INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY

H4.SMR/544 - 18

Winter College on Ultrafast Phenomena

18 February - 8 March 1991

Ultrafast Spectroscopy of the Primary Processes in Photosynthesis

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ULTRAFAST SPECTROSCOPY OF THE PRIMARY PROCESSES IN PHOTOSYNTHESIS

W. ZINTH
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I) BACKGROUND
- PROTEINS AND THEIR FUNCTION
- MATHEMATICAL DESCRIPTION OF TRANSIENT ABSORPTION CHANGES

II) PHOTOSYNTHESIS WITH BACTERIOCHLOROPHYLL
- PRIMARY ELECTRON TRANSFER IN NATIVE REACTION CENTERS (RC)
- PROPERTIES OF MODIFIED RC's
- OPTIMIZATION PRINCIPLE

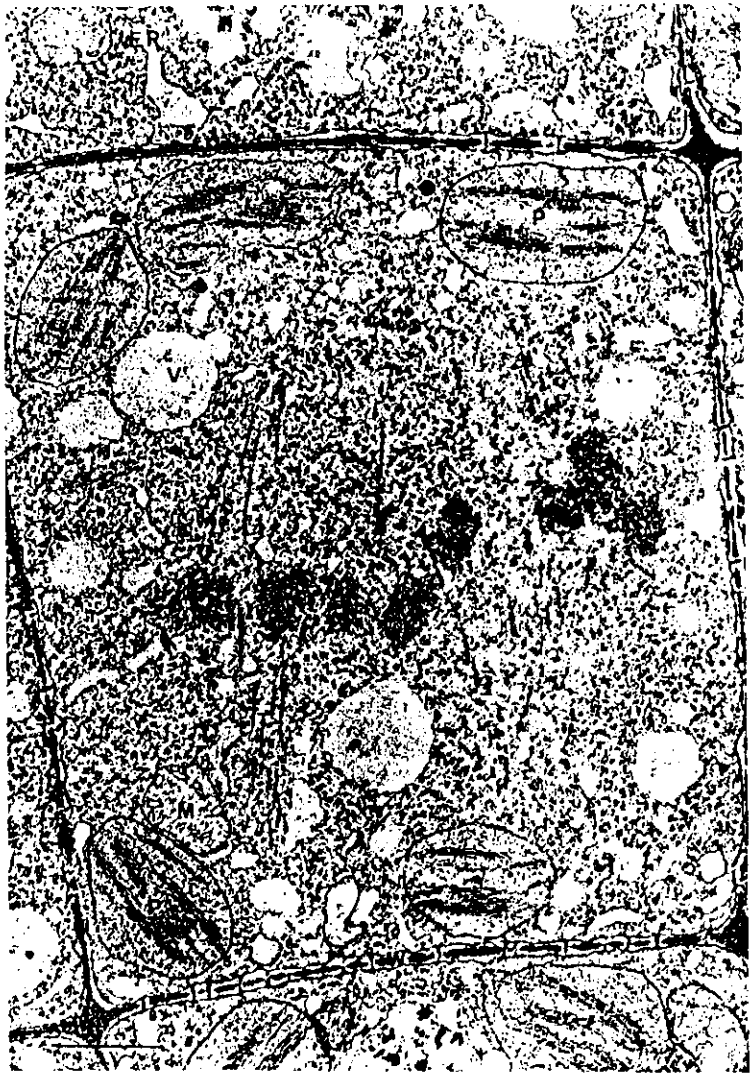


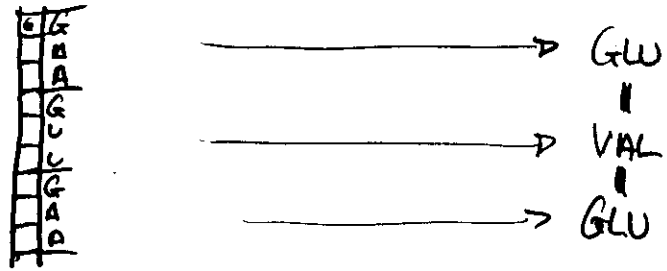
Abb. 1.7. Zelle aus dem Blättchen eines Mooses (*Sphagnum*) in Mitose (Metaphase). Die Chromosomen *CH* sind in der Äquatorialplatte geordnet. Im Grundplasma viele freie Ribosomen. *ER* endoplasmatisches Retikulum, z. T. etwas aufgebläht; *M* Mitochondrium; *P* Chloroplasten; *T* Mikrotubuli (in der Spindel längs, an der Zellwand quer getroffen); *W* Zellwand mit zahlreichen Plasmodesmen. Marke 1 µm. Fixierung: Glutaraldehyd-OsO_4

THE CELL:

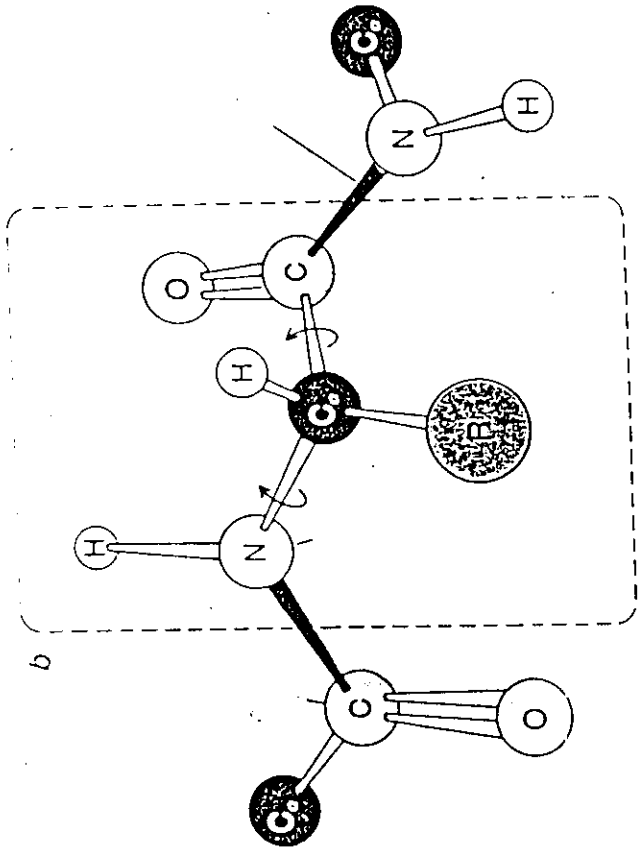
INFORMATION:	FUNCTION:
NUCLEIC-ACIDS	PROTEINS / ENZYMES
DNA / RNA	POLYPEPTIDES
4 NUCLEOTIDES:	20-L-AMINOACIDS
URACIL	
CYTOSIN	
ADENIN	
GUANIN	

TRANSLATION

RNA-SEQUENCE → AMINOACID-SEQUENCE

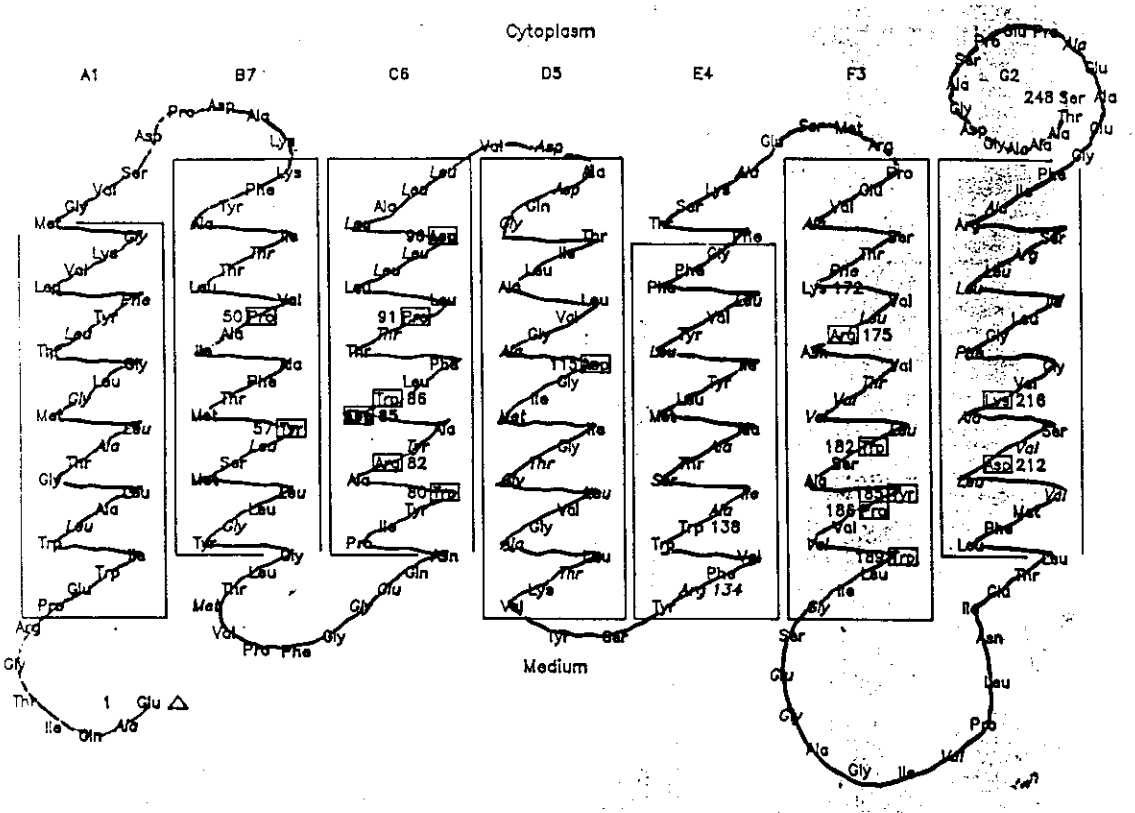


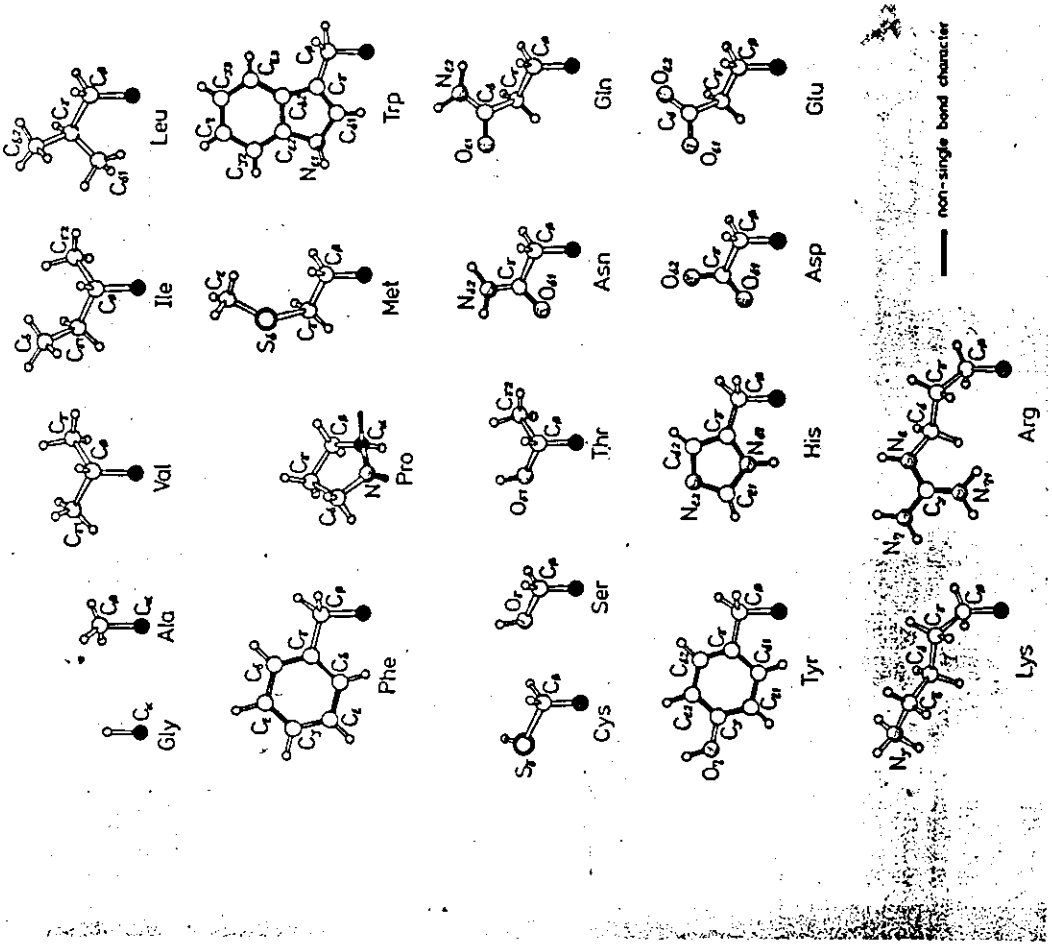
First base	Second base: U	Second base: C	Second base: A	Second base: G	Third base
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	End	End	A
	Leu	Ser	End	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

