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Contents

vii Preface

I. Generation of Pico- and Femtosecond Pulses

a) New Mode-Locking Techniques

- 1–8 Femtosecond laser sources for near-infrared spectroscopy
W Sibbett
- 9–14 Femtosecond pulse generation from solid-state lasers
Ch Spielmann, F Krausz, T Brabec, E Wintner and A J Schmidt
- 15–18 Coupled cavity mode-locking of a neodymium-doped fiber laser
C Unger, G Sargsjan, U Stamm and M Müller
- 19–22 Numerical analysis of pulse formation in solid-state lasers mode-locked with a linear external cavity
M Müller and U Stamm
- 23–26 Feedback-controlled mode-locking operation of a Nd:YLF laser at $1.047 \mu\text{m}$
K Wolfrum and P Heinz
- 27–30 Antiresonant-ring mirror passive mode-locking of solid state lasers
A Agnesi, G Gabetta and G C Reali
- 31–34 The mode-locking technique using intracavity frequency doubling
K A Stankov
- 35–38 Mode-locking of a Nd:YAG laser by a frequency-doubling crystal and saturable absorber
Zhen-guo Lü, Qi Wu, Qing-xing Li and Zhen-xin Yu
- 39–42 Chirped pulse formation in mode-locked solid state lasers with intracavity harmonic generation
S F Bogdanov, G I Onishchukov, P G Konvisar, S D Ryabko, S R Rustamov and A A Fomichov
- 43–46 A method for compensating the group-velocity mismatch in the frequency-doubling modelocker
K A Stankov, V P Tzolov and M G Mirkov
- 47–50 Study of ultrashort pulse generation in a pulsed Nd:YAG laser with an auxiliary nonlinear cavity
Zhen-guo Lü, Qi Wu, Qing-xing Li and Zhen-xin Yu

b) Ti:Sapphire Lasers and Parametric Oscillators

- 51–54 Femtosecond passively mode-locked Ti:sapphire lasers
P Georges, T Lépine, G Roger and A Brun
- 55–58 Cavity considerations and intracavity second harmonic generation in Kerr-lens mode-locked titanium-doped sapphire lasers
D Georgiev, U Günzel, J Herrmann, V Petrov, U Stamm and K-P Stolberg
- 59–62 Mode-locking of a flashlamp pumped Ti:sapphire laser using the frequency doubling nonlinear mirror
K Hamal, K A Stankov, H Jelinkova, I Prochazka and M Koselja
- 63–66 Generation of ultrashort pulses from the visible to the infrared
R Laenen, H Graener and A Laubereau
- 67–70 Parametric generation of femtosecond pulses by LBO crystal in the near IR
S A Akhmanov, I M Bayanov, V M Gordienko, V A Dyakov, S A Magnitskii, V I Pryalkin and A P Tarasevitch
- 71–74 Picosecond BBO optical parametric oscillator
V Kubecek, Y Takagi, K Yoshihara and G C Reali
- 75–78 Performance of a barium borate parametric oscillator in the picosecond regime with different cavity configurations
G P Banfi, M Ghigliazza and P Di Trapani
- 79–82 Multiphoton ionization of atoms with parametrically amplified femtosecond infrared pulses
W Joosen, P Agostini, G Petite, J P Chambaret and A Antonetti

c) Dye Lasers

- 83–88 Coherent photon seeding: A scheme for ultra stable ultrashort pulse generation
H P Weber, W Hodel, J Q Bi, P Beaud and D S Peter
- 89–92 Femtosecond pulse generation in a cw pumped passive mode-locked linear rhodamine 6G—DODCI dye laser
A Penzkofer and W Bäumlner
- 93–96 Prismatic pulse compressor for synchronously pumped mode-locked lasers
K Osvay, Z Bor, A Kovács, G Szabó, B Rácz, H A Hazim and O E Martinez
- 97–100 A simple technique for generation of frequency shifted femtosecond pulses
D Grosenick, F Noack, F Seifert and B Wilhelmi
- 101–104 Ultrashort pulse generation in a DFB-laser with a saturable absorber
A A Afanas'ev, M V Korol'kov and T V Veremeenko

