Prof. Dr. C. von Borczyskowski

Aspekte der modernen Optik

Vorlesung vom 20.05.2010

Spektroskopie

Energieumrechnung

30.000	cm^{-1}	$\hat{=}$	3 [illegible], 3.7eV
1	cm^{-1}	$\hat{=}$	1.4 °K
0.1	cm^{-1}	$\hat{=}$	3 GHz
10	cm^{-1}	$\hat{=}$	0.12 K] / mol

Spektroskopie

- Absorption, Emission von elektromagnetischer Strahlung (Optisch, Infrarot, Raman, Magnetische Resonanz, Photoelektronen), Dieelektrische Spektroskopie, Akustische Spektroskopie
- Quantenmechanischer Ansatz: (Eigen-) Energien, Wellenfunktionen, Übergangsmomente
- Born-Oppenheimer Näherung: Separation von Elektron-, Kernbewegungen (Schwingungen)
- Heisenbergsche Unschärfe-Relation
- Kohärenz
- Kontinuums Ansatz: Dielektrische Konstante, Absorption, Brechungsindex, Reflexion, Polarisation
- ***Spektrale-, zeitliche Auflösung, Empfindlichkeit, Mikroskopie***

Molecular Orbitals

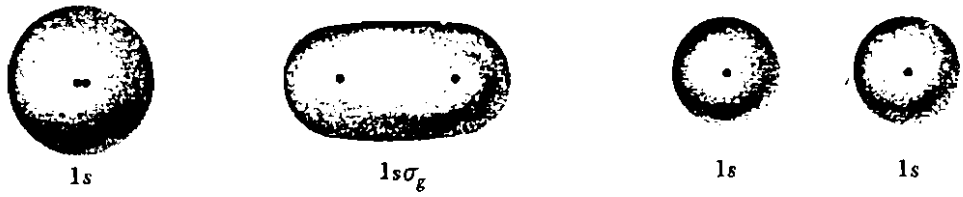
- Covalent bonds, Ionic bonds, Hydrogen bonds
- Linear Combination of Atomic Orbitals (LCAO)
- Hybridisation
- Important Atoms:
  - H 1 s , 2
  - C 2 x (2 s) ; 2 x (2 p)
  - N 2 x (2 s) ; 3 x (2 p)
  - O 2 x (2 s) ; 4 x (2 p)
  - S 2 x (3 s) / 4 x (3 p)
  - Metalls: Fe, Zn, Mg, Mn, ...

C

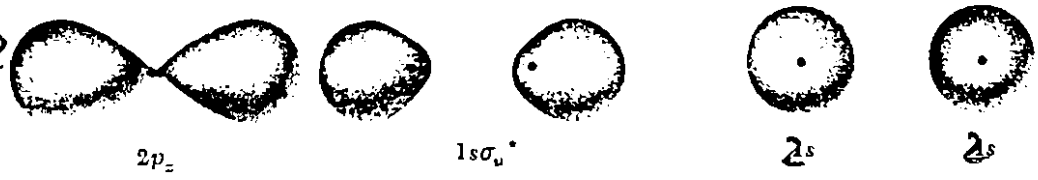
Elektronen

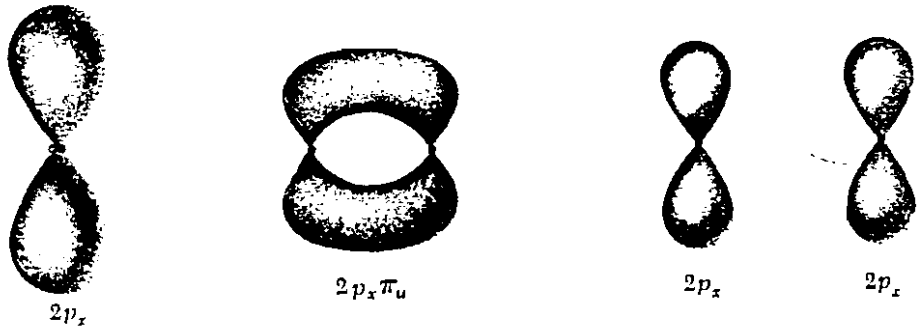
verschmolzenes Atom | Molekül | getrennte Atome

2 $n = 1$



4 $n = 2$





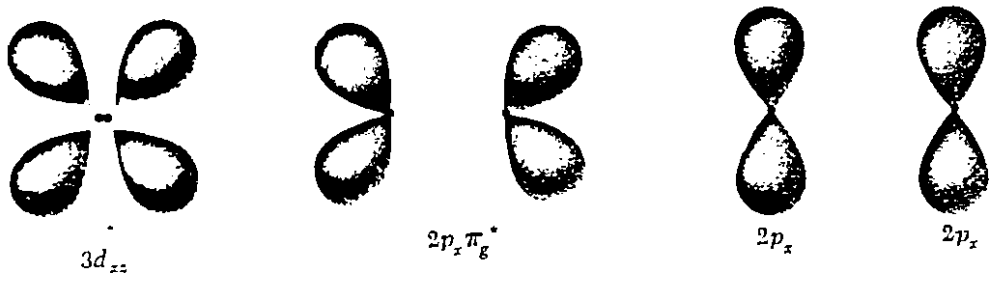
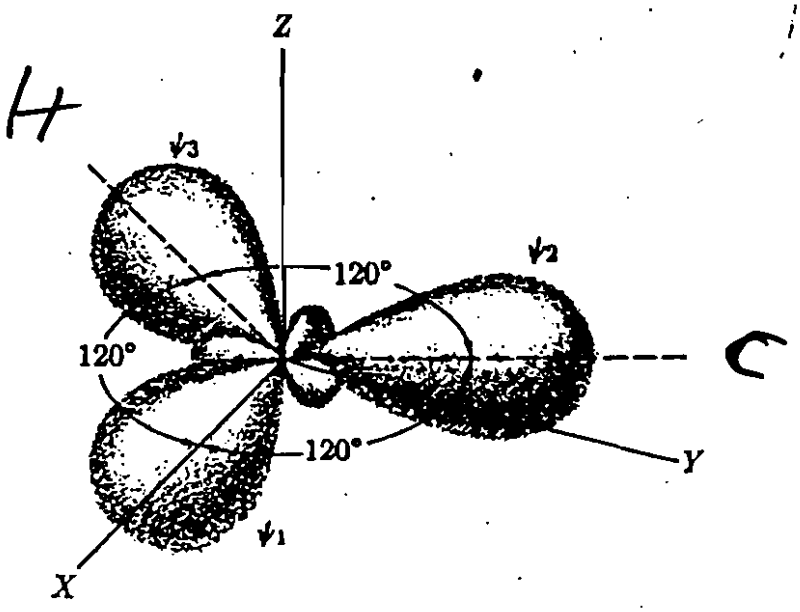
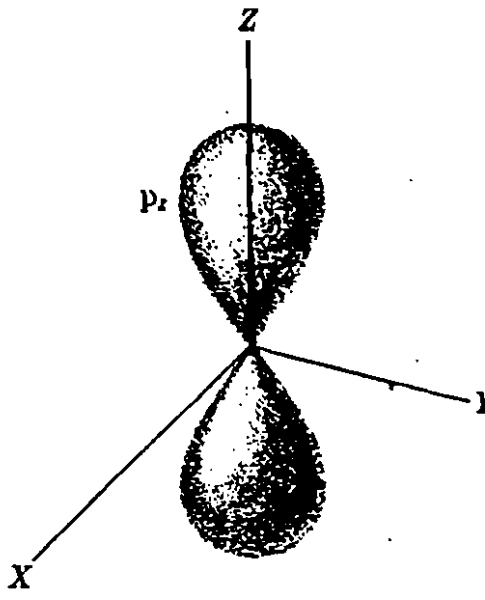


Bild 11.3 Beziehung zwischen den Orbitalen getrennter H-Atome, von H_2-Molekülen und den Orbitalen des verschmolzenen He-Atoms



(a) sp^2-Hybridwellenfunktionen



(b) p_z Wellenfunktion

Abb. 5-20. Wellenfunktionen, die aus sp^2-Hybridisierung resultieren.

$$\psi_1 = \frac{1}{\sqrt{3}}(s + \sqrt{2}\, p_x),$$

$$\psi_2 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}} p_x + \sqrt{\tfrac{3}{2}}\, p_y\right), \tag{5.10}$$

$$\psi_3 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}} p_x - \sqrt{\tfrac{3}{2}}\, p_y\right).$$

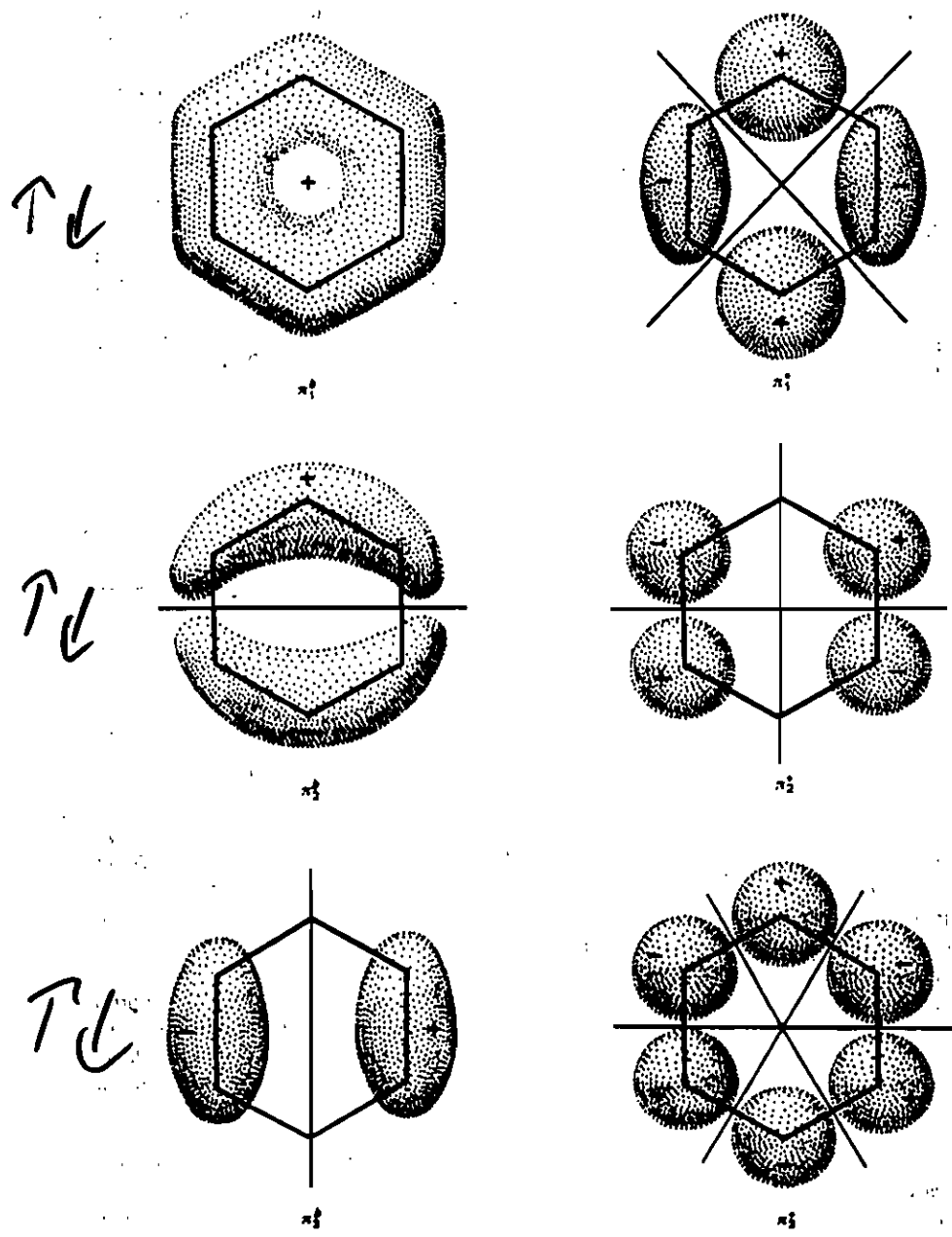
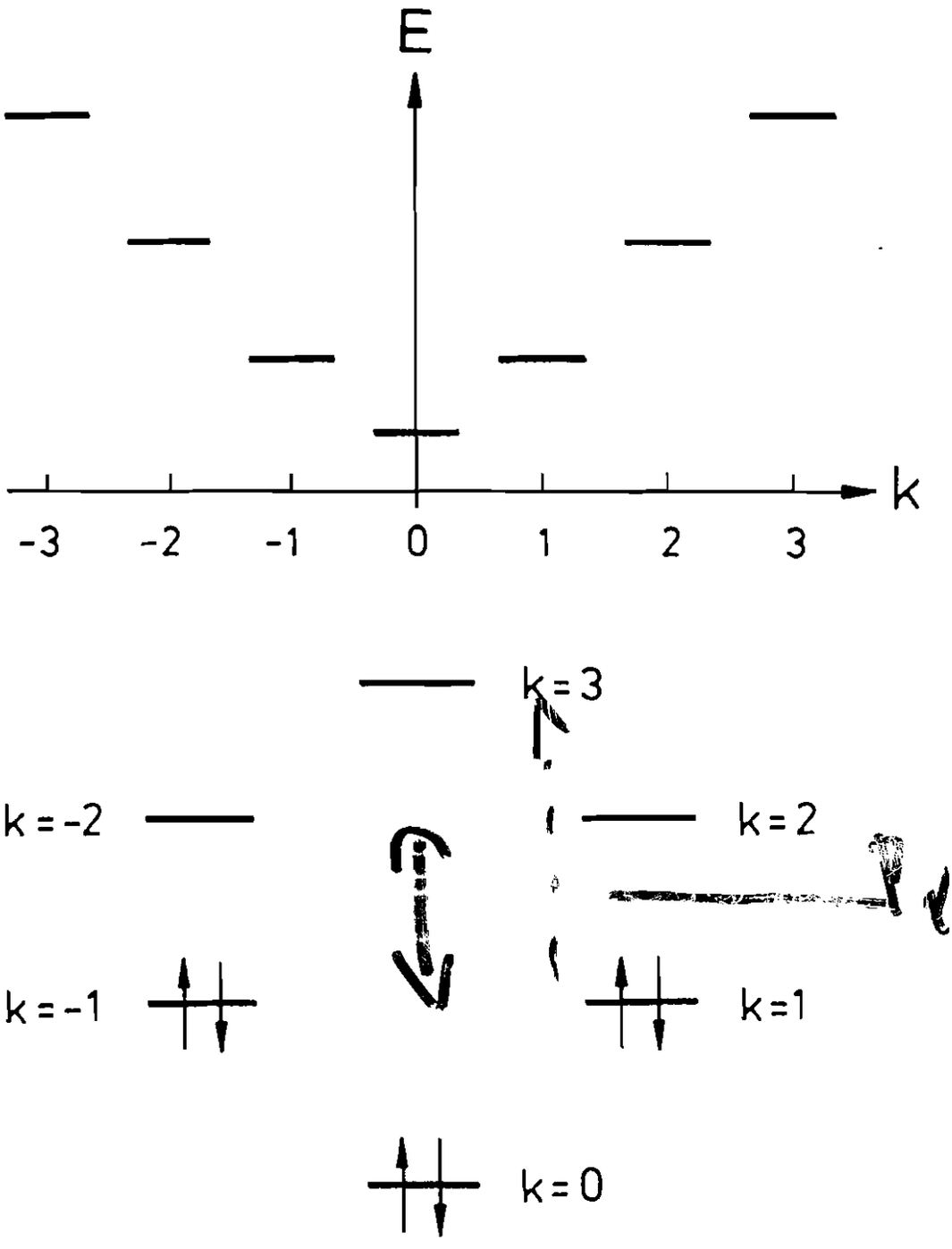
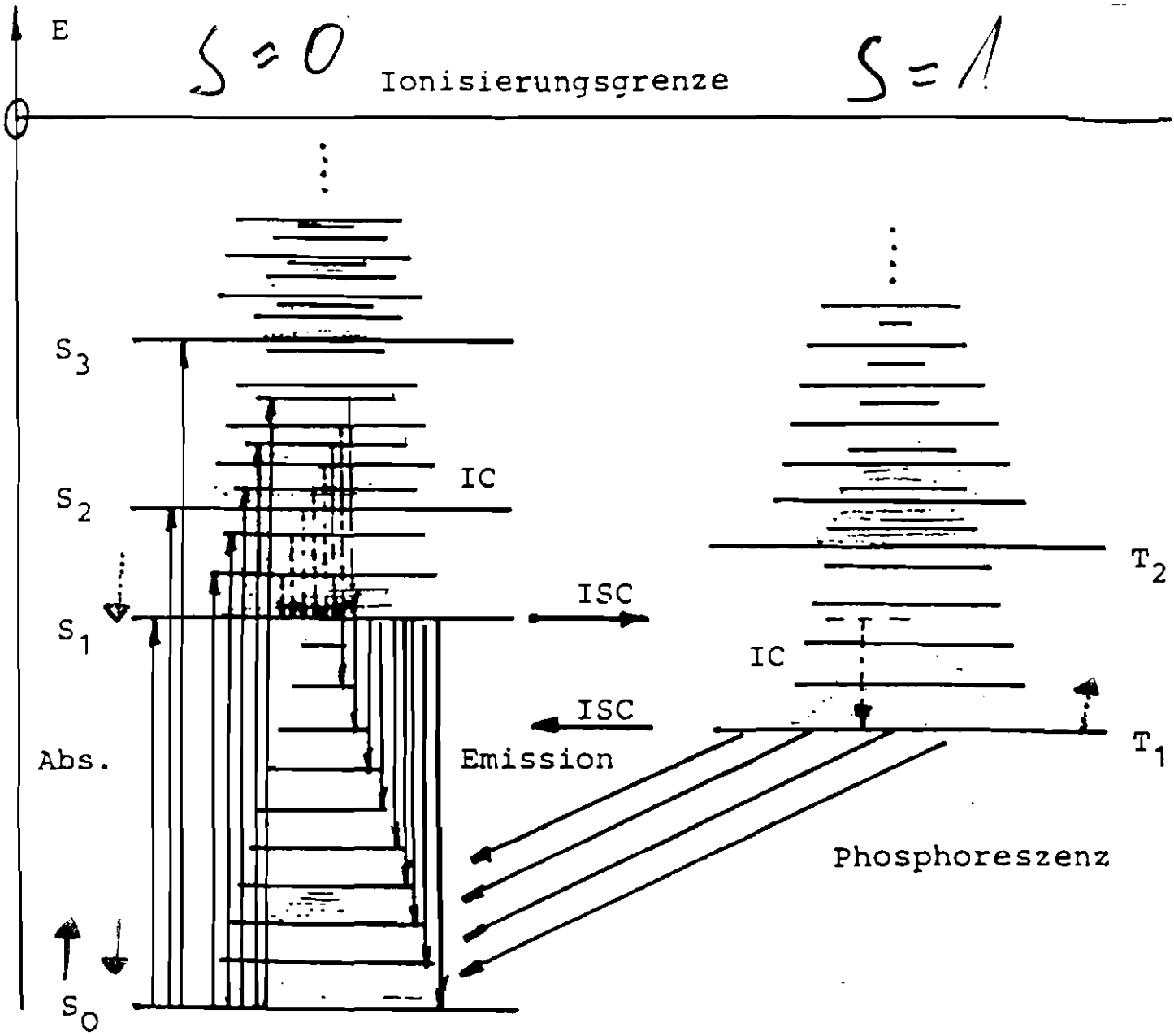


Abb. 2.26. Form der bindenden und antibindenden MO im Benzolmolekül


E
k
-3
-2
-1
0
1
2
3
k = 3
k = -2
k = 2
k = -1
k = 1
k = 0

"Jablonski-Diagramm"



