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SMR 1302 - 12

WINTER SCHOOL ON LASER SPECTROSCOPY AND APPLICATIONS

19 February - 2 March 2001

Ultrafast Dynamics in Model Molecular Systems - Excited State Intramolecular Proton Transfer

Lecture IV

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Ultrafast dynamics in model molecular systems
- excited state intramolecular proton transfer -

- observation of ultrafast chemical processes in real time
- spectroscopy of a transient species: keto TINUVIN P
- excited state intramolecular proton transfer (ESIPT) in TINUVIN P
- wavepacket dynamics during and after ESIPT in HBT

Elementary Processes of Chemistry

- breaking of bonds in the educt

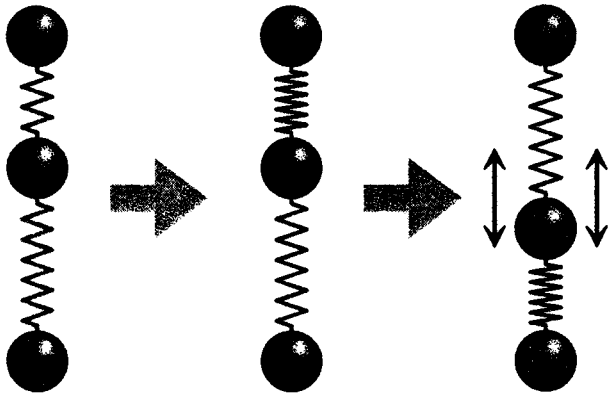
  \+ formation of bonds to form the product

- both processes are accompanied by large scale motions of atoms (compared to molecular vibrations)

- momentum conservation will lead to "ringing"

- normal modes ?

- change of the molecular geometry due to ultrafast photoinduced processes (educt → product)
- coherent ringing of the product in those modes that correlate strongly with the change in geometry
- investigation and understanding of the microscopic reaction mechanism



optically induced process

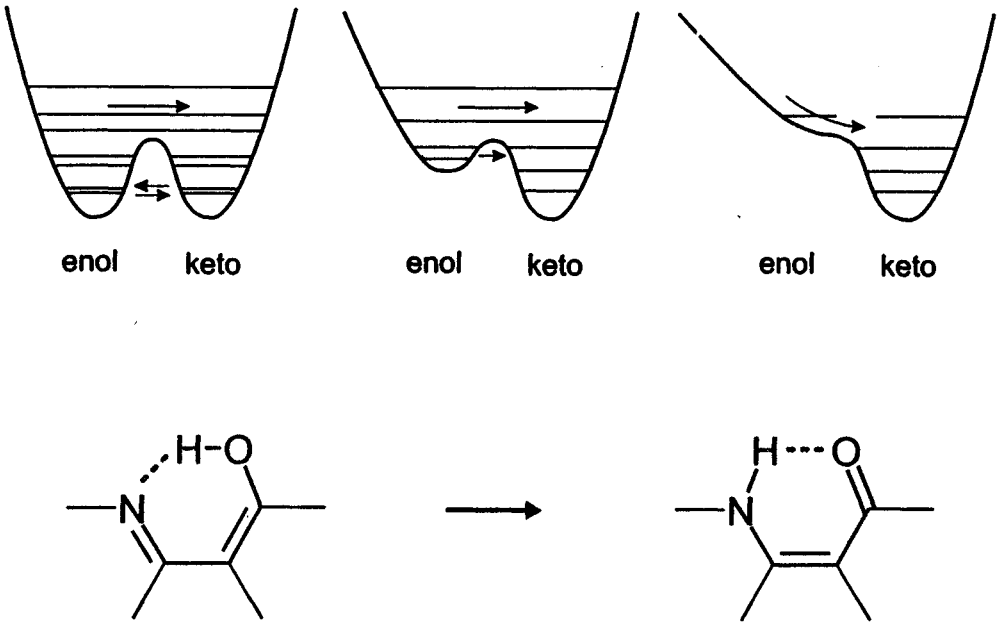
"ringing"

molecular ringing

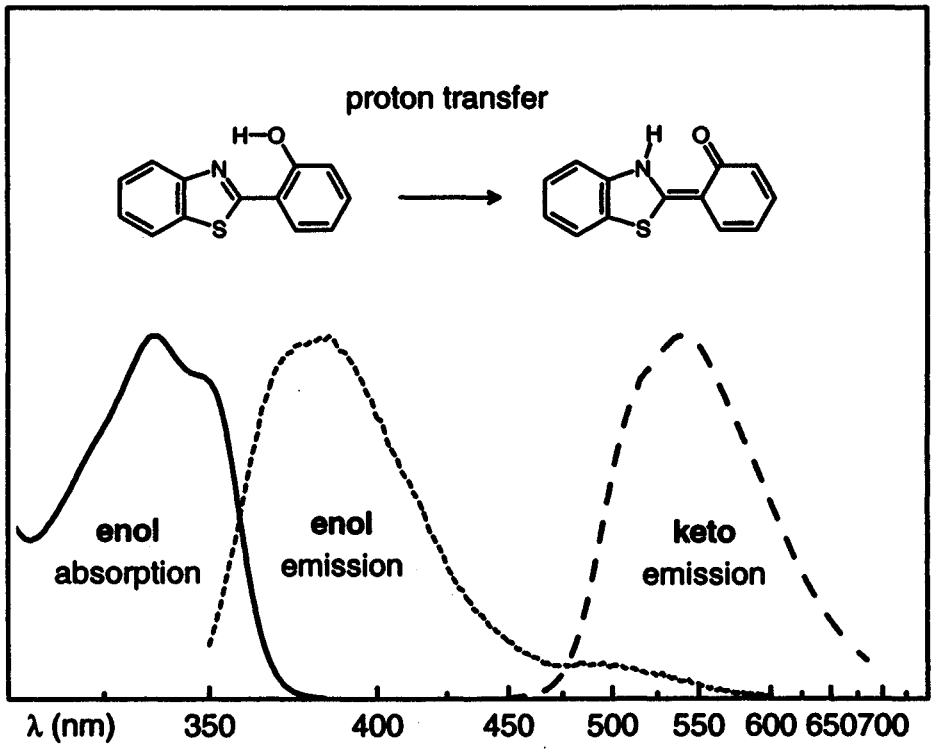
Molecular vibration

	$\tilde{\nu}$ (cm^{-1})	ν (THz)	T (fs)
C≡C–C	300	9	111
C≡C–H	700	21	48
⩾C–C⩽	900	27	37
> C=C <	1650	50	20
– C≡C –	2050	62	16
⩾C–H	2960	89	11

Excited State Intramolecular Proton Transfer (ESIPT)

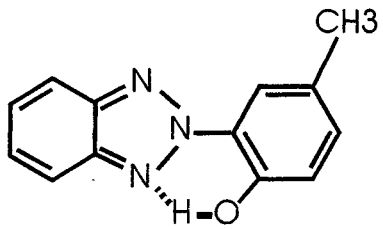


Charakterisierung der cw-Spektren von ESIPT-Molekülen

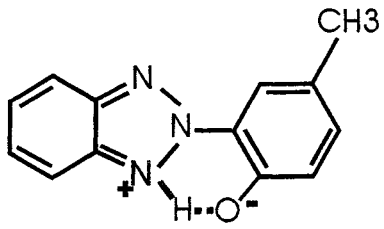


Proton transfer in TINUVIN P

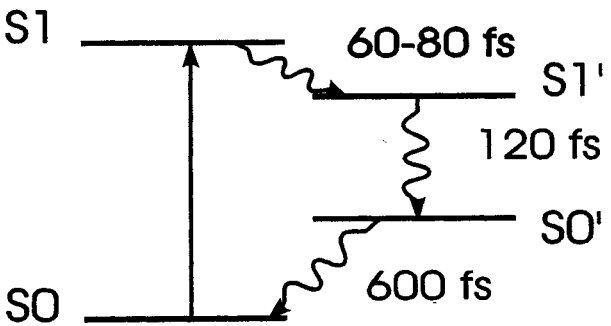
2-(2'-hydroxy-5'-methylphenyl) benzotriazole

