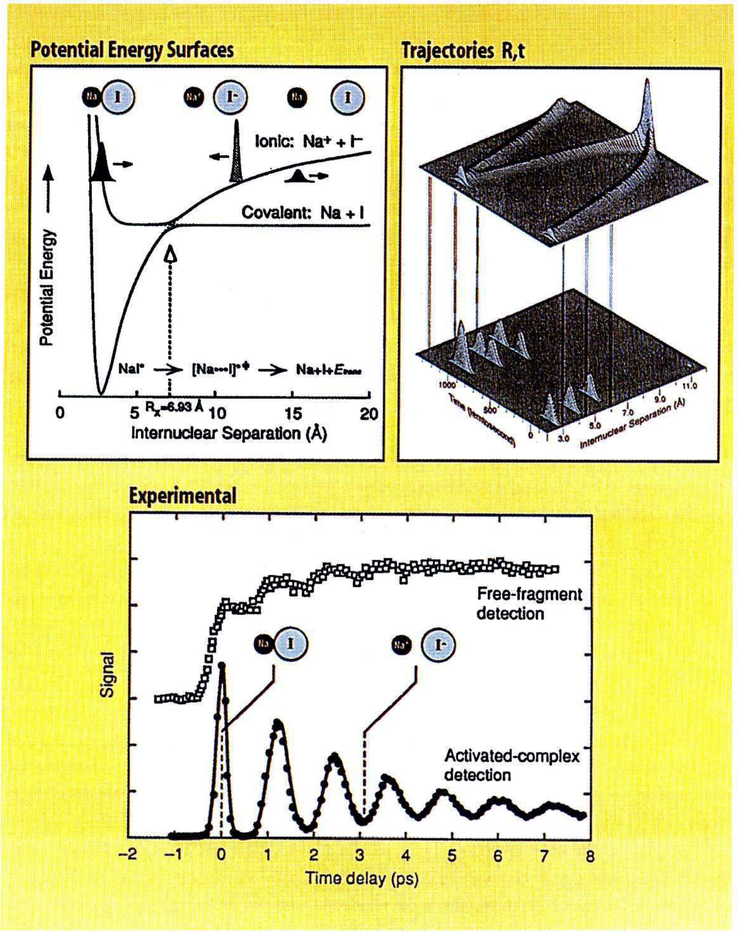


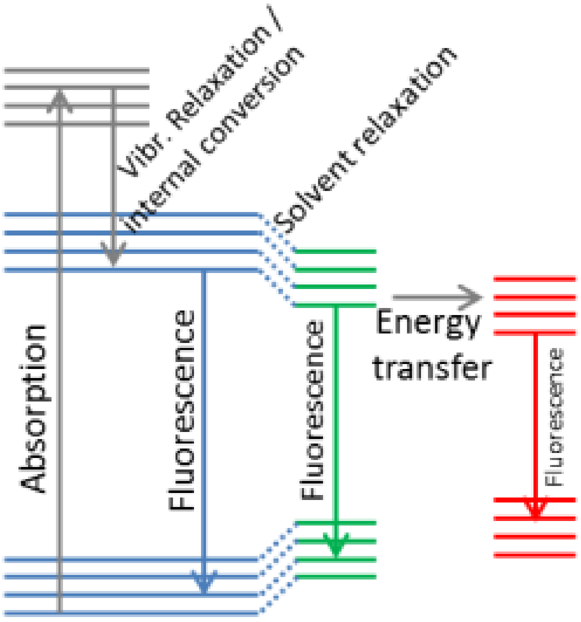
Figure 15. Femtochemistry of the NaI reaction, the paradigm case. The experimental results show the resonance motion between the covalent and ionic structures of the bond, and the time scales for the reaction and for the spreading of the wave packet. Two transients are shown for the activated complexes in transition states and for final fragments. Note the "quantized" behavior of the signal, not simply an exponential rise or decay of the ensemble. The classical motion is simulated as trajectories in space and time (top). [Ref. B1, B4, B12, B14, B17, B19, B28, 56]