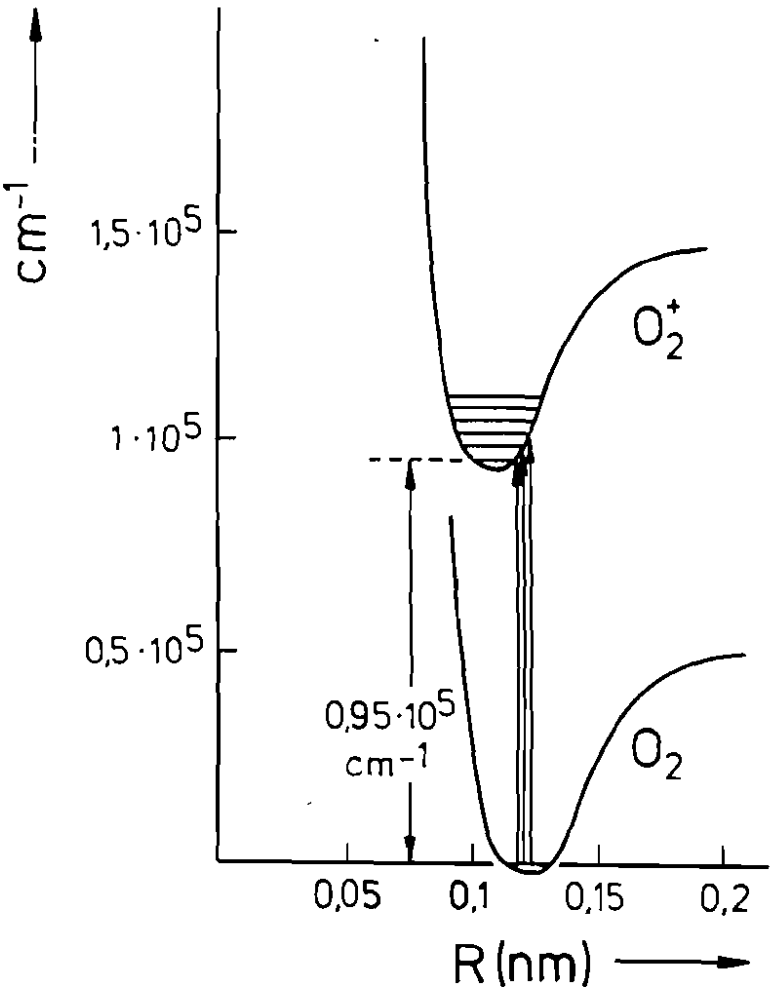
Singlettzustände
S = 0

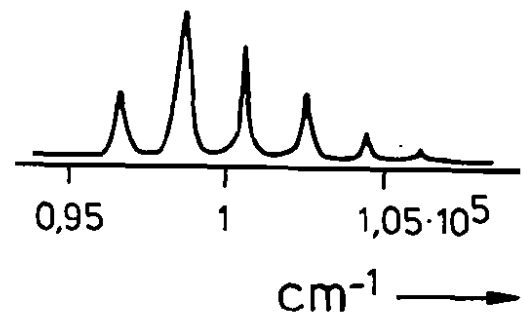
Triplettzustände
S = 1

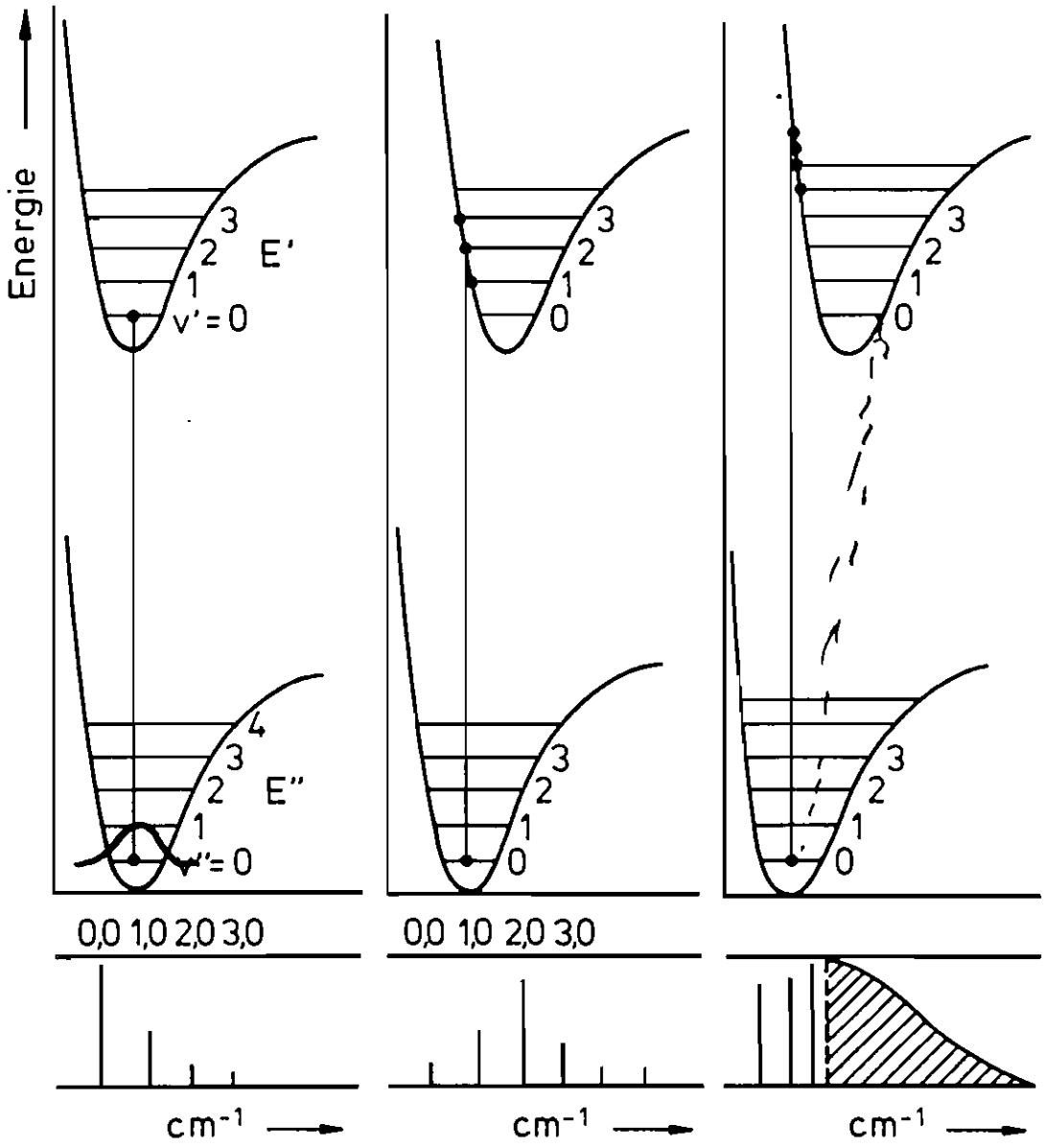
Energy Scheme: Jabonsky Diagram

- LCAO
- Hybridisation
- 2-Electron Levels
- Pauli Principle
- HOMO – Lumo Orbitals (Highest occupied molecular orbital – lowest occupied molecular orbitals)
- Born-Oppenheimer Approximation

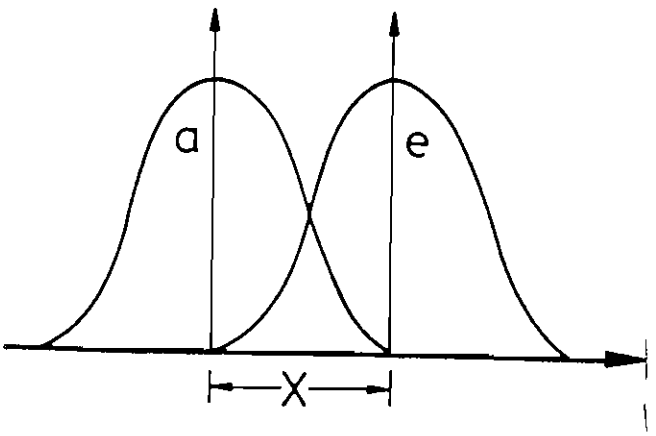
- Vibrations:
  - Bending
  - Stretching
  - Scetal modes
  - Phonon modes


cm⁻¹
1,5·10⁵
1·10⁵
0,5·10⁵
0,95·10⁵
cm⁻¹
O_2^+
O_2
0,05
0,1
0,15
0,2
R (nm)


0,95
1
1,05·10⁵
cm⁻¹



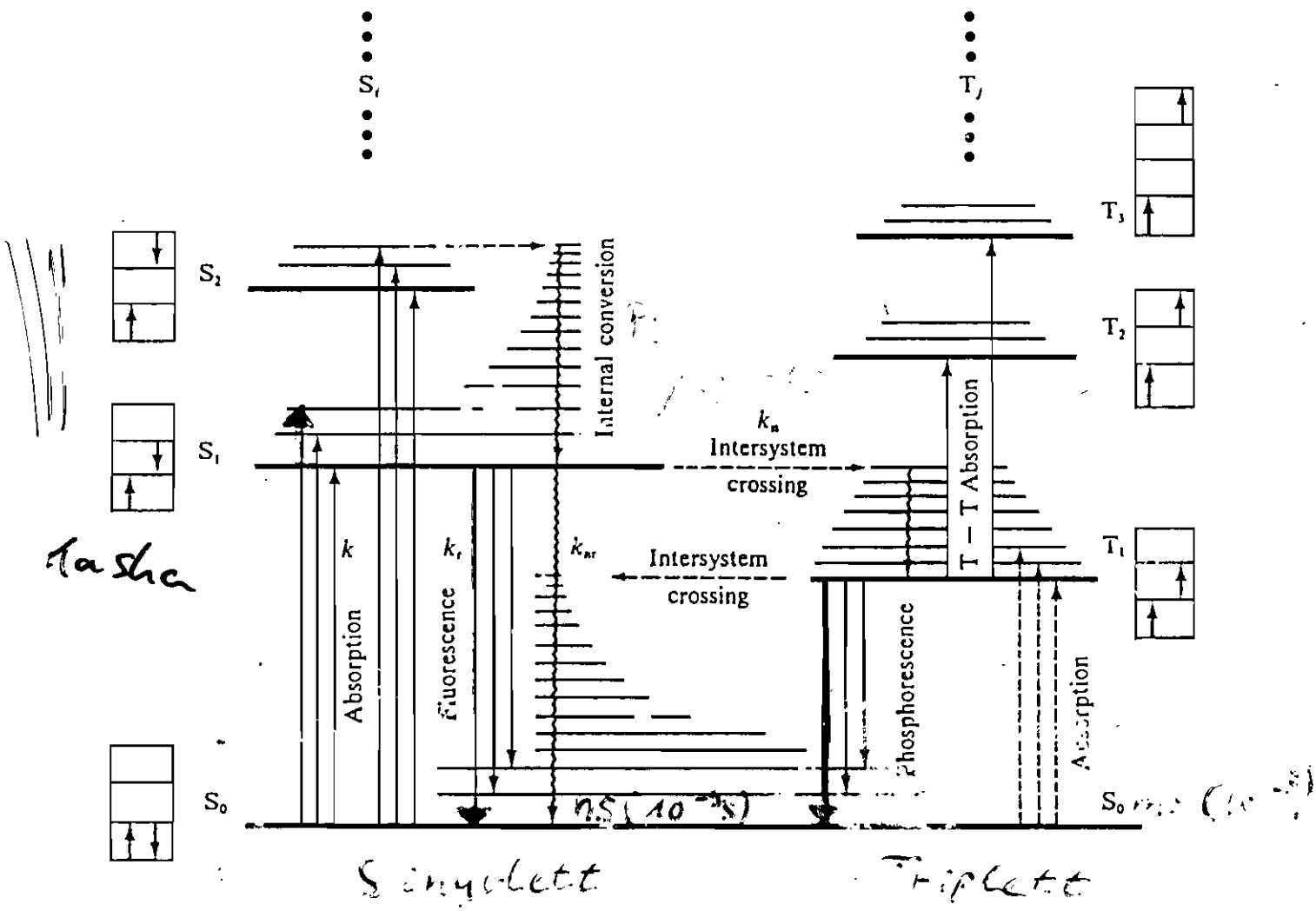
Franck-Condon-Integral

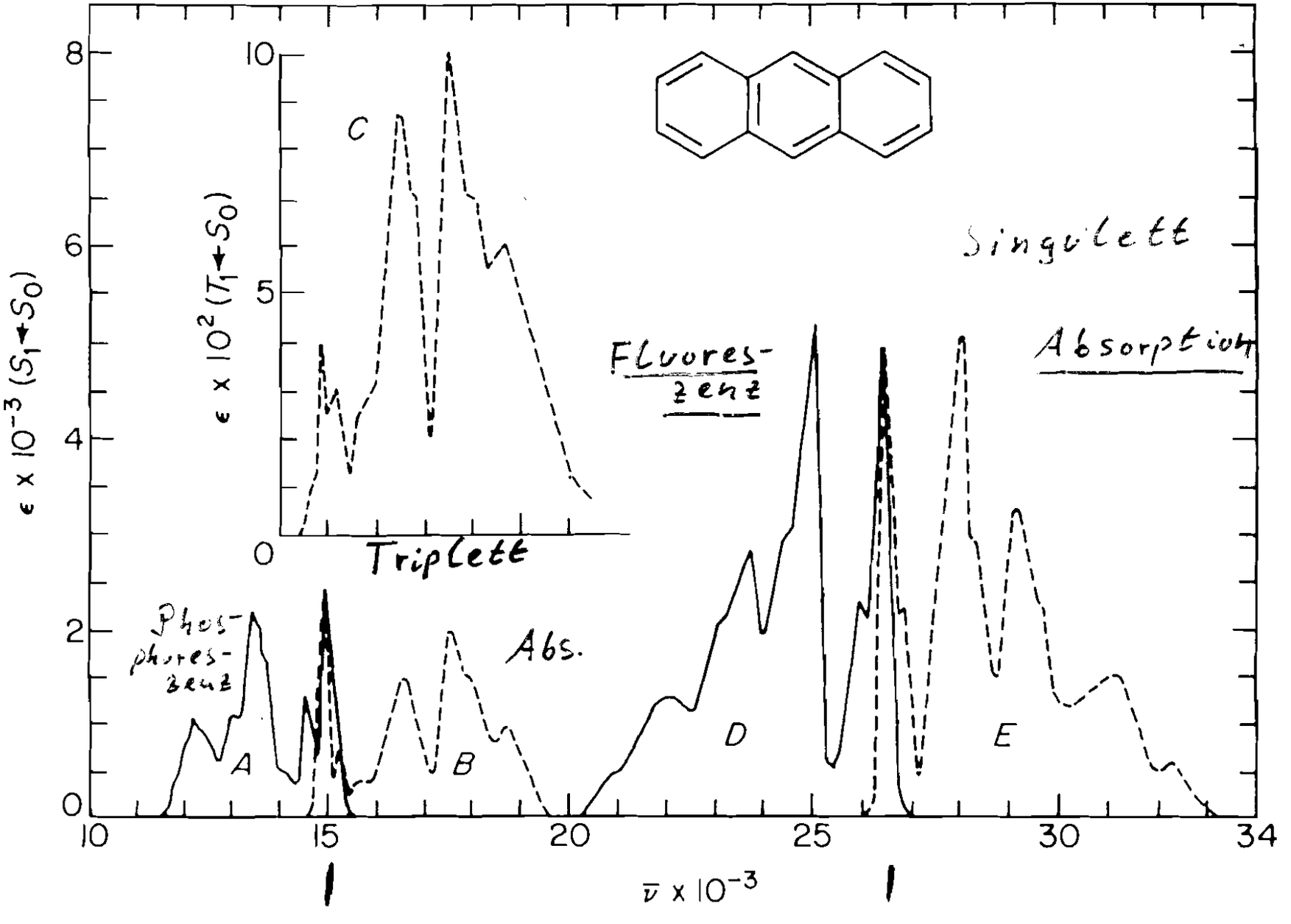


Molekule

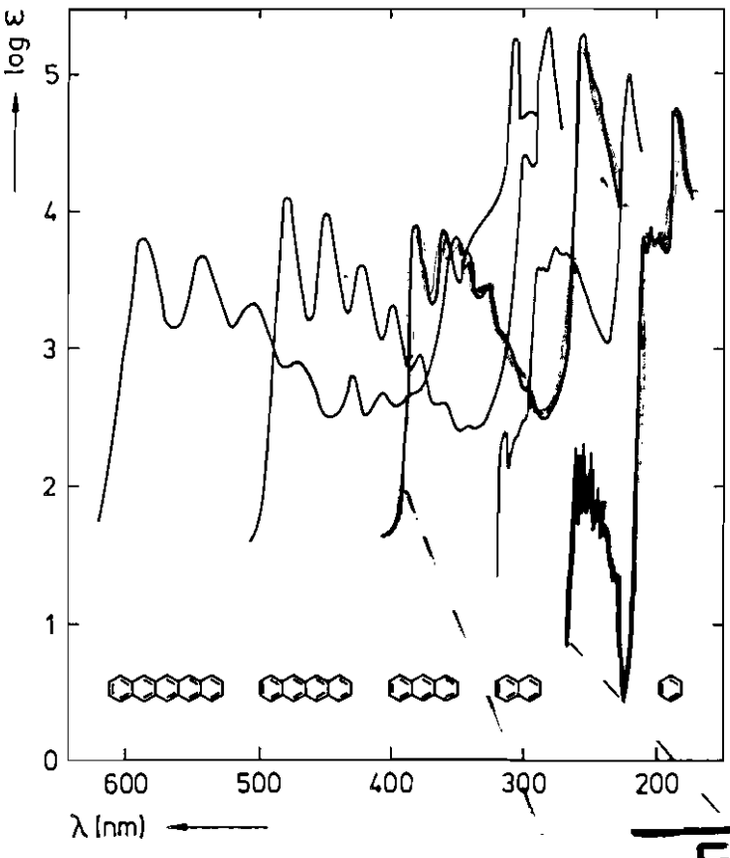
- Elektronenzustände

Optical properties of organic molecules and crystals




$\epsilon \times 10^{-3}\,(S_1 \rightarrow S_0)$
$\epsilon \times 10^{2}\,(T_1 \rightarrow S_0)$
$\bar{\nu} \times 10^{-3}$
Singulett
Absorption
Fluores-
zenz
Triplett
C
Phos-
phores-
zenz
Abs.
A
B
D
E

Optische Spektren

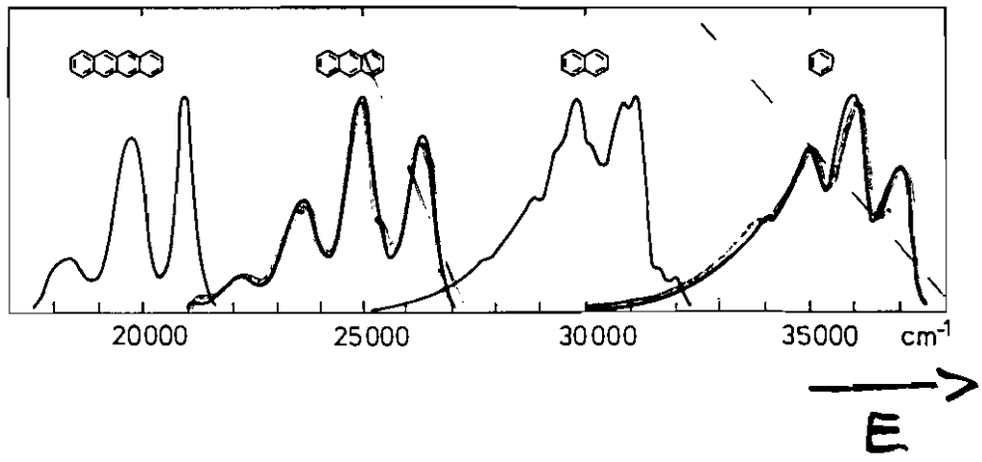


Molekül	Absorption
Benzol	2550 Å
Naphthalin	3150 Å
Anthracen	3800 Å
Tetracen	4800 Å
Pentacen	5800 Å

Absorption

E

Fluoreszenz



E

Zeitauflösung, Empfindlichkeit

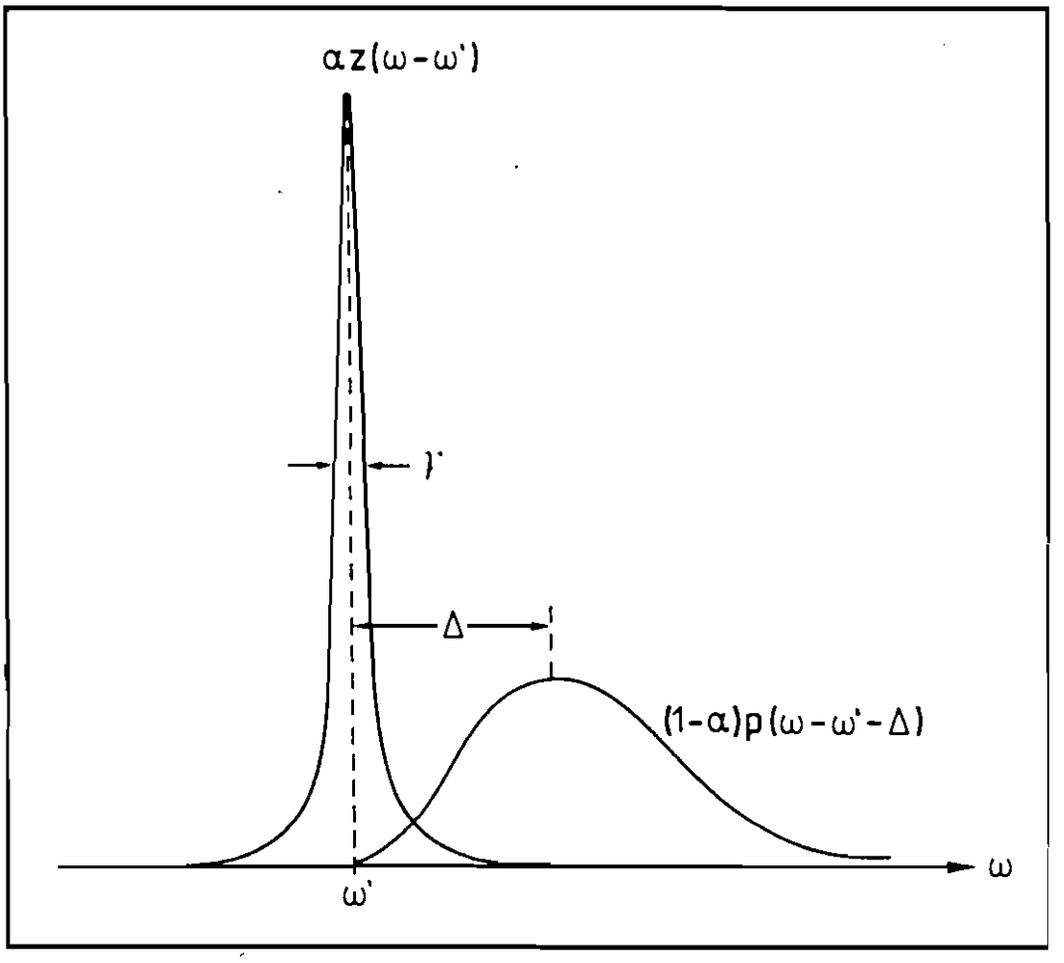
- Femtosekunden - Monate (22 Größenordnungen)