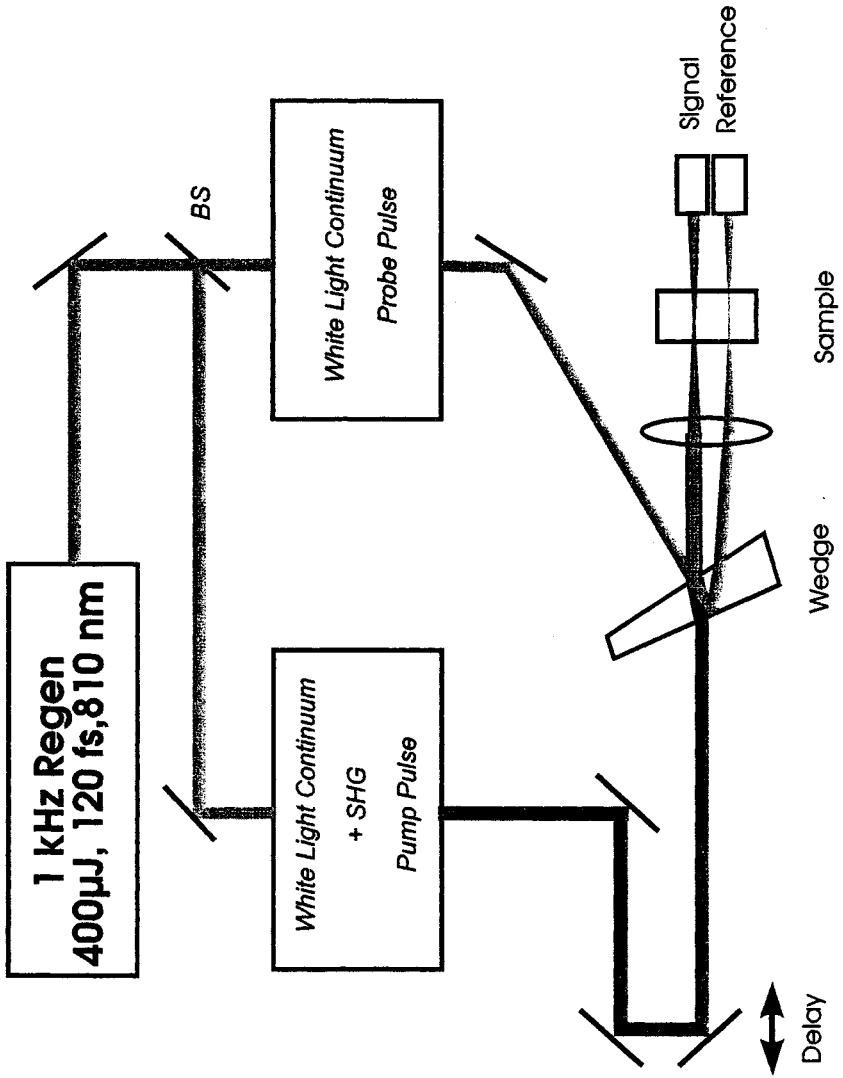


enol

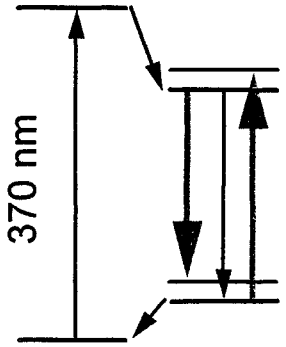


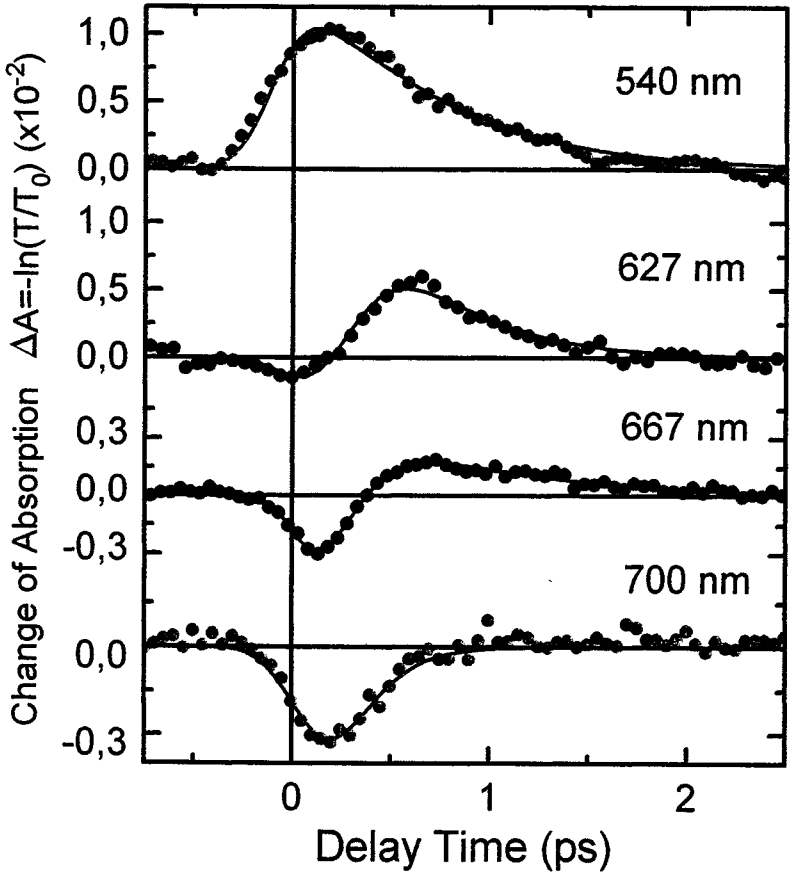
keto-type





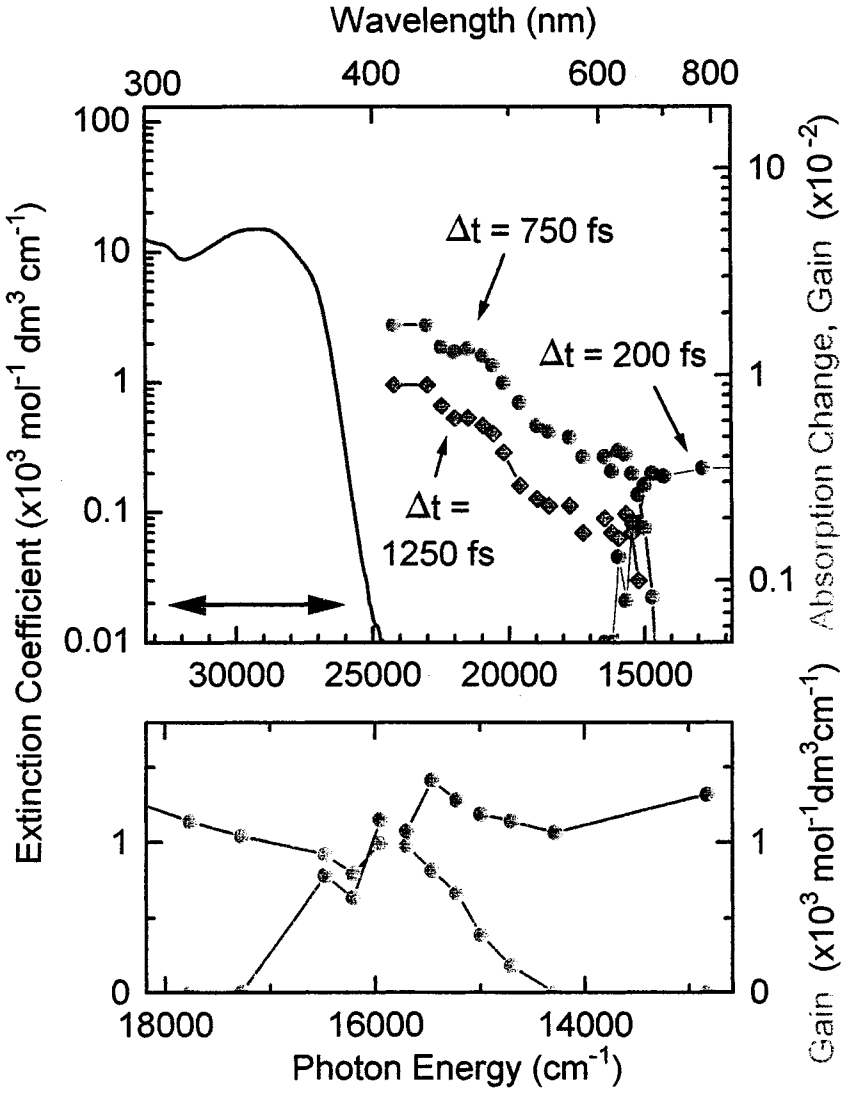
Transient emission and absorption of keto-type TIN