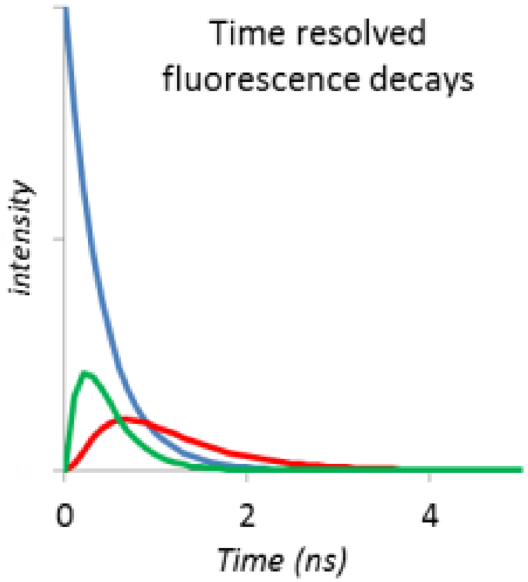
$\text{NaI}^* \longrightarrow \text{Na} + \text{I}$

(Zewail & co (1989))

- many oscillations between covalent and ionic states

Time-Resolved Fluorescence





- often provides complementary information to transient absorption
- suitable to monitor FRET (Fluorescence Resonance Energy Transfer)

Intramolecular charge transfer (ICT): DMABN (dimethylaminobenzonitrile)

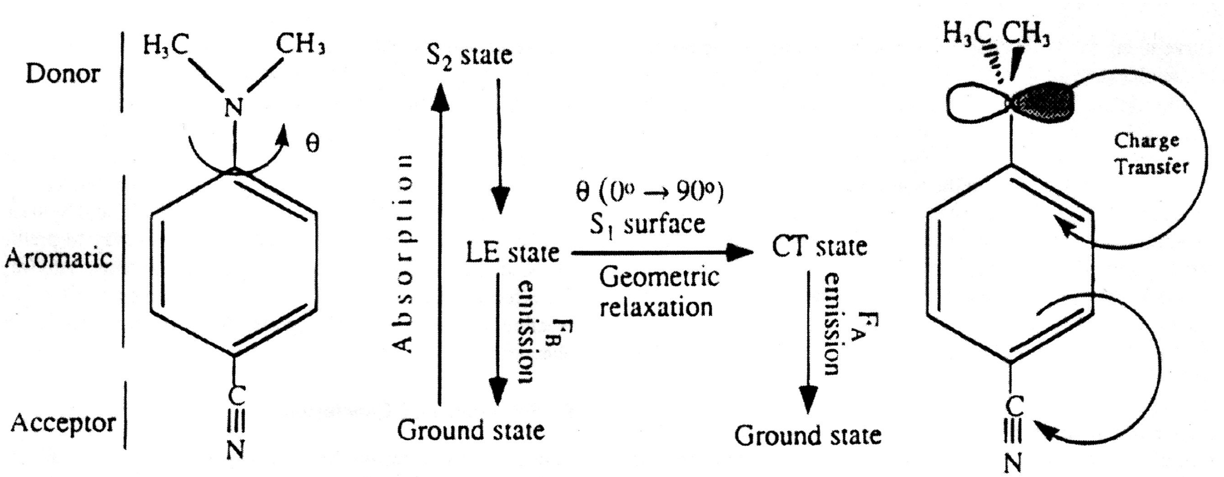
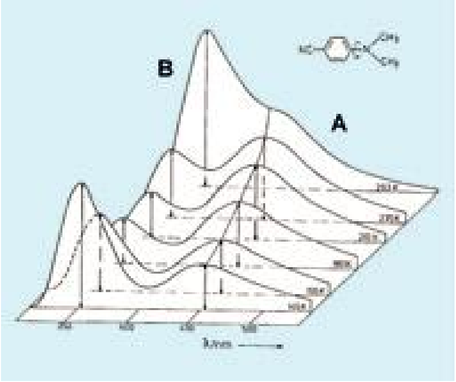


Figure 5. The dual fluorescence mechanism (TICT model) in DMABN.