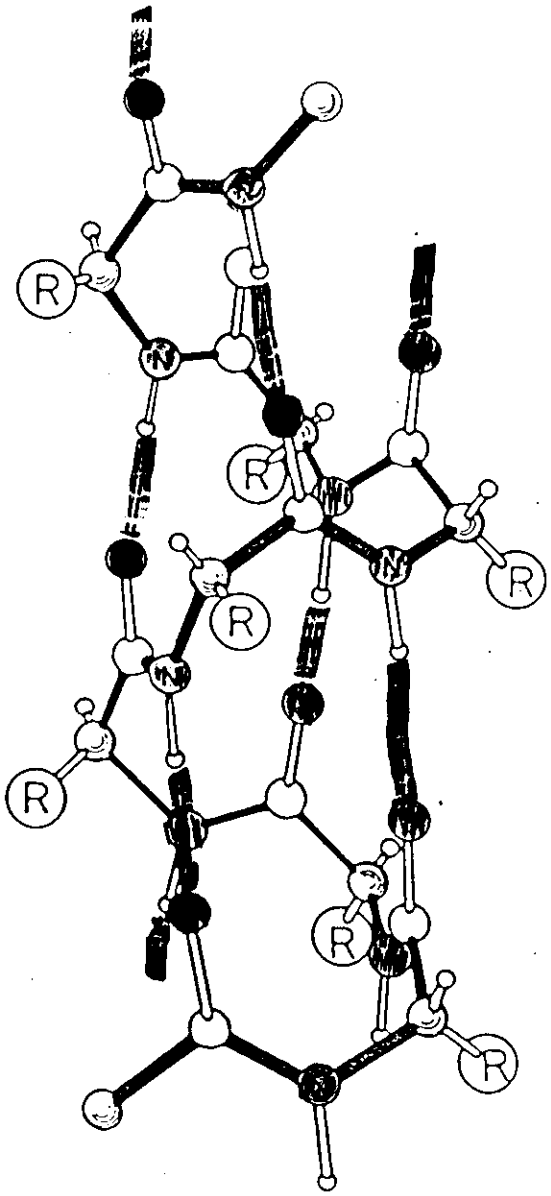


AMINOACID-SEQUENCE — PRIMARY STRUCTURE

BACTERIORHODOPSIN

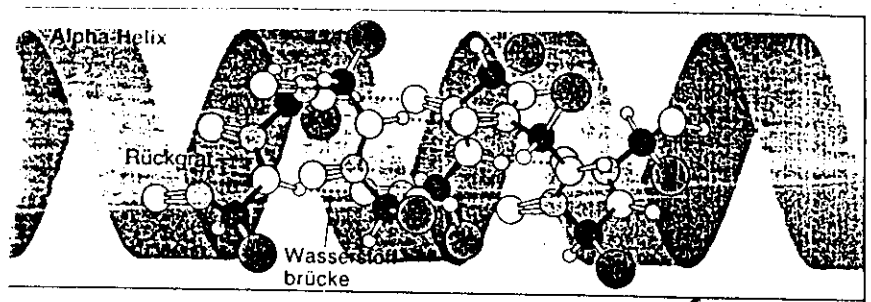


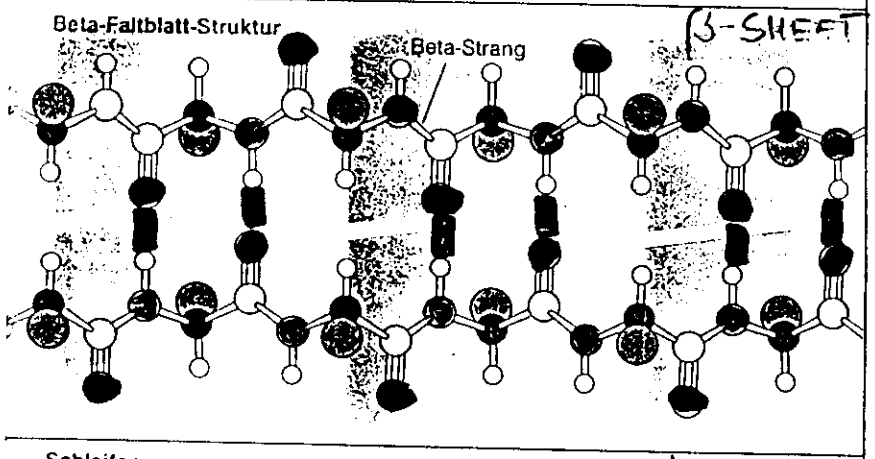


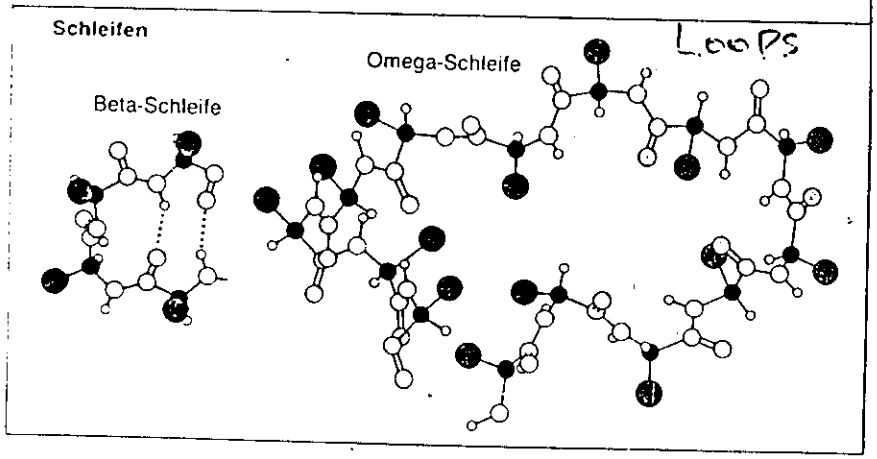


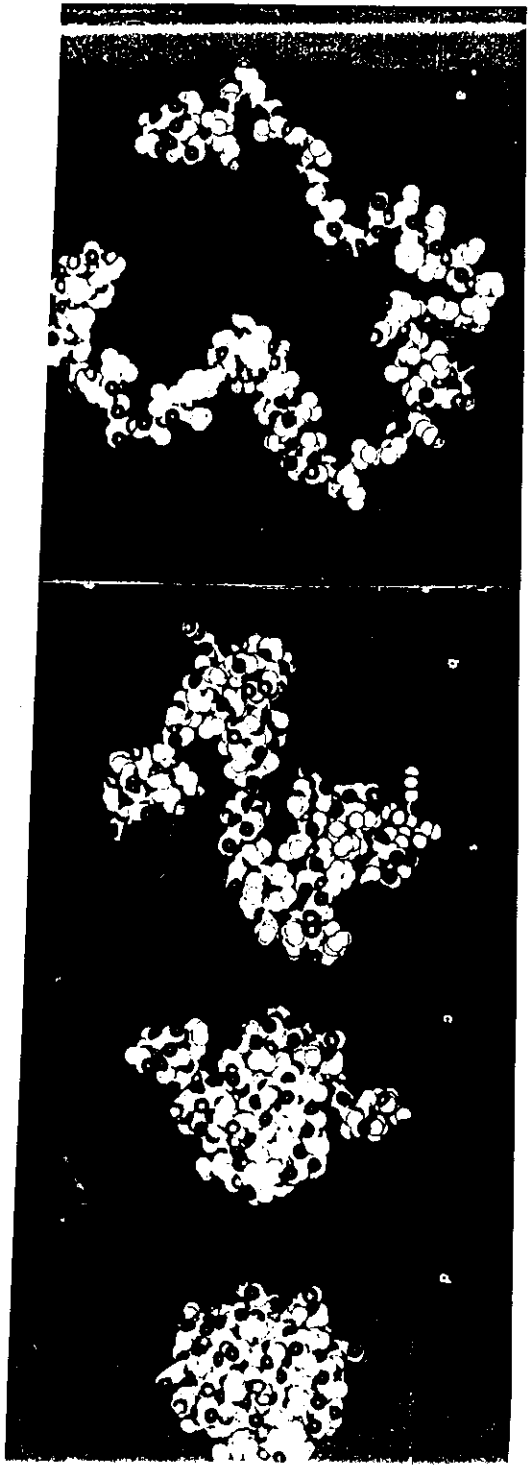
X - HELIX

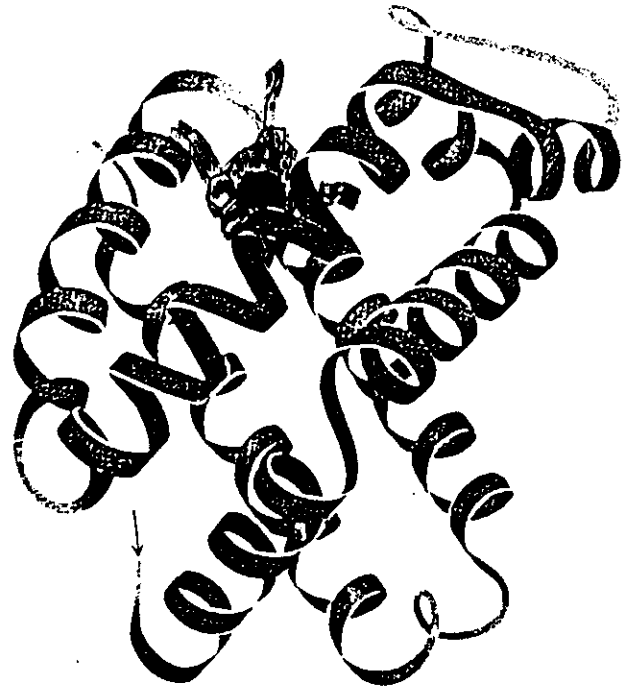
SECONDARY STRUCTUR









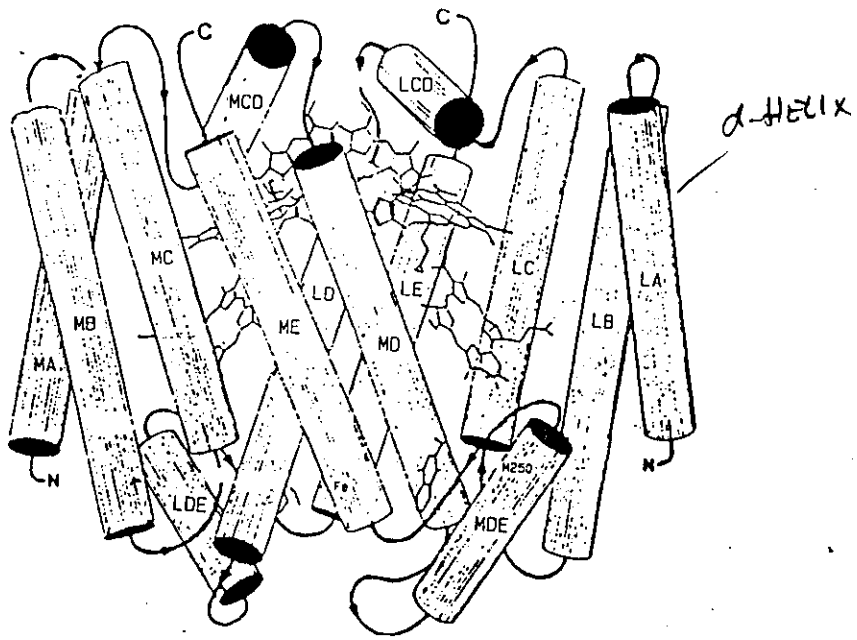


Hämoglobin (β-Kette)

AMINO-ACIDS + [redacted]

(CHROMOPHORES)

→ FUNCTIONAL PROTEIN



BACTERIAL REACTION CENTERS

OBJECTIVES:

UNDERSTANDING OF THE

- FUNCTION OF PROTEINS
- RELATION BETWEEN STRUCTURE AND FUNCTION

METHODES:

BIOCHEMICAL

SPECTROSCOPIC:

PROTEINS: VIBRATIONAL SPECTROSCOPY (IR, RAMAN)
ULTRA-VIOLETT SPECTROSCOPY

CHROMO PROTEINS:

VISIBLE / NIR SPECTROSCOPY

SPECTROSCOPY OF CHROMOPROTEINS

IR + RAMAN: AMINO ACIDS (CHROMOP.)
C=O, NH, CH, ...

UV: AMINO ACIDS
AROMATIC-AC
TRANSFER/INTERACTIONS
TO CHROMOPHORES

VISIBLE + NEAR IR: CHROMOPHORES
(ABSORPTION
EMISSION)

RESONANCE RAMAN: CHROMOPHORE-MODES

TIME-RESOLVED SPECTROSCOPY OF CHROMO PROTEINS

1. LIGHT TRIGGERS THE FUNCTIONAL REACTION

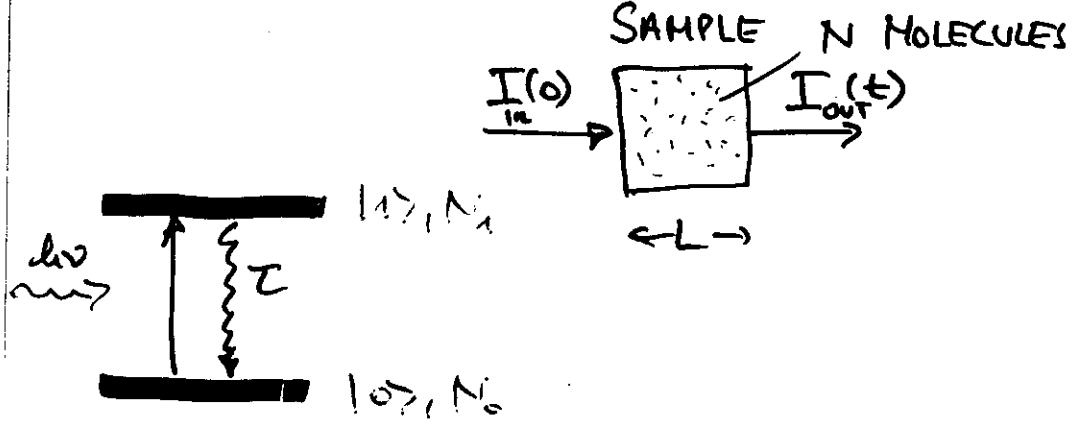
2. THE REACTION CHANGES THE ABSORPTION SPECTRUM

3. LIGHT DETECTS THE ABSORPTION CHANGES

4. OBSERVED ABSORPTION CHANGES ARE RELATED TO MICROSCOPIC REACTION

THEORY OF TRANSIENT ABSORPTION CHANGES

① SIMPLE TWO-LEVEL SYSTEMS



$$I_{out} = I_{in} \exp\left[-\sigma N_0 L + \sigma N_1 L\right]$$

$$\frac{dN_1}{dt} = -\gamma N_1 = -\frac{1}{\tau} N_1$$

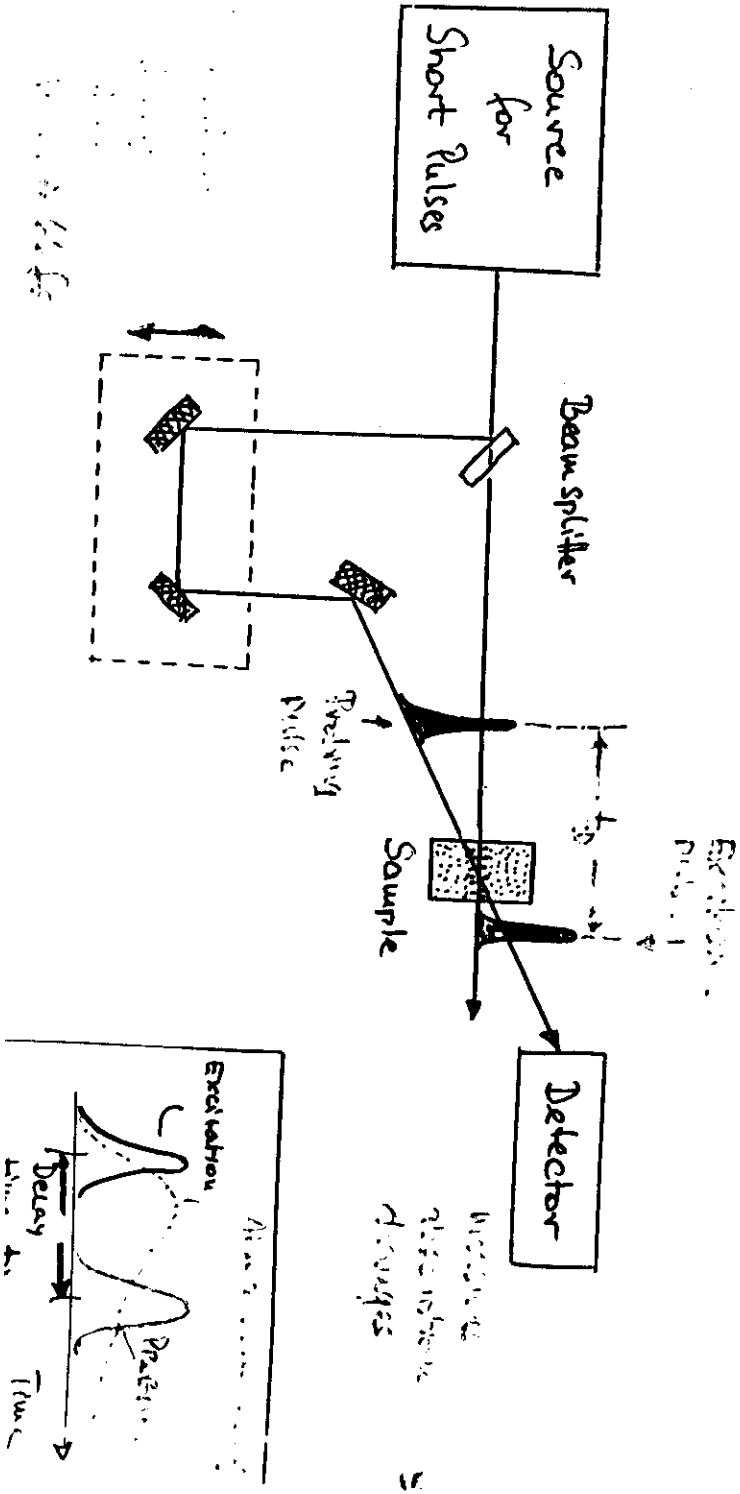
LOW LIGHT

SPONTANEOUS DECAY

TIME DEPENDENT OCCUPATION:

$$N_1(t) = N_1(0) \exp(-\gamma t)$$

$$N_0(t) = N - N_1(t)$$



ÄBSORBANCE:

$$\log\left(\frac{I_{out}}{I_{in}}\right) = +\sigma L\left(N_1(t) - N_0(t)\right)$$

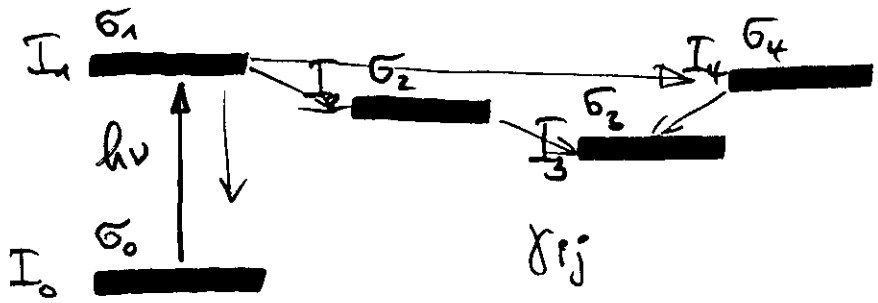
$$= \sigma L\left(2N_1(t) - N\right)$$

$$= \sigma L\left(2N_1(0)\exp[-\gamma t] - N\right)$$

ABSORBANCE CHANGE $\Delta A(t)$ REFLECTS THE POPULATION CHANGE $N_1(t)$

$$\Delta A = 2\sigma L \underbrace{\exp[-\gamma t]\, N_1(0)}_{N_1(t)}$$

2. MULTI-LEVEL SYSTEM



POPULATION CHANGES:

STARTING CONDITION $N_1(0) = N_{10}$

$N_i(0) = 0$

$i > 1$

$$\frac{dN_i}{dt} = -\gamma_{ij} \sum_j N_j$$

$$\begin{pmatrix} \frac{dN_1}{dt} \\ \vdots \\ \frac{dN_i}{dt} \\ \vdots \end{pmatrix} = \begin{pmatrix} +\gamma_{11} & \gamma_{12} & \cdots & \gamma_{1n} \\ \gamma_{21} & \gamma_{22} & & \\ \vdots & & \ddots & \\ \gamma_{n1} & & & \gamma_{nn} \end{pmatrix} \begin{pmatrix} N_1 \\ N_2 \\ \vdots \\ N_n \end{pmatrix}$$

RATE-EQUATION-SYSTEM

SOLUTION OF THE RATE EQUATIONS:

$$N_i(t) = \sum_j^n B_{ij} \exp[-t/\tau_j]$$

WITH: $\alpha_j = \frac{1}{\tau_j}$ IS THE j^{th} EIGENVALUE OF THE RATECONSTANT MATRIX (γ_{ij})

B_{ij} DEPEND ON EIGENVECTORS OF (γ_{ij}) AND STARTING CONDITIONS

ABSORBANCE CHANGE:

$$\Delta A(t) = A_0 \sum_{i=1}^n \{\sigma_i - \sigma_0\} N_i(t) =$$

$$= A_0 \left(\sum_{i=1}^n \{\sigma_i - \sigma_0\} \sum_{j=1}^n B_{ij} \exp[-t/\tau_j] \right)$$

$$\Delta A(t) = \sum_{j=1}^n a_j \exp(-t/\tau_j)$$

FOR FINITE DURATIONS OF EXCITING AND PROBING PULSES AND "WEAK" * LIGHT INTENSITIES:

$$\Delta A(t_D) = \int_0^\infty kk(t_D - t)\, \Delta A(t)\, dt$$

INSTRUMENTAL RESPONSEFUNCTION

MEASURED ΔA IS CONVOLUTION OF INSTRUMENTAL RESPONSE FUNCTION AND MOLECULAR RESPONSE

* WEAK: PROBING AND EXCITATION PROCESSES DO NOT CHANGE N_i CONSIDERABLY $\Delta N_i \ll N_i$

TYPICAL EXCITATION $\Delta N_0 \leq 0.1\, N_0$

DATA HANDLING PROCEDURE:

I) MEASURE $\Delta A(t_D)$ AT DIFFERENT WAVELENGTHS

II) USE SHORT PULSES ($\Delta kk \ll \tau_j$)

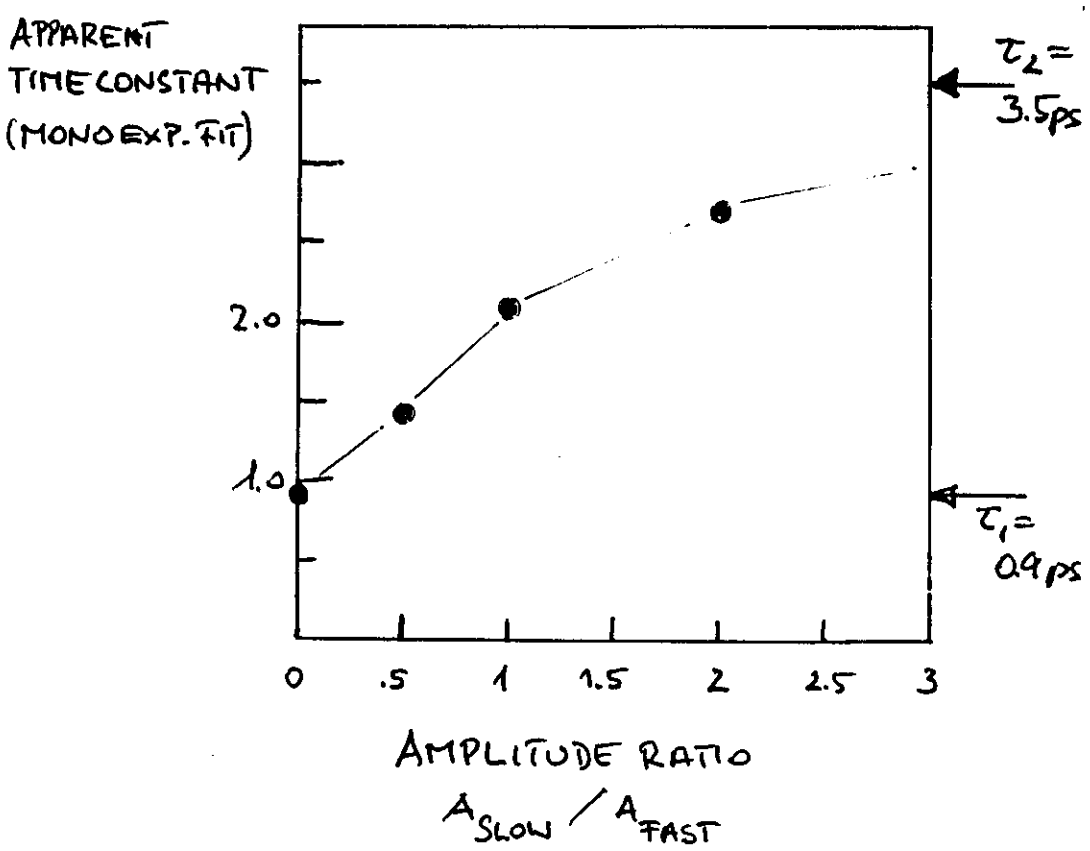
III) FIT THE EXPERIMENTAL-DATA WITH n EXPONENTIAL FUNCTIONS

IV) DETERMINE SMALLEST NUMBER OF n WHICH EXPLAINS ALL DATA

PROBLEM:

- THE MORE TIME-CONSTANT YOU USE, THE BETTER IS THE AGREEMENT OF FIT AND DATA

* HINT: IF YOU FIND A WAVELENGTH-DEPENDEN RATE YOU MAY BE USING NOT ENOUGH INTERMEDIATES



SPECTROSCOPICALLY ACCESSIBLE QUANTITIES ⟷ MOLECULAR MODEL

- DIFFERENT TIME CONSTANTS τ_j $(j = 1 \dots n)$
- NUMBER OF TIME CONSTANTS n
- FIT AMPLITUDES $a_j(\lambda)$ $j = 1 \dots n$

$$\Delta A(\lambda, t) = \sum_j a_j(\lambda) \exp(-t/\tau_j)$$

MAIN PROBLEM:

ONE MEASURES THE EIGENVALUES OF THE RATE CONSTANT MATRIX k_{ij} $(i = 1 \dots N)$

BUT NOT THE MATRIX ELEMENTS

→ N QUANTITIES MEASURED BUT N(N-1) INDEPENDENT ELEMENT k_{ij}

THE SOLUTION REQUIRES ASSUMPTION ON THE RATE EQUATION SYSTEM:

MODEL ASSUMPTION REQUIRED!