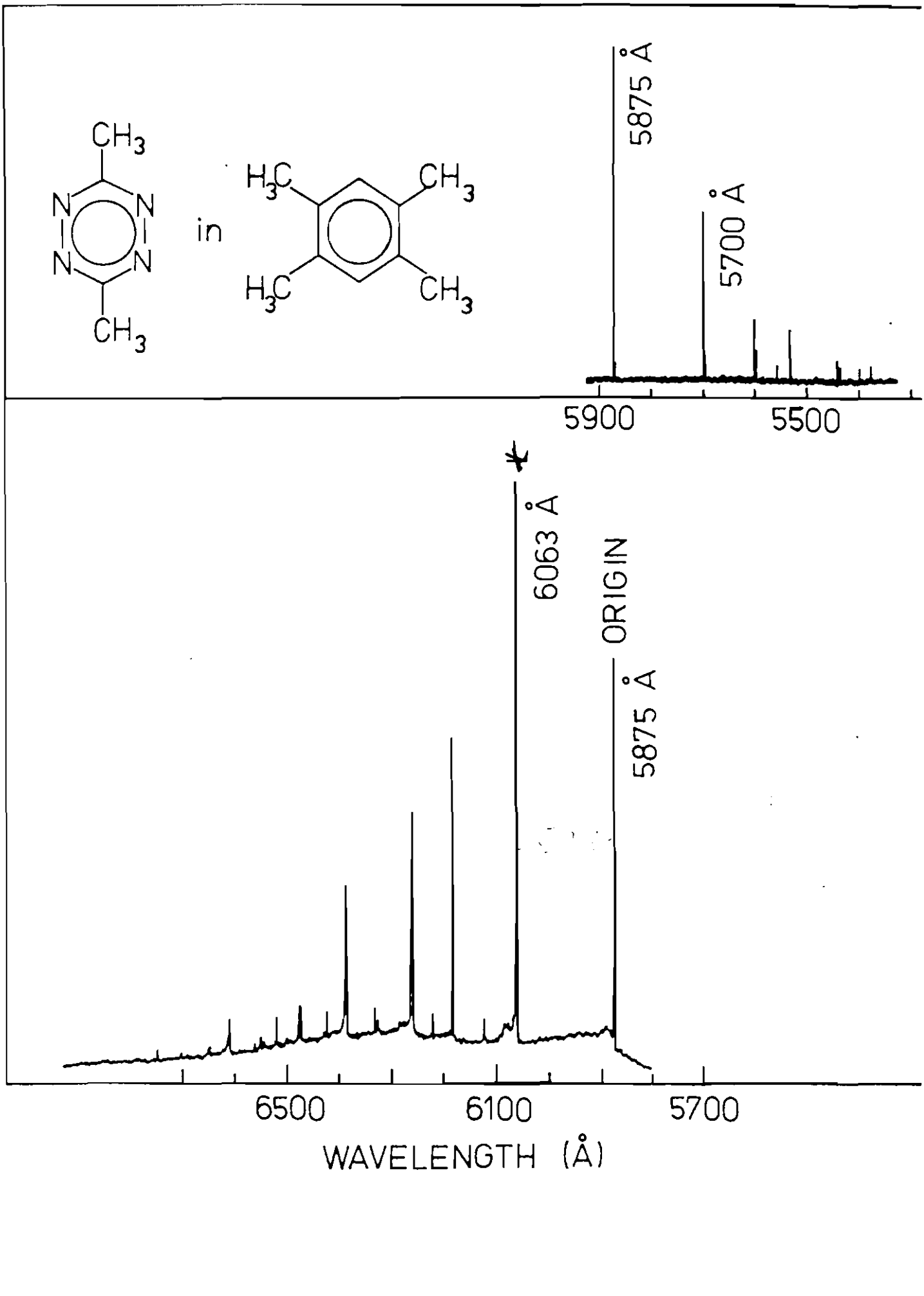
- Isolation
- Stabilität
- Detektoren
- „Effekt“ - Modulation
- Kodierung
- Markierung

Spektrale Auflösung

- Heisenbergsche Unschärferelation
- Homogene Verbreiterung durch dynamische Prozesse
- Inhomogene Verbreiterung durch statische „Unordnung“
- Ensemble- Zeitmittelung

- ***Kohärente Verfahren, Doppel-“Resonanz“verfahren***
- ***Spektrale Selektion Lochbrennen), Einzelmolekültechniken***


αz(ω-ω')
Γ
Δ
(1-α)p(ω-ω'-Δ)
ω
ω'


CH3
N
N
N
N
CH3
in
H3C
CH3
H3C
CH3
5875 Å
5700 Å
5900
5500
6063 Å
ORIGIN
5875 Å
6500
6100
5700
WAVELENGTH (Å)

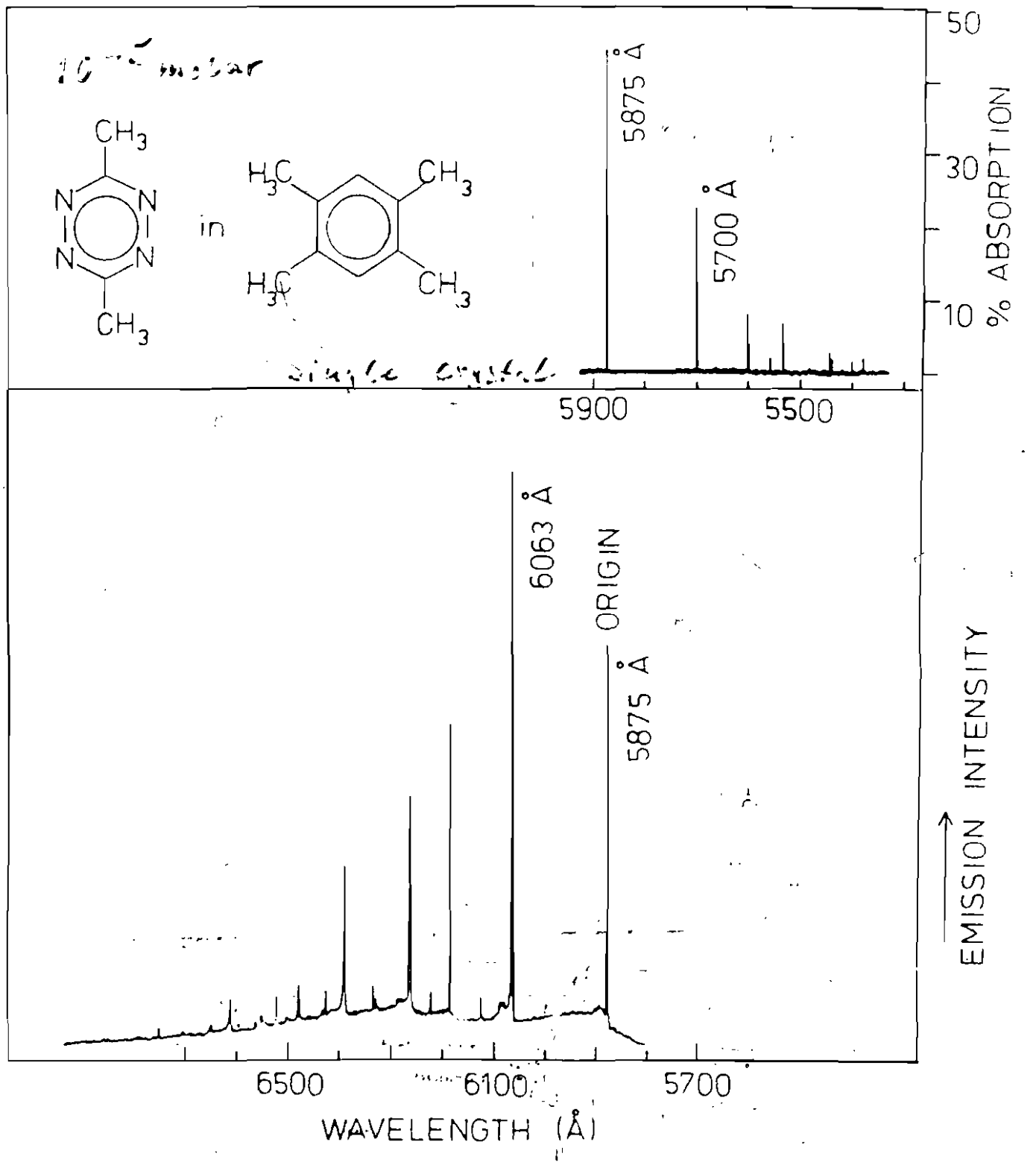
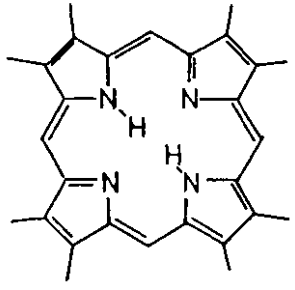


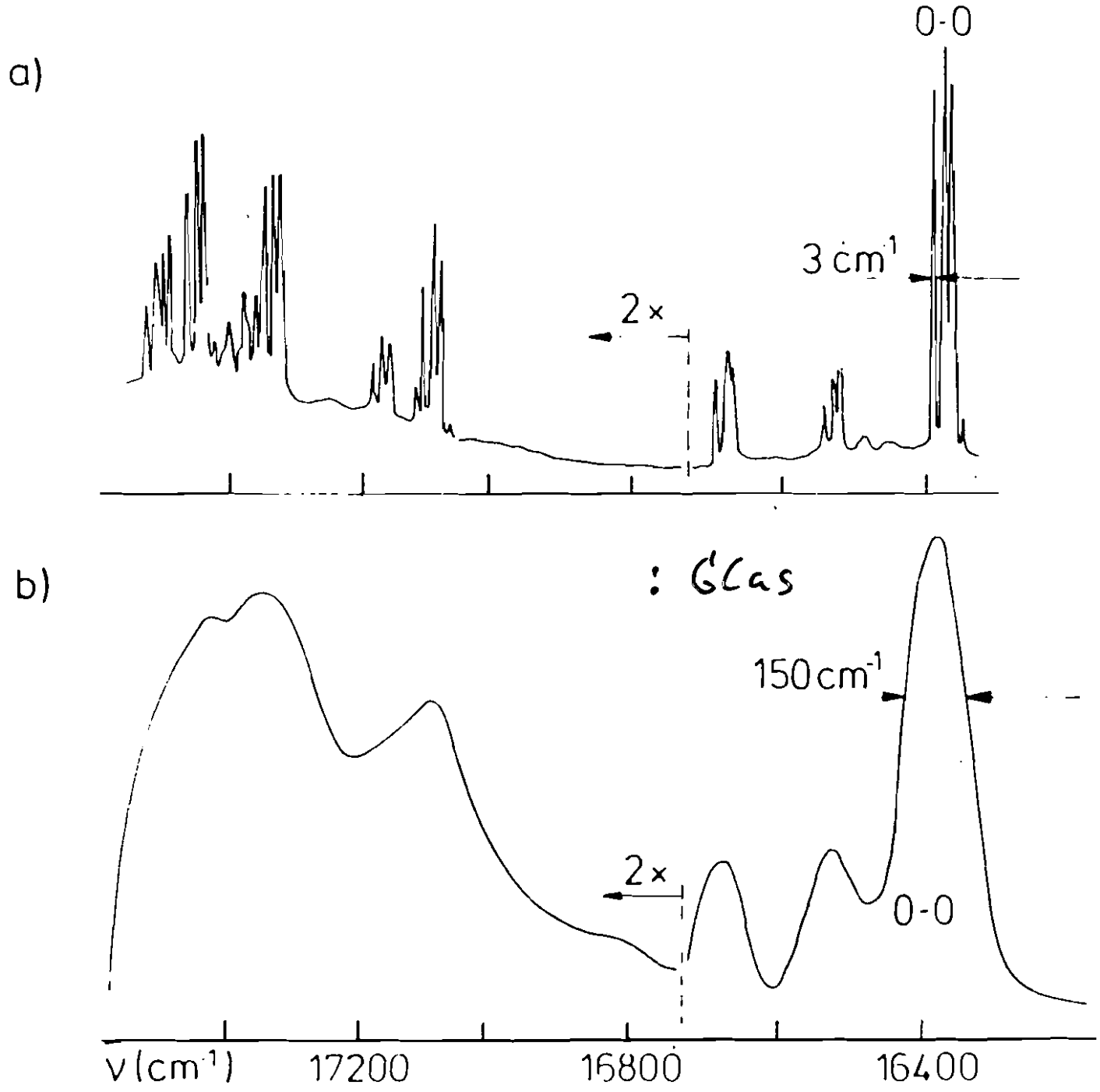
FIG. 1. The absorption and laser-induced (at 5700 Å) emission spectra of DMST in durene at 2 K.

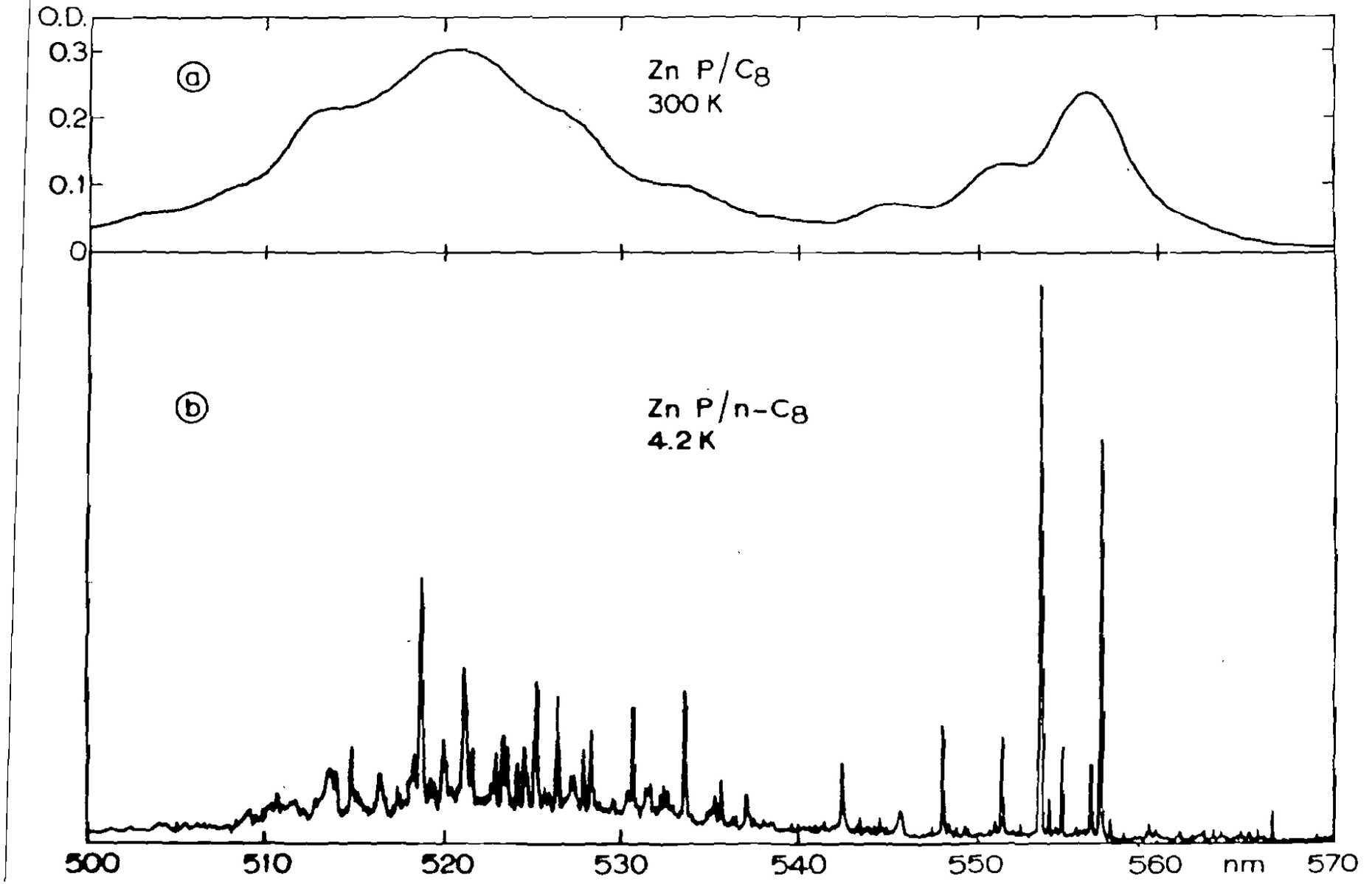
(From H. de Vries and D.A. Wiersma, Phys. Rev. lett. 36, 91, 1976).

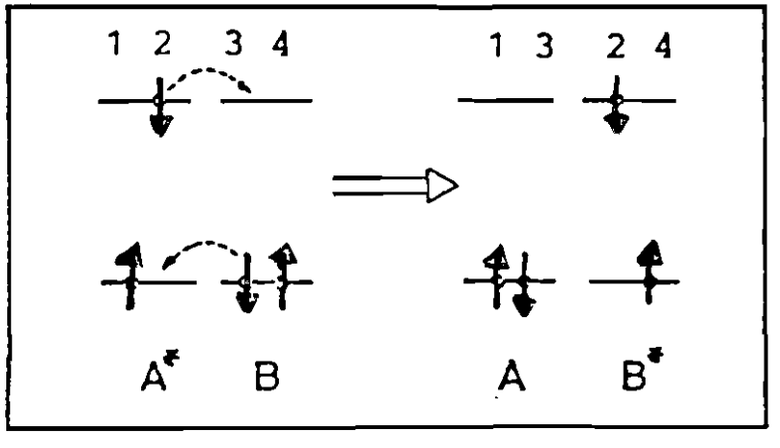
Matrix : Kristall



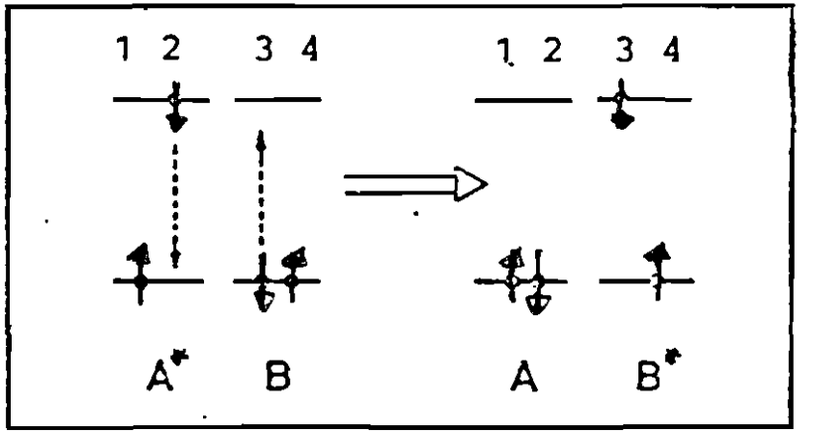
H_2P



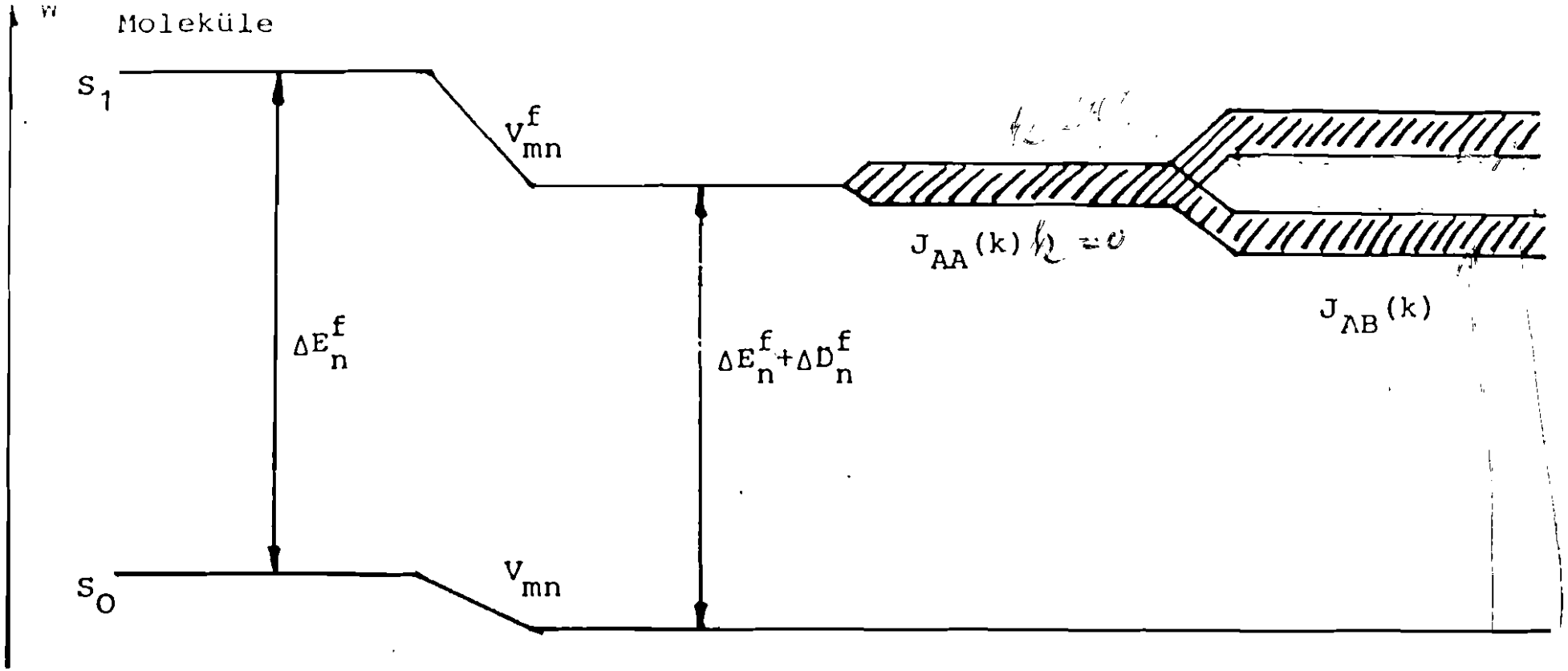

O.D.
0.3
0.2
0.1
0
ⓐ
Zn P/C8
300 K
ⓑ
Zn P/n-C8
4.2 K
500
510
520
530
540
550
560
nm
570