- 105–108 Passively mode-locked dye laser with spatial dispersion in the gain medium
N I Michailov
- 109–112 Investigation of chirped pulse amplification in a dye amplifier system
O Kittelmann, G Korn, J Ringling and F Seifert

d) High Power Lasers

- 113–118 Femtosecond second harmonic generation from Al at the laser intensity level up to 10^{14} W/cm²
S V Govorkov, N I Koroteev and I L Shumay
- 119–124 Femtosecond x-ray emission from laser irradiated Al targets
A Mysyrowicz, J P Chambaret, A Antonetti, P Audebert, J P Geindre and J C Gauthier
- 125–128 First results on the way to a ps multiterawatt glass laser system using fiberless CPA-technique
F Billhardt, P Nickles and I Will
- 129–131 Nonlinear quantum electrodynamics with high power ultrashort laser pulses: possibility of experimental studies
P G Kryukov

II. New Techniques and Propagation of Ultrashort Light Pulses

- 133–138 Ultra-sensitive detection with ultra-short pulse ring lasers
J-C Diels, M Lai and M Dennis
- 139–142 Novel laser schemes in gases and vapors pumped by short pulse high power lasers
A Tünnermann, K Mossavi and B Wellegehausen
- 143–146 Ultrafast time-resolved laser scanning microscopy
H Bergner, U Stamm, K Hempel, M Kempe, A Krause and H Wabnitz
- 147–149 An all solid state picosecond photon counting system for spectroscopy
I Procházka, K Hamal, B Sopko, J Říčka and M Hoebel
- 151–154 Best estimates of exponential decay parameters and the design of single-photon-counting experiments
M Köllner
- 155–158 Three-wave solitons of a new type in Raman scattering of polariton waves
A L Ivanov and G S Vygovskii
- 159–162 Spatial and temporal distribution of femtosecond pulses after tight focusing
M Kempe, U Stamm, R Gutewort, B Wilhelmi and W Rudolph

- 163–168 Behaviour of femtosecond pulses in lenses
Z Bor and Z L Horváth
- 169–171 Propagation-time-dispersion in a streak camera lens
K Osvay, Z Bor, B Rácz and G Szabó
- 173–180 Ultrafast cross-phase modulation
P Heist, J Krüger, W Rudolph, T Schröder, P Dorn, F Seifert and B Wilhelmi
- 181–184 Study of spectral narrowing for femtosecond pulses propagating in single-mode optical fibres
X Zhu and W Sibbett
- 185–188 Bistable solitons
J Herrmann and S Gatz
- 189–192 Coherent effects on soliton amplification in a doped fiber
I V Mel'nikov and R F Nabiev
- 193–196 Memory effects assisted phase-conjugation of sub-nano and picosecond pulses in optical fibers
N I Minkovski and T P Mirtchev

III. Coherent Spectroscopy and Nonlinear Optics

- 197–202 Pressure induced vibrational relaxation in molecular crystals by picosecond coherent Raman spectroscopy in a diamond anvil cell
E L Chronister and R A Crowell
- 203–206 Time-resolved investigation of LO-phonon dynamics in semi-insulating and n-type GaAs
F Bogani and F Vallée
- 207–211 Dephasing of excitons in polar semiconductors—The cuprous chloride case
F Vallée, F Bogani and C Flytzanis
- 213–216 Analysis of experimental data on time-domain spectroscopy of molecular gases
D V Kolomoitsev and S Yu Nikitin
- 217–222 Time-domain spectroscopy of molecular vapors with subpicosecond pulses of THz radiation
H Harde and D Grischkowsky
- 223–226 Two-photon processes with chirped pulses: spectral diffraction and focussing
B Broers, L D Noordam and H B van Linden van den Heuvell
- 227–230 Using of broad-bandwidth stimulated Raman scattering in subpicosecond transient spectroscopy of optical Kerr effect
P A Apanasevich, V P Kozich, A I Vodchitz and B L Kontsevov