Serrano-Andrés et al., J. Chem. Phys. 117, 3189 (1995)

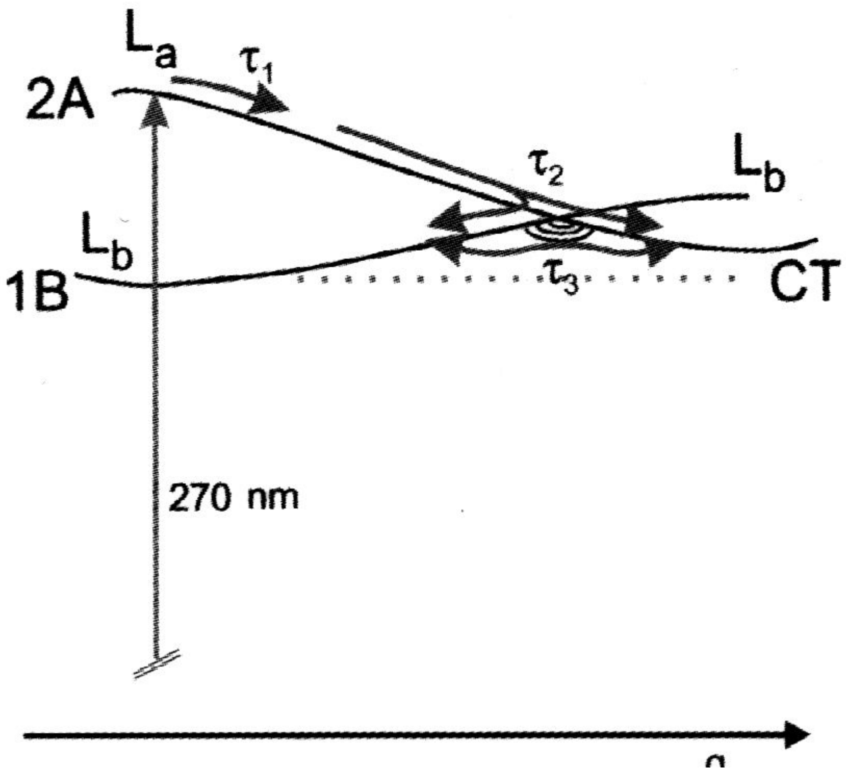


Observe dual fluorescence:

LE (locally excited) state
+ CT (charge transfer) state

ICT mechanism

Fuss et al., Faraday Discuss. 127, 23 (2004)



reaction coordinate

typical time scales (measured in femtosecond time-resolved experiments):

τ_1 = 5-10 fs
τ_2 = 30-50 fs
τ_3 = 500 fs - 1 ps

The reaction coordinate mainly involves the twist, but also other modes and the solvent

Also, there's a conical intersection!

“Do fluorescence and transient absorption probe the same intramolecular charge transfer state of 4-(dimethylamino)benzonitrile?”

031101-2 Gustavsson *et al.* J. Chem. Phys. **131**, 031101 (2009)