Austausch - Wechselwirkung



Coulomb - Wechselwirkung



Anregungsenergie für eine Molekülanregung am Molekül n.

$$\Delta E_n^f = (\langle\varphi_n^f|\hat{H}_n|\varphi_n^f\rangle - \langle\varphi_n|\hat{H}_n|\varphi_n\rangle).$$

$0.000\ cm^{-1} < \Delta E_n^f < 30.000\ cm^{-1}$

Bandverschiebung durch die Ww mit den anderen Molekülen im Kristall.

$$\Delta D_n^f = \sum_{m\neq n}(\langle\varphi_n^f\varphi_m|\hat{V}_{mn}|\varphi_n^f\varphi_m\rangle - \langle\varphi_m\varphi_n|\hat{V}_{mn}|\varphi_m\varphi_n\rangle).$$

ΔD_n^f typisch $\approx 1.000\ cm^{-1}$

Bandstruktur und Davydov-Aufspaltung

$$E^f_{\pm}(k) = 2J_{AA}\cos\vec{k}\vec{b} \pm 2J_{AB}[\cos\vec{k}(\vec{a}+\vec{b})/2 + \cos\vec{k}(\vec{a}-\vec{b})$$

Davydov-Aufspaltung T_1 typisch $10\ cm^{-1}$

S_1 -"- $100\ cm^{-1}$

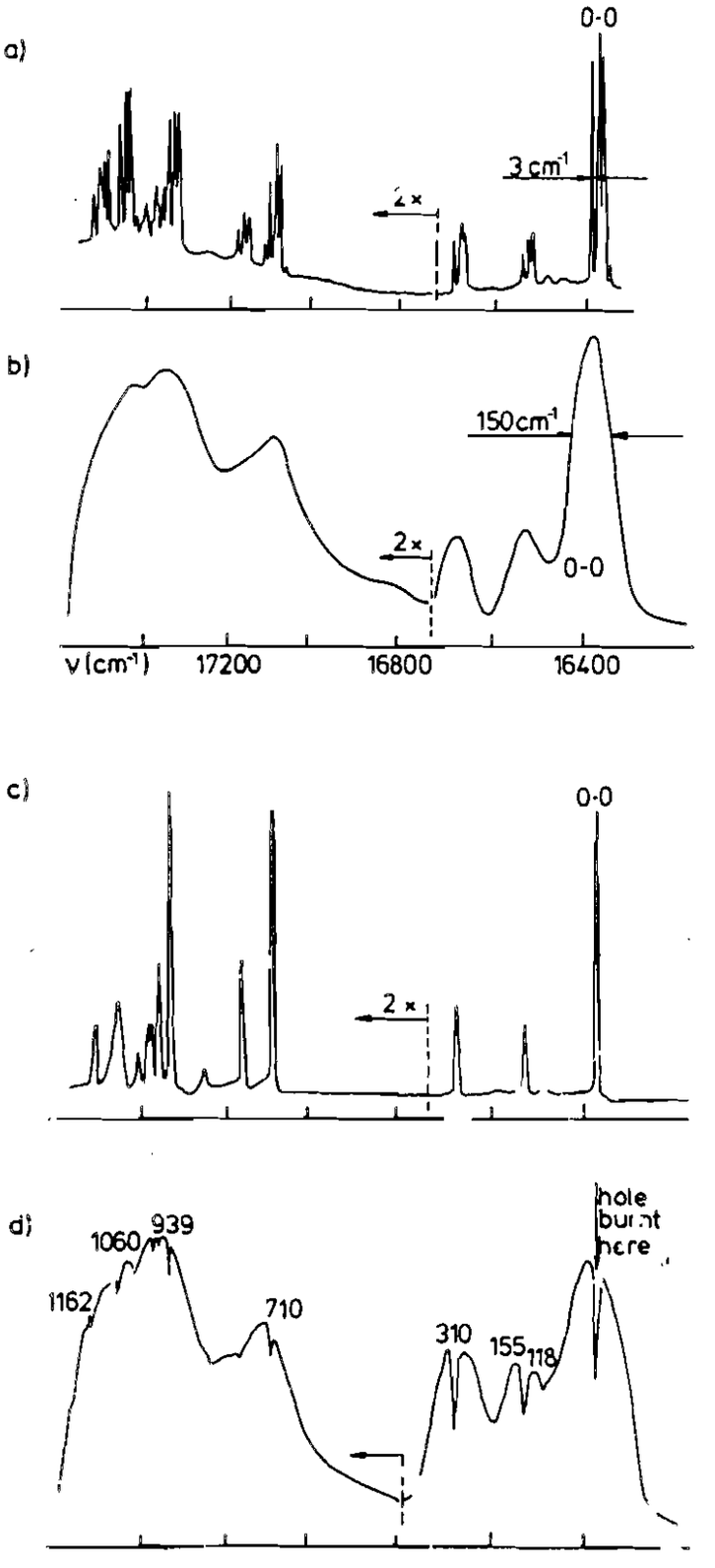
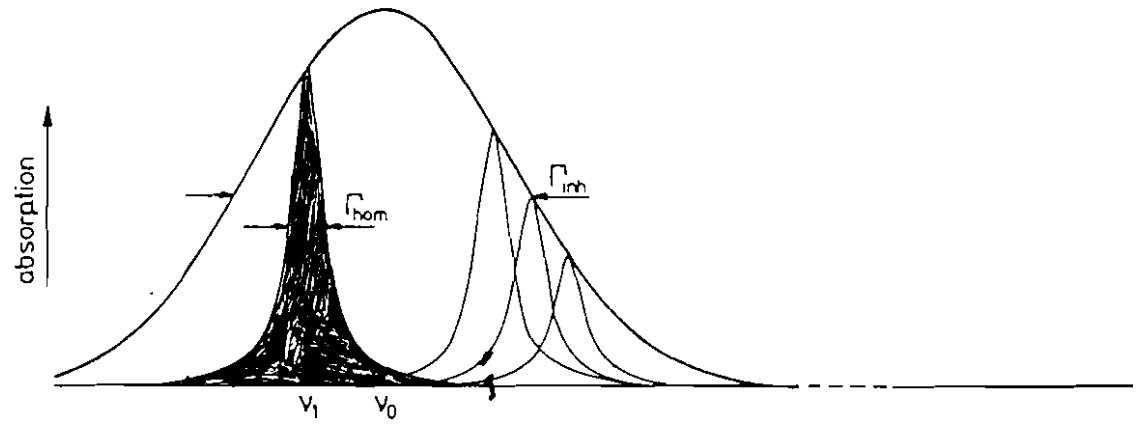
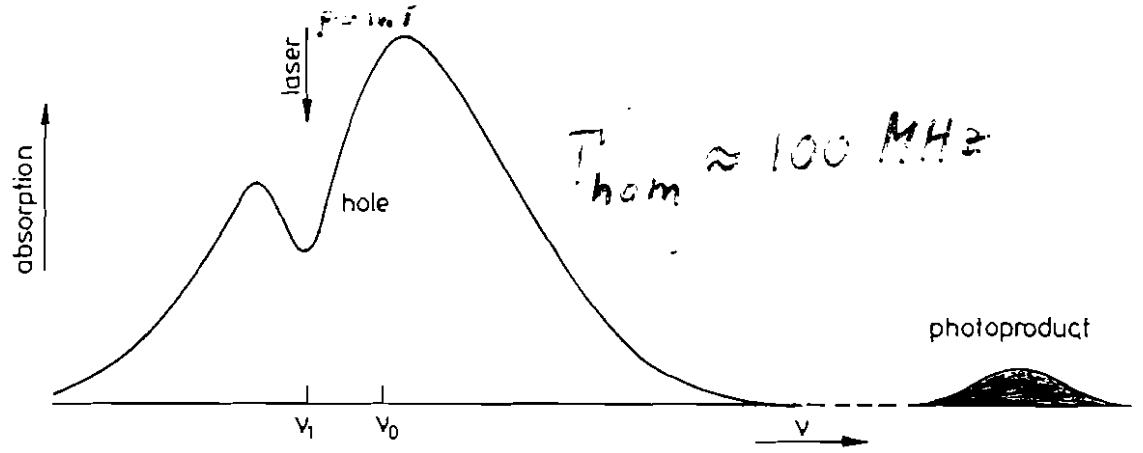
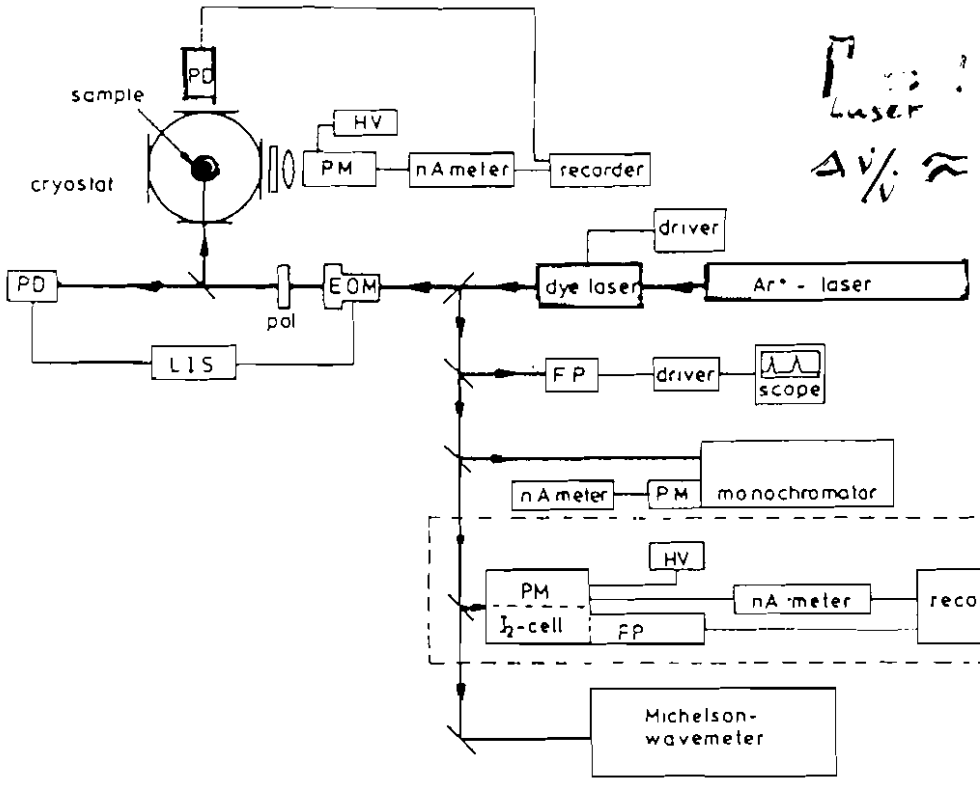


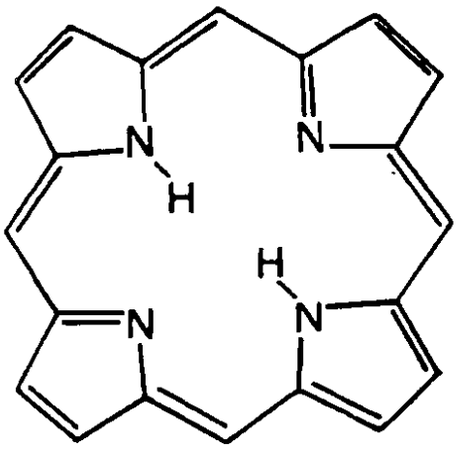
Fig. 1. Excitation spectrum of free-base porphin (H_2P) at: T = 4.2 K: (a) in *n*-heptane (crystal) with broadband detection of fluorescence; (b) in MTHF (glass) with broadband detection of fluorescence; (c) in MTHF (glass) with narrowband detection of fluorescence; (d) in MTHF (glass) with a photochemical hole burnt in to the 0–0 transition and broadband detection of fluorescence.


absorption
Γ_{hom}
Γ_{inh}
ν_1
ν_0

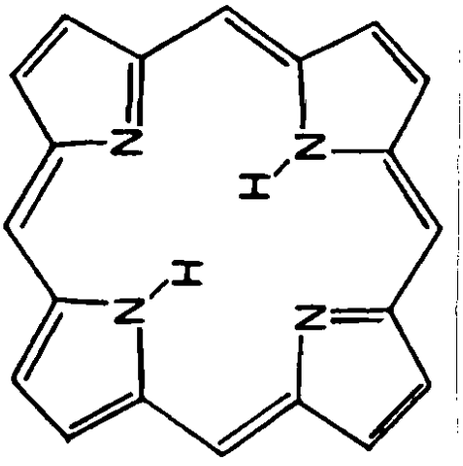

laser
absorption
hole
photoproduct
ν_1
ν_0
ν
"probe"

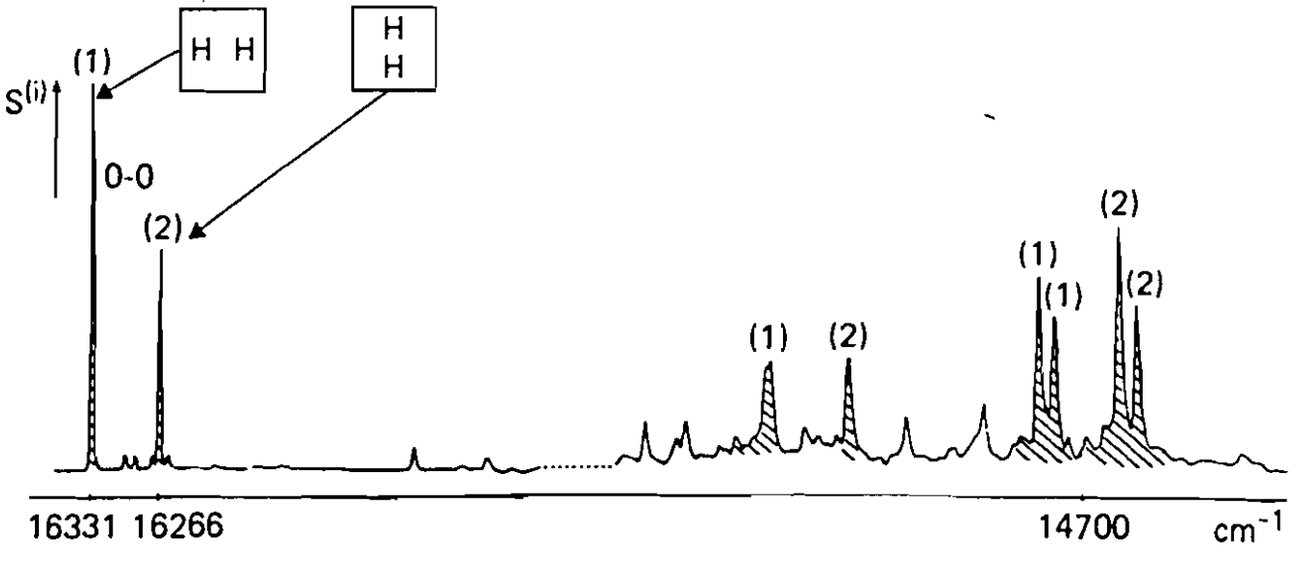

PD
sample
cryostat
HV
PM
nA meter
recorder
driver
PD
EOM
pol
dye laser
Ar⁺ - laser
LIS
FP
driver
scope
nA meter
PM
monochromator
HV
PM
I_2-cell
FP
nA meter
recorder
Michelson-
wavemeter

Kristallachse



H_2P



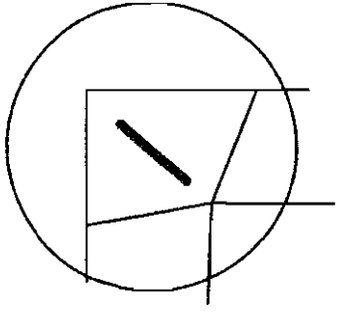


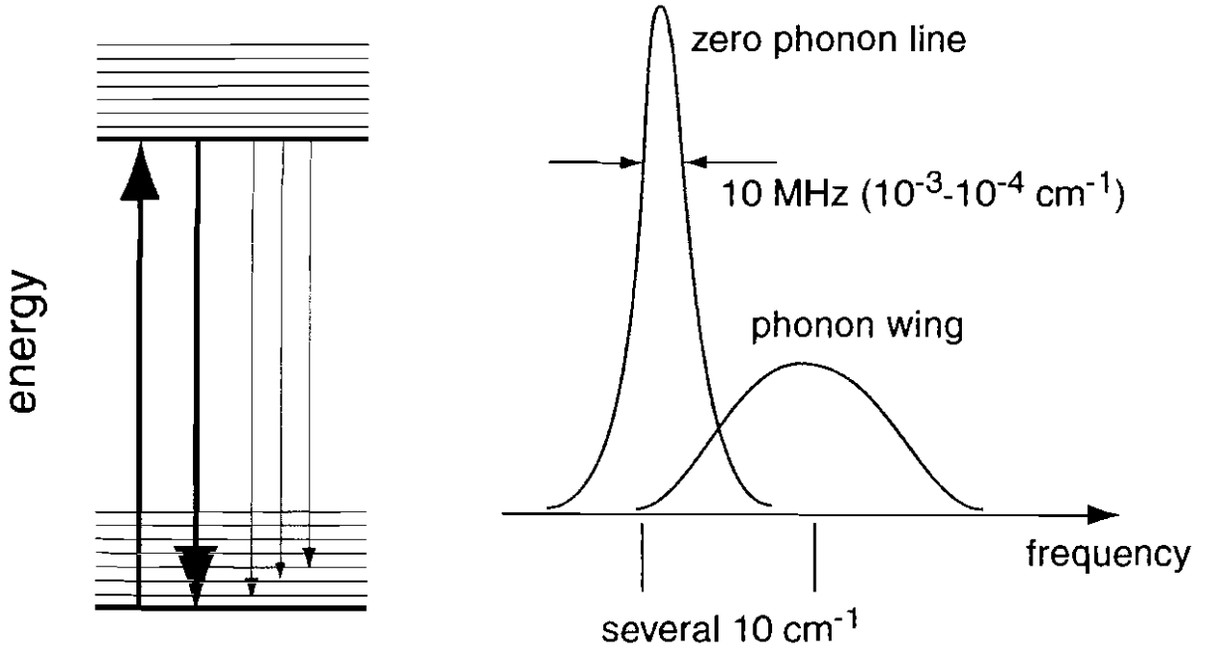
Single Molecule Detection

- Principles of Optical Spectroscopy of Organic Molecules and Nanoparticles
- Single Molecule Detection Schemes
- Application to Molecules
- Application to Nanoparticles