- 231–234 Third order nonlinear optical properties of substituted poly(p-phenylene vinylene) derivatives
H L Li, S Rentsch and H Bergner
- 235–238 Four wave mixing processes in strontium vapour generated by tunable femtosecond pulses
J Ringling, O Kittelmann, F Seifert and J Herrmann
- 239–242 Laser pulses shortening at transient backward SRS and forward scattering suppression
R G Zaporozhchenko, I S Zakharova, A V Kachinskii, G G Kotaev and I V Pilipovich
- 243–246 Synchronization of quantum transitions by light pulses: Raman transitions in highly excited hydrogen atom
V A Ulybin
- 247–250 Intracavity laser spectroscopy of fast running processes
M V Pyatakhin
- 251–254 Optical implementation of a Hopfield-type neural network by the use of persistent spectral hole burning media
O Ollikainen and A Rebane

IV. Applications to Solid State Physics and Surface Dynamics

- 255–260 Femtosecond generation of coherent optical phonons in condensed media
H Kurz
- 261–266 Femtosecond spectroscopy of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: electron–phonon interaction measurement and energy gap observation
S V Chekalin, V M Farztdinov, V V Golovlev, V S Letokhov, Yu E Lozovik, Yu A Matveets and A G Stepanov
- 267–270 Investigation of melting processes in GaAs in the femtosecond time domain
T Schröder, W Rudolph, S Govorkov and I Shumay
- 271–274 Time-resolved spectroscopic investigations of Ti doped YAlO_3 and pure YAlO_3 crystals
H Chosrovian, S Rentsch and U-W Grummt
- 275–278 Pulsed propagation of luminescence in anthracene
T Reinot and J Aaviksoo
- 279–282 Photoinjected charge carrier trapping and recombination in one-dimensional conducting polymers
I Zozulenko

- 283–288 Ultrafast relaxation of plasma oscillations in Ag islands studied by second-harmonic generation
D Steinmüller-Nethl, R A Höpfel, E Gornik, A Leitner and F R Aussenegg
- 289–292 Laser induced electron emission processes of an Au-surface irradiated by single picosecond pulses at $\lambda = 2.94 \mu\text{m}$ in the intermediate region between multiphoton and tunneling effects
C Tóth, G Farkas and K L Vodopyanov

V. Applications to Semiconductors

a) Carrier Dynamics in Bulk Semiconductors

- 293–298 Ultrafast electronic and thermal processes in hydrogenated amorphous silicon
D Hulin, P M Fauchet, R Vanderhaghen, A Mourchid, W L Nighan Jr, J Paye and A Antonetti
- 299–302 Femtosecond spectroscopic study of free carrier induced optical nonlinearities in crystalline silicon
A Esser, A Ewertz, T Zettler, W Kütt and H Kurz
- 303–308 Picosecond infrared studies of hot holes in germanium
W Kaiser, M Woerner and T Elsaesser
- 309–312 Nonthermalized electron distribution at low density in GaAs
D W Snoke, W W Rühle, Y-C Lu and E Bauser
- 313–316 Carrier thermalization in GaAs and InP studied by femtosecond luminescence spectroscopy
T Elsaesser, J Shah, L Rota and P Lugli
- 317–324 Femtosecond nonlinearities and hot-carrier dynamics in GaAs
T Gong and P M Fauchet
- 325–328 Optical nonlinearities at the bandedge of CaAs at room temperature
H Heesel, T Zettler, A Ewertz and H Kurz
- 329–332 Transient reflectivity and transmission spectra of gallium arsenide: dependence on doping and excitation density
G Böhne, S Freundt, S Lehmann and R G Ulbrich
- 333–338 Femtosecond relaxation of photoexcited single-species carriers in bulk doped semiconductors
G M Gale, A Chébir, E Fazio and J Chesnoy
- 339–342 Hot carrier relaxation in doped III–V compounds studied by femtosecond luminescence
X Q Zhou and H Kurz