TIME CONSTANTS τ_j AND AMPLITUDES a_j MAY BE USED:

TO CONSTRUCT A REACTION SCHEME:
- SEQUENCE OF STATES
- LINEAR / BRANCHED / PARALLEL

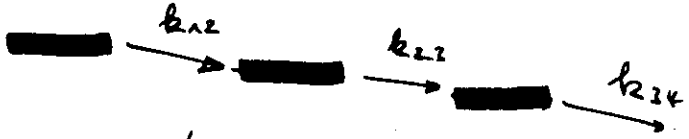
TO CALCULATE DIFFERENCE SPECTRA

TO OBTAIN A MICROSCOPIC PICTURE

USE ADDITIONAL EXPERIMENTS TO CHECK THE MICROSCOPIC MODEL:

- DICHROIC ABSORPTION CHANGE
- FLUORESCENCE EMISSION
- MODIFIED SAMPLES

LINEAR REACTION MODEL WITHOUT BACKREACTIONS



$$k_{ij} = \begin{pmatrix} -k_{12} & 0 & 0 \\ k_{12} & -k_{22} & 0 \\ 0 & k_{23} & -k_{34} \end{pmatrix}$$

$$\alpha_1 = k_{12} \qquad \alpha_2 = k_{22} \qquad \alpha_3 = k_{34}$$

ONLY THE ORDER OF THE RELAXATION MUST BE DETERMINED!

↳ DIFFERENT SPECTRA OF THE INTERMEDIATES FOR DIFFERENT ORDER OF THE PROCESSES

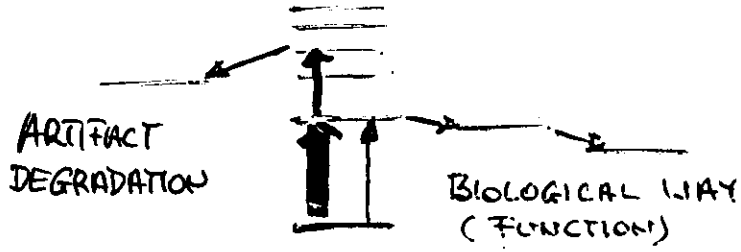
ALL OTHER REACTION MODELLS CONTAIN MORE ARBITRARY ASSUMATIONS

BIOLOGICAL SAMPLES:

SPECIAL REQUIREMENTS

1) WEAK EXCITATION

- PREVENT NON-PHYSIOLOGICAL REACTIONS



- PREVENT MULTI PHOTON PROCESSES

2) HIGHLY SENSITIVE DETECTION

- WEAK EXCITATION ⇒ SMALL ABSORPTION CHANGE

3) LOW REPETITION RATES

- LONG CYCLE TIMES OF 10^{-3} s – s

4) HIGH TIME RESOLUTION

5) HIGH AMPLITUDE RESOLUTION

- COMPLEX REACTION MODELS

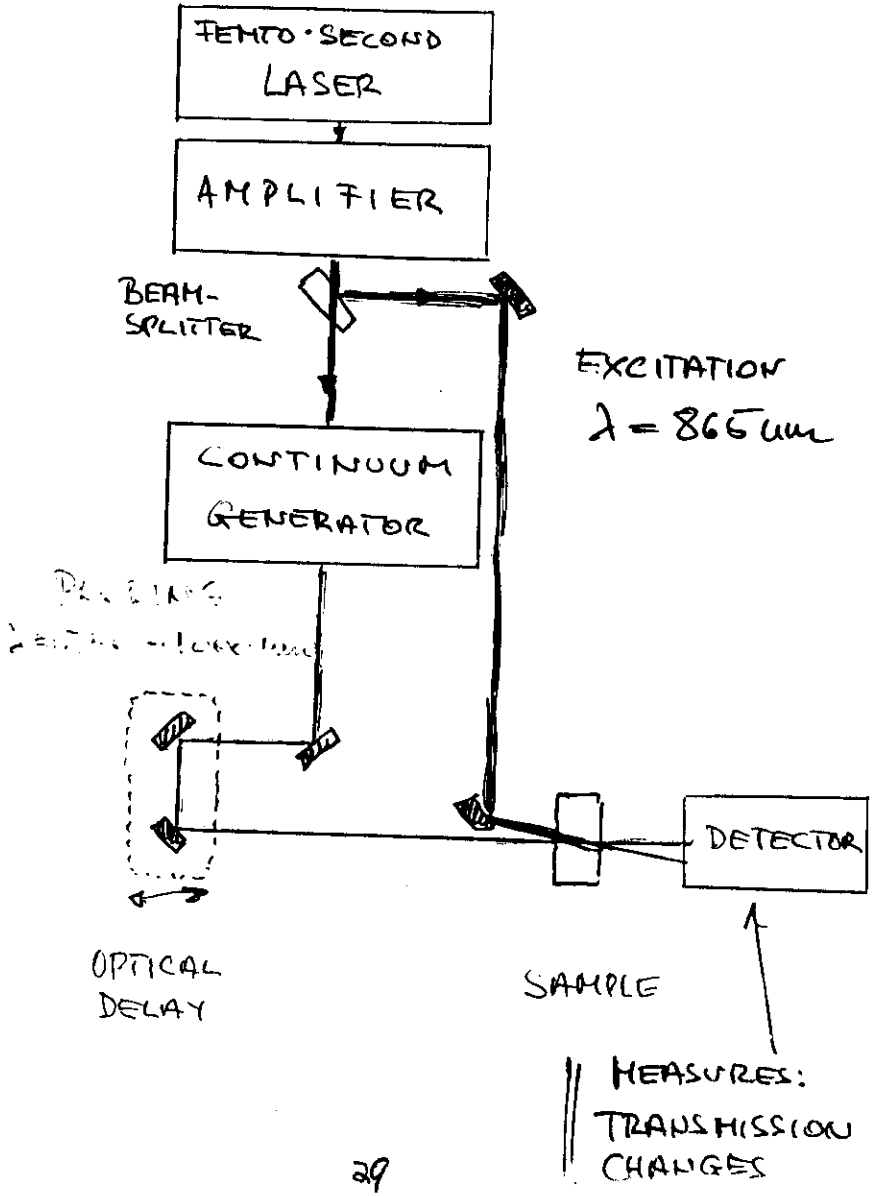
PARAMETER OF A TYPICAL SET-UP

1) EXCITATION:
- WAVELENGTH ADJUSTED TO PROBLEM
- SHORT PULSES $\sim$ 50fs $\sim$ 200fs
- WEAK EXCITATION $\Delta N_0 < 0.1 N_0$

2) PROBING:
- HIGH SENSITIVITY $\Delta A \approx 10^{-3}$ -
- MANY WAVELENGTHS
- LONG DELAY TIMES $\sim 10^{-9} - 10^{-8}$ s
- POLARIZATION DEPENDENT DETECTION

TECHNIQUE:

FEMTOSECOND EXCITE-AND-PROBE EXPERIMENT OF THE SAMPLE TRANSMISSION:



PHOTOSYNTHESIS WITH BACTERIOCHLOROPHYLL

THE PRIMARY ELECTRON TRANSFER IN BACTERIAL REACTION CENTERS

- PHOTOSYNTHESIS
- BACTERIAL REACTION CENTERS (RC)
- ELECTRON TRANSFER IN NATIVE RC
- MODIFICATIONS OF RC
- THE OPTIMIZATION OF PHOTOSYNTHESIS

COWORKERS:

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	FRANKFURT

PHOTOSYNTHESIS —

WHAT DOES PHOTOSYNTHESIS ?

CONVERTS SUNLIGHT INTO

CHEMICAL ENERGY

[illegible] 100TW

HUMAN ENERGY CONSUMPTION 7.5TW
(PETROLEUM, COAL ...)

REACTION EQUATION:

$$CO_2 + 2\,H_2A \xrightarrow{\text{SUNLIGHT}} CH_2O + H_2O + 2A$$

CONSUMES CO_2

CONVERTS + STORES ENERGY

THE EVOLUTION OF PHOTOSYNTHESIS

$3-4\ 10^9$ a BC

BUILD-UP OF SELF-REPRODUCING SPECIES

BACTERIA LIVING ON GEOCHEMICAL RESOURCES

$2-3\ 10^9$ a BC

FIRST ENERGY CRISIS:

GEOCHEMICAL RESOURCES EXHAUSTED

USE OF NEW ENERGY SOURCES → SUNLIGHT

BUILD-UP OF PHOTOSYNTHETIC SPECIES

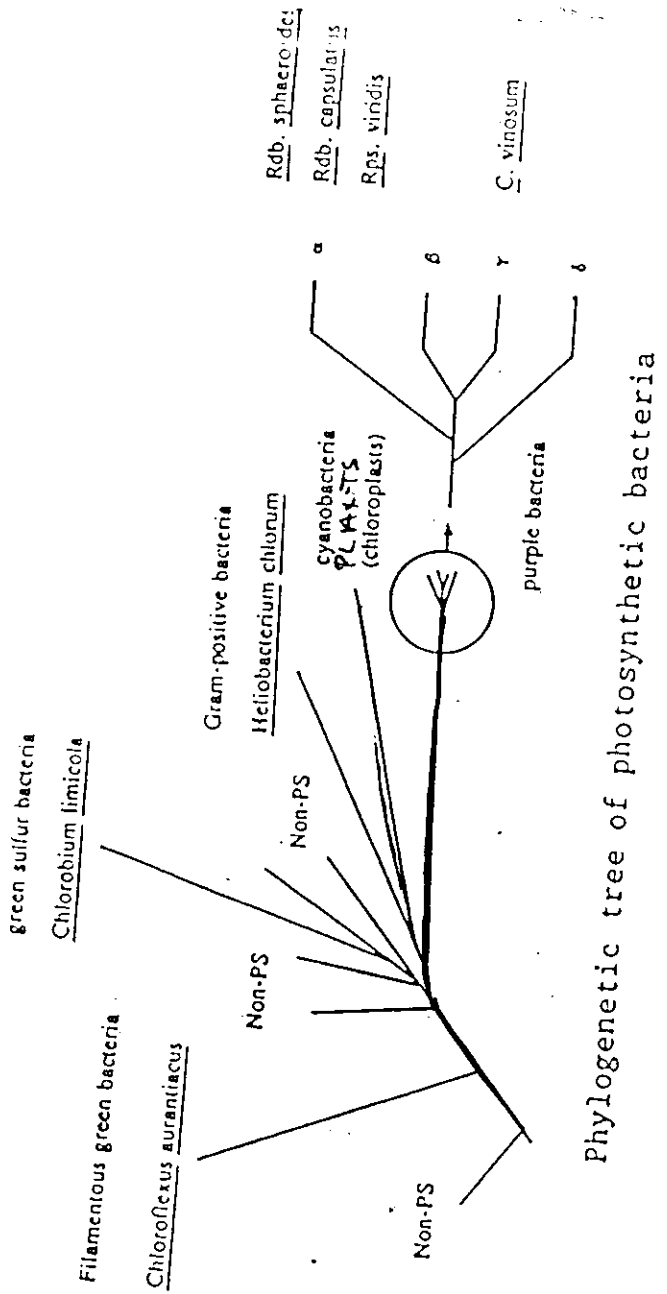
→ POISONING OF THE ATMOSPHERE BY O_2

→ ATMOSPHERE BECOMES OXIDIZING

→ MANY SPECIES DIE

→ BUILD-UP OF LARGE CARBON RESERV (COAL, PETROLEUM)

BUILD-UP OF SPECIES "BURNING" PHOTOSYN. MATERIAL BY OXIGEN



Phylogenetic tree of photosynthetic bacteria

1900 - 2000 a. AC (TODAY)

- SECOND ENERGY CRISES:
  FOSSILE RESOURCES EXHAUSTED
- OVERPRODUCTION OF CO_2
- DESTRUCTION OF FORESTS

→ INCREASE OF ATMOSPHERIC CO_2

→ GREEN-HOUSE-EFFECT
GLOBAL TEMPERATURE CHANGE

DEVELOPMENT OF REGENERATIVE ENERGY SYSTEMS

E.G. USE OF PHOTOSYNTHETIC SYSTEMS

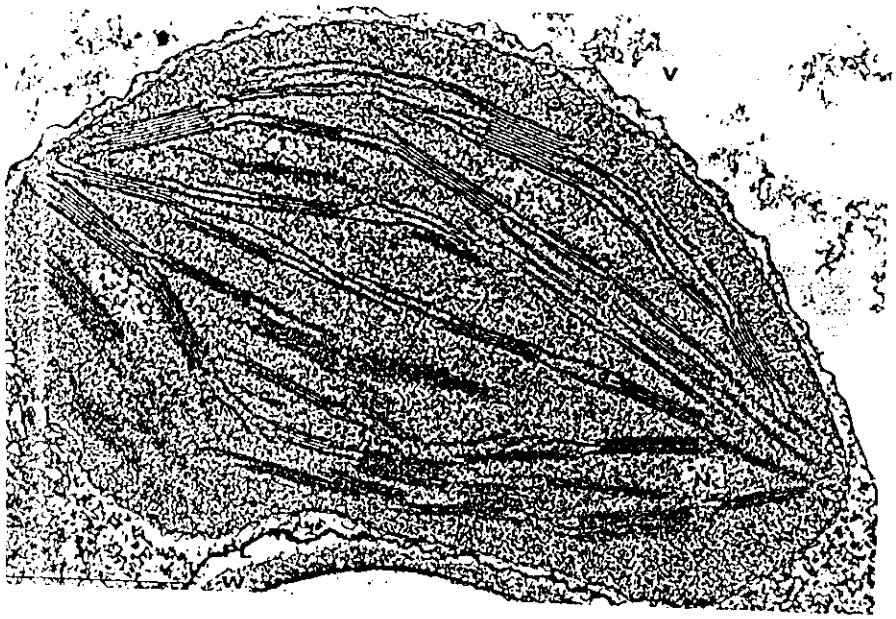


Fig. 1. Section of *Rhodopseudomonas sphaeroides* after semi aerobic culture in the dark. Cell has a few distinguishable chromatophores, but is packed with numerous poly β hydroxybutyrate (PHB) granules. Bar represents 0.2 μm. Reprinted from Peters and Cellarius (1972) by permission.

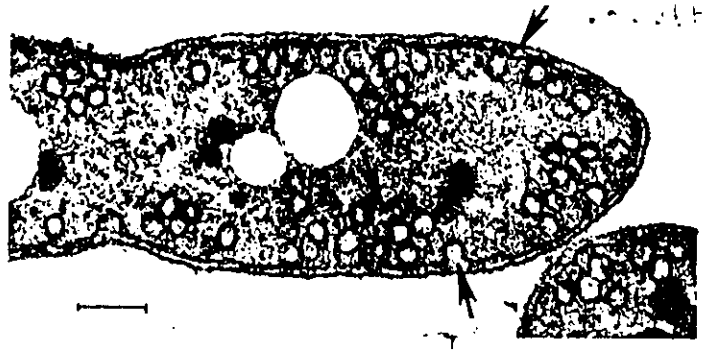


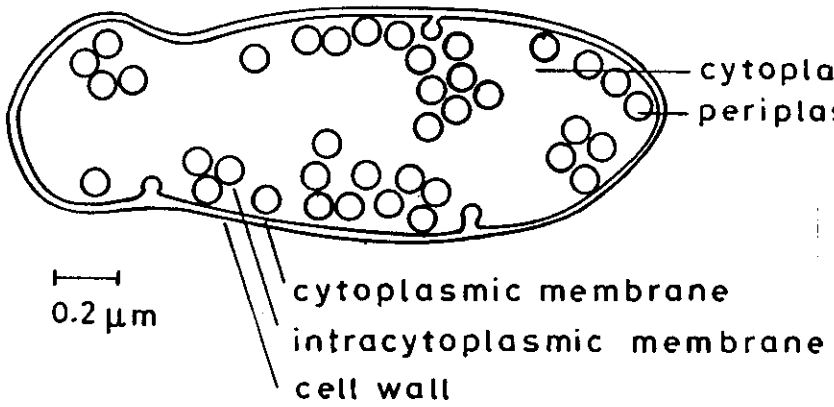
Fig. 2. Section of *Rhodopseudomonas sphaeroides* grown anaerobically at moderate light intensity. Areas of chromatophore continuity with the cytoplasmic membrane and proliferating vesicles are indicated by arrows. Bar represents 0.2 μm. Reprinted from Peters and Cellarius (1972) by permission.

vesicular or tubular invaginations and extends inward in the form of connected vesicles and bulged tubes (Holt and Marr, 1965*a–c*; Peters and Cellarius, 1972; Drews and Giesbrecht, 1963; Cohen-Bazire and Kunisawa, 1963; Boatman, 1964). Under aerobic conditions, intracytoplasmic membrane development is minimal (Fig. 1), since growth is achieved through oxidative metabolism and the extent of Bchl synthesis is determined by the oxygen partial pressure. When cells are grown anaerobically at moderate light intensities, however, the vesicular intracytoplasmic membrane system becomes well developed (Fig. 2). The Rhodospirillaceae that have this type of intracytoplasmic membrane system include *Rp. capsulata*, *Rp. globiformis*, *Rp. sphaeroides*, and *Rhodospirillum rubrum*.