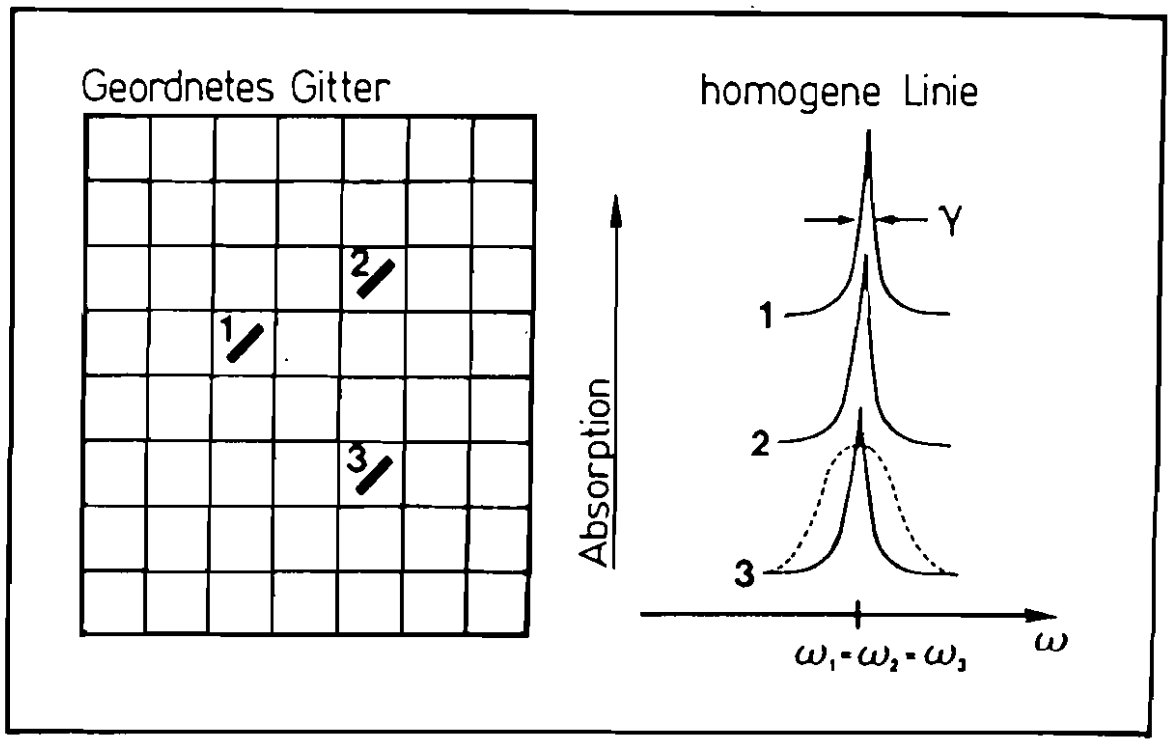
Single Emitter

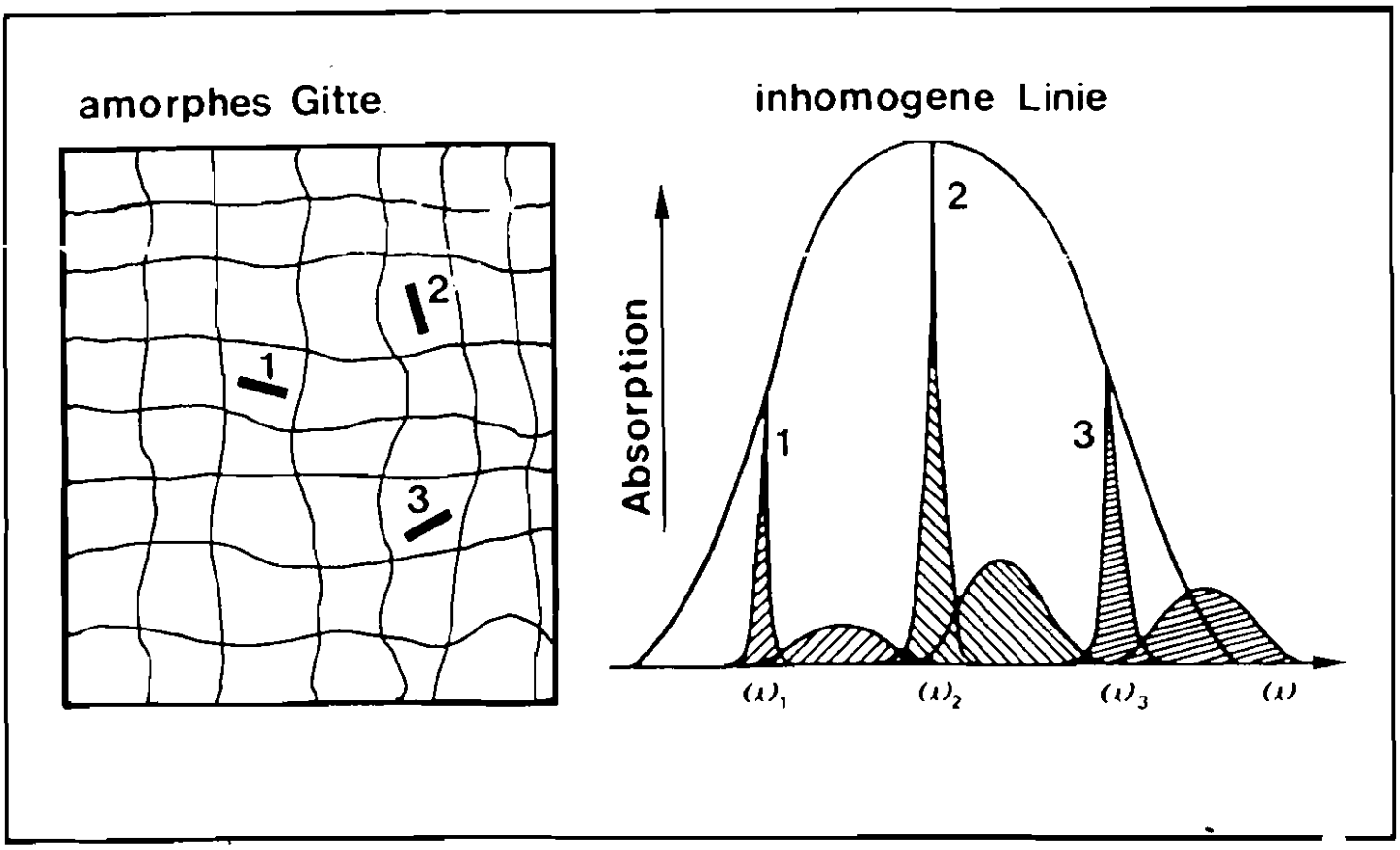
Single Emitter in a Crystal at low T



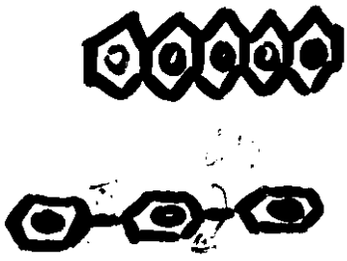


- probes nano-environment
  static & dynamic properties
- providies information on the members of an ensemble
- may show up new physical effects
  - blinking
  - photobleaching in one step
  - bunching/anti-bunching of photons

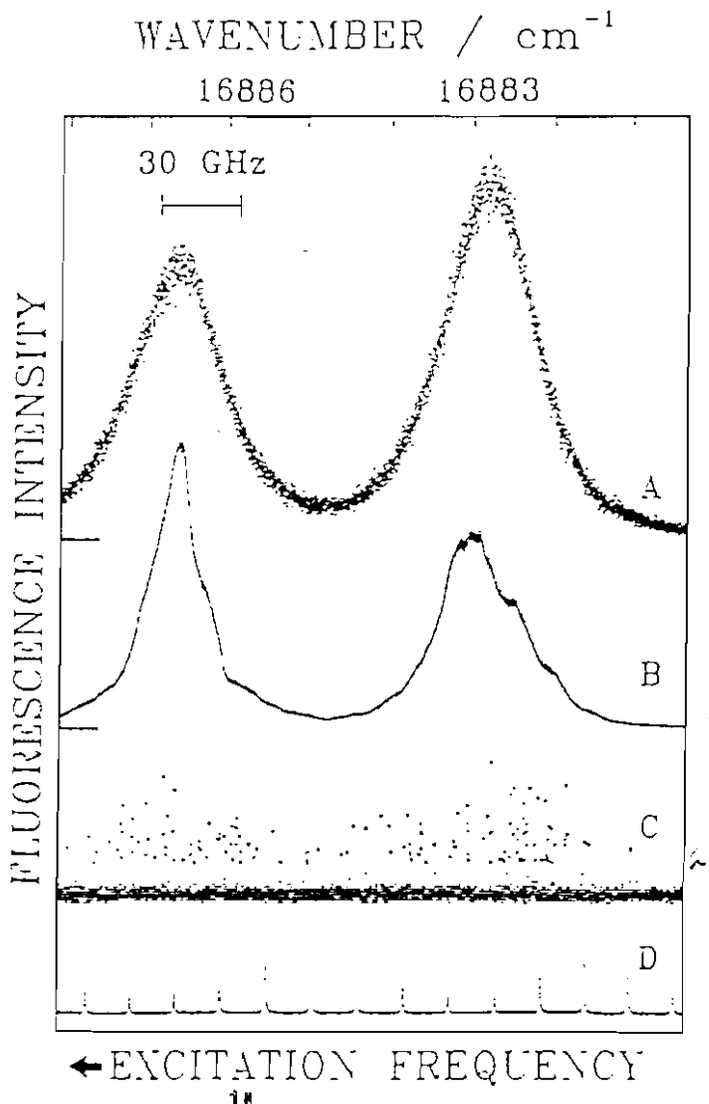

Geordnetes Gitter
1
2
3
homogene Linie
Absorption
Y
1
2
3
$\omega_1 = \omega_2 = \omega_3$
ω

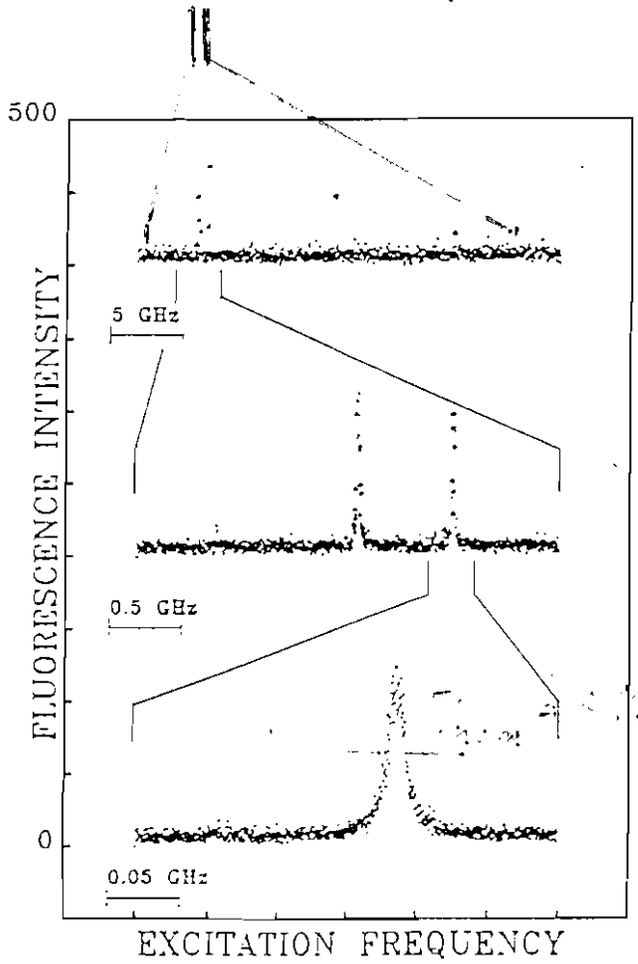

amorphes Gitte
1
2
3
inhomogene Linie
Absorption
1
2
3
$(\omega)_1$
$(\omega)_2$
$(\omega)_3$
(ω)

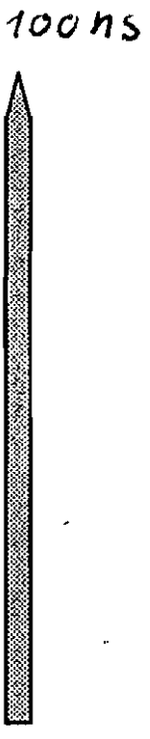
Pentacen

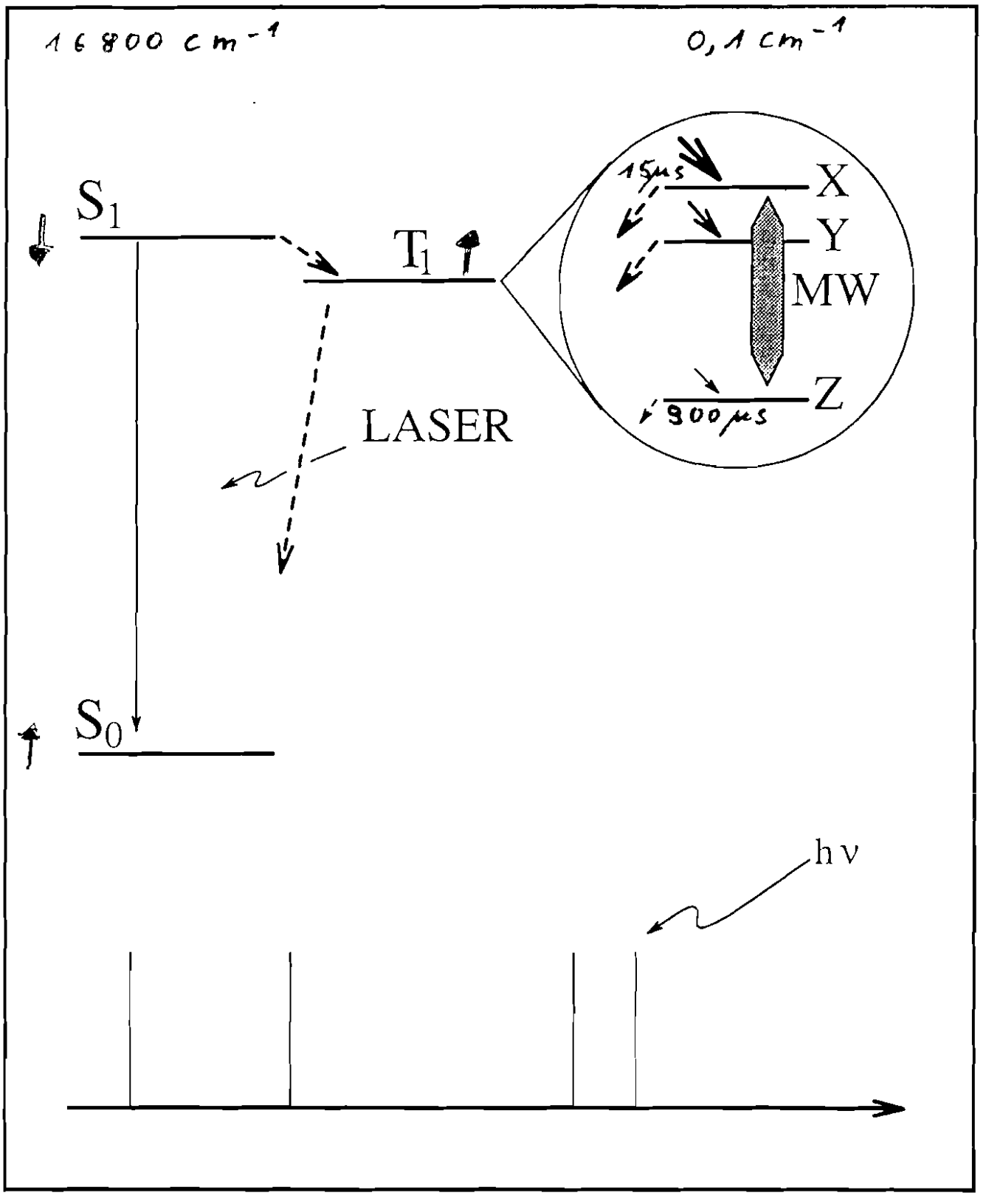


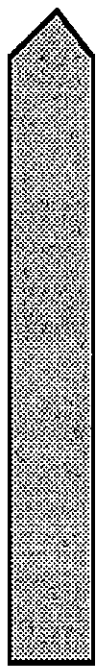
p-Terphenyl

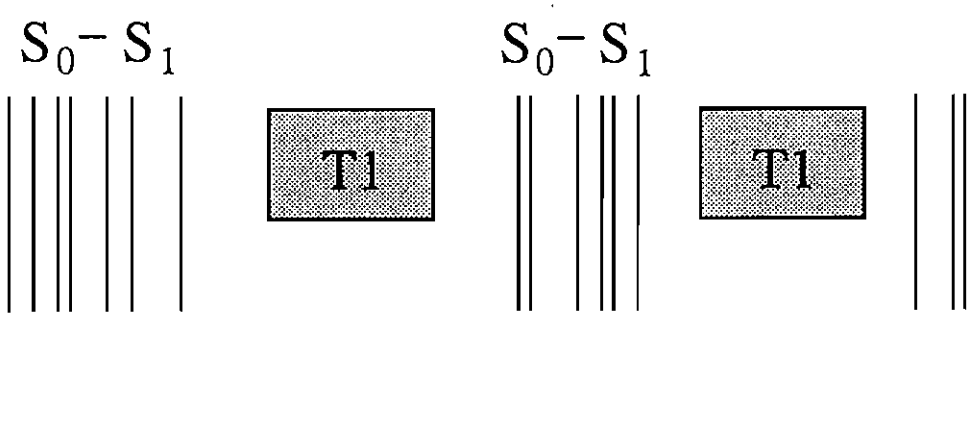


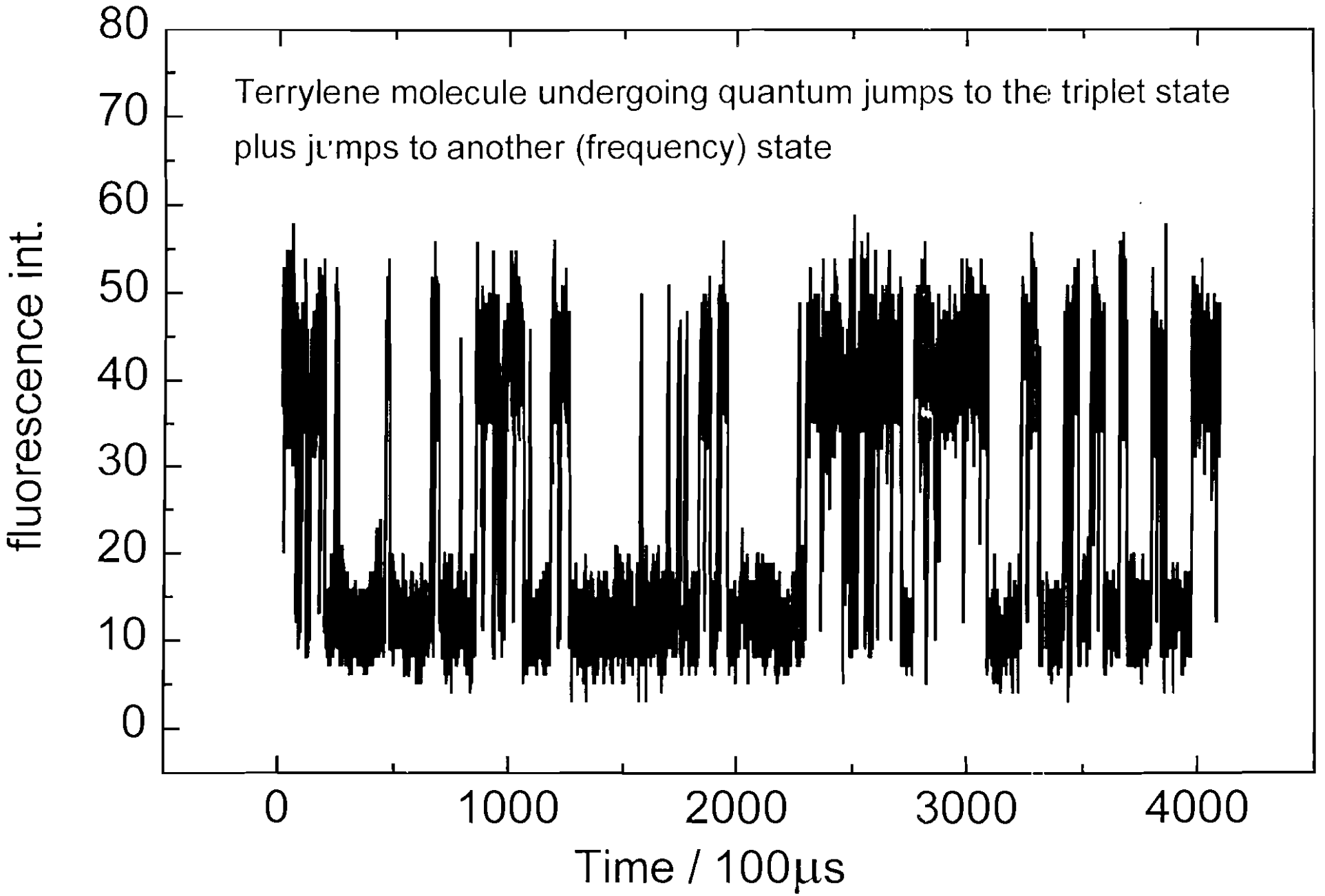



100 ns


16800 cm⁻¹
0,1 cm⁻¹
S1
T1
15µs
X
Y
MW
Z
900µs
LASER
S0
hν




$S_0 - S_1$
T1
$S_0 - S_1$
T1
τ


Terrylene molecule undergoing quantum jumps to the triplet state
plus jumps to another (frequency) state
fluorescence int.
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
Time / 100µs