- 343–344 Reversible gallium arsenide bleaching under the action of picosecond light pulses
N N Ageeva, I L Bronevoi, S E Kumekov and V A Mironov
- 345–348 Theory of hot LO–phonon decay in laser excited direct-gap semiconductors
U Wenschuh, E Heiner and K W Becker
- 349–352 Dynamic Burstein–Moss effect in InAs at room temperature and passive mode-locking of a 3 μm Er laser
K L Vodopyanov, H Graener, C C Phillips and I T Ferguson
- 353–356 Kinetics and relaxation of nonequilibrium electron–hole system in direct gap semiconductors
V Dneprovskii, V Klimov and M Novikov
- 357–360 Investigation of carrier temperature relaxation with femtosecond transient grating experiments in $\text{CdS}_x\text{Se}_{1-x}$ -semiconductors
D van Lap, U Peschel, H E Ponath and W Rudolph

b) Carrier Dynamics in Semiconductors of Low Dimensionality

- 361–366 Nonlinearity near half-gap in bulk and quantum well GaAs/AlGaAs waveguides
M N Islam, C E Soccolich, R E Slusher, W S Hobson and A F J Levi
- 367–370 Resonant electron and hole tunneling between GaAs quantum wells
A P Heberle, W W Rühle and K Köhler
- 371–374 Dynamical aspects of pressure induced Γ –X electron transfer in a $(\text{GaAs})_{15}/(\text{AlAs})_5$ type-I superlattice
J Nunnenkamp, K Reimann, J Kuhl and K Ploog
- 375–378 Hot luminescence and nonlinear effects in shortperiod superlattices under picosecond excitation
E A Vinogradov, A V Zayats, D N Nikogosyan and Yu A Repeyev
- 379–382 Coulomb relaxation kinetics in a dense quasi-twodimensional electron plasma
K El-Sayed, T Wicht, H Haug and L Bányai
- 383–388 An infrared spectrometer for time-resolved intersubband spectroscopy
A Seilmeier, T Dahinten, U Plödereeder and G Weimann
- 389–392 Femtosecond relaxation of excited carriers in microcrystallites in a glassy matrix at excitation intensity 10^{10} – 10^{13} W/cm^2
S V Chekalin, V M Farztdinov, V V Golovlev, Yu E Lozovik, Yu A Matveets, A G Stepanov and A P Yartsev
- 393–396 Time-resolved studies on the carrier dynamics in quantum dots
V Jungnickel, J Puls and F Henneberger

397–400 Nonlinear picosecond spectroscopy of zero-dimensional semiconductor
V S Dneprovskii, V I Klimov and Ju V Vandyshev

401–404 Absorption saturation and nonlinear diffraction of laser pulses in the
commercial $\text{CdS}_x\text{Se}_{1-x}$ -doped glasses
*V A Zaporozhchenko, R G Zaporozhchenko, I V Pilipovich,
A E Kazachenko and V A Zyulkov*

c) Exciton Dynamics

405–410 Phase relaxation of excitons in semiconductor mixed crystals
U Siegner and E O Göbel

411–414 Subpicosecond spectroscopy of excitons in GaAs/AlGaAs
heterostructures
K Leo, J Shah, S Schmitt-Rink and K Köhler

415–418 Tunneling versus exciton formation of photo-induced carriers in
asymmetric double quantum wells
R Strobel, R Eccleston, J Kuhl and K Köhler

419–422 Exciton relaxation dynamics in GaAs/AlGaAs single quantum well
heterostructures
P Roussignol, A Vinattieri, L Carraresi, M Colocci and C Delalande

423–426 The exciton interband scattering and LA-phonon interaction dynamics
in GaAs quantum wells
R Eccleston, J Kuhl, R Strobel, W W Rühle and K Ploog

427–430 Carrier-induced shifts of exciton energies in CdTe/CdZnTe superlattices
M K Jackson, D Hulin, J-P Foing, N Magnea and H Mariette

431–436 Nonlinear optical response of interacting excitons
A L Ivanov, L V Keldysh and V V Panashchenko

437–440 Exciton-exciton inelastic collision dynamics in CuBr microcrystals
G Tamulaitis, R Baltramiejunas, S Pakalnis and A I Ekimov

d) Opto-Electronics

441–444 Ultrafast polarization switching in ridge-waveguide laser diodes
*A Klehr, A Bärwolff, R Müller, G Berger, J Sacher, W Elsässer and
E O Göbel*