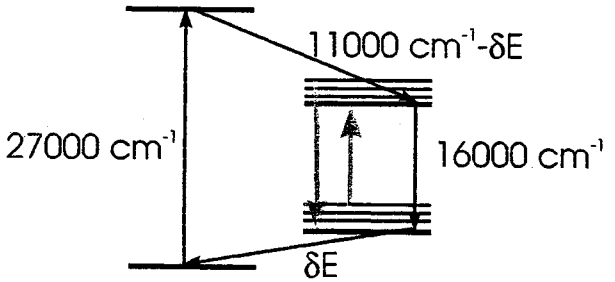
Chudoba, Lutgen, Jentzsch, Riedle, Wörner, Elsässer CPL 240, 35 (1995)

Transient absorption and emission spectra of keto-type TINUVIN



Chudoba et al., CPL **240**, 35 (1995)

Energetic widths of hot vibrational distributions



- **Excess energy**

⇨ Bose statistics and 78 normal modes

⇨ Max. temperatures and energy widths:

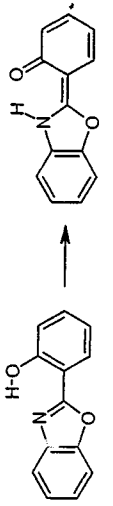
T_{S1max} = 600 K ⇨ kT_{S1max} = 400 cm^{-1}

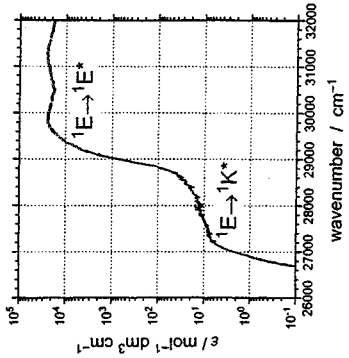
T_{S0max} = 1000 K ⇨ kT_{S0max} = 670 cm^{-1}

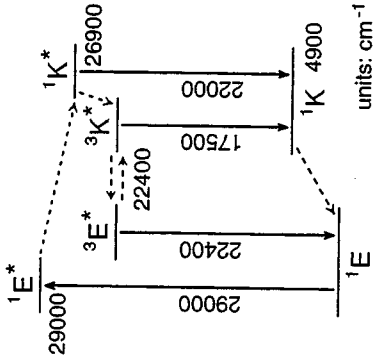
☝ experimental overlap: **2000 cm^{-1}**