Autocorrelation

- Photon correlation Function

$$g^{(2)}(\tau) = \frac{\langle I(t)\, I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

  - Photon-Antibunching
  - Rabi-Oscillation/Dephasing
  - Photonbunching

Densitymatrix 5 - Level System

→ Microwave - optical Blochequation

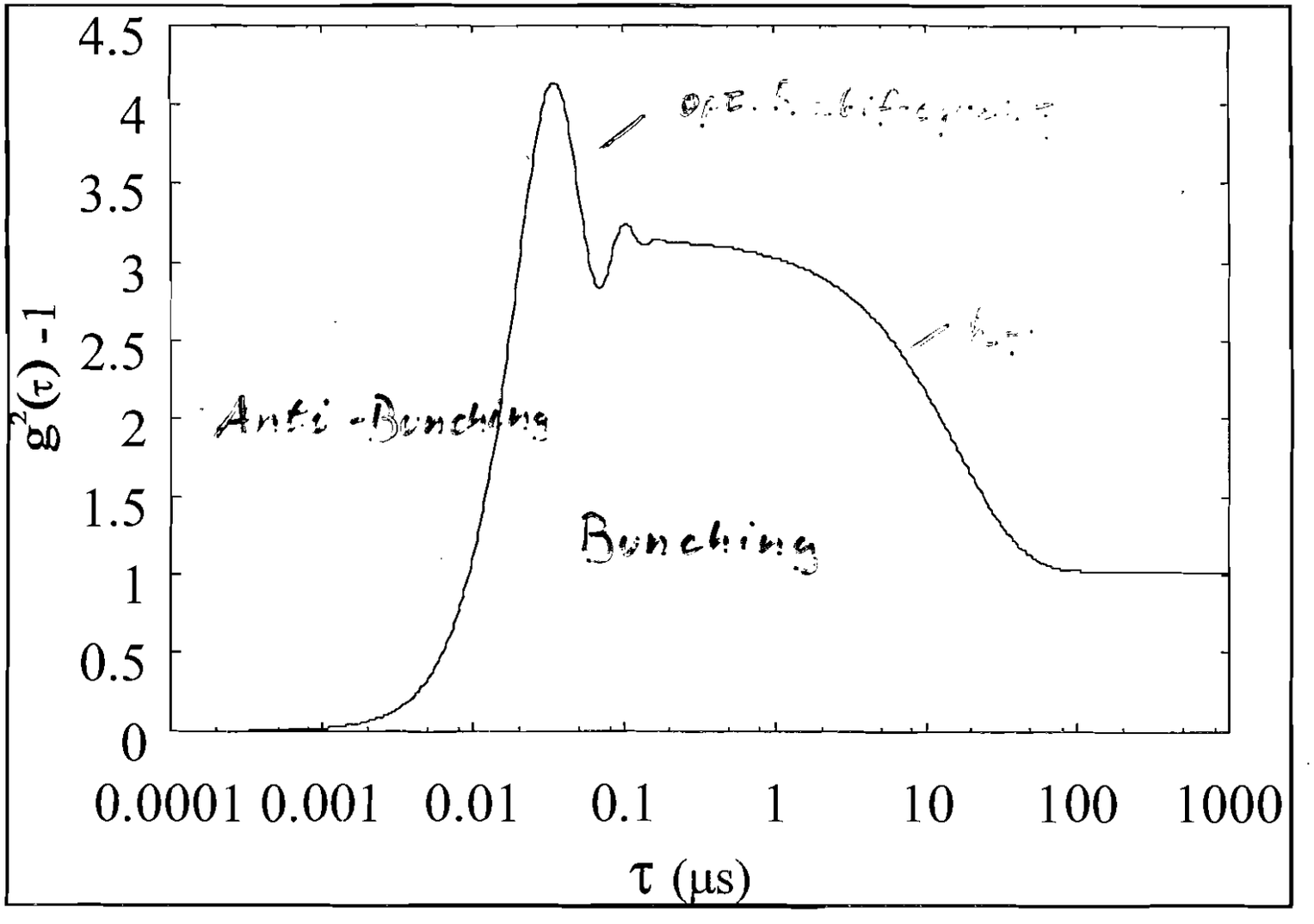
$$H/h \begin{bmatrix} \omega_{11} & -\Omega \cos \omega_L t & \\ -\Omega \cos \omega_L t & \omega_{22} & \\ & & \omega_{xx} \\ & & \omega_{yy} \\ & & -\Lambda \cos \omega_M t \end{bmatrix} \quad \Lambda \cos \omega_M t \quad \omega_{zz}$$

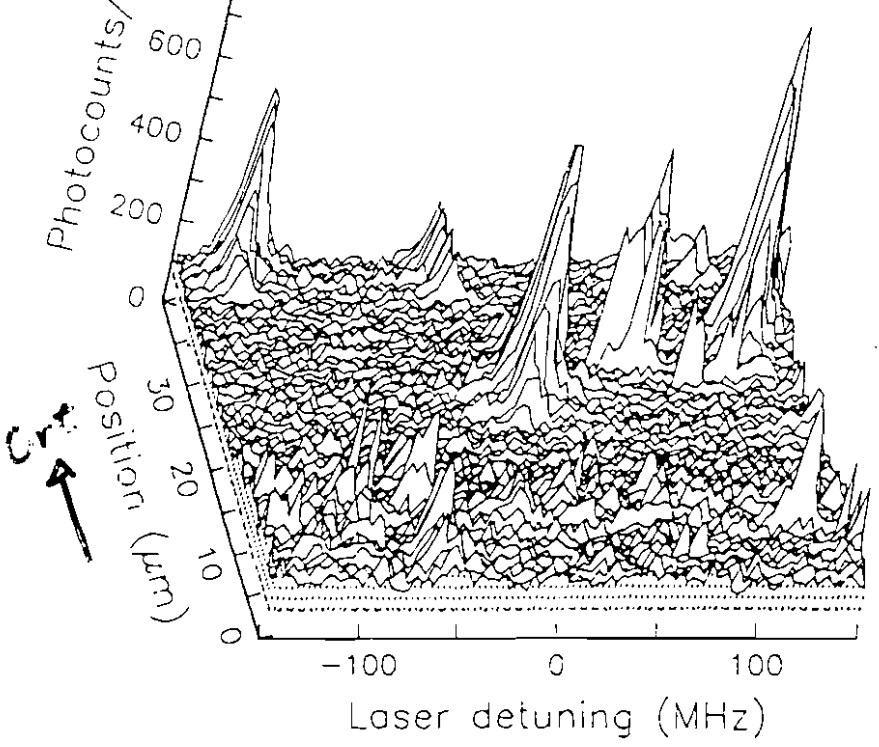
Brown et al.
J. C. P. 1994

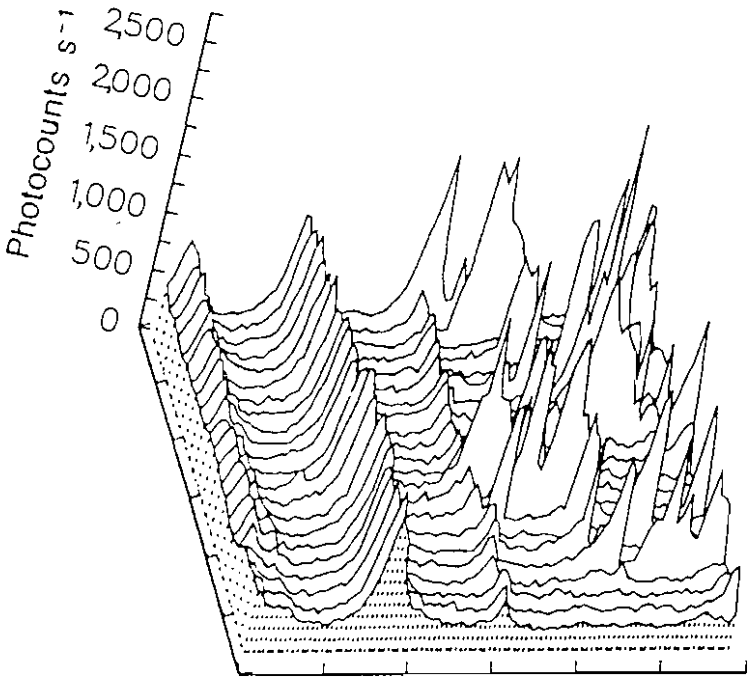
Correlationfunction

$$g^2(\tau) = \frac{\langle I(t)\, I(t+\tau) \rangle}{\langle I(t) \rangle^2}$$

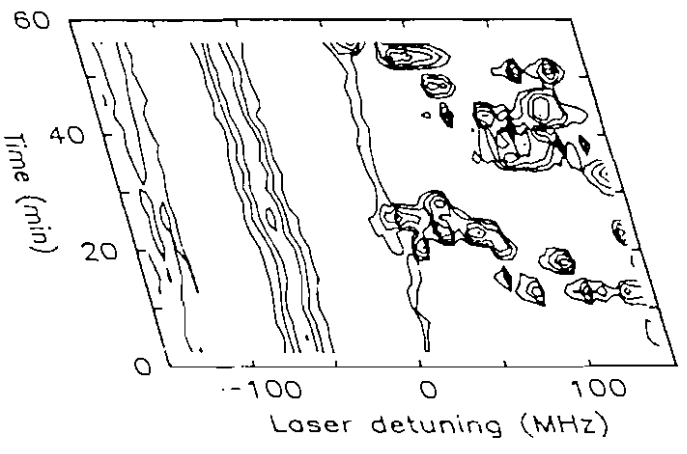
Korrelationsfunktion

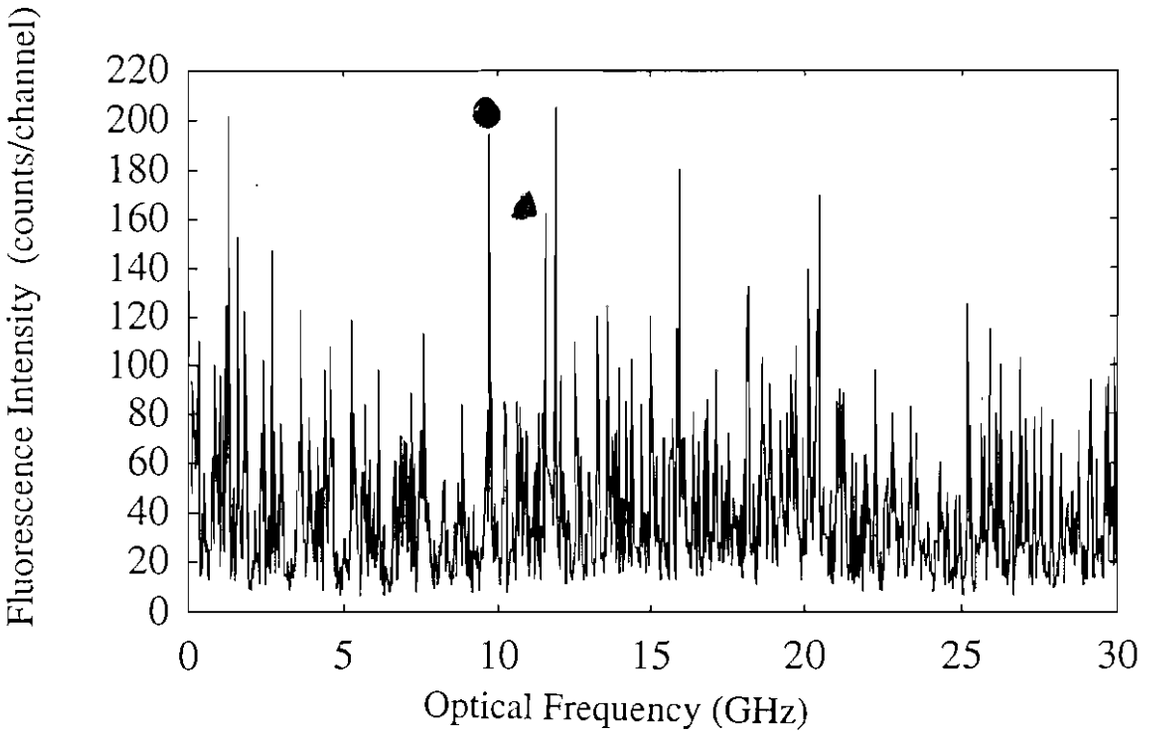


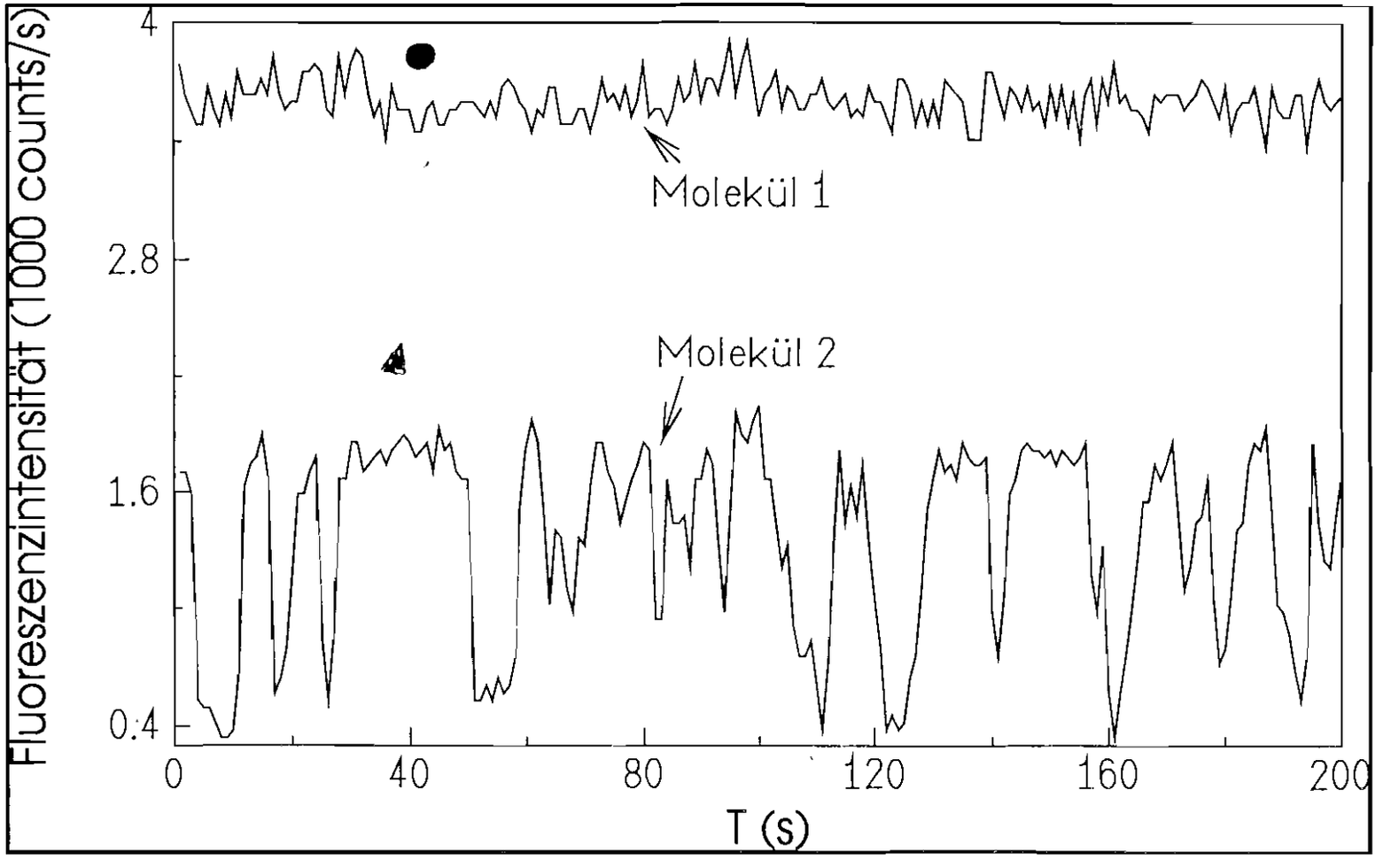

Photocounts s⁻¹
600
400
200
0
Position (μm)
30
20
10
0
−100
0
100
Laser detuning (MHz)


Photocounts s⁻¹
2500
2000
1,500
1,000
500
0

1.5 K

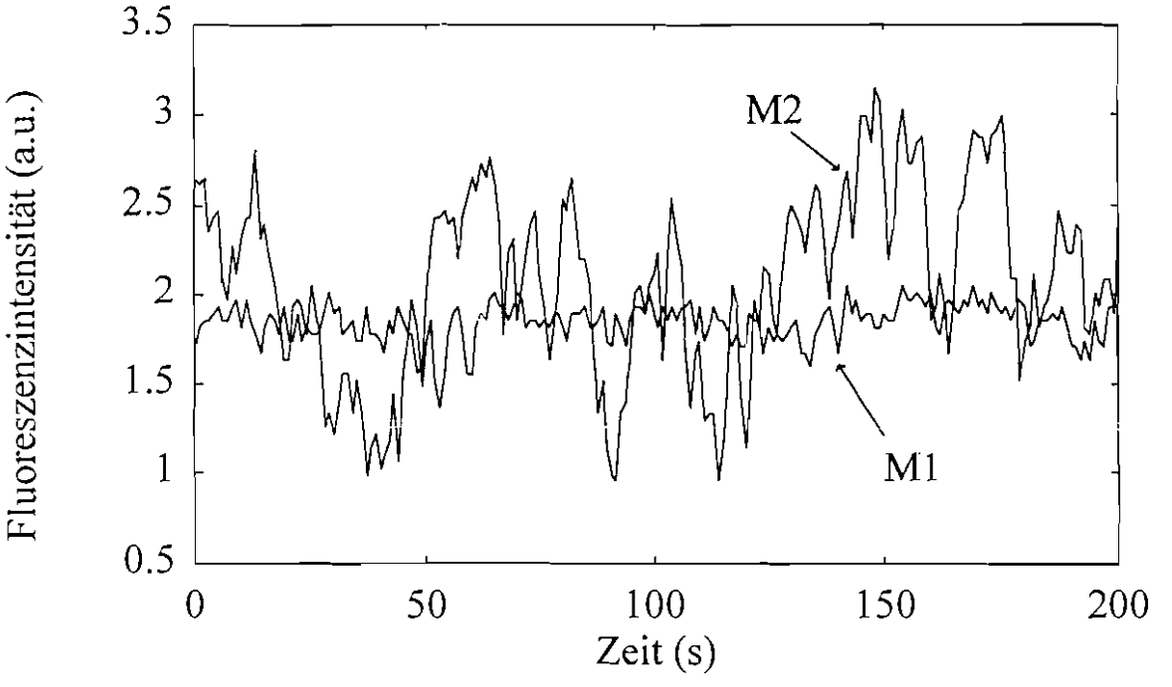

Time (min)
60
40
20
0
−100
0
100
Laser detuning (MHz)


Fluorescence Intensity (counts/channel)
220
200
180
160
140
120
100
80
60
40
20
0
0
5
10
15
20
25
30
Optical Frequency (GHz)

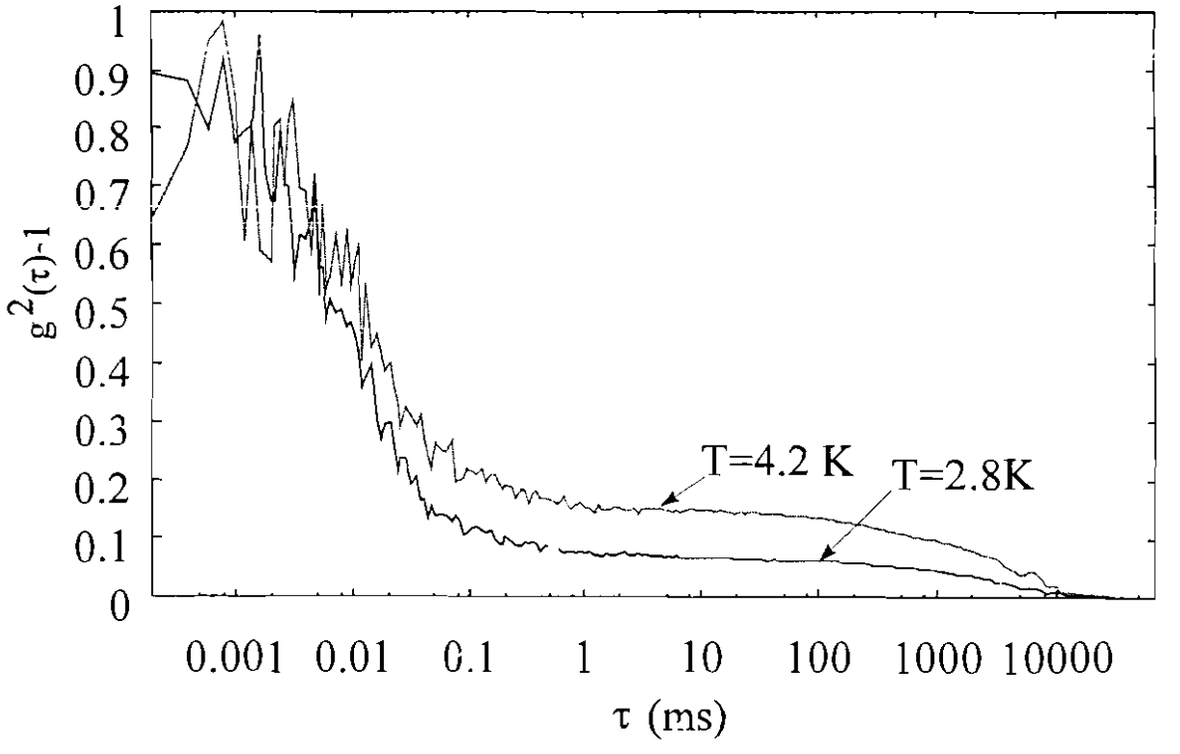

Fluoreszenzintensität (1000 counts/s)
4
2.8
1.6
0.4
Molekül 1
Molekül 2
0
40
80
120
160
200
T (s)