445–448 Generation of picosecond pulses by optically pumped short- and ultra-
short-cavity semiconductor lasers (theory)
Yu D Kalafati and V A Kokin

449–454 Picosecond photodetectors fabricated on low temperature GaAs
*M Klingenstein, J Kuhl, R Nötzel, K Ploog, J Rosenzweig, C Moglestue,
J Schneider, A Hülsmann and K Köhler*

- 455–456 Picosecond optical diagnostic of semiconductors and elements of integrated circuits
V V Simanovich, G I Onishchukov and A A Fomichev
- 457–460 Investigation of electrical pulse propagation in a n-MOS device by time-resolved laser scanning microscopy
A Krause, H Bergner, K Hempel and U Stamm
- 461–464 Spectral and temporal holography of ultrashort light pulses and its possible applications in opto-electronic systems and devices
Yu T Mazurenko

VI. Applications to Molecular Systems

a) Ultrafast Photo-Excitation of Molecules

- 465–470 Measurement and conjecture concerning IVR acceleration by methyl group. CH_3 vs CD_3
D B Moss, C S Parmenter, T A Peterson, C J Pursell and Zhong-Quan Zhao
- 471–476 Infrared transient hole burning with picosecond pulses
H Graener
- 477–480 Resonance interactions of 10 μm picosecond pulses with polyatomic molecules
V M Gordienko, Z A Biglov, E O Danilov and V A Slobodyanyuk
- 481–484 Photophysics of the higher excited singlet state of diphenylacetylene
Y Hirata, T Okada, N Mataga and T Nomoto
- 485–488 Time-resolved optical spectroscopy of donor-acceptor-substituted polyenes
G Quapil and H Port
- 489–494 Nonlinear excited state dynamics of J-aggregates on the femtosecond time-scale
R Gagel, R Gadonas and A Laubereau
- 495–498 Ultrafast optical dynamics and nonlinear susceptibility for resonant transitions of excited molecules and aggregates
V Bogdanov, S Kulya and A Spiro
- 499–502 Picosecond relaxation processes in photoexcited metallophthalocyanine aggregates
V Butvilas, V Gulbinas and A Urbas
- 503–508 Ultrafast relaxation dynamics of photoexcitations in one-dimensional conjugated polymers
M Yoshizawa and T Kobayashi

- 509–512 Ultrafast processes in thiophene oligomers studied by ps absorption measurements
D Grebner, H Chosrovian, S Rentsch and H Naarmann

b) Solvation Dynamics and Orientational Relaxation

- 513–518 Classical and quantum solvation
E Neria, A Nitzan, R N Barnett and U Landman
- 519–522 Solvation dynamics of Nile blue studied by time-resolved gain spectroscopy
M M Martin, N Dai Hung, L Picard, P Plaza and Y H Meyer
- 523–526 Decay time distribution of fluorescence kinetics in systems with inhomogeneous broadening of electronic spectra
D M Gakamsky, E P Petrov and A N Rubinov
- 527–530 Orientational dynamics of molten $2[\text{Ca}(\text{NO}_3)_2] - 3[\text{KNO}_3]$ measured by time-resolved optical Kerr effect
M Ricci, R Torre, P Foggi and R Righini
- 531–534 Orientational relaxation dynamics of polar dye probes in n-alkylnitriles
G B Dutt and S Doraiswamy
- 535–538 Direct observation of femtosecond angular-velocity dynamics in molecular liquids
T Hattori, A Terasaki, T Kobayashi, T Wada, A Yamada and H Sasabe
- 539–542 Direct observation of the orientational motion of small molecules in condensed matter
G Seifert and H Graener