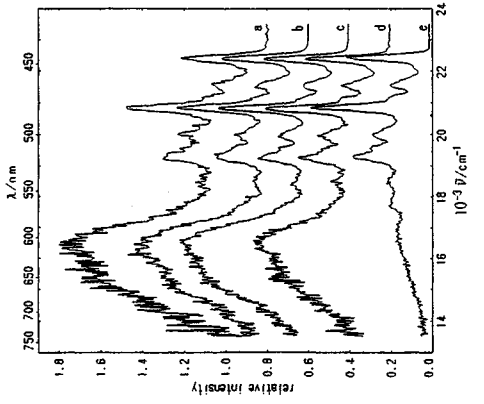
⇨ non equilibrium population

ESIPT of 2-(2'-Hydroxyphenyl)benzoxazol (HBO): Phosphorescence Studies





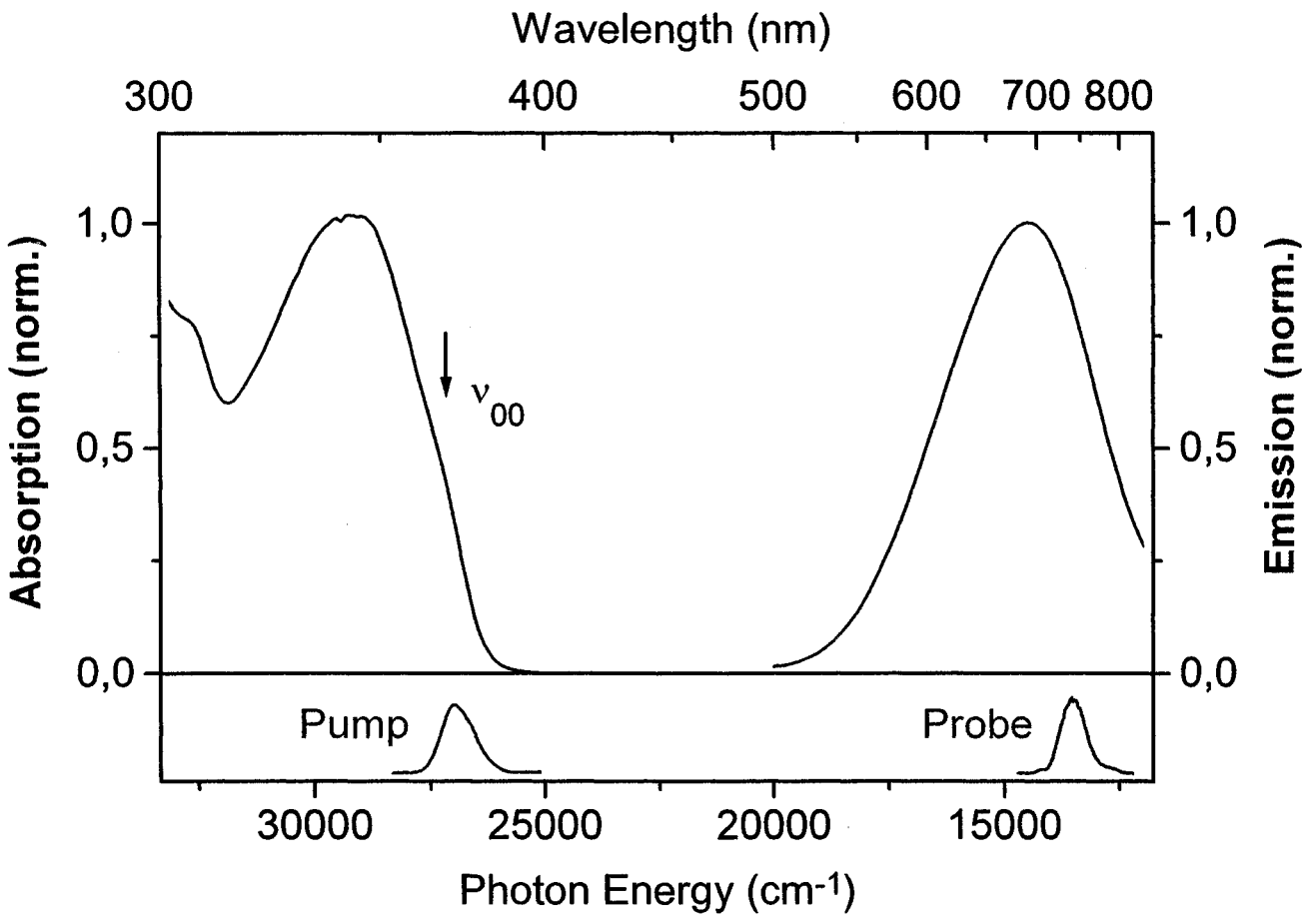


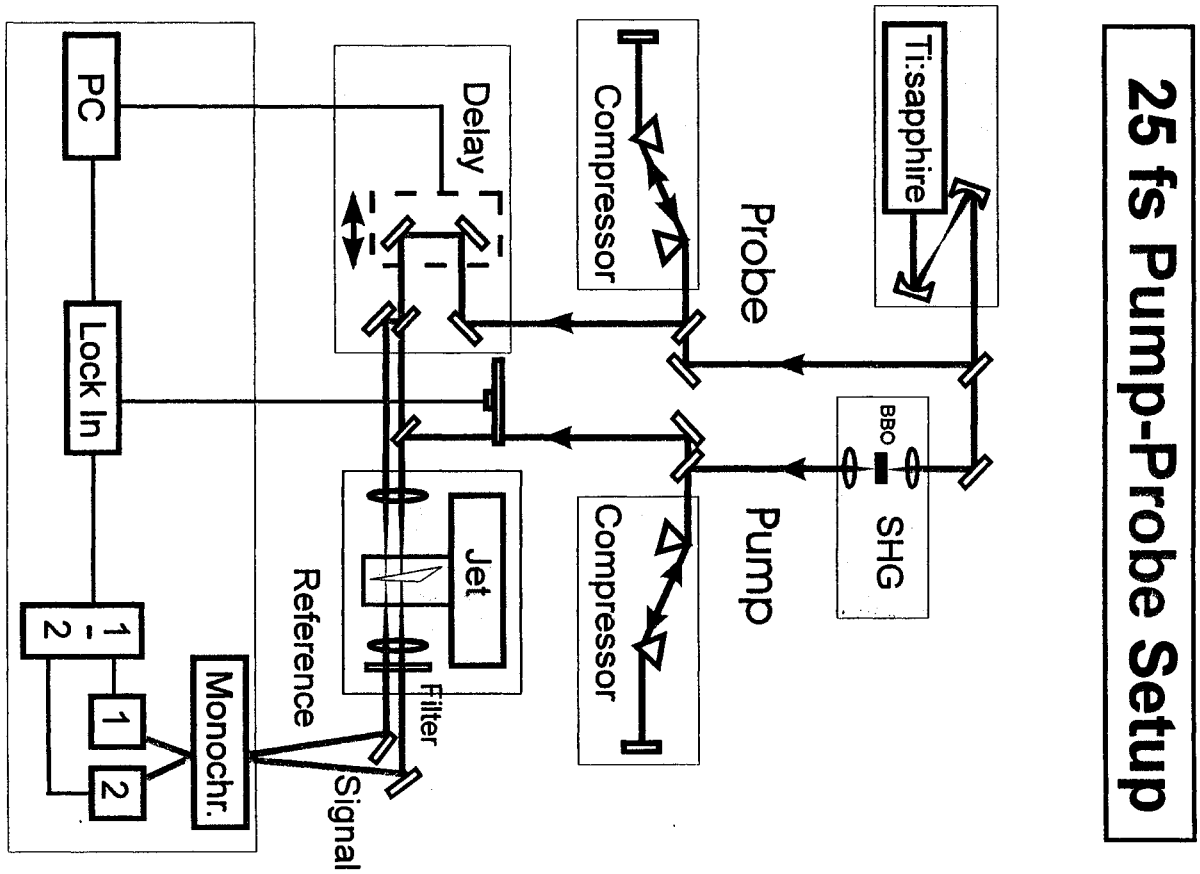


M.F. Rodríguez Prieto, B. Nickel, K.H. Grellmann, A. Mordzinski; Chem. Phys. Lett. **146** (1988), 387

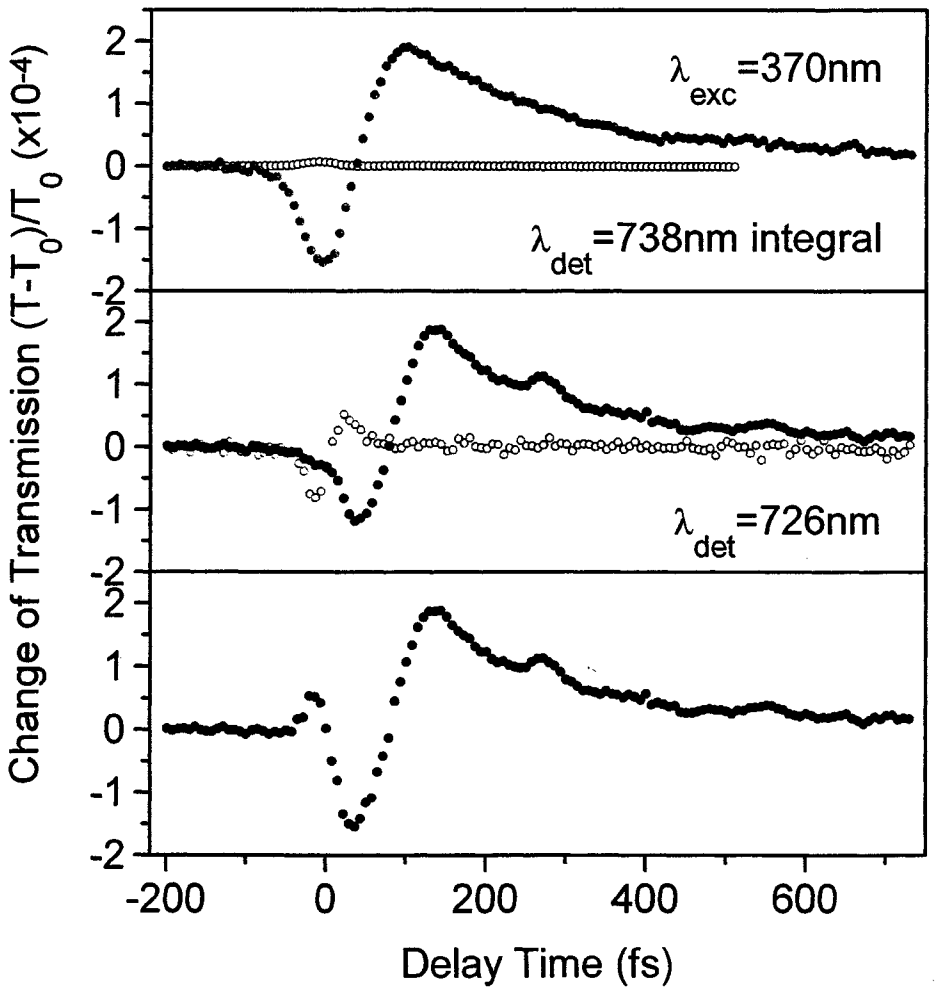
B. Nickel, P.J. Walla; Chem. Phys. **237** (1998), 237