Correlation spectroscopy on molecules undergoing frequency shifts

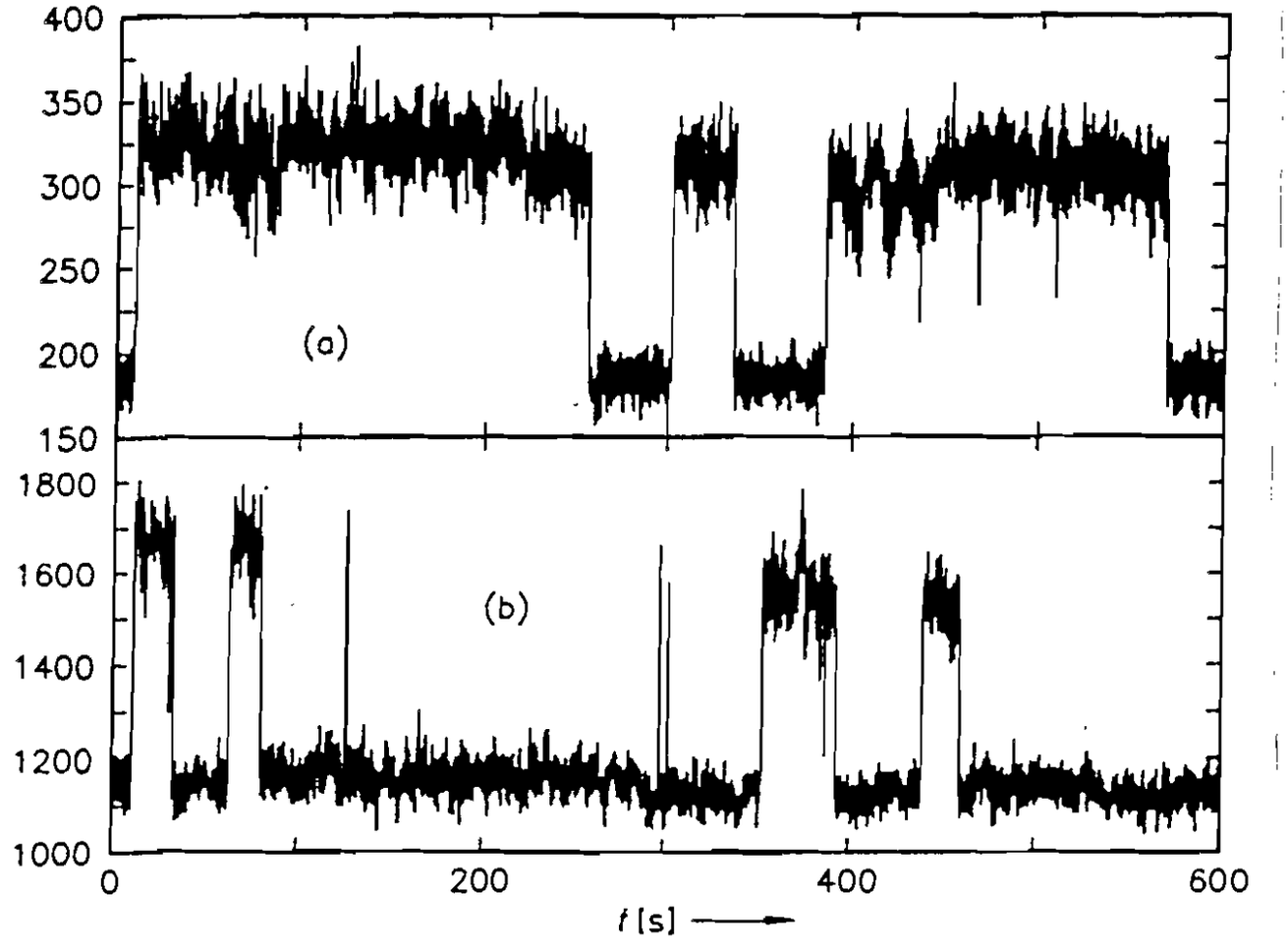
System: Pentacene in p-Terphenyl



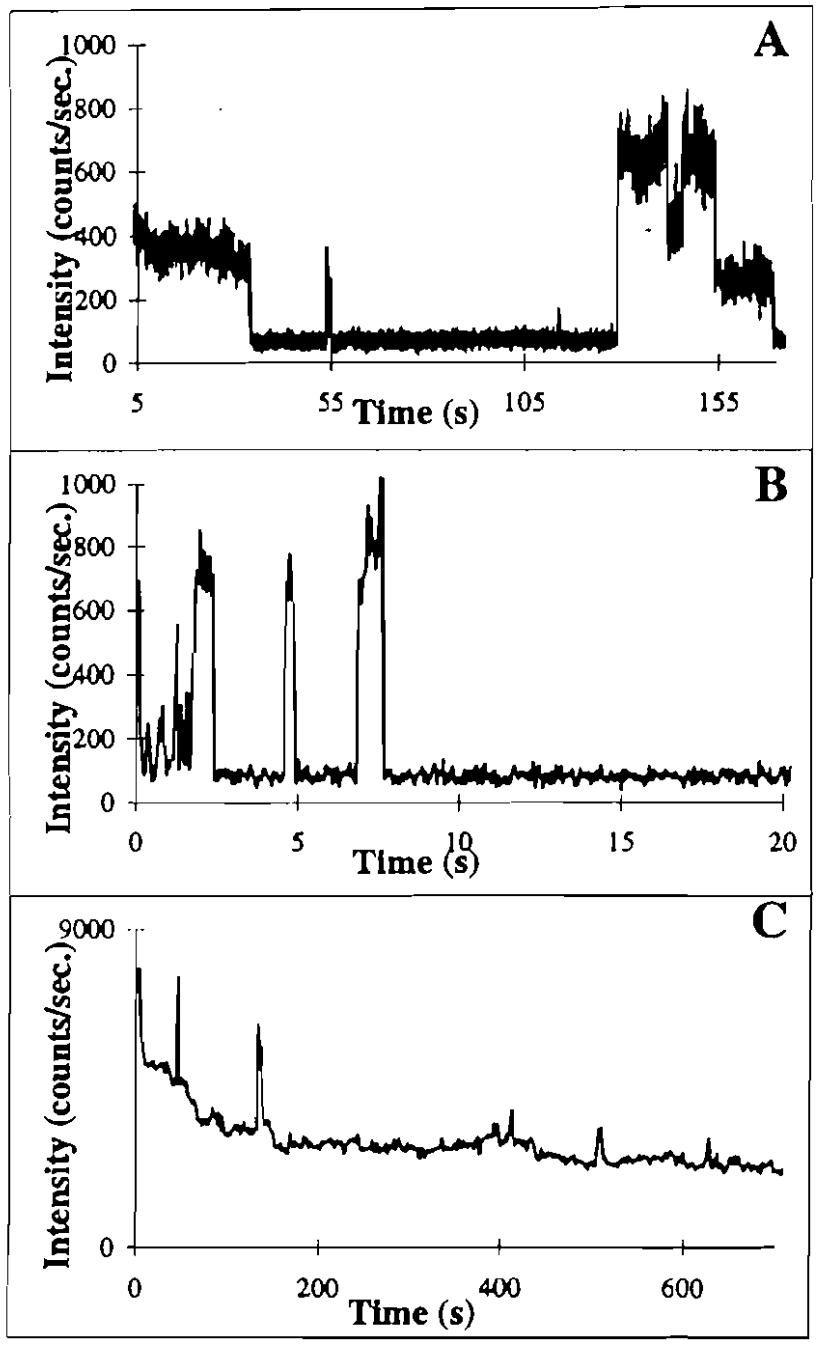
Autocorrelation function of fluorescence intensity yields typical correlation times:

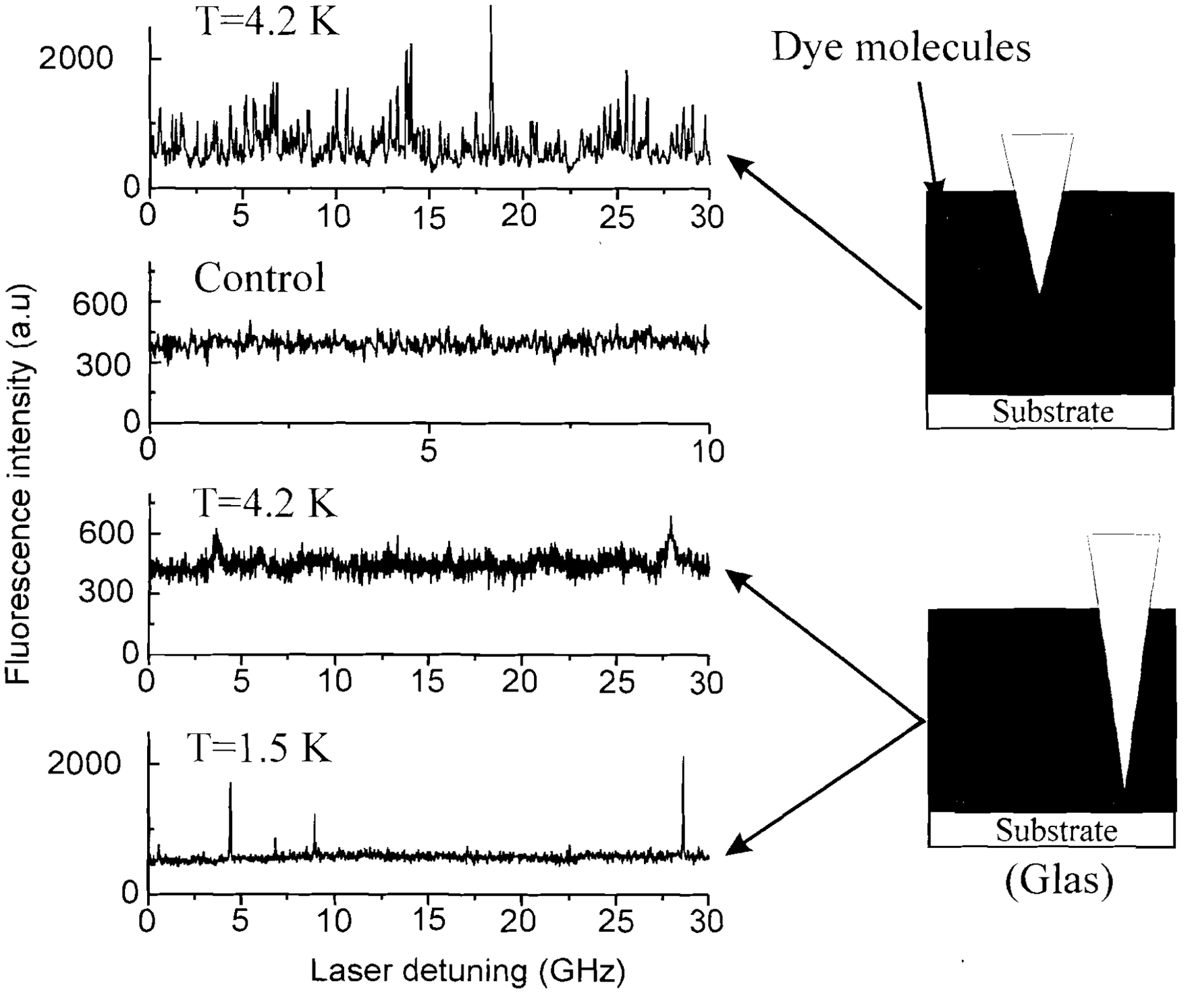


Optisches Schalten von Molekülen



$P_1 \neq P_2$

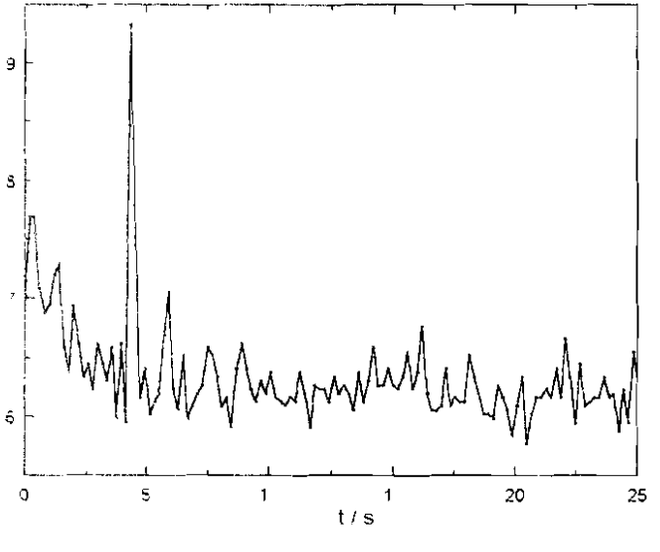

A
Intensity (counts/sec.)
1000
800
600
400
200
0
5
55
105
155
Time (s)
B
Intensity (counts/sec.)
1000
800
600
400
200
0
0
5
10
15
20
Time (s)
C
Intensity (counts/sec.)
9000
0
0
200
400
600
Time (s)

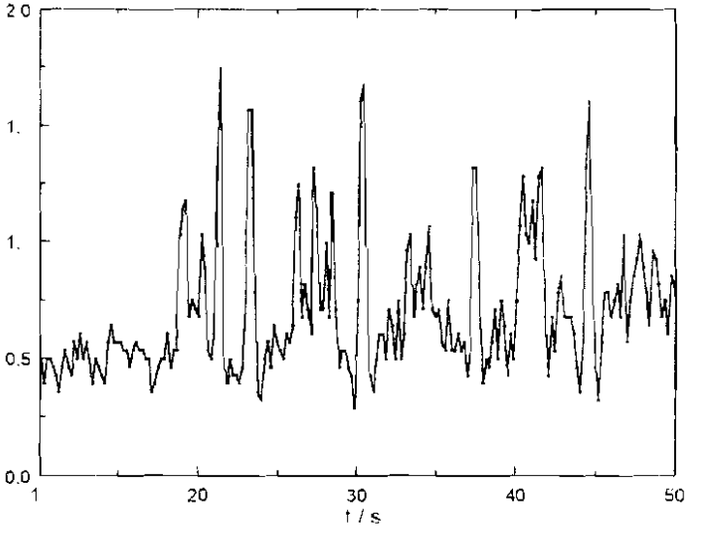

T=4.2 K
2000
0
0
5
10
15
20
25
30
Control
600
300
0
0
5
10
T=4.2 K
600
300
0
0
5
10
15
20
25
30
T=1.5 K
2000
0
0
5
10
15
20
25
30
Fluorescence intensity (a.u)
Laser detuning (GHz)
Dye molecules
Substrate
Substrate
(Glas)

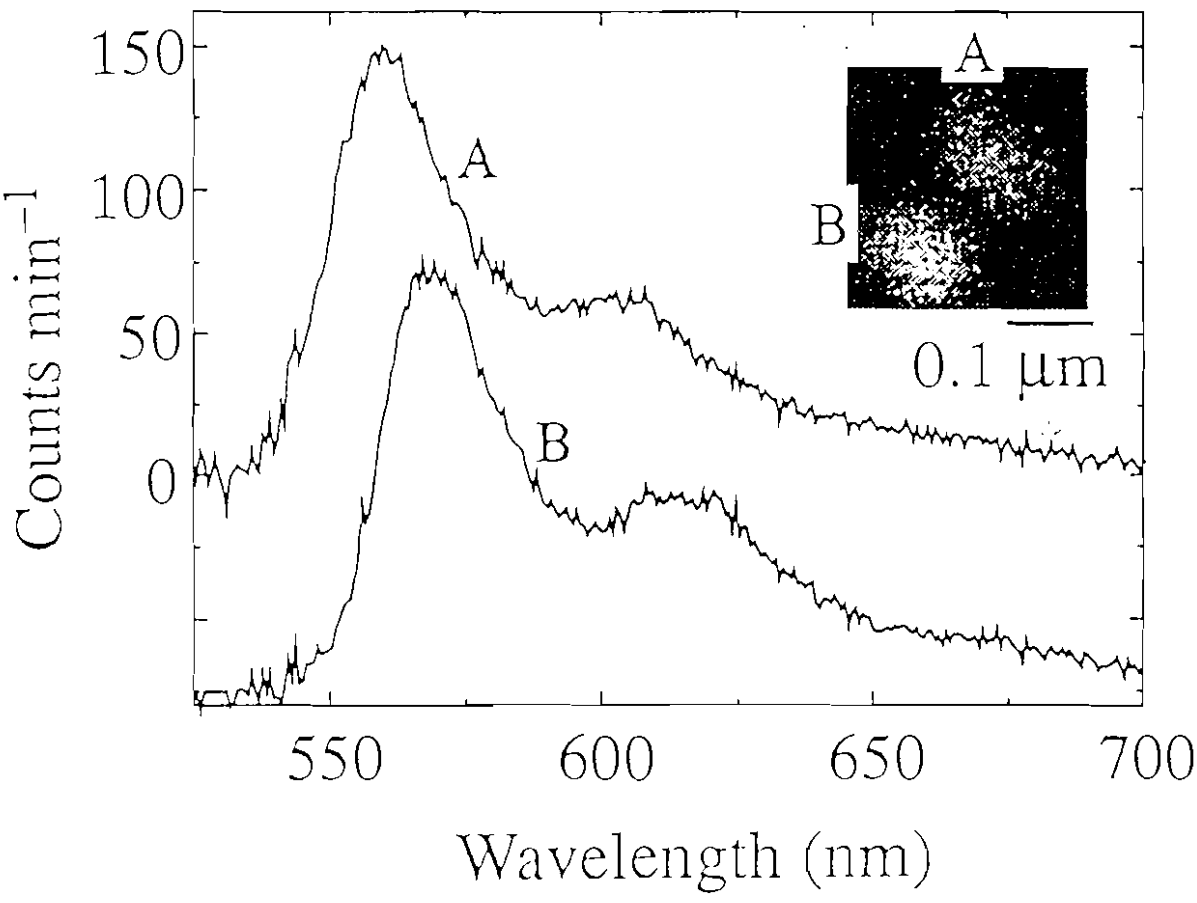
Dynamics of fluorescence intensity of single molecules