VII. Dynamical Photochemical Processes

- 543–548 Femtosecond proton and deuterium transfer in aromatic molecules
T Elsaesser, F Laermer and W Frey
- 549–552 Intermolecular proton transfer via intramolecular proton transfer: The photodissociation of 2-naphthol-3,6-disulfonate
A Masad and D Huppert
- 553–556 Molecular dynamics study of the picosecond photostimulated conformational dynamics
B A Grishanin, V D Vachev and V N Zadkov
- 557–560 Time-resolved CARS spectroscopy of the series of bisdimethylamino-methine photoisomers
W Werncke, M Pfeiffer, A Lau, L Holz and T Hasche
- 561–566 Femtosecond-picosecond laser photolysis studies on photoinduced charge transfer and electron ejection dynamics
N Mataga, H Miyasaka and Y Hirata

- 567–570 Energy transfer phenomena in low and high molecular alkanes
O Brede and R Hermann
- 571–574 Analysis of molecular dissociation by a chirped infrared laser pulse
B A Grishanin, V D Vachev and V N Zadkov
- 575–578 Coherence effects on selective ionization of three-level systems driven by pulse sequences of two lasers
K Johst
- 579–582 Fast relaxation processes in aromatic free radicals
N Borisevich, S Melnichuck, S Tikhomirov and G Tolstorozhev
- VIII. Applications to Biology**
- 583–588 Femtosecond photoisomerization of rhodopsin as the primary event in vision
R W Schoerlein, C V Shank, L A Peteanu and R A Mathies
- 589–594 Low temperature reaction dynamics in the primary electron transfer of photosynthetic reaction centers
W Zinth, C Lauterwasser and U Finkle
- 595–598 Femtosecond absorption studies of 14-fluorobacteriorhodopsin
M Taiji, K Bryl, N Sekiya, K Yoshihara and T Kobayashi
- 599–604 Picosecond time-resolved resonance CARS of bacteriorhodopsin
G H Atkinson and L Ujj
- 605–608 Primary processes in isolated photosynthetic bacterial reaction centers from *chloroflexus aurantiacus* studied by picosecond fluorescence spectroscopy
A R Holzwarth, L Griebenow and M G Müller
- 609–612 Time-resolved fluorescence studies of isolated photosynthetic reaction centers from *chloroflexus aurantiacus* at low temperatures
M Hucke, G Schweitzer, K Griebenow, M G Müller and A R Holzwarth
- 613–616 Picosecond fluorescence of photosystem II D1/D2/cyt b559 and D1/D2/cyt b559/CP47 pigment-protein complexes
K Timpmann, A Freiberg, A A Moskalenko and N Yu Kuznetsova
- 617–622 Laserspectroscopic investigations of nonlinear optical effects in molecular aggregates of pigment–protein complexes
J Voigt, Th Bittner, G Kehrberg and G Renger
- 623–626 Aggregation of chlorophyll *a* in hydrocarbon solution
V Helenius, J Erostyák and J Korppi-Tommola
- 627–630 Energy transfer and charge separation at 15 K in membranes of *heliobacterium chlorum*; temperature dependence of secondary electron transfer
P J M van Kan and J Amesz

- 631–634 Femtosecond energy transfer processes in allophycocyanin and C-
phycoyanin trimers
*E V Khoroshilov, I V Kryukov, P G Kryukov, A V Sharkov, T Gillbro,
R Fischer and H Scheer*
- 635–638 Photo-activation of a molecular proton crane
C J Jalink, A H Huizer and C A G O Varma
- 639–642 Fluorescence decay studies of probe molecules distribution throughout
the lipid membranes and the determination of ‘micropolarity’
N A Nemkovich, A N Rubinov and M G Savvidi
- 643–646 Author Index
- 647–650 Keyword Index

Low temperature reaction dynamics in the primary electron transfer of photosynthetic reaction centers

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ABSTRACT: The primary electron transfer in reaction centers of *Rhodobacter (Rb.) sphaeroides* is investigated as a function of temperature with subpicosecond time resolution. The experimental results indicate that the electron transfer is not thermally activated and that the same transfer mechanisms are active at low temperatures and at room temperature.