Absorption- and Fluorescence Spectra

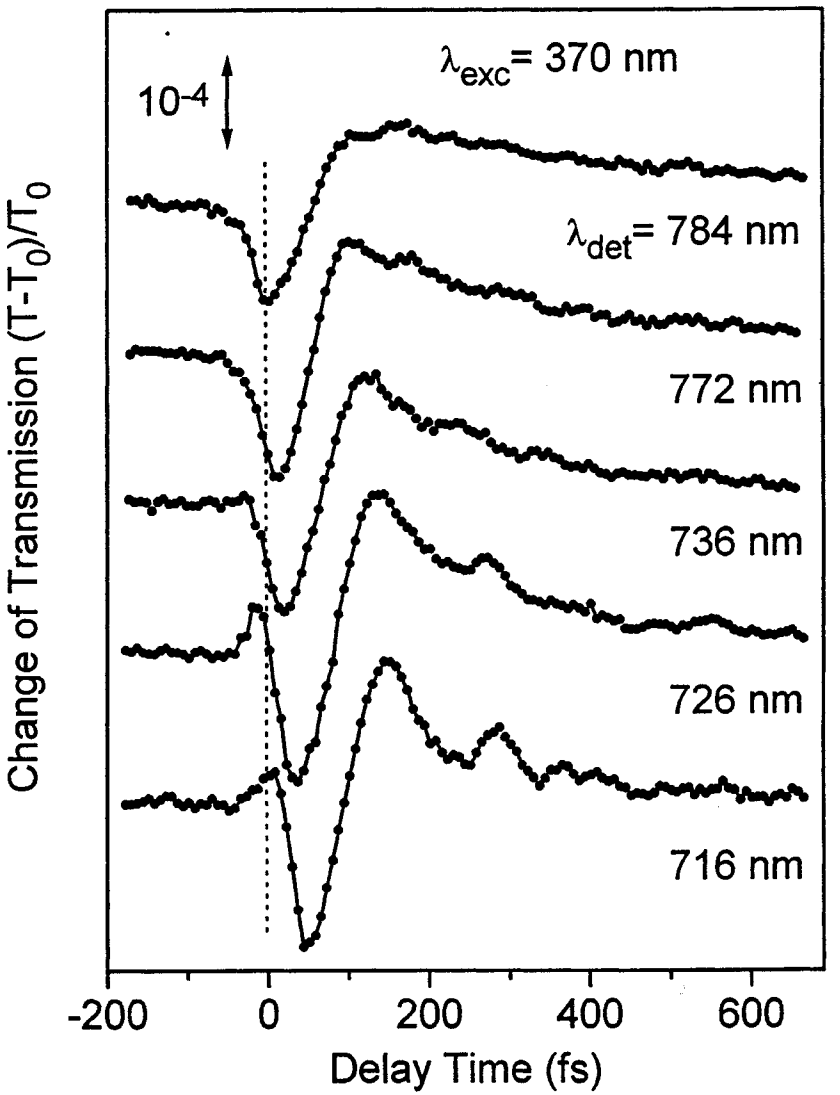




Transient absorption and emission of TIN + solvent contributions

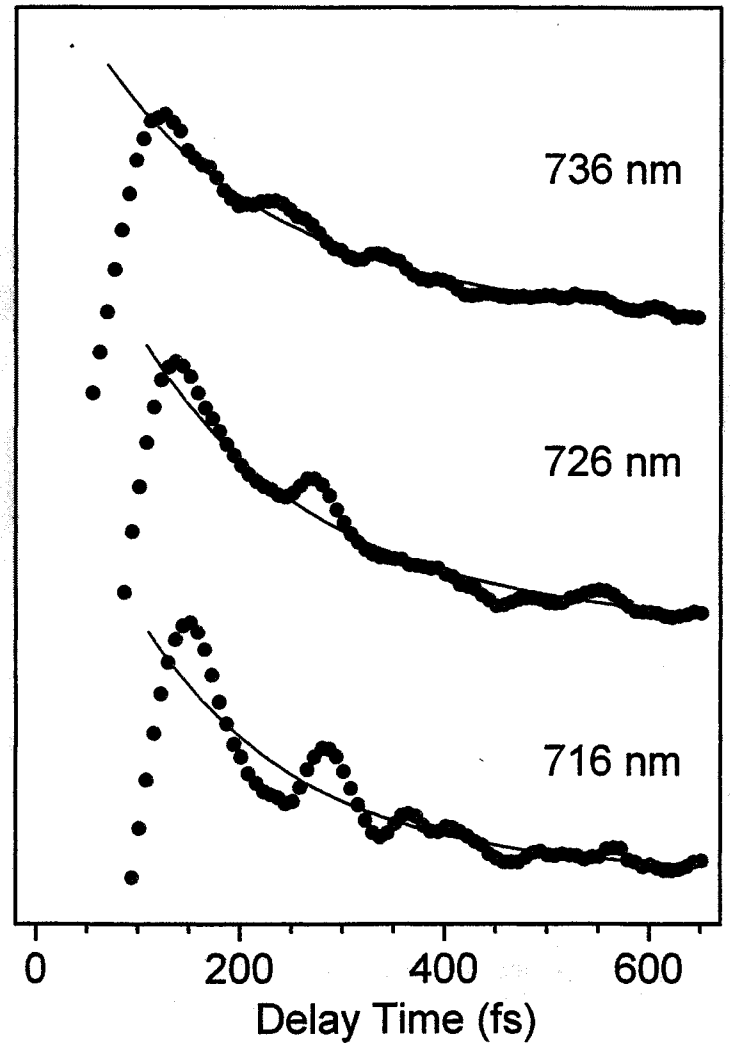


Spectrally resolved transient absorption and emission of TIN

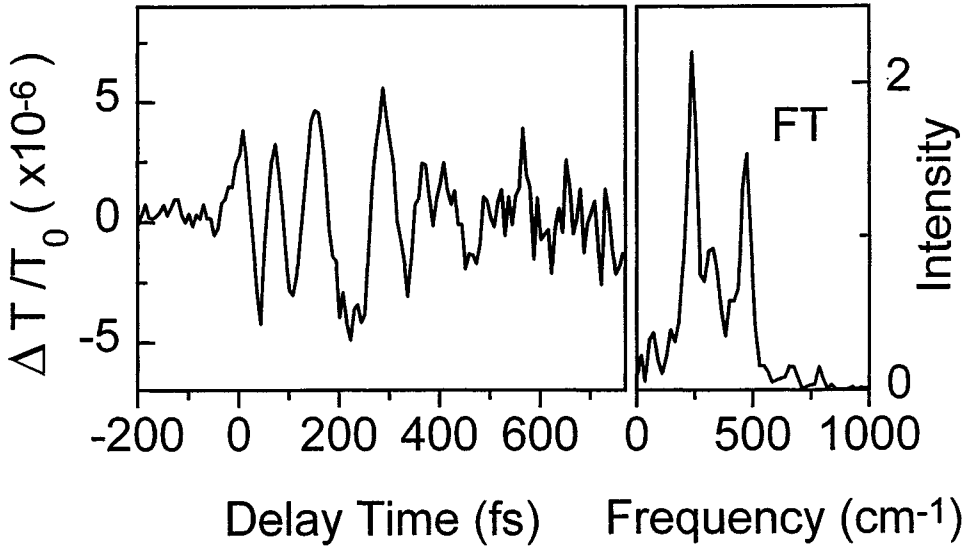


CPL 262, 622 (1996)

Wave Packet Dynamics during and after Proton Transfer



Oscillatory transmission change at λ_{det}=716 nm

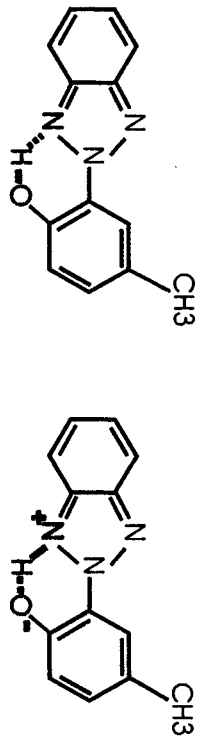


Summary of TINUVIN P results

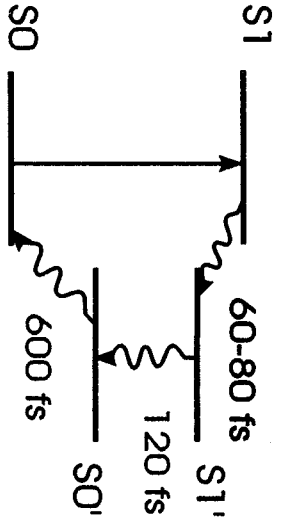
- ESIPT (excited state intramolecular proton transfer) in TINUVIN P within 60 - 80 fs
- observation of oscillatory signals - coherent wavepacket dynamics - during and after the proton transfer
- small effective barrier for ESIPT that is modulated by low frequency vibrational modes
- irreversible process due to additional modes (IVR = intramolecular vibrational redistribution)
- ultrafast return (τ ~ 120 fs and 700 fs) to the ground state surface (IC = internal conversion)
- proton back transfer in the electronic ground state within 600 fs