When these vesicular chromatophores were first observed, it was suggested that they were free cytoplasmic organelles, i.e., that they were discrete and not continuous with the cytoplasmic membrane (Vatter and Wolfe, 1958). However, it was demonstrated quite clearly by subsequent investigators (Cohen-Bazire and Kunisawa, 1963; Drews and Giesbrecht, 1963; Holt and Marr, 1965*a–c*; Boatman, 1964; Peters and Cellarius, 1972) that this is not the case. The vesicles first appear as simple membrane protrusions, which then invaginate and become constricted, resulting in a stalked, more-or-less spherical vesicle that is open at the cell-wall end (Fig. 3). Finally, these vesicles penetrate more deeply into the cytoplasm of the cell, often assuming a tubular appearance, and proliferate into a branched network (Fig. 4). New protrusions

from Clayton: the photosynth. bacteria

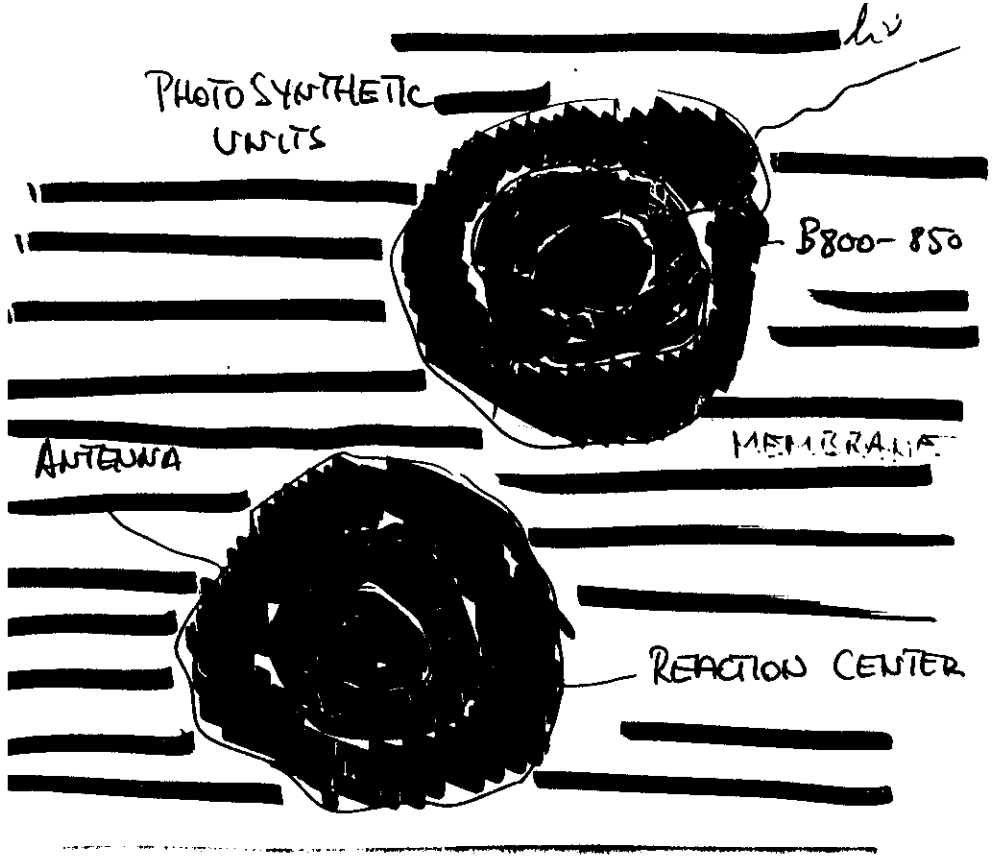
Rb. sphaeroides



BASIC FUNCTIONS OF PHOTOSYNTHETIC SYSTEMS:

LIGHT ABSORPTION: ANTENNA

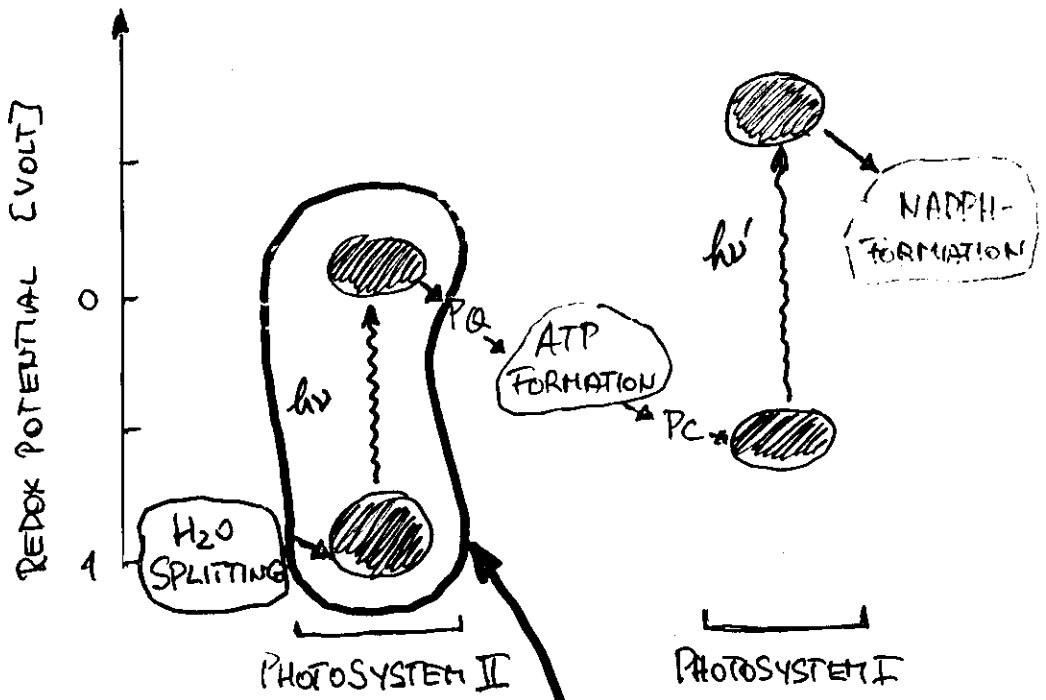
ENERGY CONVERSION: REACTION CENTERS



REACTION SCHEME OF CHLOROPHYLL-MEDIATED PHOTOSYNTHESIS

$$6\,CO_2 + 6\,H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\,O_2$$

PLANTS



PLANTS: COMPLEX REACTION SCHEME WITH TWO REACTION-CENTERS ≙ PHOTOSYSTEM I + II
USE H_2O AS ELECTRON SOURCE

BACTERIA: USE H_2S AS ELECTRON SOURCE
SIMPLIFIED SCHEME:

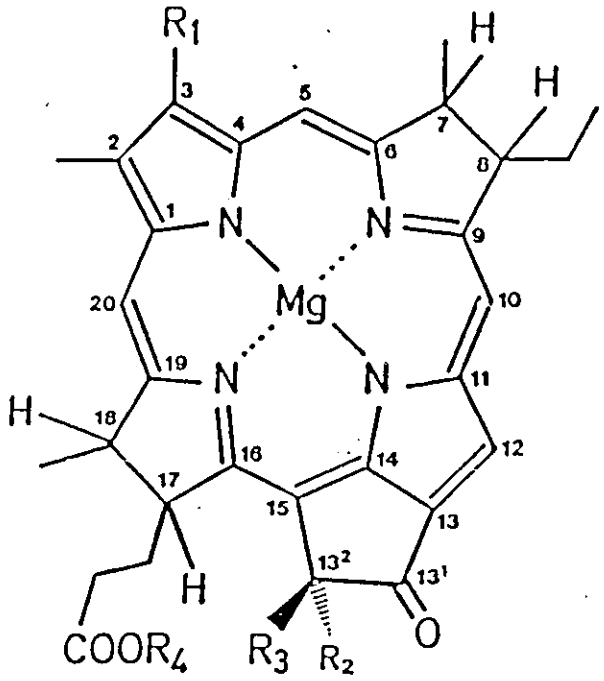
1 REACTION CENTER ≙ PHOTOSYSTEM I

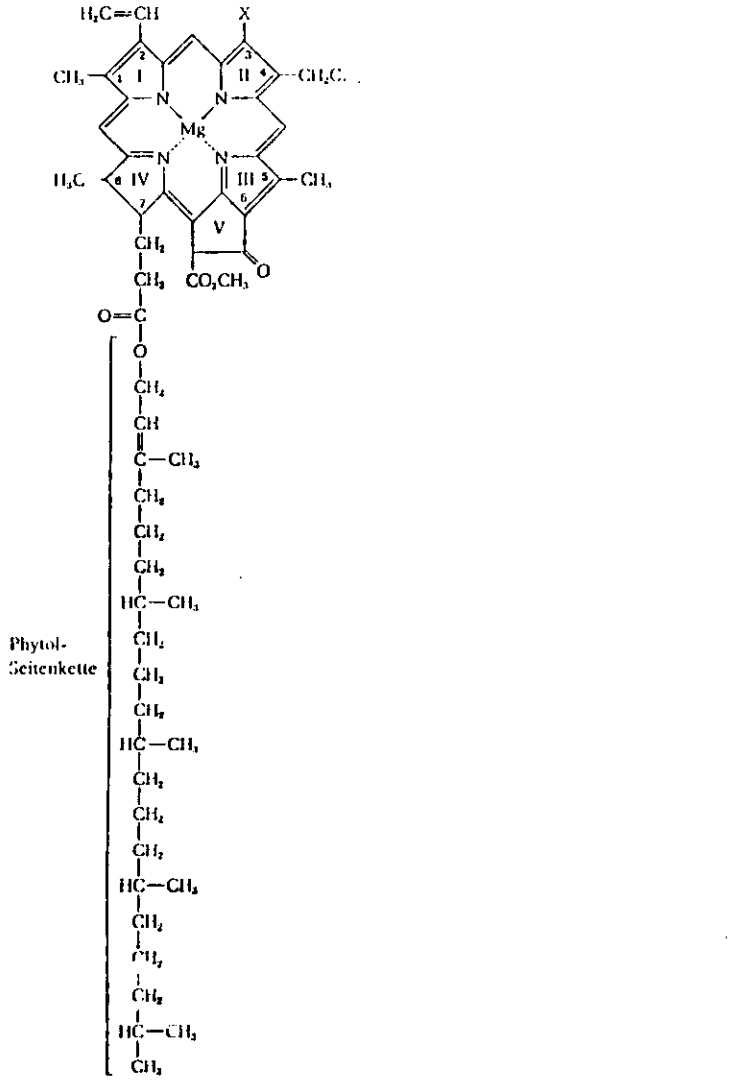
PROPERTIES OF THE REACTION CENTERS:

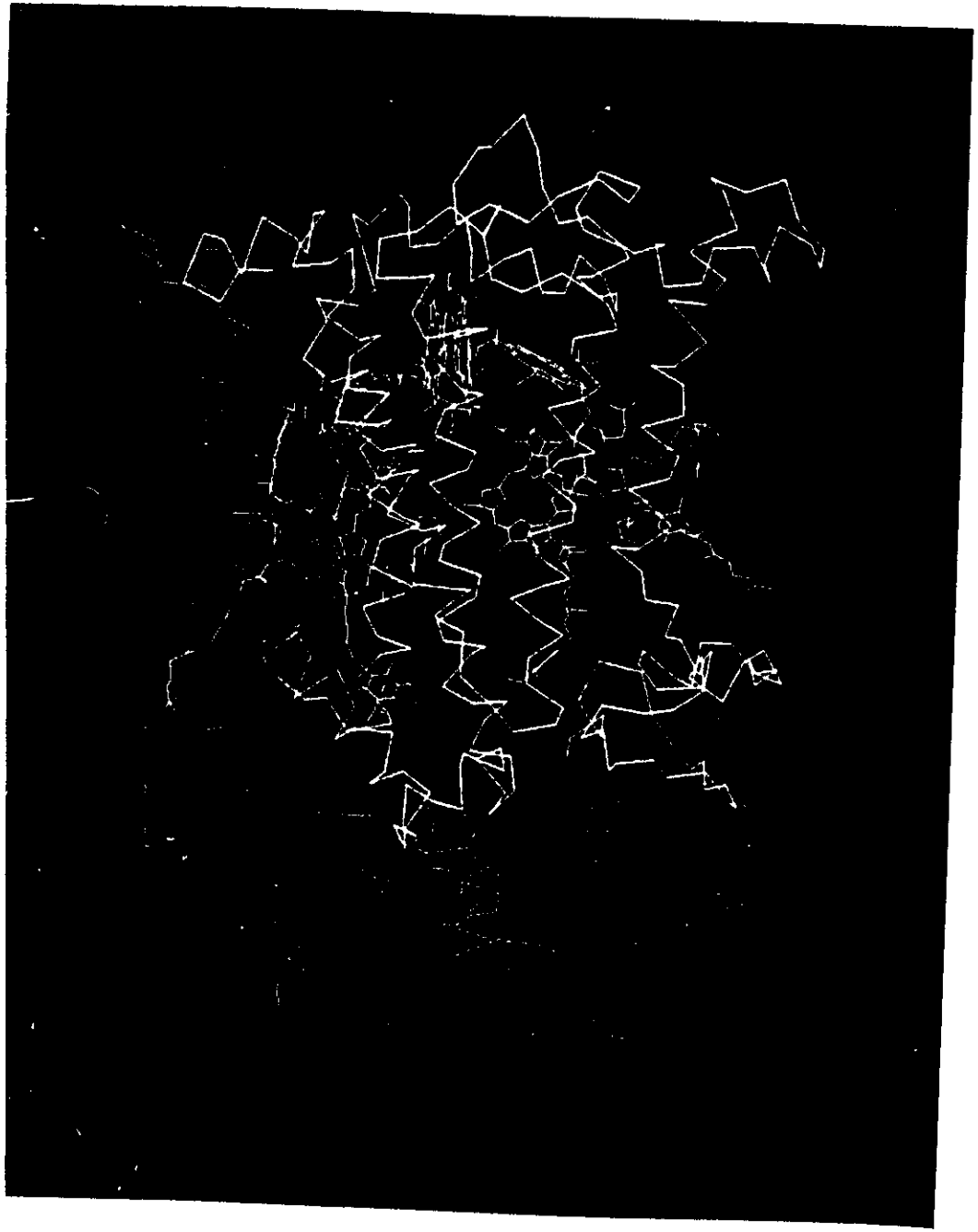
- MEMBRANE PROTEIN
- WEIGHT ~ 100 000 D
- 3-4 PROTEIN SUBUNITS
- 4 BACTERIOCHLOROPHYLLS
- 2 BACTERIOPHEOPHYTINS
- 2 QUINONS

FUNCTION:

LIGHT/ENERGY ABSORPTION
CHARGE SEPARATION
CHARGE TRANSFER

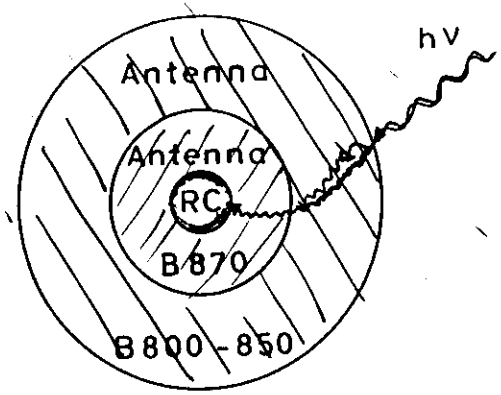

R1
H
H
Mg
N
N
N
N
H
H
COOR4
R3
R2
O

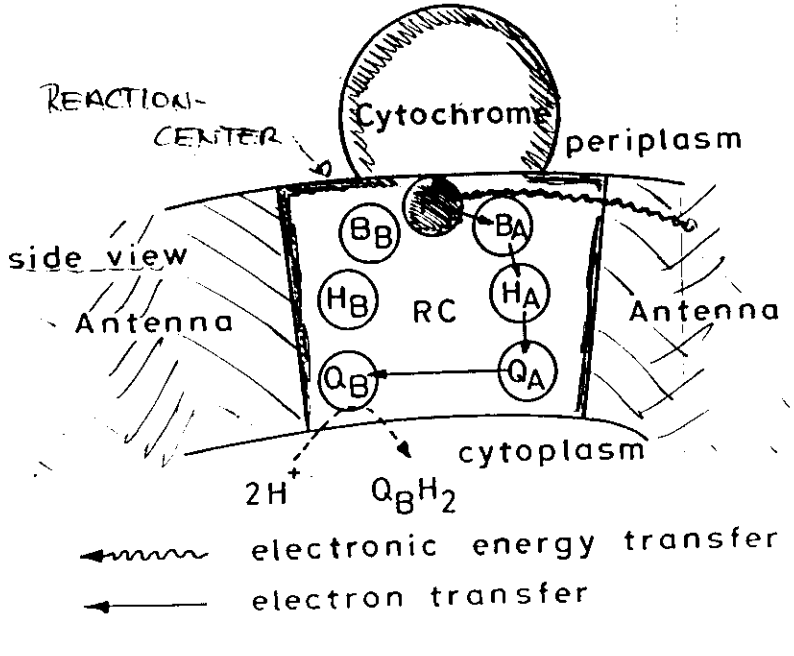

Phytol-
Seitenkette

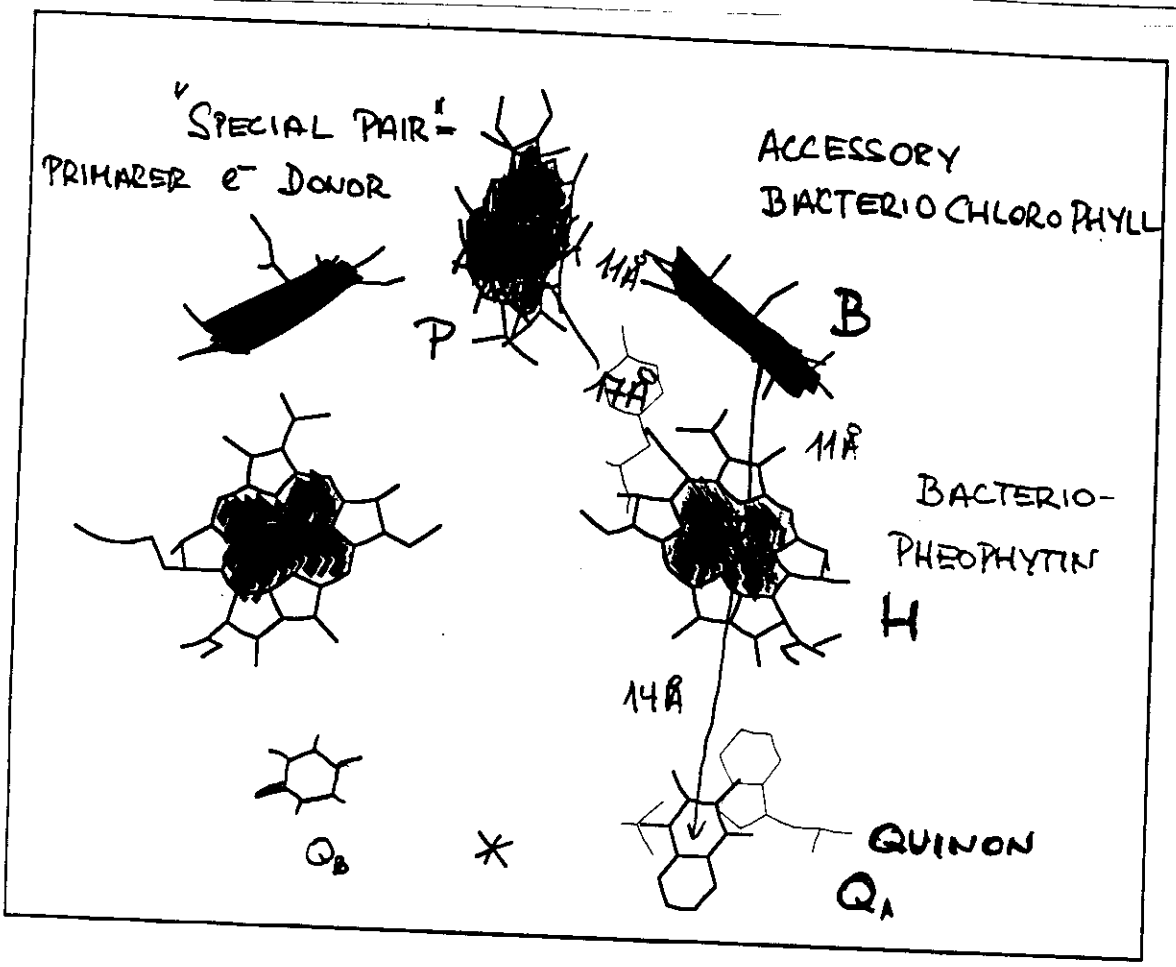


(intra) cytoplasmic membrane

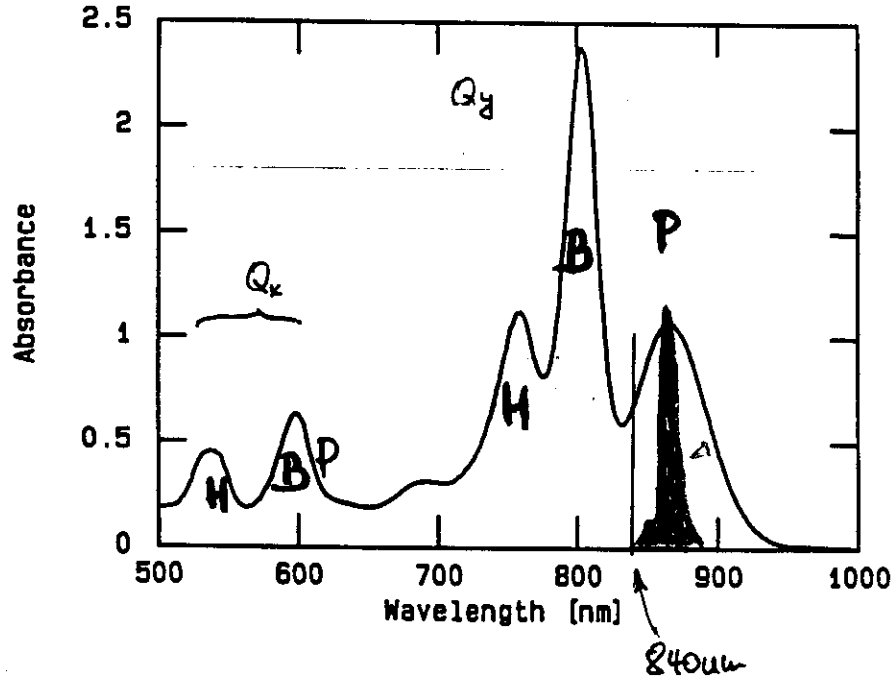
top_view







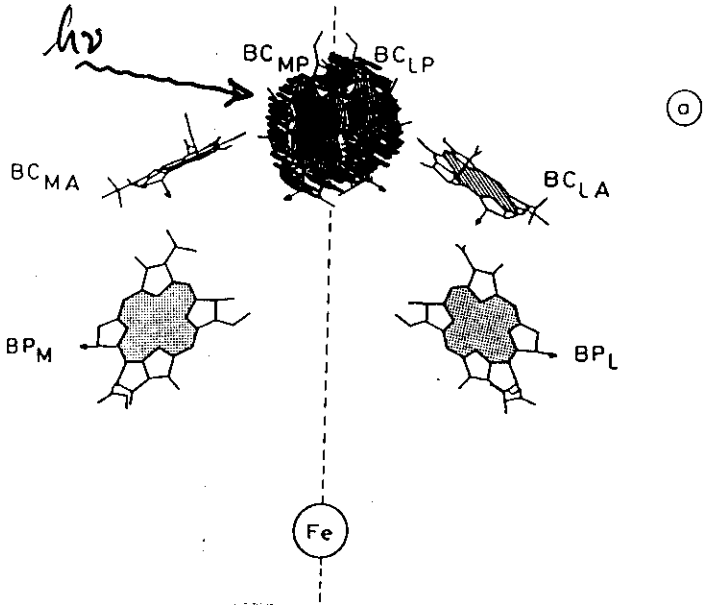
SPECTRUM OF REACTION CENTER FROM RHODOBACTER SPHAEROIDES



SPECTRUM OF THE EXCITATION PULSE

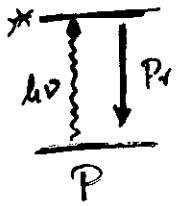
THE FIRST REACTION:

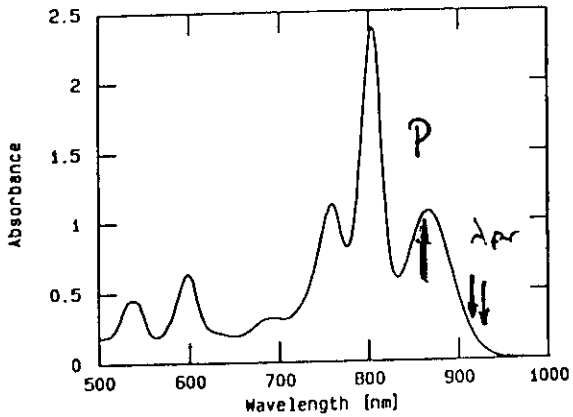
EXCITATION AND DECAY OF THE EXCITED ELECTRONIC LEVEL OF THE PAIR:

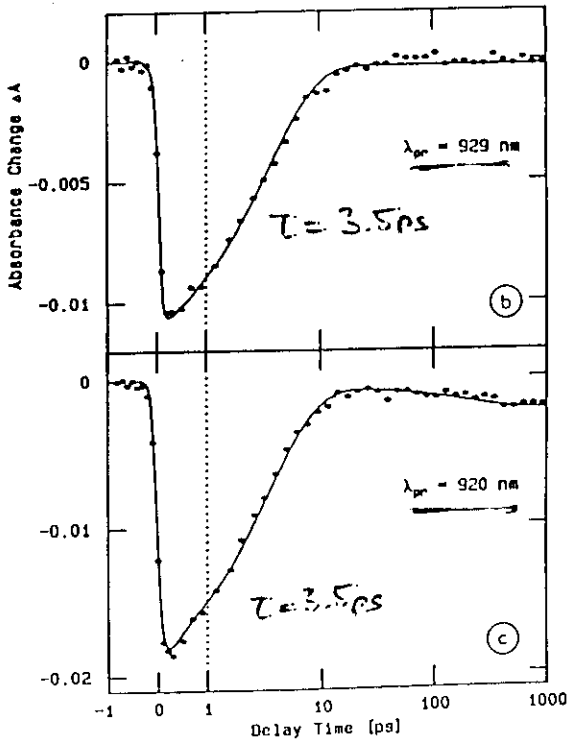


DETECTION: GAIN IN THE LONGWAVE-SIDE OF THE SPECIAL PAIR ABSORPTION BAND

THE LIFE-TIME OF THE EXCITED ELECTRONIC STATE P*:

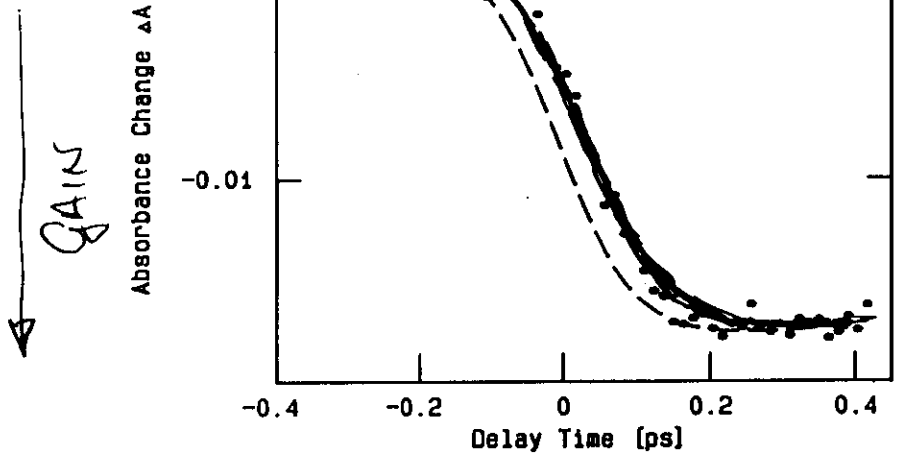






P* DECAYS NON EXPONENTIALLY

INSTANTANEOUS RESPONSE



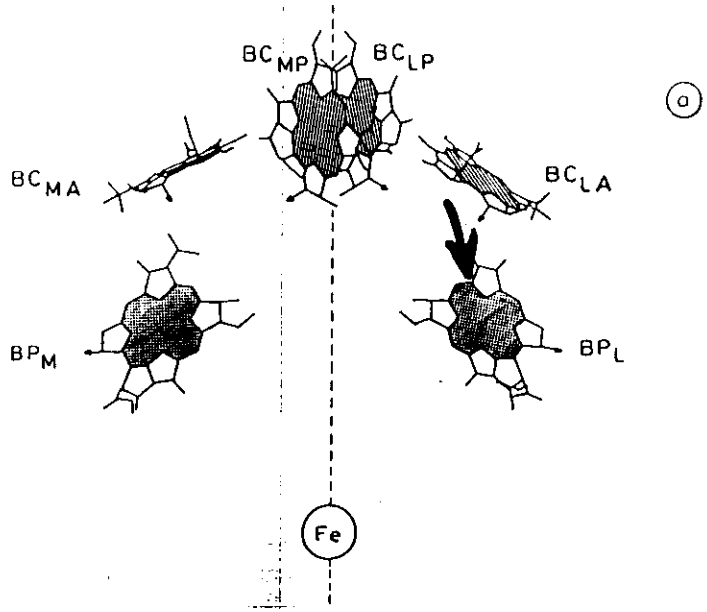
GAIN

AT 920nm

THE GAIN RISES DELAYED BY 40fs ⇒

VERY FAST S_1 REACTION OF THE SPECIAL PAIR

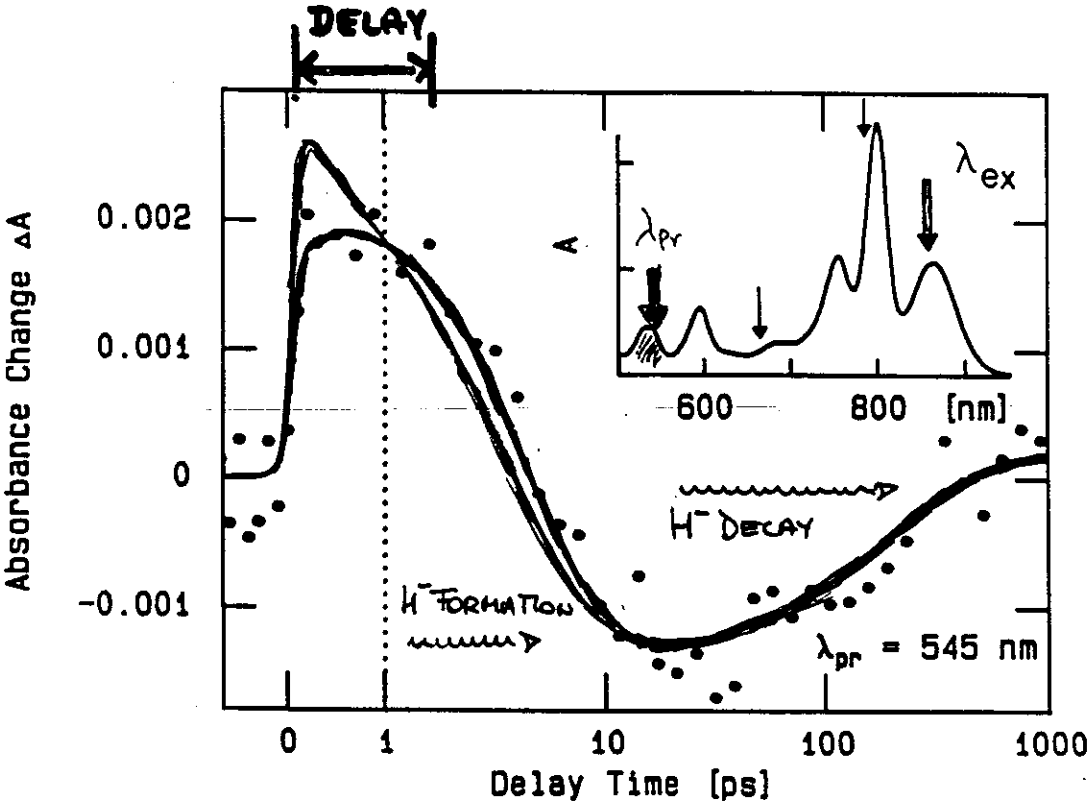
ARRIVAL OF THE ELECTRON AT THE BACTERIOPHEOPHYTINE:



DETECTION:

DISAPPEARANCE OF THE PHEOPHYTINE ABSORPTION BANDS!

REDUCTION OF THE BACTERIOPHEOPHYTIN H

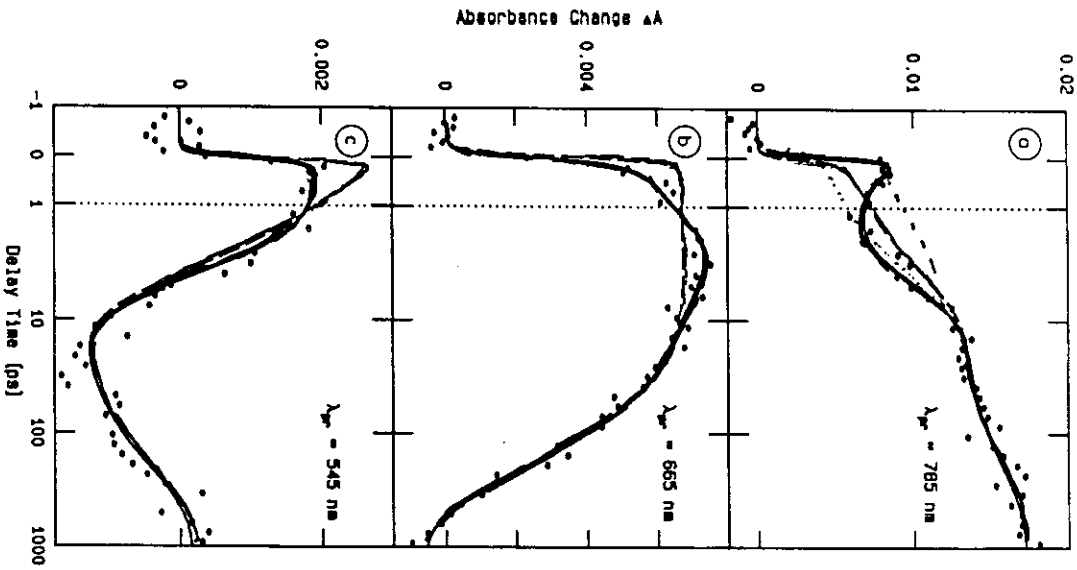


— KINETIK MODEL WITH $\tau_1 = 3.5$ps ; $\tau_2 = 200$ps

— KINETIK MODEL WITH $\tau_1 = 3.5$ps, $\tau_2 = 0.9$ps, $\tau_3 = 200$ps

— TWO STATE MODEL $\tau_1 = 2.5$ps, $\tau_2 = 200$ps

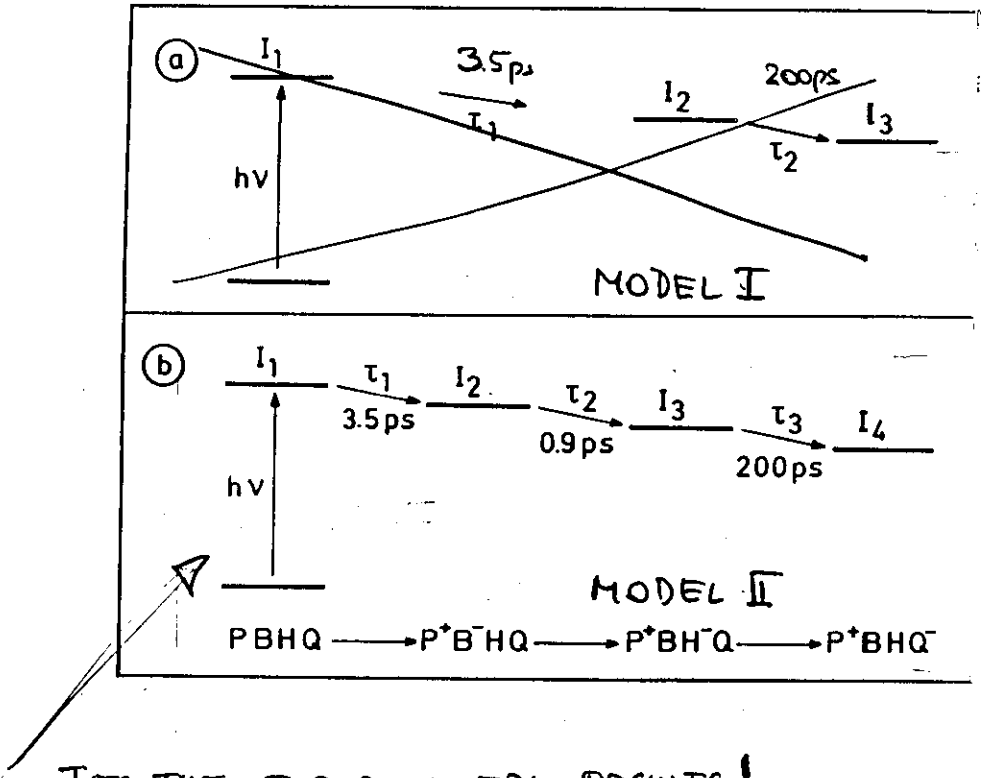
— THREE STATE MODEL $\tau_1 = 3.5$ps, $\tau_2 = 0.9$ps, $\tau_3 = 200$ps