1. INTRODUCTION

Photosynthetic conversion of light energy into chemical energy starts via several electron transfer (ET) reactions in pigment protein complexes called reaction centers (RC's). A series of recent experiments have shown that the most rapid electron transfer processes proceed on the time scale of picoseconds /1-7/. During these reactions an electron is transferred from the primary donor (P), a pair of bacteriochlorophyll molecules via a chain of chromophores to a quinone acceptor molecule. From the structural arrangement /8, 9/ of the chromophores in the reaction centers the following reaction path is suggested: Starting at the primary donor P the electron should be transferred via a monomeric bacteriochlorophyll molecule (B), a bacteriopheophytin molecule (H) to a quinone molecule (Q). A number of picosecond experiments addressed the primary reaction in the reaction centers. In these publications it was shown that several picosecond processes occur in the RC's: A process with a time constant of 200 ps is related with the electron transfer from the bacteriopheophytin to the quinone. A faster time constant of about 3.5 ps was attributed to both, the decay of the electronically excited state P* and to the electron transfer to the pheophytin H /2, 3/. The observation of an additional time constant of 0.9 picoseconds was taken as an indication that the monomeric bacteriochlorophyll is involved in the primary reaction process /5-7/. Until now the assignment of the fast kinetic constant to a molecular process is still in discussion. Most probable are the three reaction models which are shown in Figure 1 /5-7/.

2. REACTION MODELS

The structural arrangement of the reaction centers strongly suggests the stepwise electron transfer model of Figure 1 a: According to this model the electronically excited state P* of the special pair decays with the time constant of 3.5 ps. Simultaneously an electron is transferred from the special pair to the monomeric bacteriochlorophyll B. The second electron transfer is faster and carries the electron with a time constant of 0.9 ps to the bacteriopheophytin H. Finally the 200 ps process generates the radical pair P⁺Q⁻ where the electron has reached the quinone.

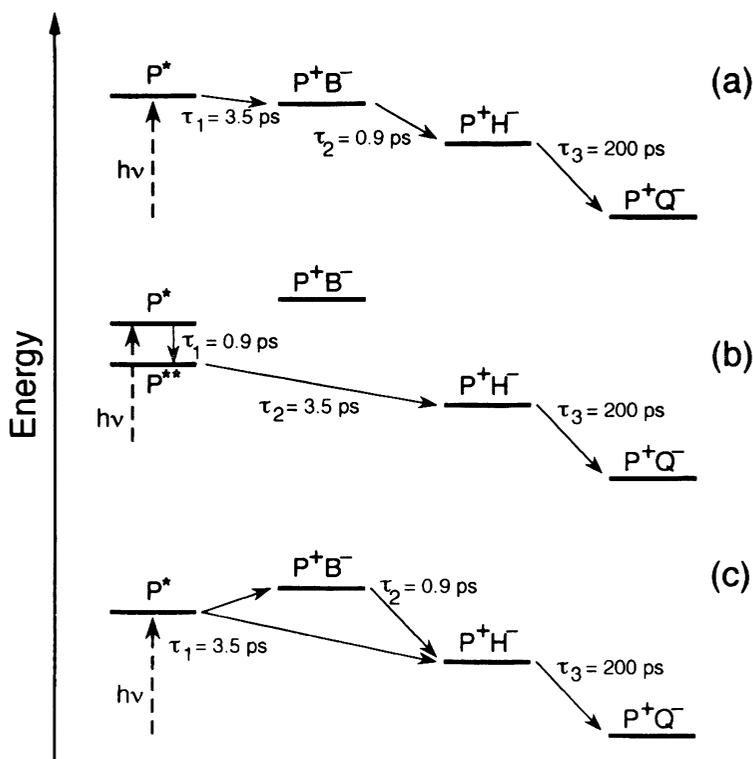


Figure 1: Schematic representation of three reaction models of the primary photosynthetic electron transfer: (a): The stepwise model. (b): unistep superexchange model with a 0.9 ps vibrational relaxation process which leads to a relaxed electronic state P^{**} . (c): branched (parallel) reaction model.

From extensive experimental studies the absorption spectra of the different intermediates of model 1a could be calculated. All these data were fully consistent with the molecular interpretation of a stepwise electron transfer.