Proton transfer in TINUVIN P

2-(2'-hydroxy-5'-methylphenyl) benzotriazole

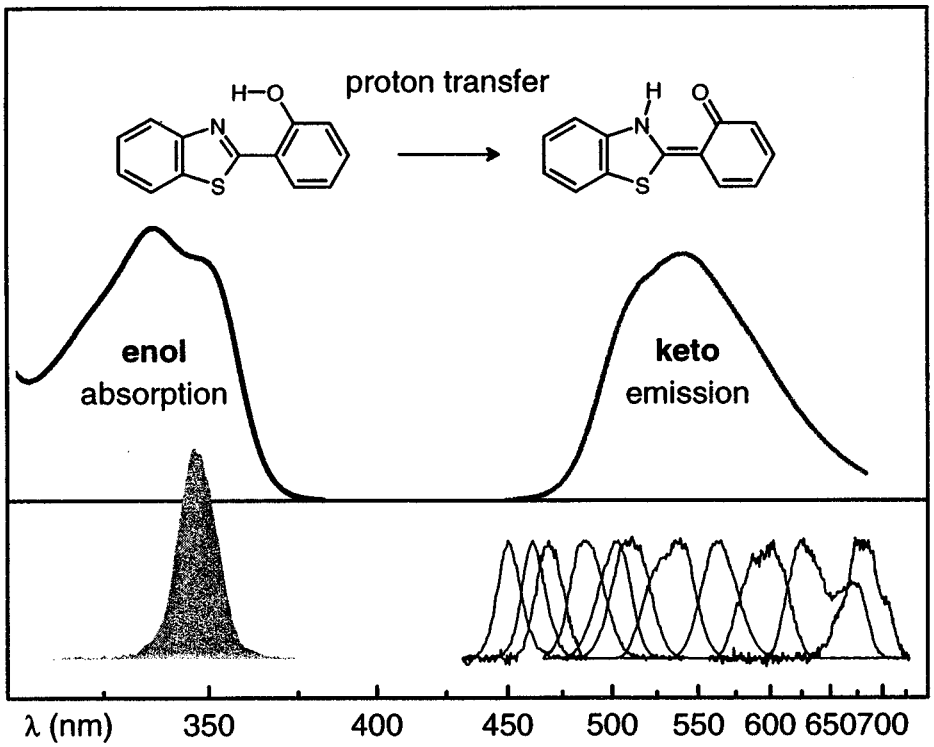


enol Keto-type

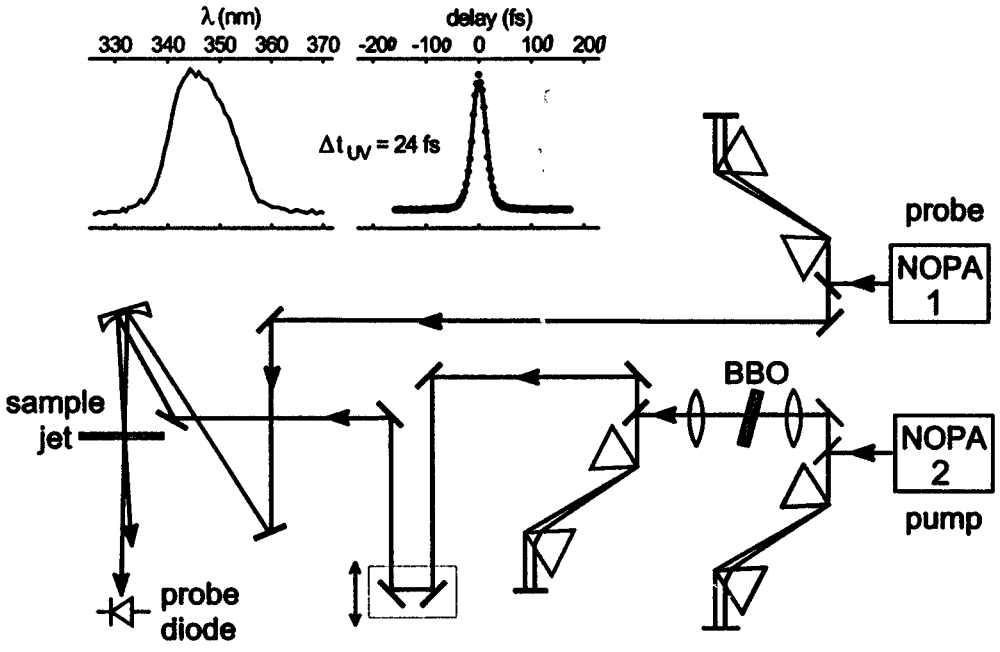


C. Chudoba, E. Riedle, M. Pfeiffer, and T. Elsaesser, Chem. Phys. Lett. **263**, 622 (1996)

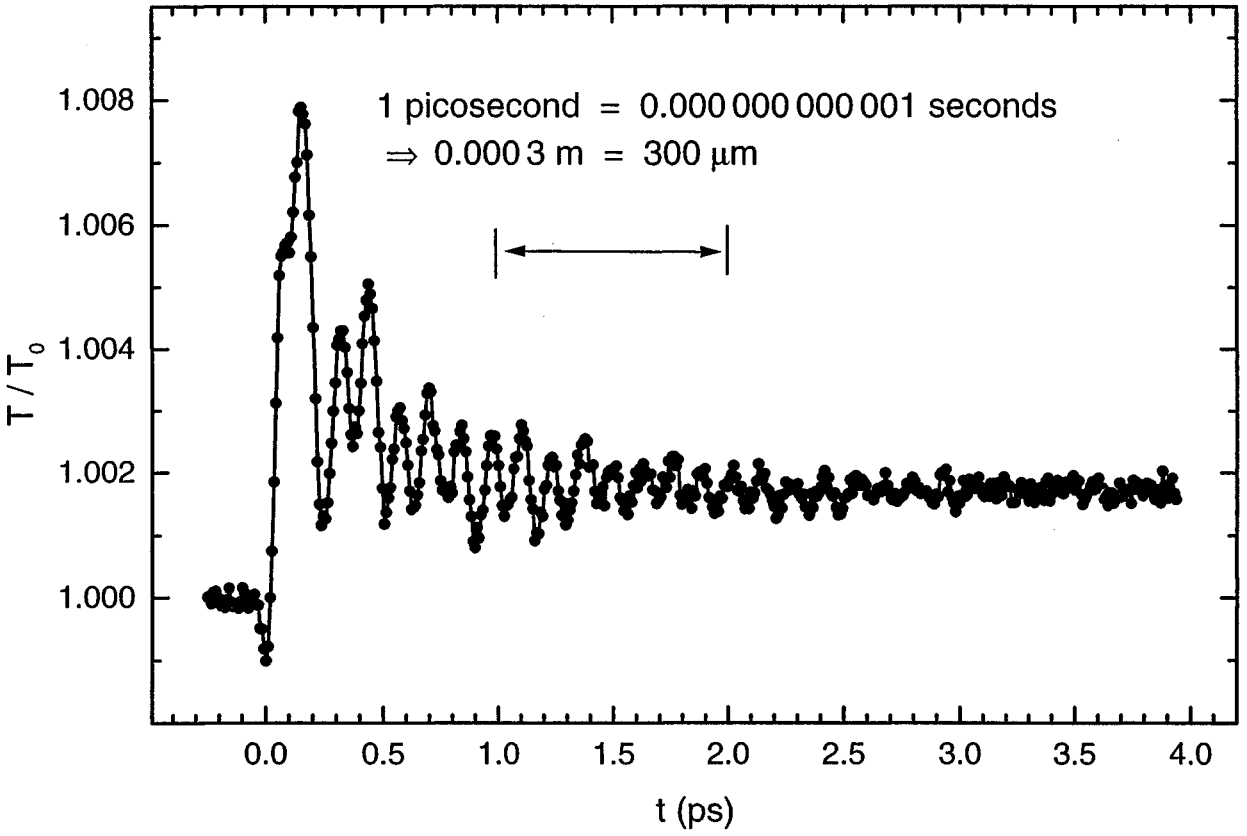
2-(2'-Hydroxyphenyl)benzothiazole (HBT)