THE SHORT-LIVED PRECURSOR OF P^+H^-

MODEL I

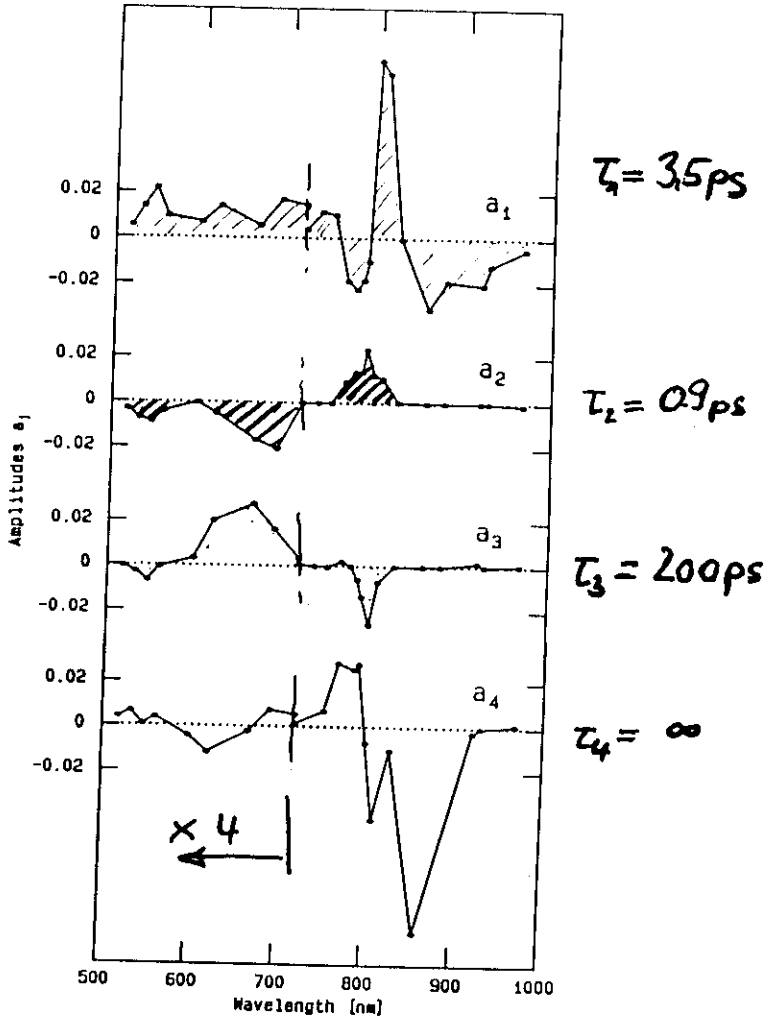
DOES NOT EXPLAIN THE EXPERIMENTS



FITS THE EXPERIMENTAL RESULTS!

WHAT IS THE MOLECULAR BACKGROUND?

FIT - AMPLITUDES



$\tau_1 = 3.5ps$

$\tau_2 = 0.9ps$

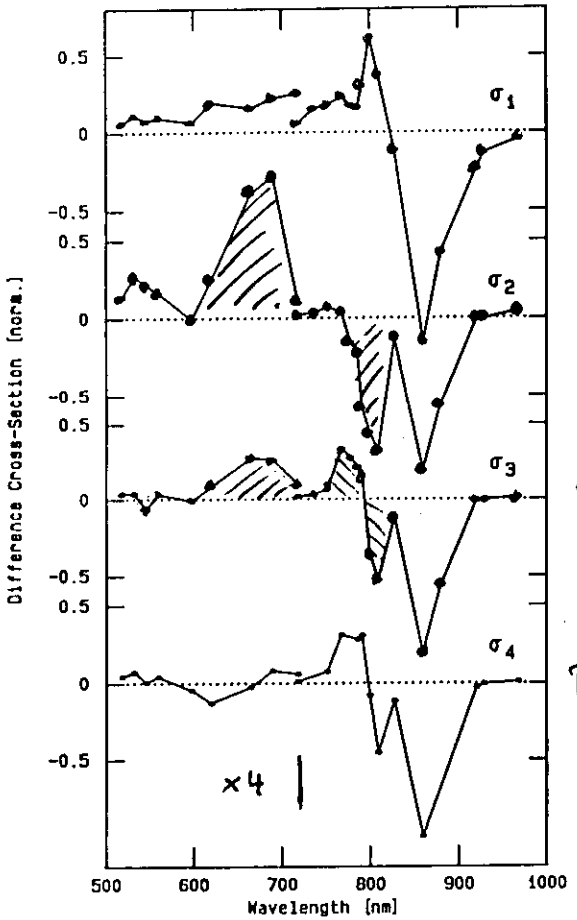
$\tau_3 = 200ps$

$\tau_4 = \infty$

ONLY ONE ASSUMPTION:

THERE ARE FOUR KINETIC COMPONENTS!

THE DIFFERENCE SPECTRA OF THE INTERMEDIATES:



P^* 3.5ps

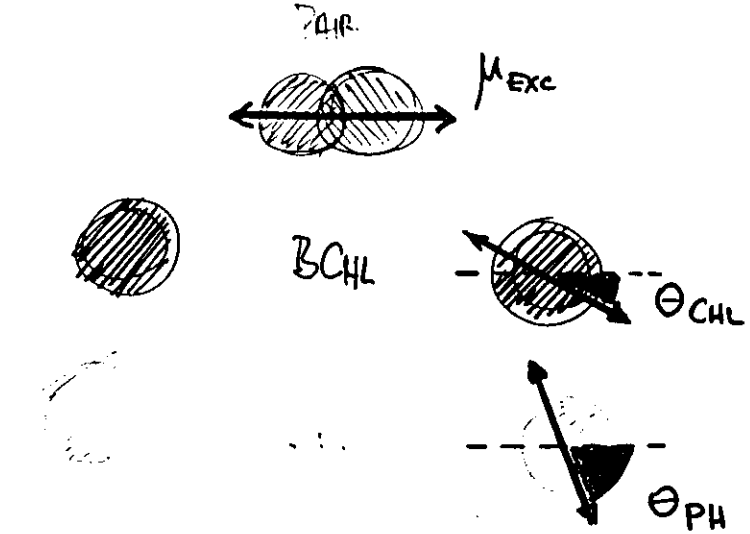
$P^+ B^-$ 0.9ps

$P^+ H^-$ 200ps

$P^+ Q^-$ ∞

$\vec{E}_{exc} \parallel \vec{E}_{probe}$

DIRECTIONS OF TRANSITION MOMENTS:



EXPERIMENT:

$E_{PR} \parallel E_{EXC} \rightarrow \Delta A_{\parallel}$ $E_{PR} \perp E_{EXC} \rightarrow \Delta A_{\perp}$

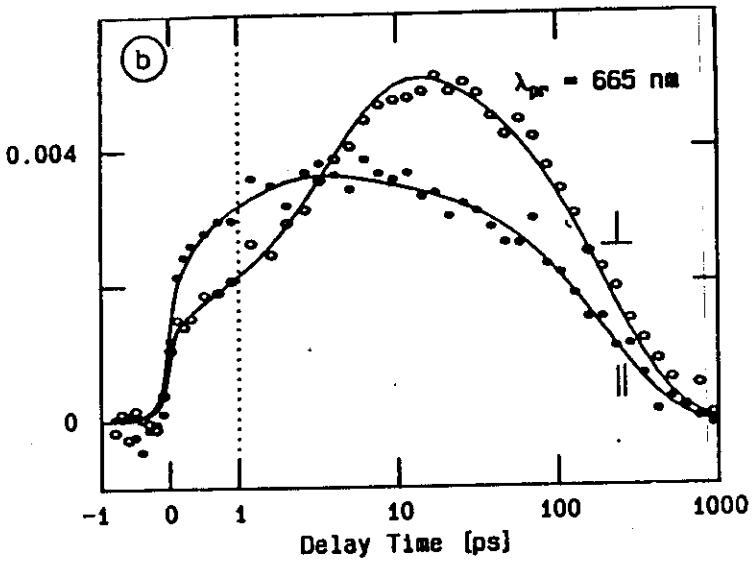
$\frac{\Delta\sigma_{\perp}}{\Delta\sigma_{\parallel}} = f(\theta)$

RECOMMENDED OBJECT:

REGIONS OF NEW BANDS

→ $\lambda \gtrsim 660$ nm

TRANSIENT DICHROISM:



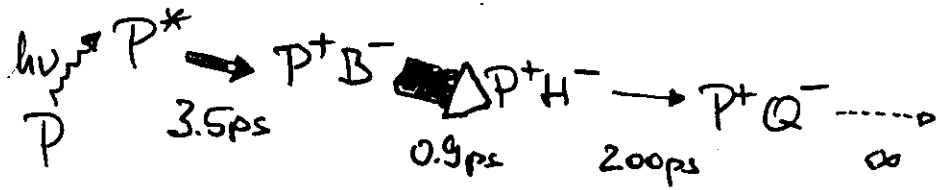
TRANSITION MOMENT ANGLES!

	CALCULATED	EXPERIMENTAL
$BCHL^{\ominus}$	29°	32° (18° – 39°)

$BCHL^{\ominus}$ AND $BPH^{\ominus}$ HAVE THE SAME ABSORPTION CROSS-SECTION AT 665 nm

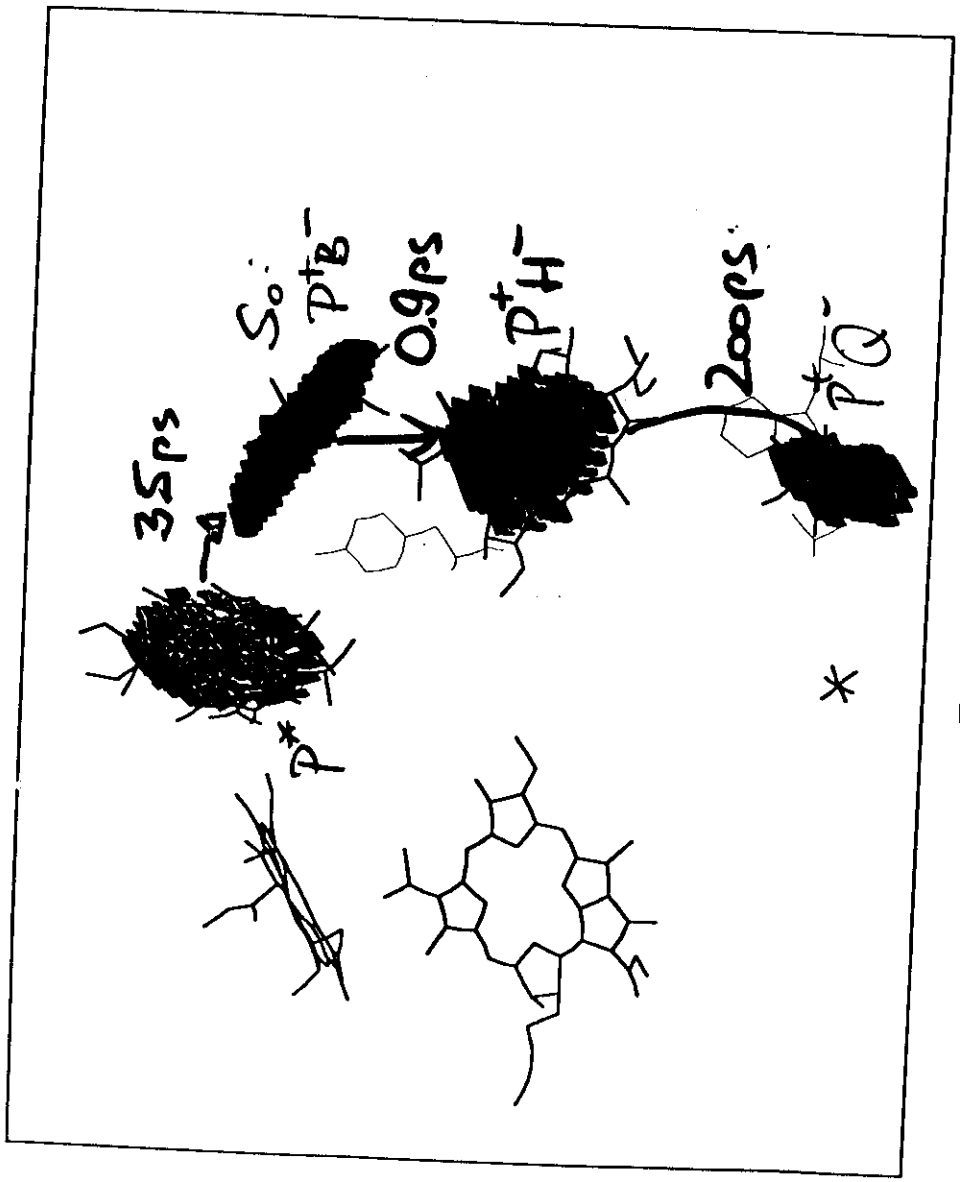
CONCLUSIONS FOR NATIVE REACTION CENTER

- THE PRIMARY PHOTOSYNTHETIC REACTION IN THE REACTION CENTERS OF RB. SPHAEROIDES INVOLVES FOUR INTERMEDIATES
- THE REACTION MODEL



EXPLAINS ALL EXPERIMENTAL DATA

WHAT IS THE MOLECULAR BACKGROUND OF THE ELECTRON TRANSFER?



THE MICROSCOPIC BACKGROUND OF THE ELECTRON TRANSFER

NON-ADIABATIC ELECTRONTRANSFER THEORY:

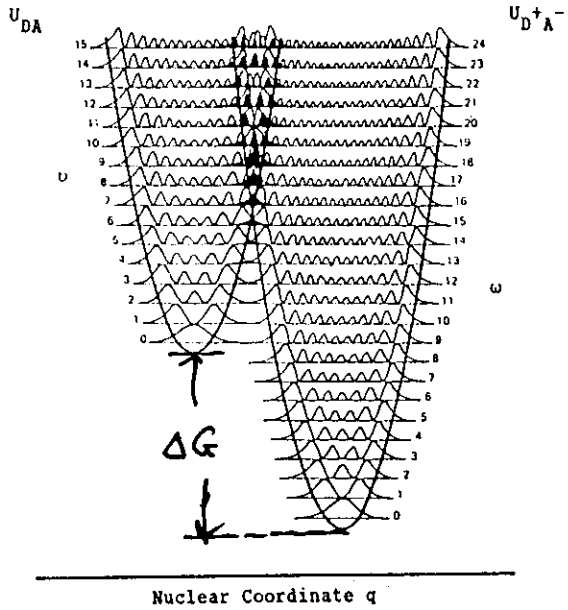
RATE $$k_{ET} = \frac{2\pi}{\hbar} |V|^2 F$$