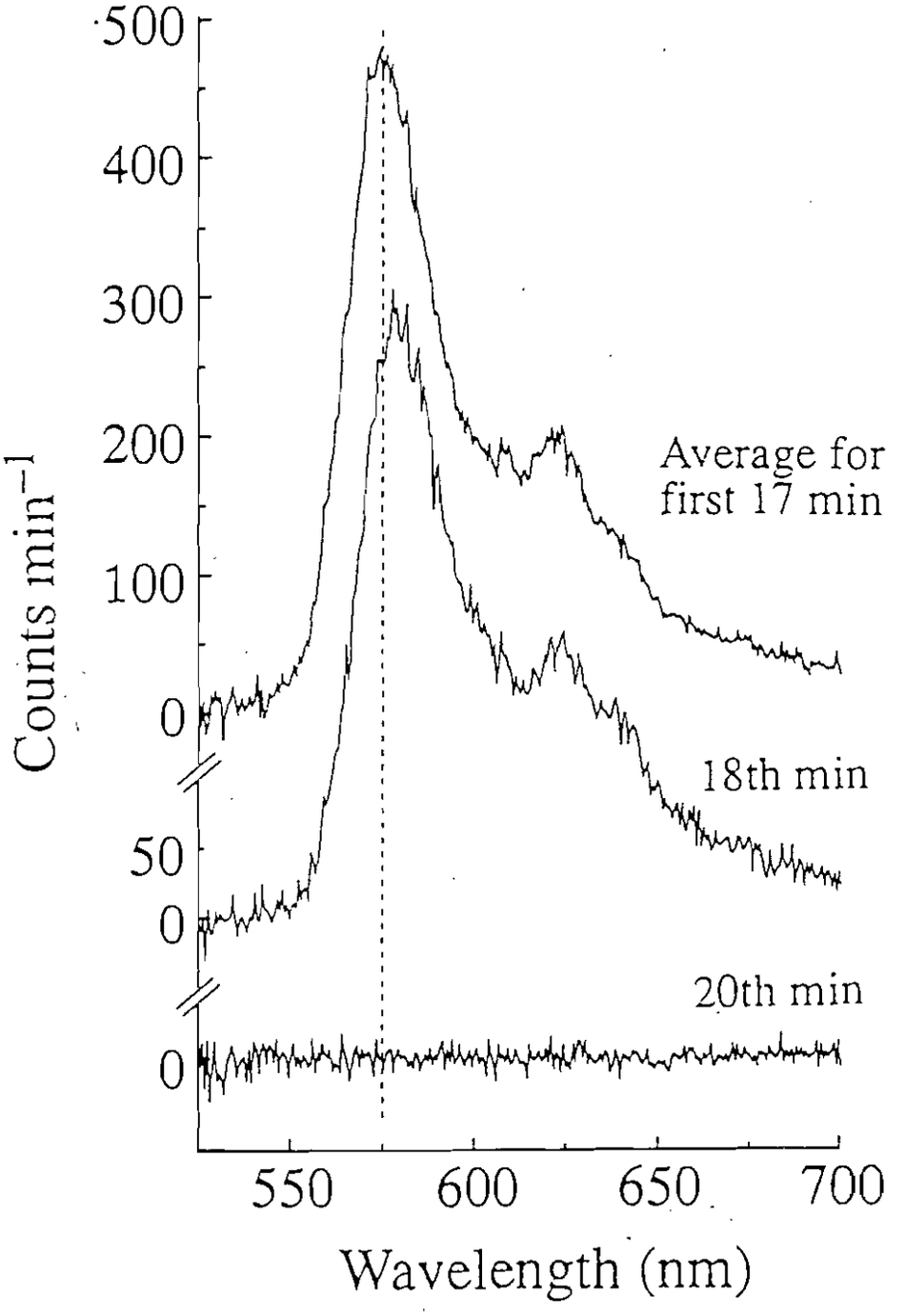
- confocal images of single R6G molecules (scan 1.2 x 1.2 μm^2)

- temporal evolution of fluorescence intensity of single molecules

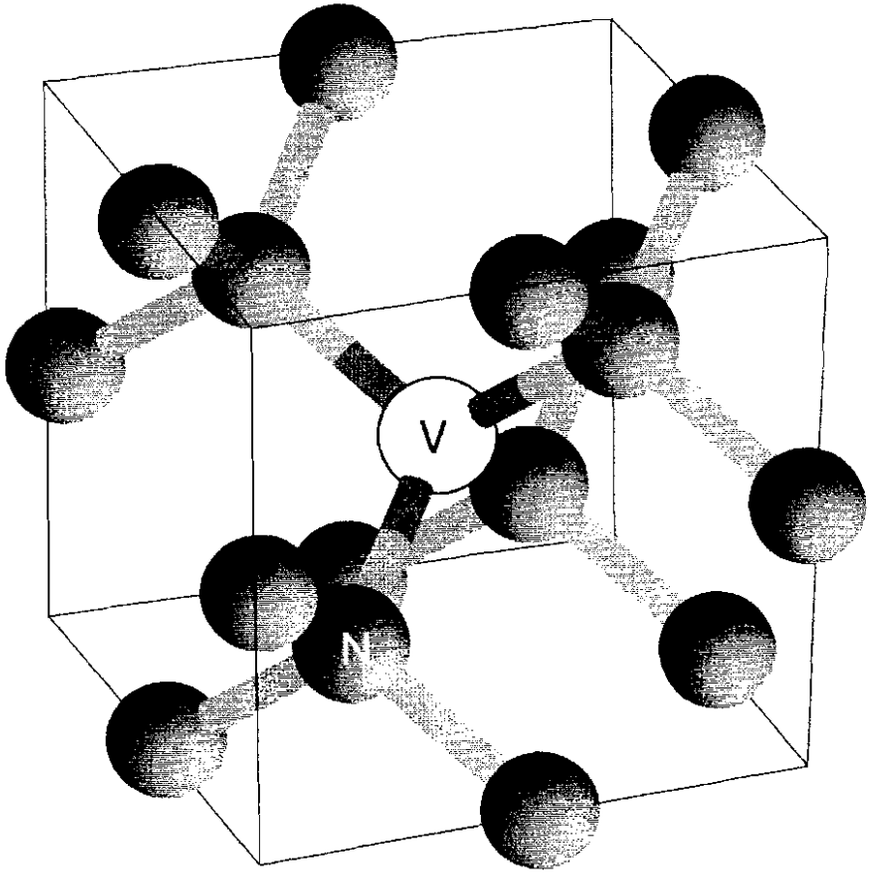




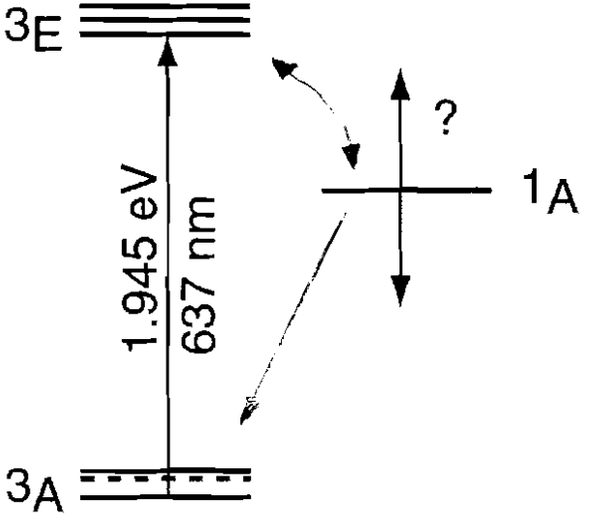

150
100
50
0
Counts min^{-1}
A
B
A
B
0.1 μm
550
600
650
700
Wavelength (nm)

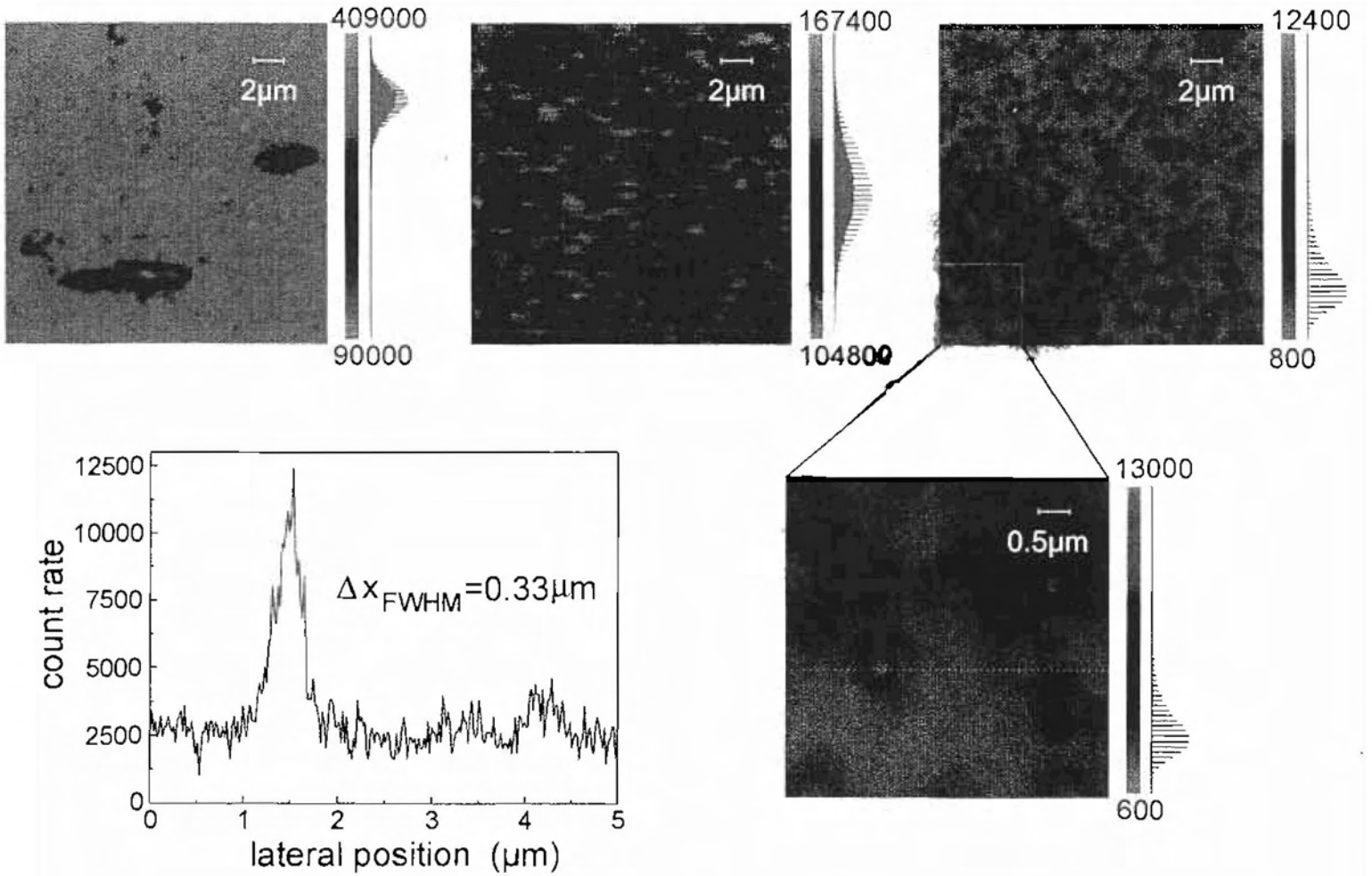

500
400
300
200
100
0
50
0
0
Counts min^{-1}
Average for
first 17 min
18th min
20th min
550
600
650
700
Wavelength (nm)

Nitrogen Vacancy Defect (N-V centre)



- induced by electron iradiation (electron energy >300 keV)
- different charge states known
- well studied by PL, RAMAN, ESR, ODMR
- high photostability

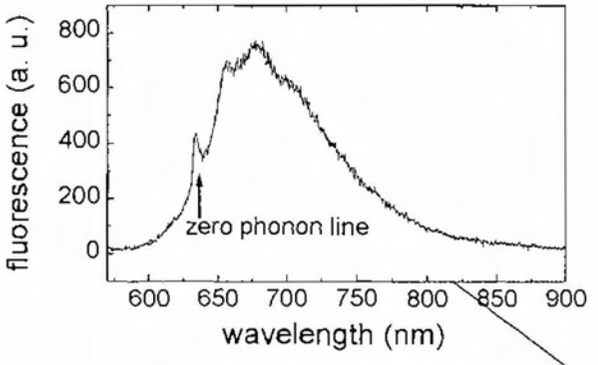




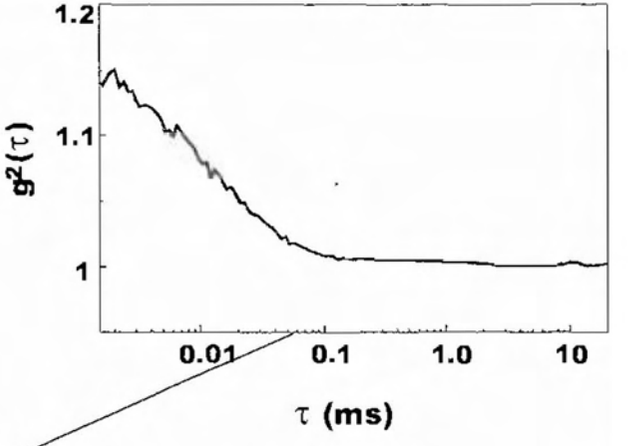
Gruber et al. Science 276 (1997) 2012

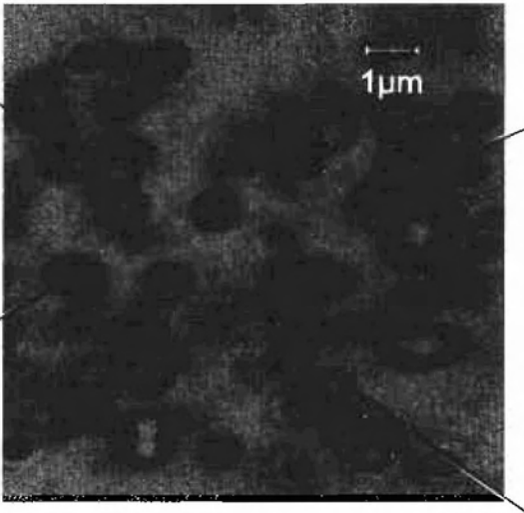
single N-V centers in diamond

fluorescence spectrum

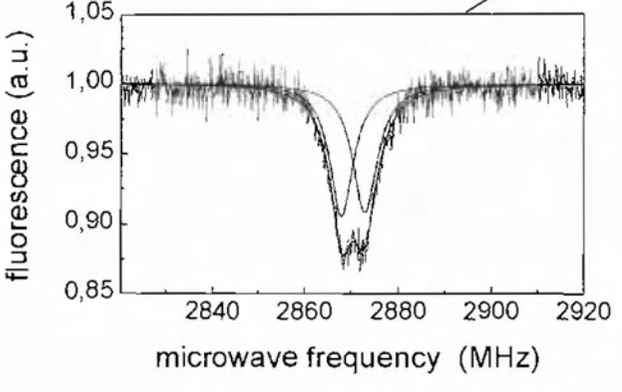


dynamics

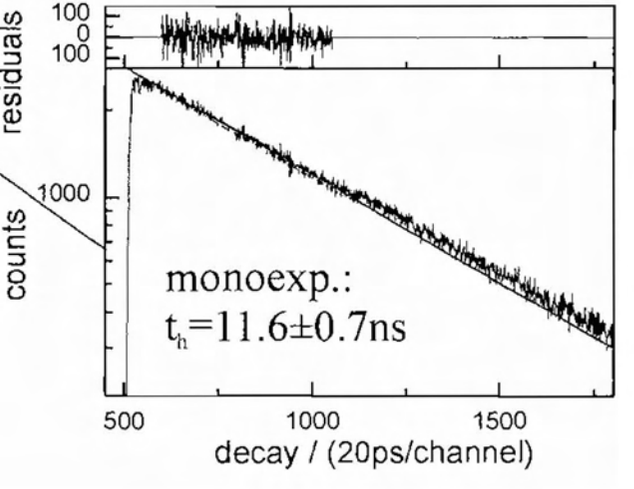


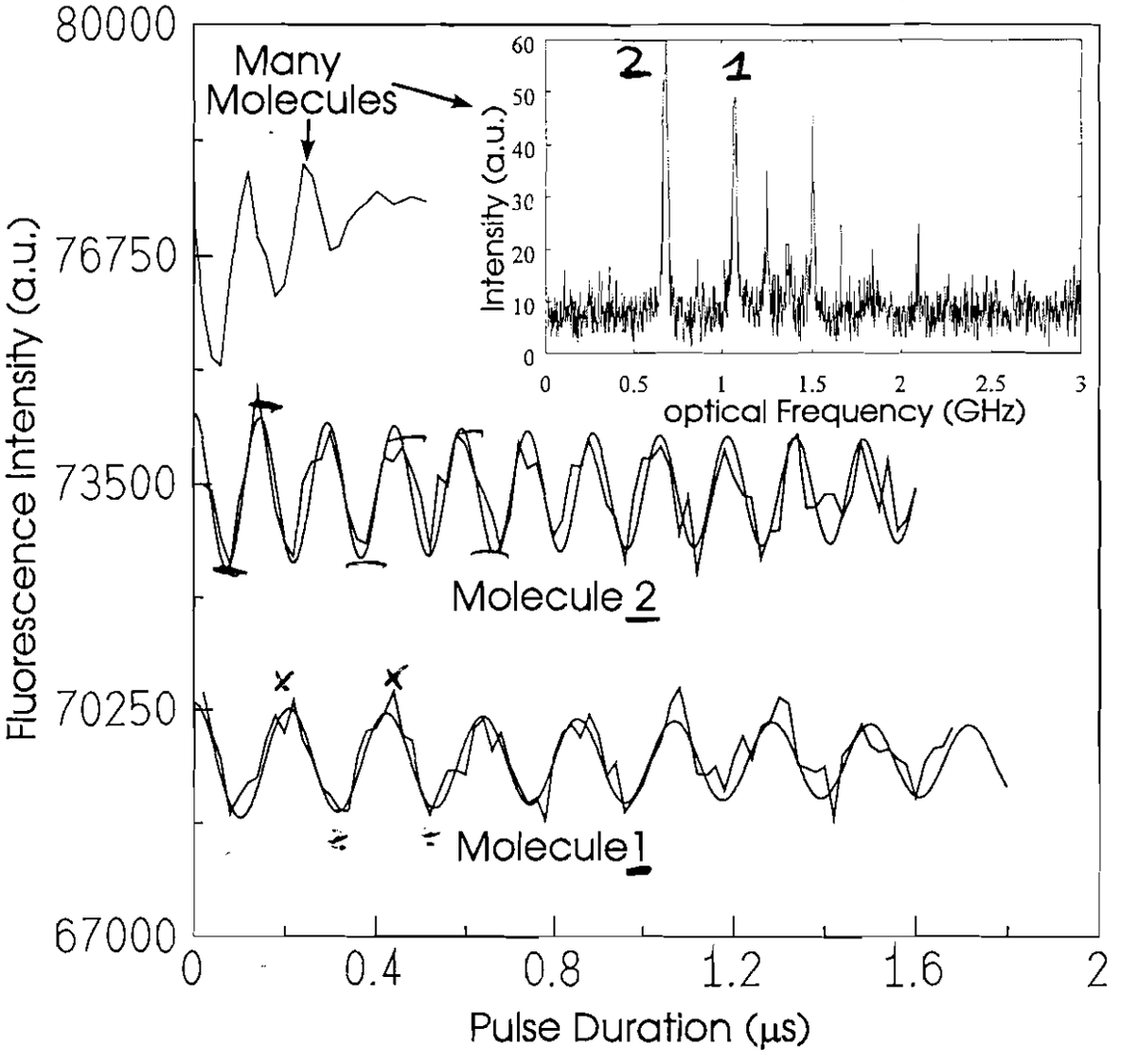


ODMR spectrum



lifetime

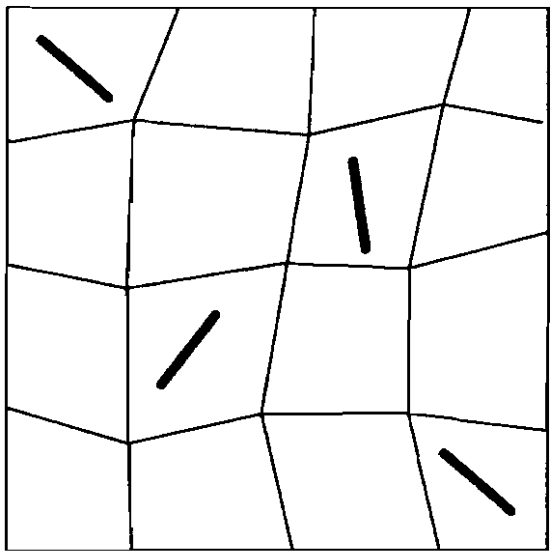




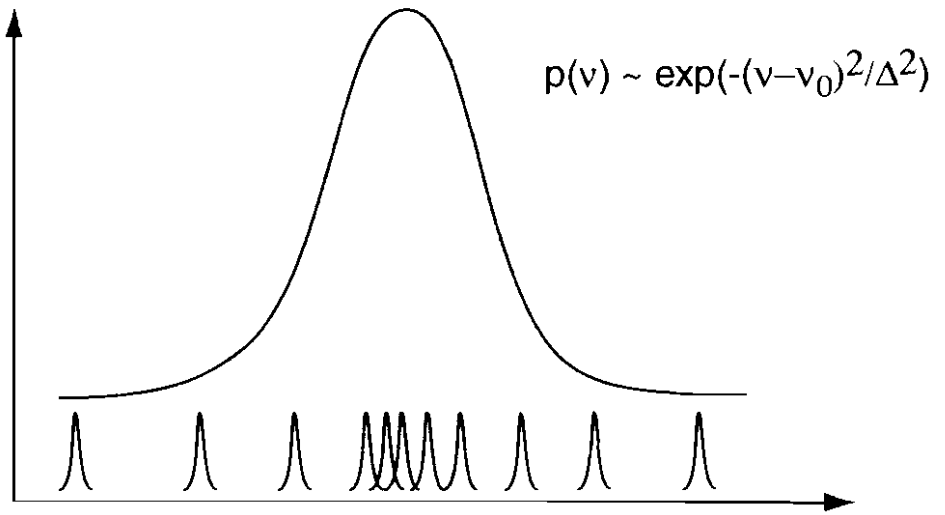
$\omega_{Nut} = \gamma_e B_1 (MW)$

Spectrum of Emitters in an Ensemble

heterogeneous environment



inhomogeneous broadened line



- information only on ensemble
- no information on the individual emitter