Transient Absorption Spectroscopy with 20 fs Time Resolution

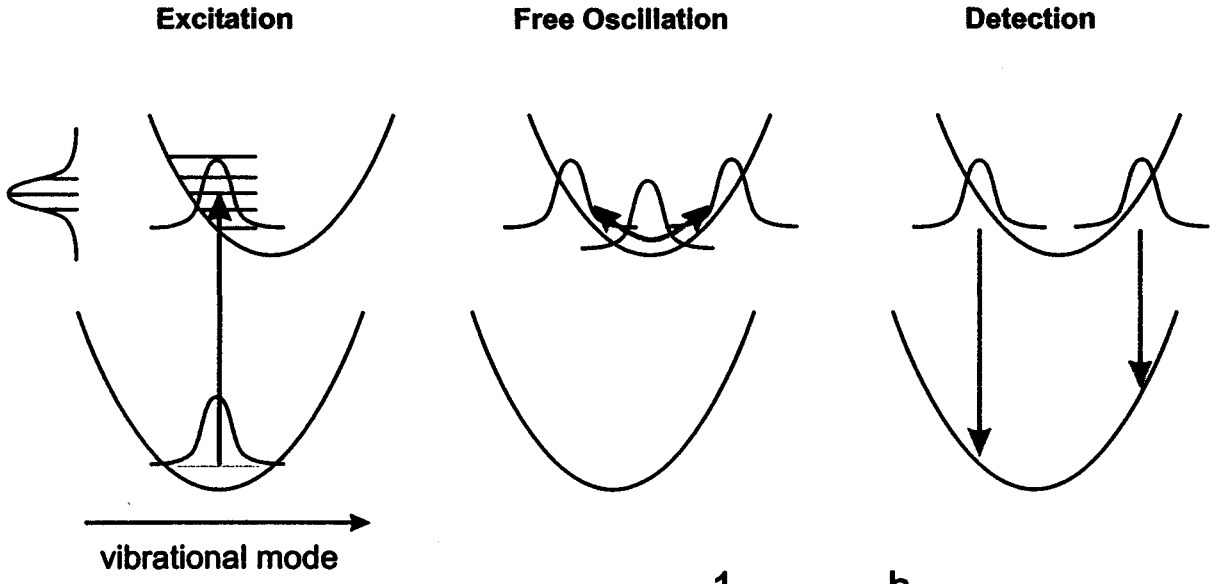


Intramolecular Proton Transfer

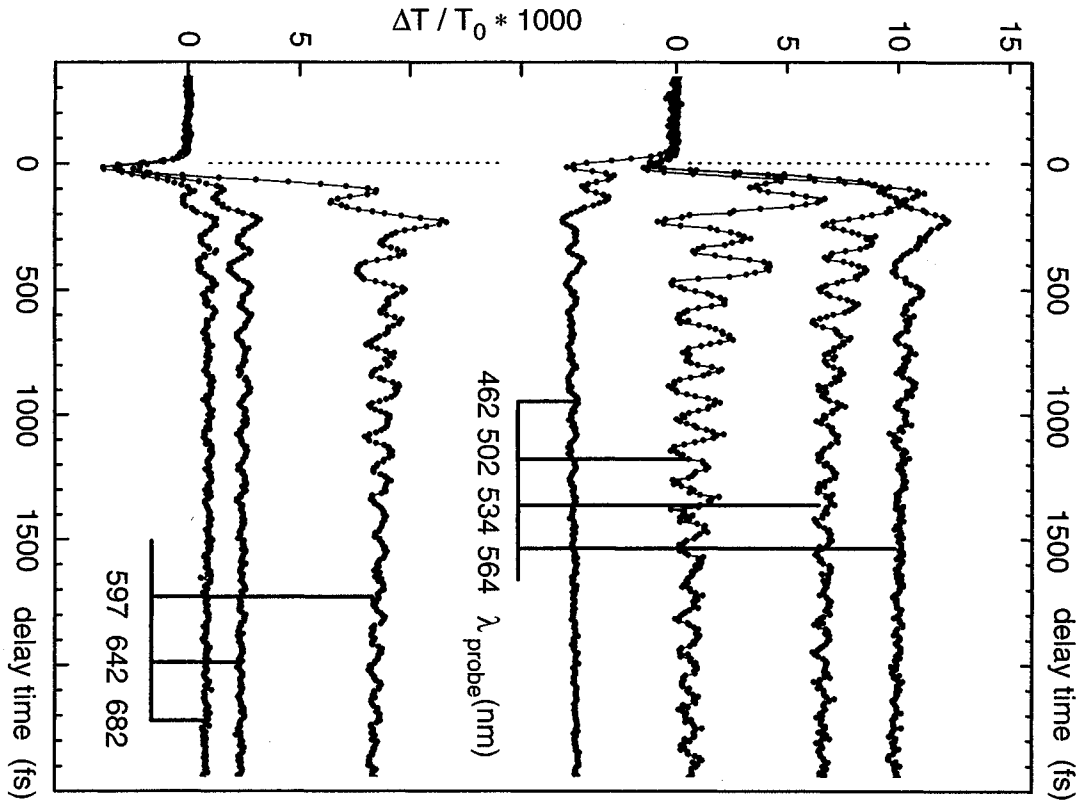


S. Lochbrunner / E. Riedle

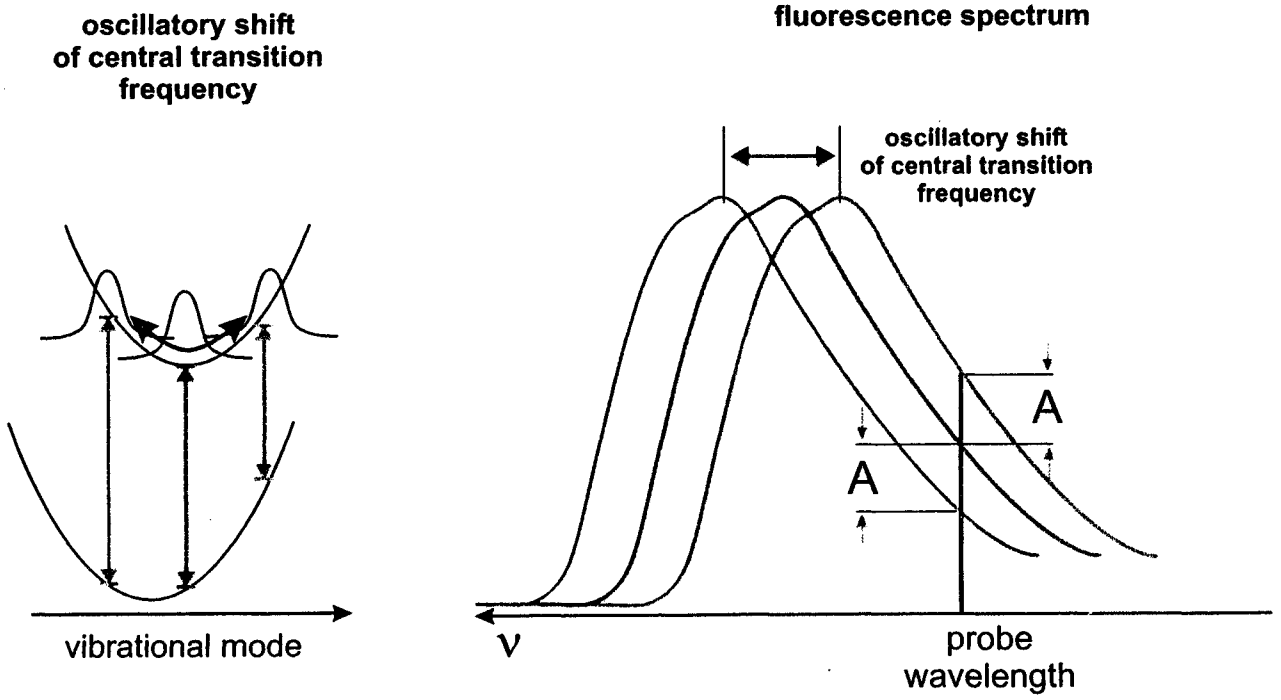
Vibronic Wavepackets



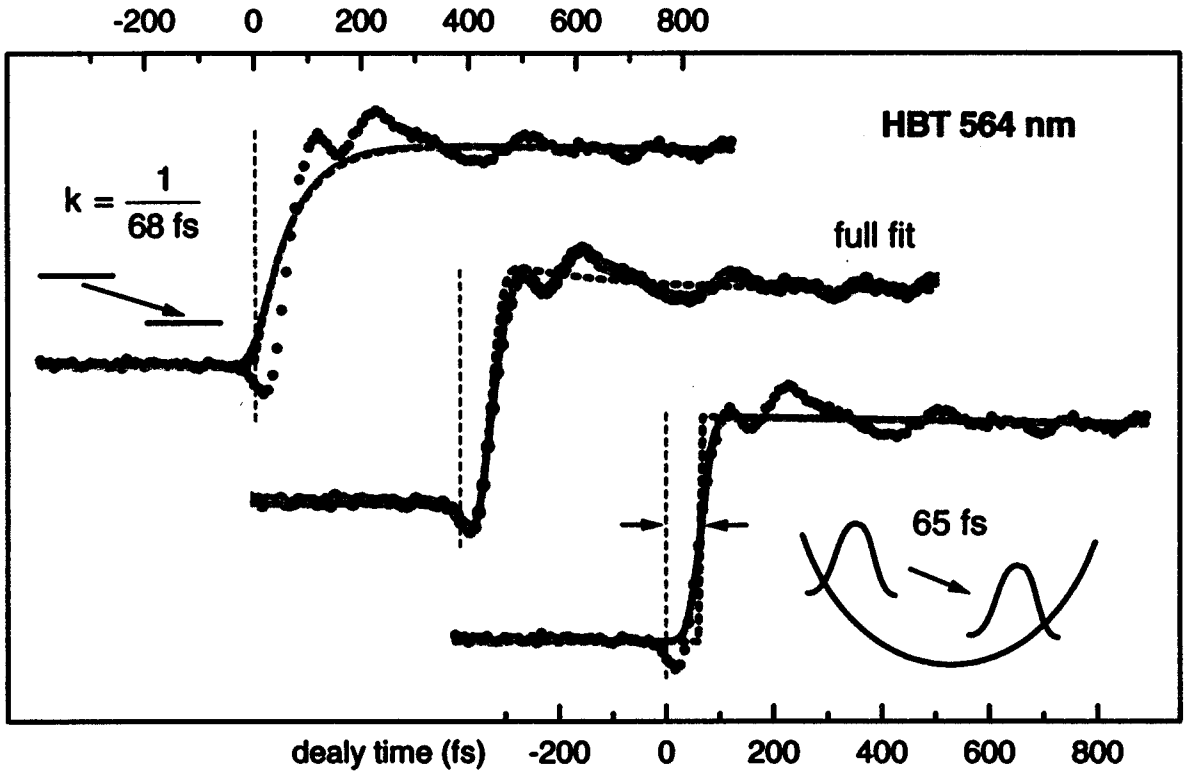
$$T_{osci} = \frac{1}{\nu_{osci}} = \frac{h}{E_{i+1} - E_i}$$