V= ELECTRONIC COUPLING :
OVERLAPP OF ELECTRONIC WAVEFUNCTIONS

$V \propto \exp(-\Delta x \alpha)$

$\Delta x \rightarrow \Delta x + 2$ Å $\quad k_{et} \rightarrow 1/10\, k_{et}$

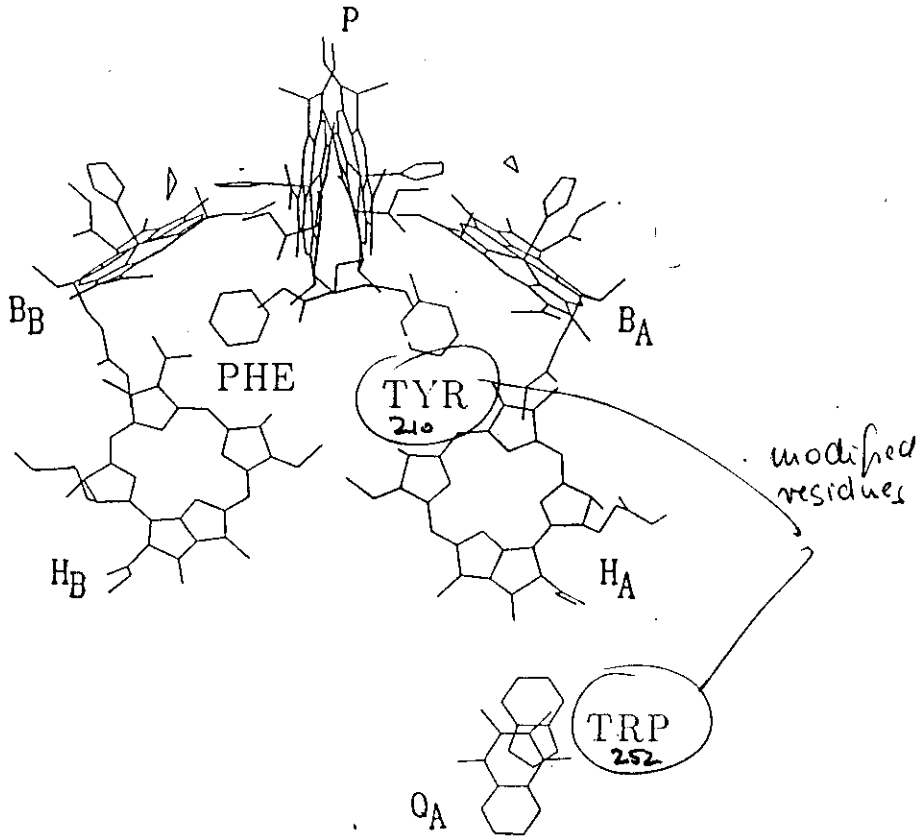
F= FRANCK – CONDON FACTOR
OVERLAPP OF NUCLEAR WAVEFUNCTION
ENERGETICS

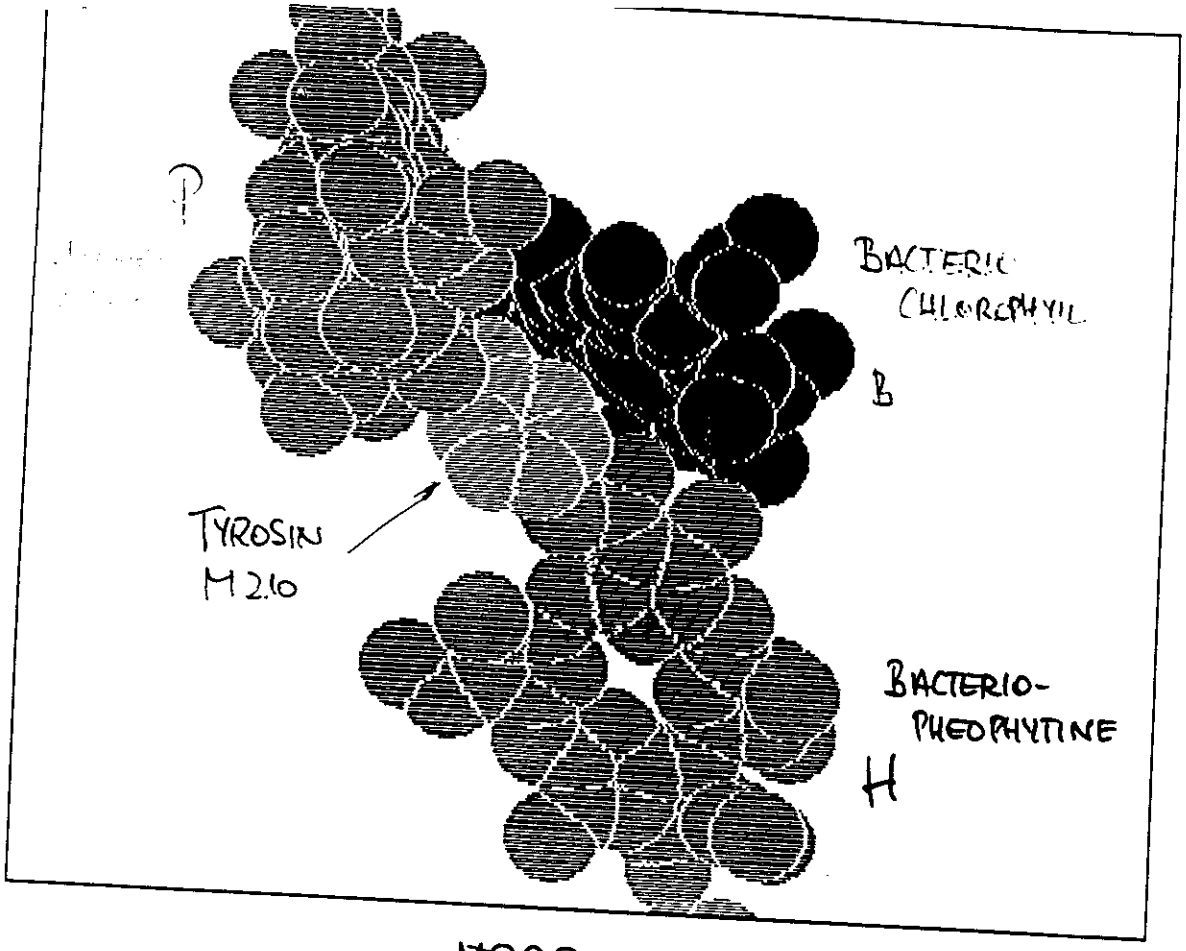


POSSIBLE MODIFICATIONS:

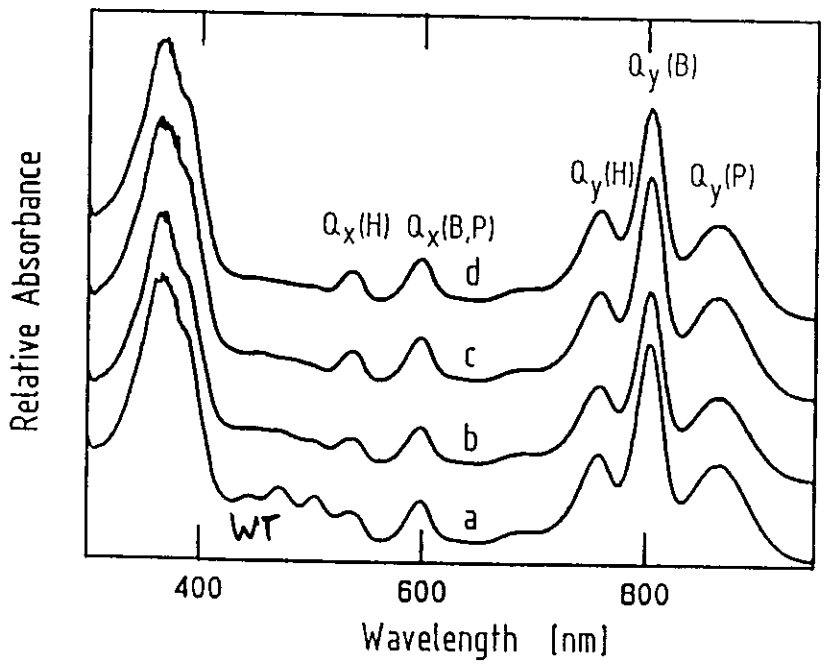
CHANGE OF V

CHANGE OF F

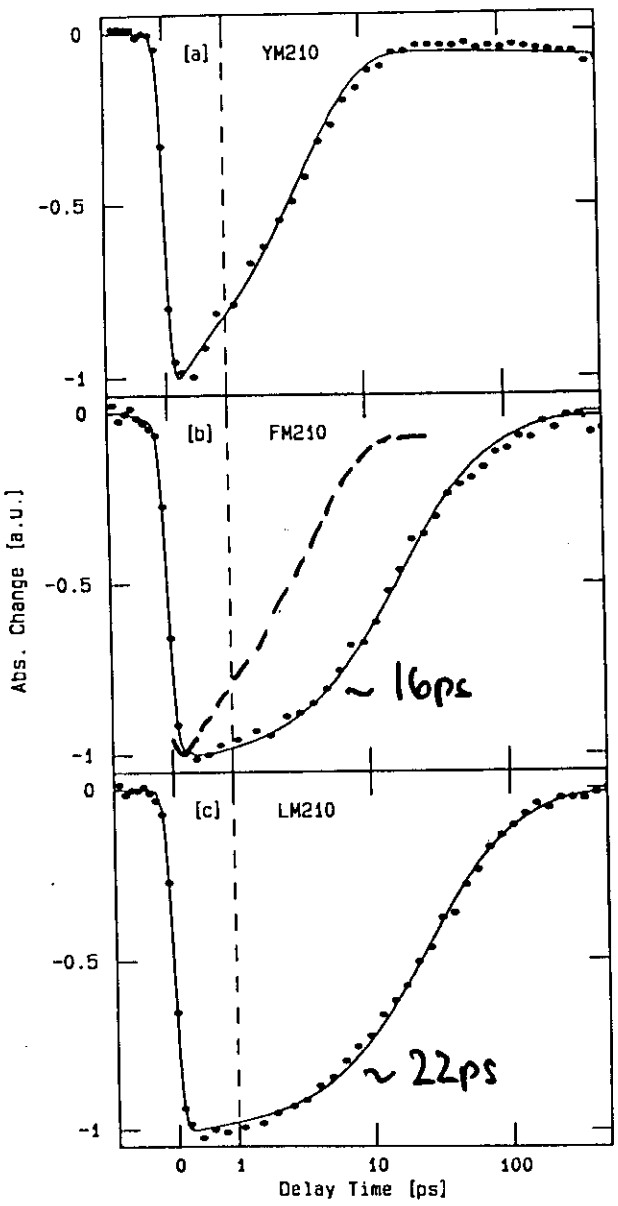



BACTERIO CHLOROPHYL
B
TYROSIN
M 210
BACTERIO-
PHEOPHYTINE
H

M208

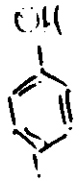

Relative Absorbance
Q_y(B)
Q_y(H)
Q_y(P)
Q_x(H) Q_x(B,P)
d
c
b
a
WT
400
600
800
Wavelength [nm]

DECAY OF P^+ $\lambda_{PR} = 420$ nm



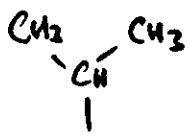
WILD TYPE

TYR.