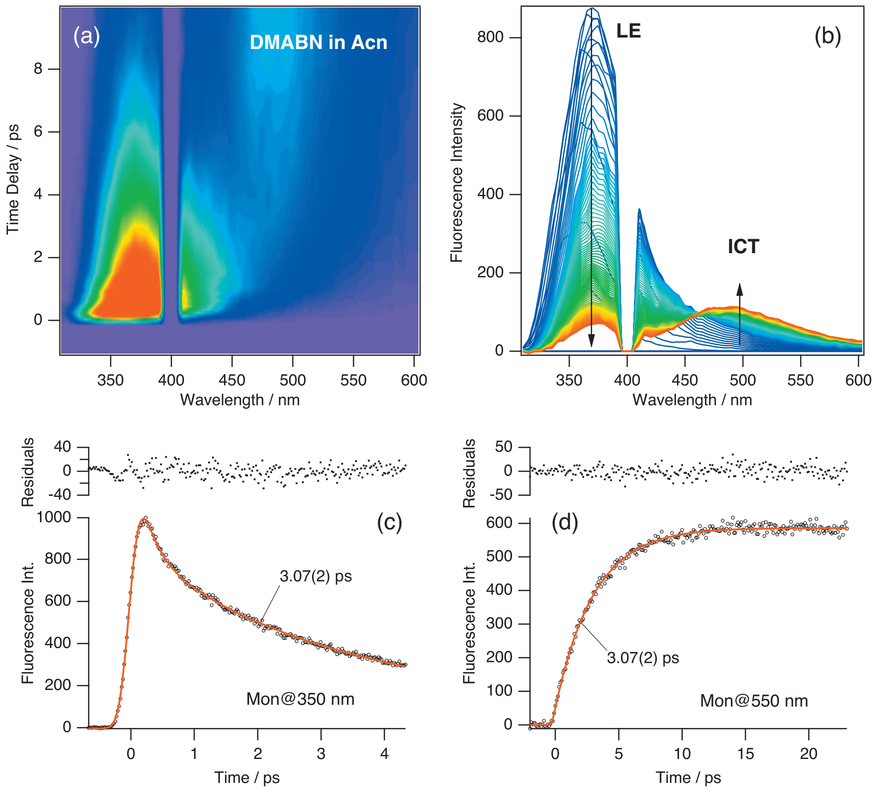


FIG. 1. The femtosecond time-resolved fluorescence upconversion spectra: (a) two-dimensional image plot and (b) its corresponding time-evoluted spectra of DMABN in acetonitrile (Acn) at room temperature. The spectral region around 400 nm was masked thoroughly to protect a detector in the excitation wavelength of 267 nm. The fluorescence decay curves of (c) the LE emission at 350 nm and (d) the ICT emission at 550 nm for DMABN in Acn. Common decay time constants were evaluated including other upconversion sets (not shown here) by a nonlinear least-squares global fit with a deconvolution procedure. The numbers in the parentheses indicate a standard deviation (1σ).

Gustavsson et al., J. Chem. Phys. 131, 031101 (2009)

Fluorescence

“Do fluorescence and transient absorption probe the same intramolecular charge transfer state of 4-(dimethylamino)benzonitrile?”

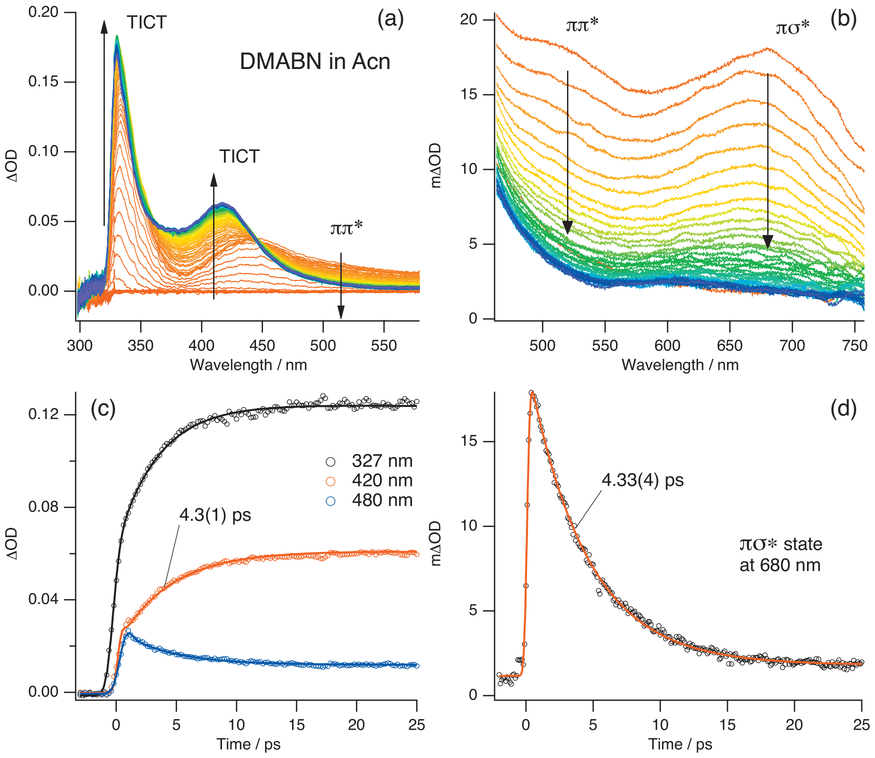


FIG. 2. The femtosecond time-resolved transient absorption spectra (−2 to 25 ps with an interval of 0.1 ps) at (a) shorter- and (b) longer-wavelength region for DMABN in Acn at room temperature. The arrows indicate the time evolution of the spectra, and assignments for the transients are also shown. Kinetics at (c) the 420 nm transient (TICT) and (d) 680 nm transient (the $\pi\sigma^*$-state absorption), which were extracted with a band integration from the time-resolved spectra [(a) and (b)]. Leaders show the fitted decay times with a standard deviation in the parentheses.

Gustavsson et al., J. Chem. Phys. 131, 031101 (2009)

Absorption