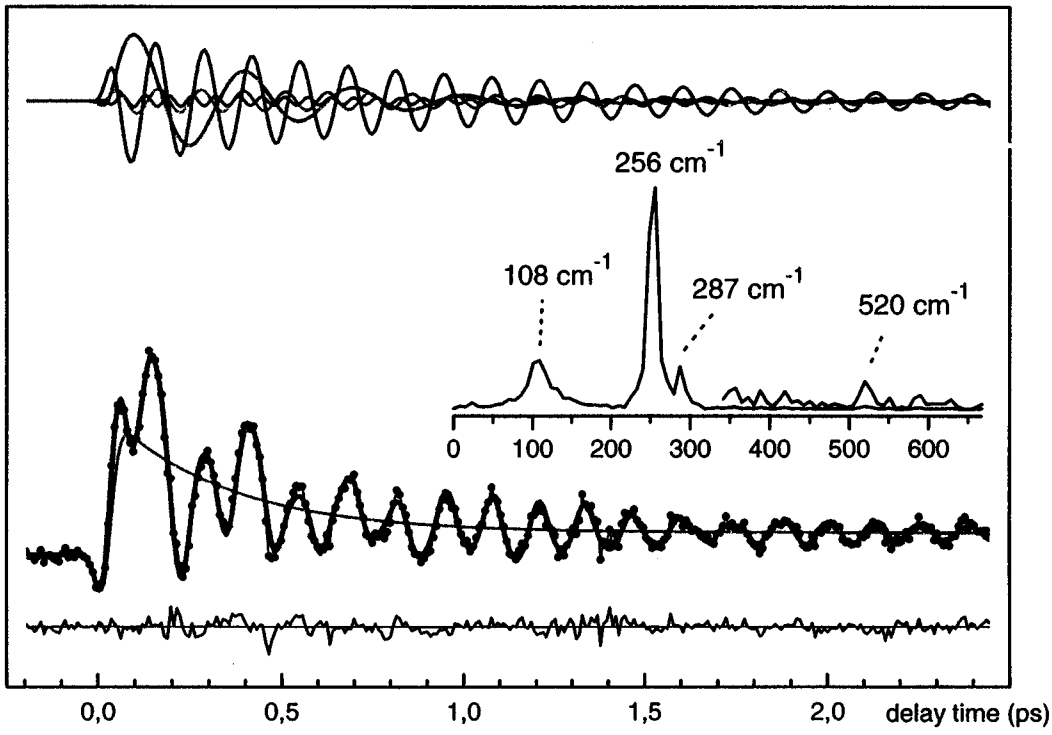


signal modulation by vibrational wavepacket motion

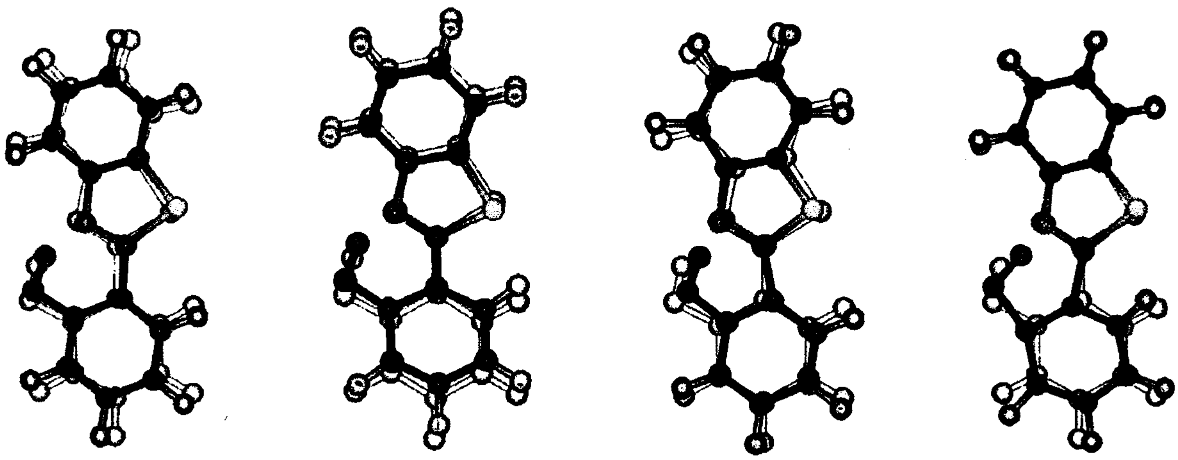


Ballistic Wavepacket Motion vs. Rate Model





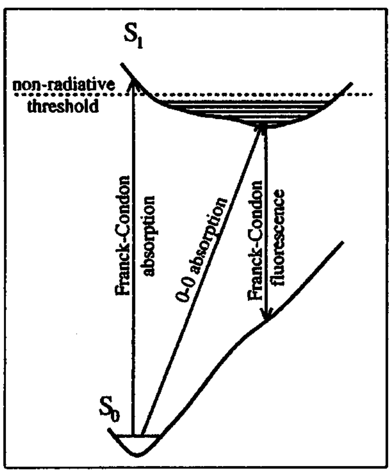
Excited State Vibrations of HBT



Experiment	118	254	289	529
scaled CIS	116	258	288	514/534

frequencies in cm^{-1}

Partitioning of Vibrational Excess Energy



PT reaction coordinate

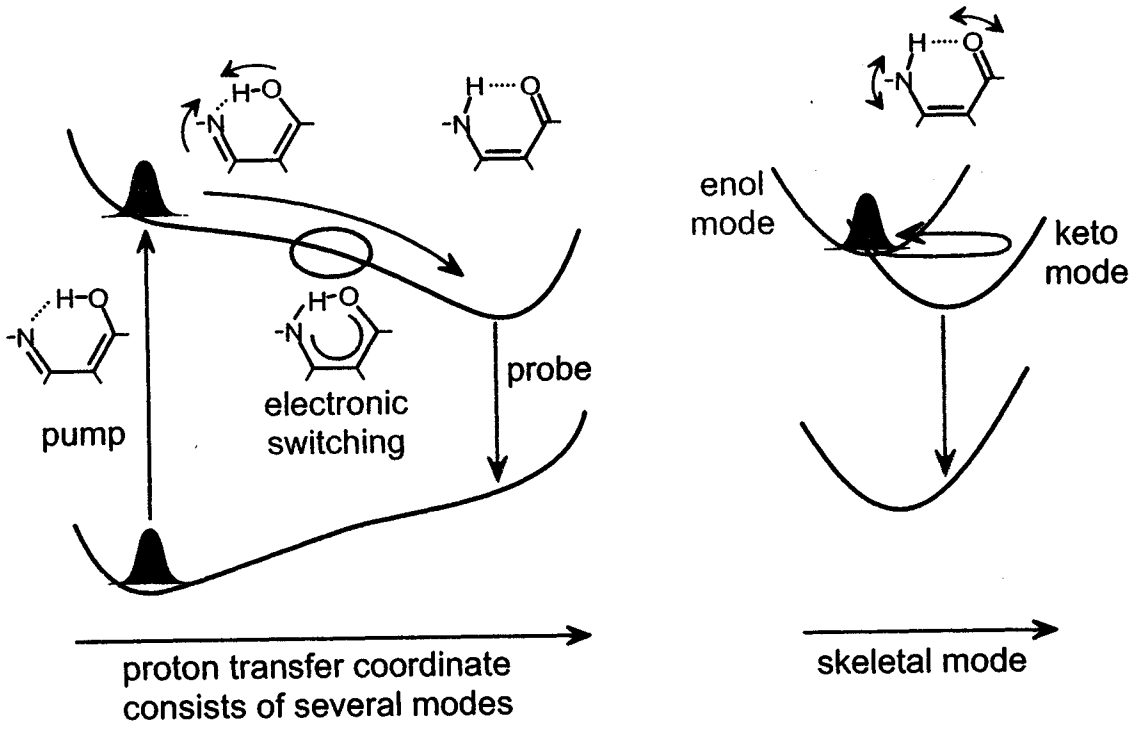
A. L. Sobolewski and W. Domcke
Phys.Chem.Chem.Phys. 1, 3065 (1999)

Stokes shift	7 500 cm^{-1}
S_0 contribution	5 000 cm^{-1}
S_1 contribution	**2 500 cm^{-1}**

observed oscillations:

5 x 110 cm^{-1}	550 cm^{-1}
5 x 253 cm^{-1}	1 265 cm^{-1}
1 x 290 cm^{-1}	290 cm^{-1}
1 x 525 cm^{-1}	525 cm^{-1}
total	**2 630 cm^{-1}**

ESIPT-Model



Conclusions

- coherent vibrational motion during and after an ultrafast photoinduced reaction observed with tunable 20 fs pulses

- in HBT we find
  - simultaneous ballistic motion of the proton and pericyclic transfer of the electron (ca. 60 fs)
  - subsequent coherent vibration of the H-chelate ring
  - excitation of 4 low frequency modes
  - "no" excitation of OH / NH vibrations
  - relaxation of the bath modes in about 300 fs
  - **proton follows all changes adiabatically**

- high level multidimensional quantum chemistry calculations for the excited state confirm this picture

- "excitation" of normal modes corresponding to the geometry change between the "transition state" and the product