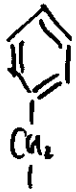


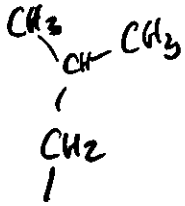
PHE

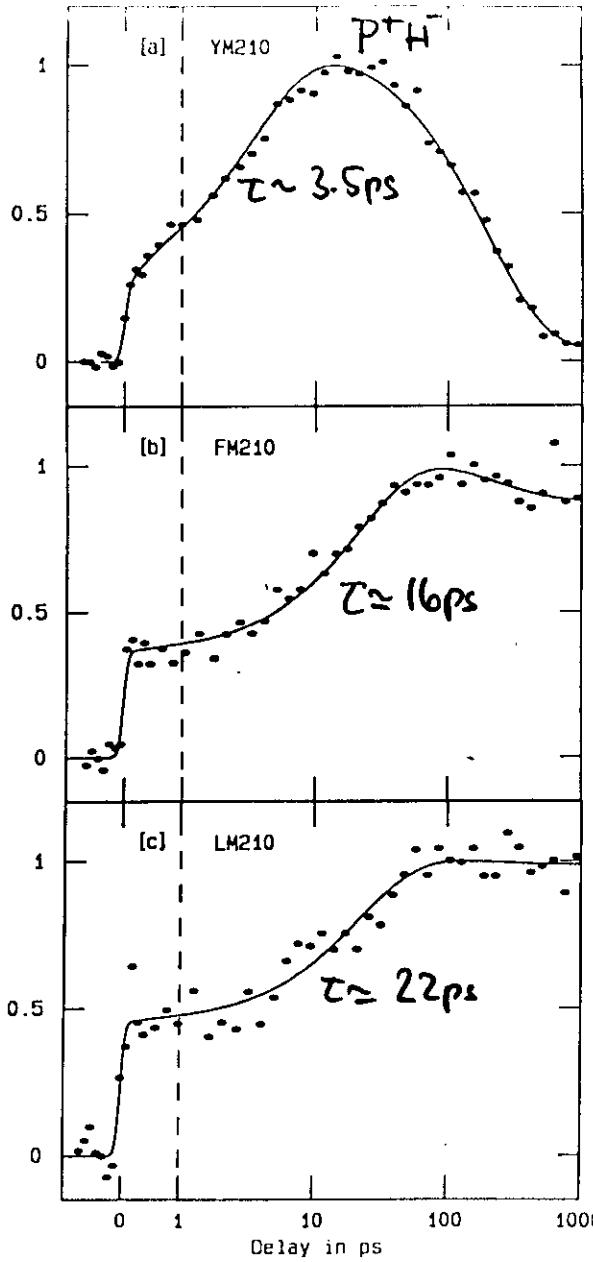
LEU



WILD TYPE





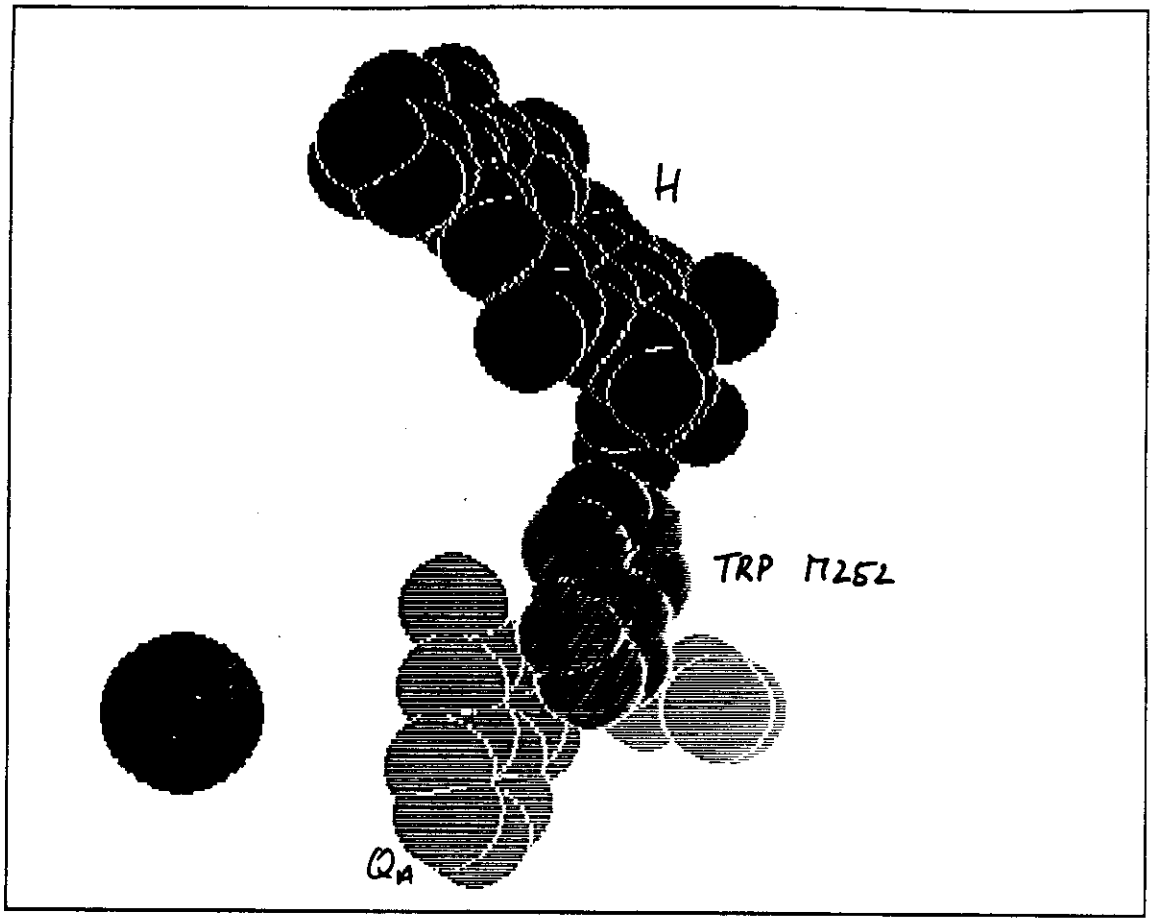


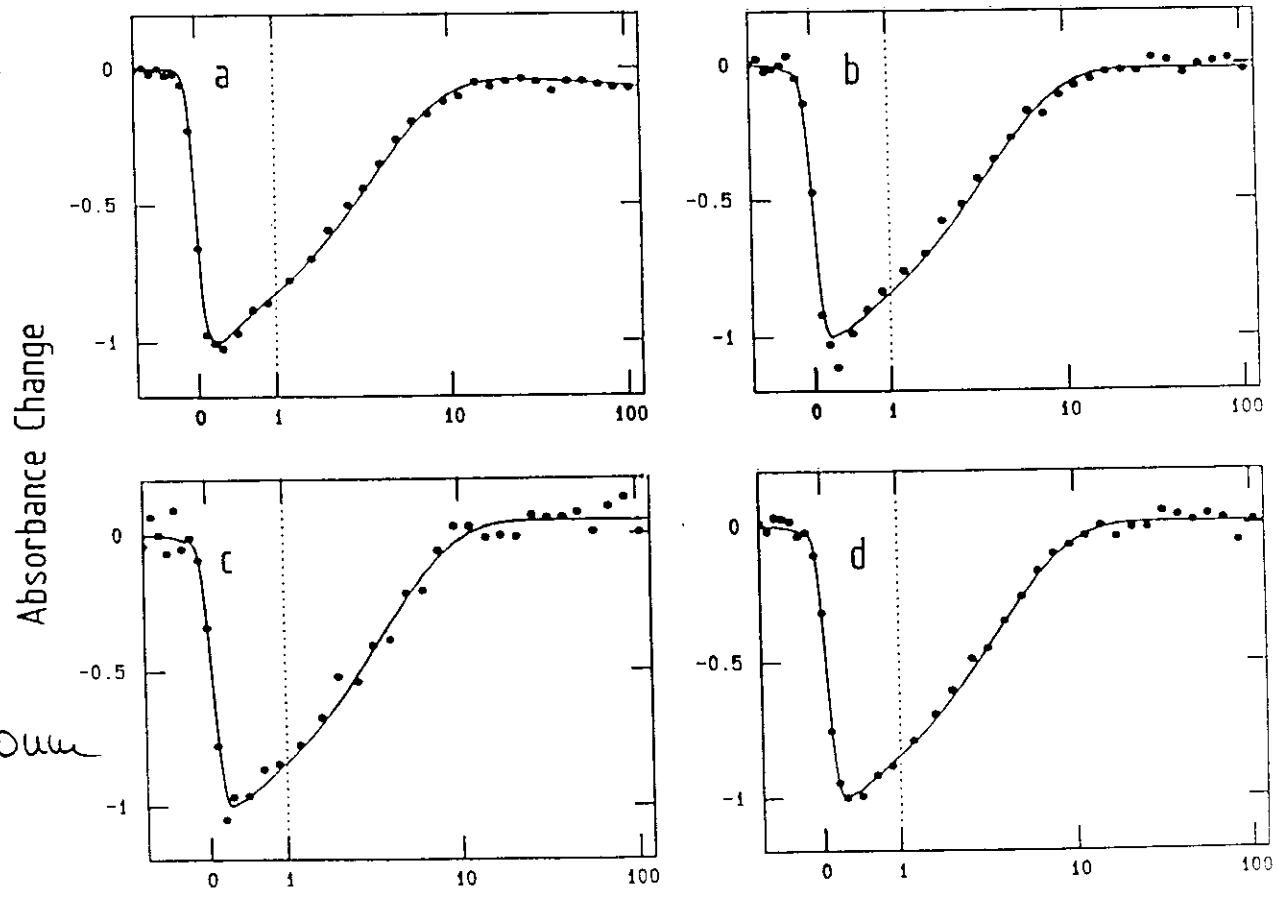
NO CHANGE OF ELECTRON OVERLAP

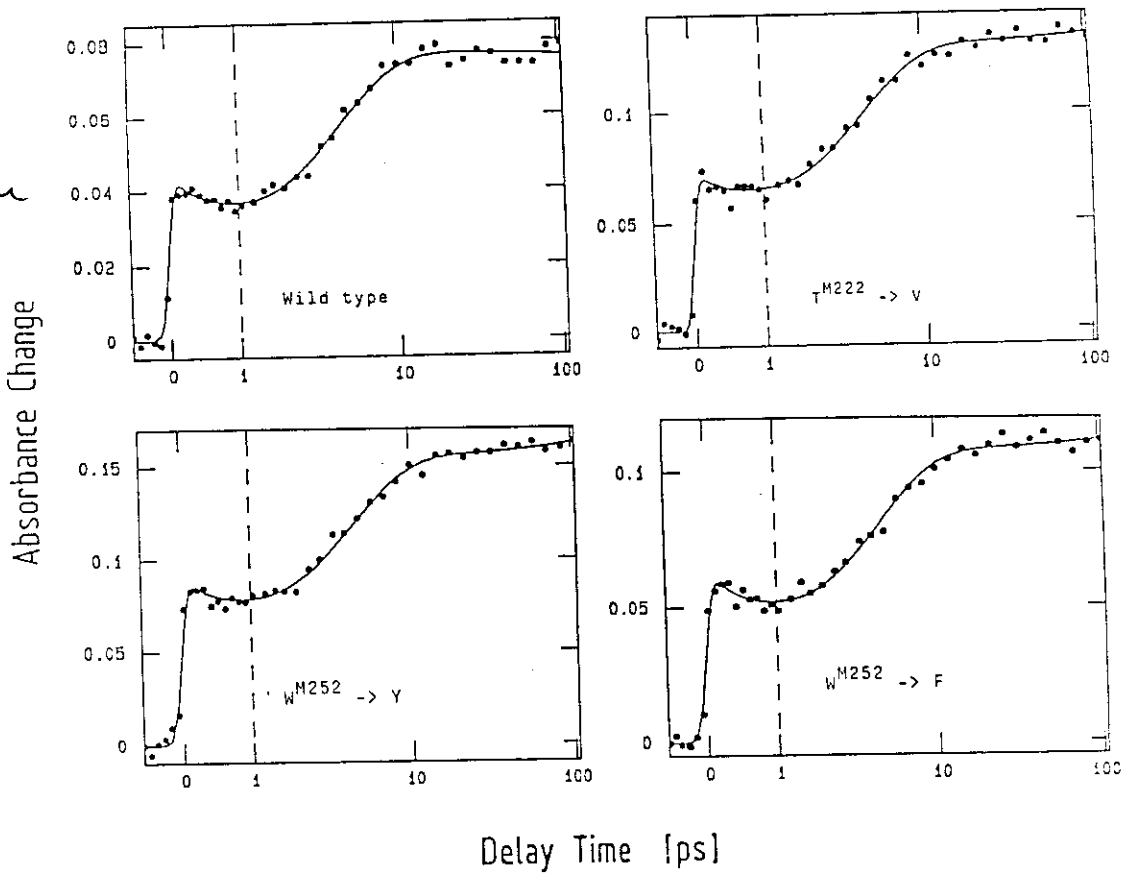
68

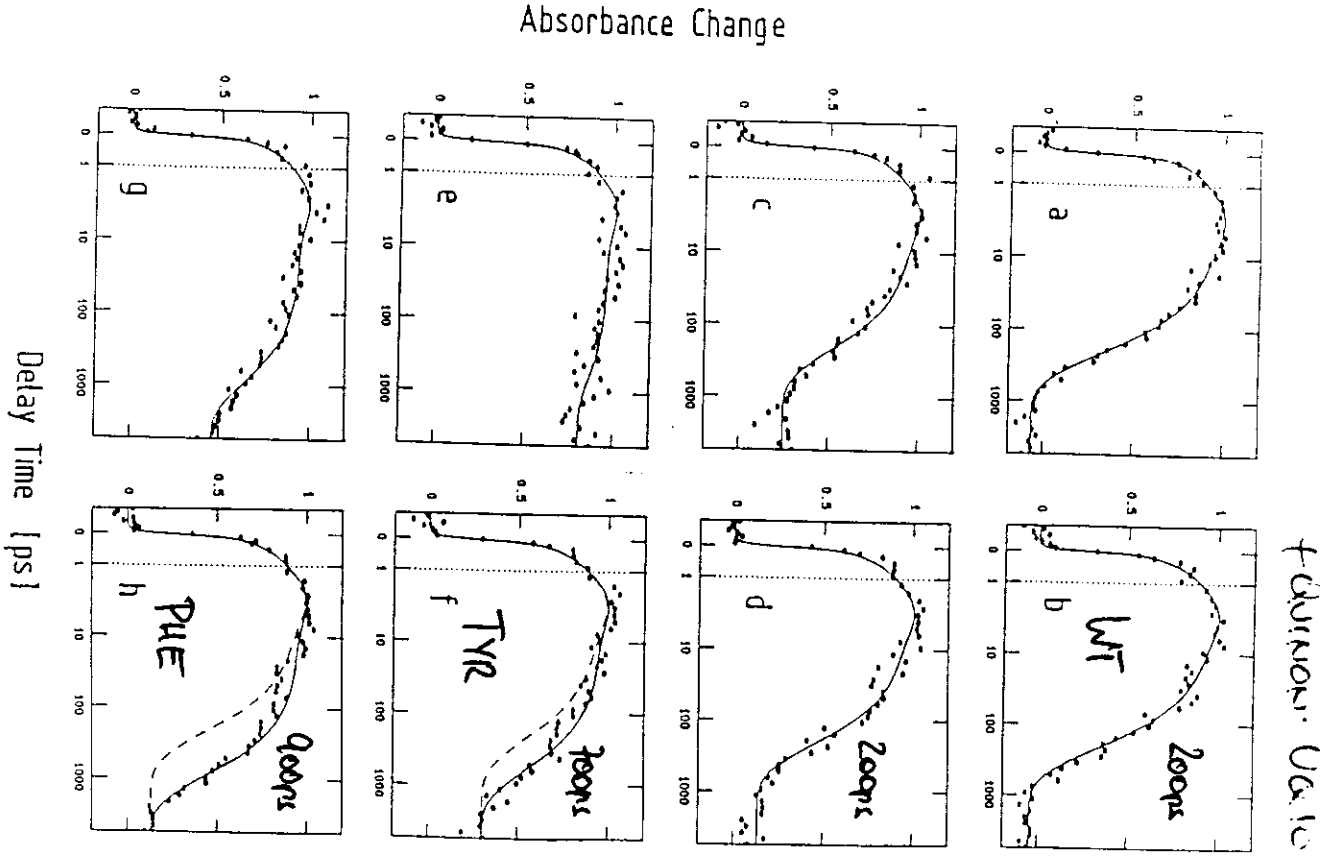
CHANGED ENERGETICS → CHANGED ET

69


H
TRP M252
Q_A


a
b
c
d
0
-0.5
-1
0
1
10
100
Absorbance Change
Delay Time [ps]


λ = 785 nm
Absorbance Change
Wild type
T M222 -> V
W M252 -> Y
W M252 -> F
Delay Time [ps]


Absorbance Change
Delay Time [ps]
a
b WT 200ps
c
d 200ps
e
f TYR 700ps
g
h PHE 900ps

λ = 660 nm

EXCHANGE OF TRP M252

CHANGE TO PHE, TYR

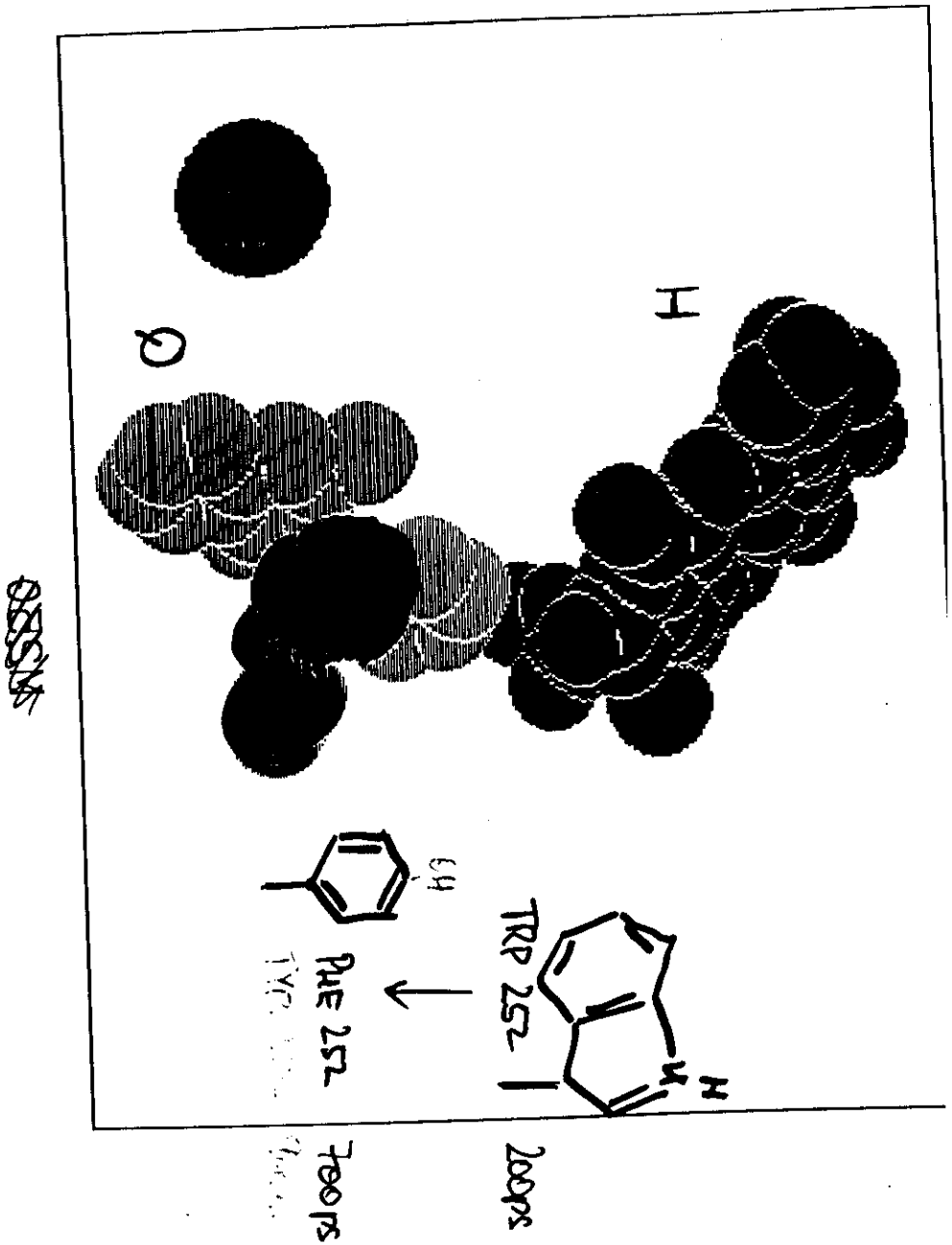
SMALLER ELECTRONIC OVERLAPP

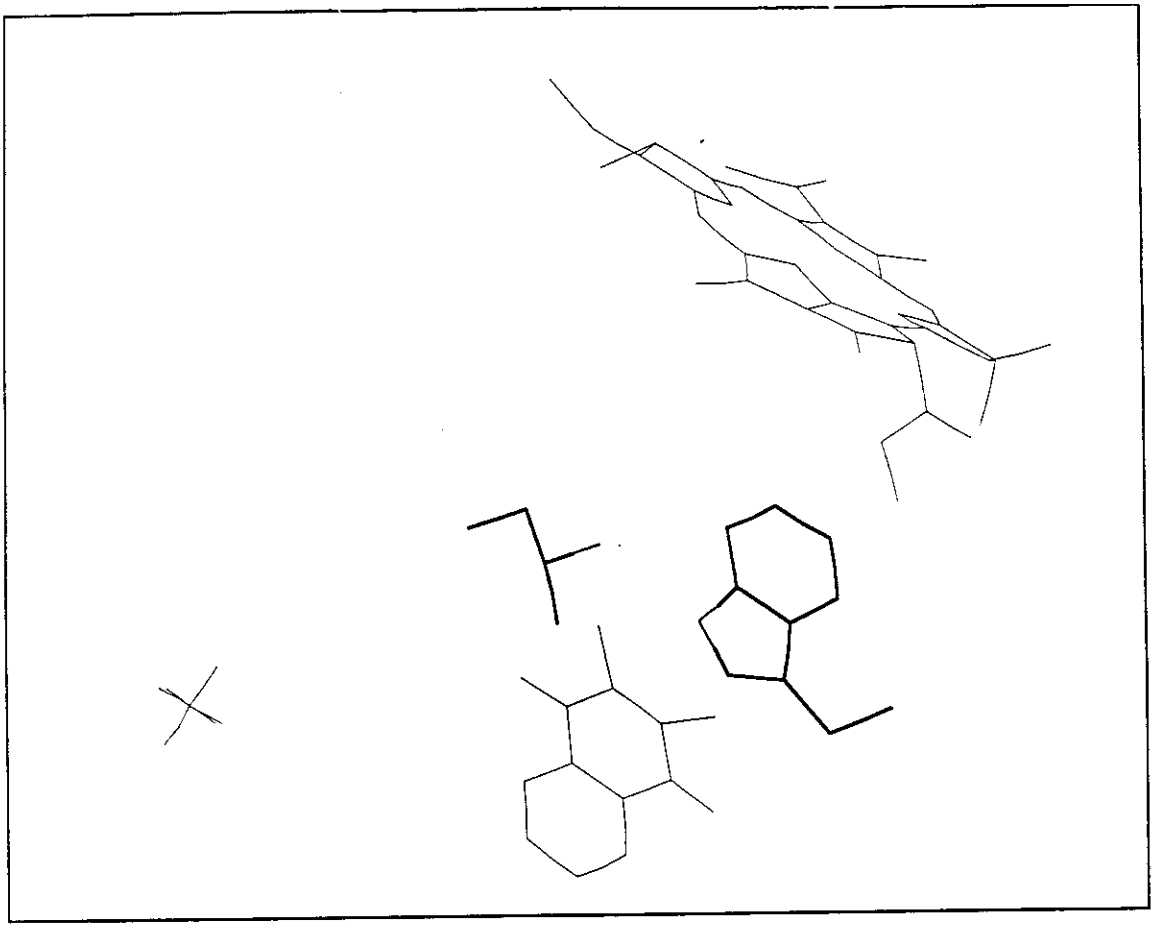
CHANGED ENERGETICS

SLOWING DOWN OF THE KINETICS:
$P^+I^- \rightarrow P^+Q^-$

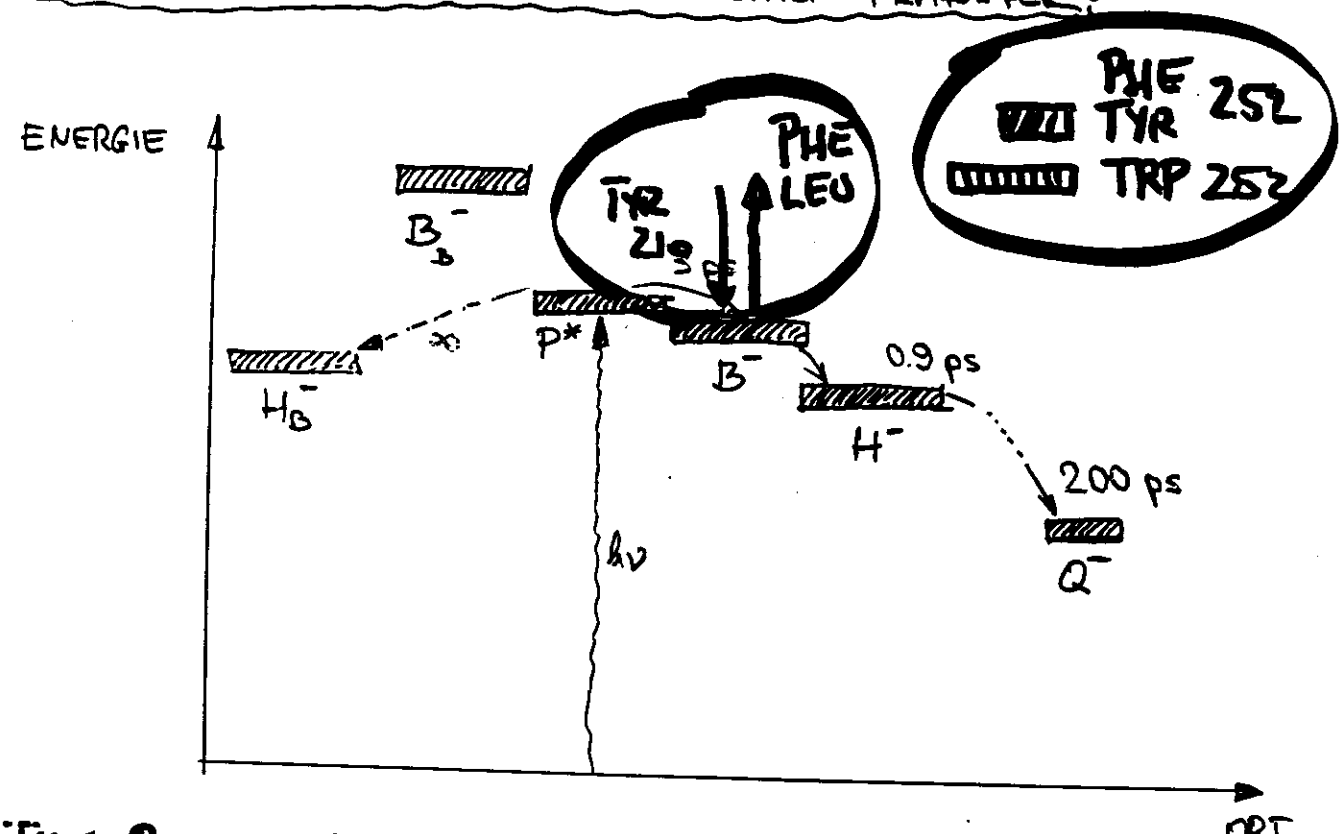
I (TRP)	200ps
TYR	900ps
PHE	700ps

CHANGE OF ELECTRONIC OVERLAPP
DOMINATE SLOWING DOWN OF ET





ENERGETICS OF THE PRIMARY ELECTRON TRANSFER:



THE ROLE OF SINGLE AMINOACIDS

THE PRIMARY REACTION –
AN OPTIMISED PROCESS:

	COMPETITION:
$A^* \longrightarrow P^*$	INTERNAL CONVERSION
ENERGY TRANSFER FROM ANTENNA	~ 500ps – 1ns
2.0 ps	
$P^* \longrightarrow P^+B^-$	– BACK TRANSFER TO ANTENNA
FIRST CHARGE SEPARATION	– INTERNAL CONVERSION ~200ps
3.5ps	1,5% Loss
$P^+B^- \longrightarrow P^+H^-$	FAST RECOMBINATION:
CHARGE TRANSPORT	~ 100ps
0.9 / 0.65 ps	1% Loss
$P^+H^- \rightarrow P^+Q^-$	RECOMBINATION + TRIPLETT FORMATION
220ps	~30 ns
	1% Loss
QUANTUM EFFICIENCY	$\geq$ 95%
ENERGY EFFICIENCY	$\geq$ 50%

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METHODS: W. KAISER (EDITOR):
ULTRASHORT LASER PULSES AND APPLICATIONS, SPRINGER 1988

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– J. DEISENHOFER, H. MICHEL
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SPRINGER SERIES IN BIOPHYSICS VOL 6. (1991)