In model 1b the fast time constant of 0.9 ps is assigned to an excited state relaxation process of the special pair. Presumably this process is vibrational relaxation from the initially populated Franck-Condon-state. In this reaction model the first electron transfer drives the electron with a time constant of 3.5 ps directly to the bacteriochlorophyll H. This fast long-distance electron transfer is only possible if the monomeric bacteriochlorophyll is involved as a virtual intermediate in a superexchange interaction.^{10-12/} In this case the energy level of the corresponding radical pair P^+B^- is higher than the energy of P^* .

When the energy level of state P^+B^- is close to the energy of state P^* a branched reaction model becomes possible (see Figure 1c) ^{12/}. In this model two reactions occur in parallel: a direct ET from the special pair P^* to the bacteriochlorophyll H as well as a stepwise ET via the real intermediate P^+B^- . In this model the 3.5 ps kinetic would reflect the depopulation of the excited special pair while the 0.9 ps time constant is related with the population of the intermediate state P^+B^- . From room temperature experimental data one could conclude that at least 50 % of the reaction centers should use the stepwise reaction path via P^+B^- ^{5, 6/}.

It is the purpose of the present paper to present experimental data on the low temperature reaction dynamics. From the temperature dependence of the observed rates we draw conclusions on the molecular mechanisms of the electron transfer.

3. EXPERIMENTAL

The measurements presented in this paper are obtained on quinone depleted reaction centers from the carotenoid free strain R26.1 of *Rb.sphaeroides*. Details of the preparation procedures are published in reference /13/. The time resolved absorption experiments are performed using the excite and probe technique with weak subpicosecond pulses (pulse duration ≈ 150 fs) generated by a laser-amplifier-system with a repetition rate of 10 Hz. Details of the experimental system are described in reference /6, 13/. The temporal width of the instrumental response function is below 300 fs.

4. RESULTS

In a first set of time resolved experiments the temperature dependence of the decay of the excited state P^* is investigated. In these experiments the transient absorption changes induced by stimulated emission of the radical pair are monitored at a probing wavelength of 920 nm (see Figure 2). At the investigated low temperatures of 25 K the signal closely follows a model function with a single exponential time constant $\tau_1 = 1.4 \pm 0.3$ ps. This time constant as well as the temperature dependence of this time constant is in agreement with the results of previous experimental studies /14/. The most important topic addressed here is the temperature dependence of the fast kinetic component. For this purpose we studied the transient absorption changes at probing wavelengths around 795 nm. In this wavelength range the amplitude of the 3.5 ps kinetic component is very weak and the additional fast kinetic component is clearly visible at room temperature. In Figure 3 we present the experimental data for a probing wave-

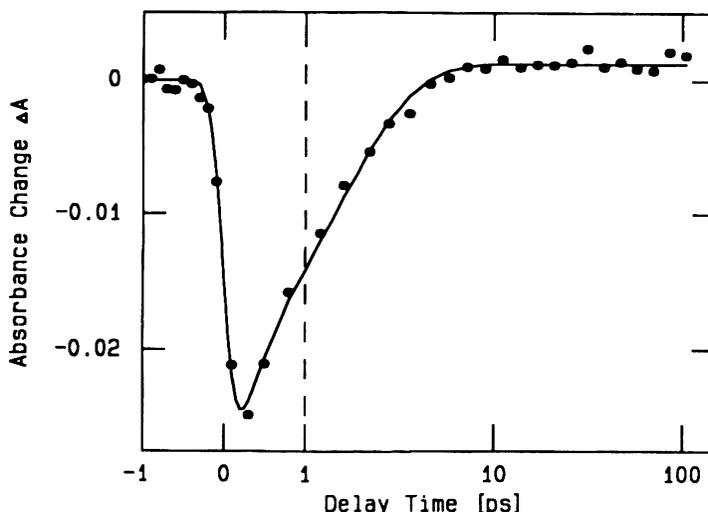


Figure 2: Transient absorption data on RC from *Rb. sphaeroides* at 25 K. The absorbance change is plotted on a linear scale for delay times $t_D < 1$ ps and on a logarithmic scale for longer delay times. Probing wavelength 920 nm. The signal reflects the decay of the excited electronic level P^* which is monoexponential with a time constant of $\tau = 1.4$ ps.

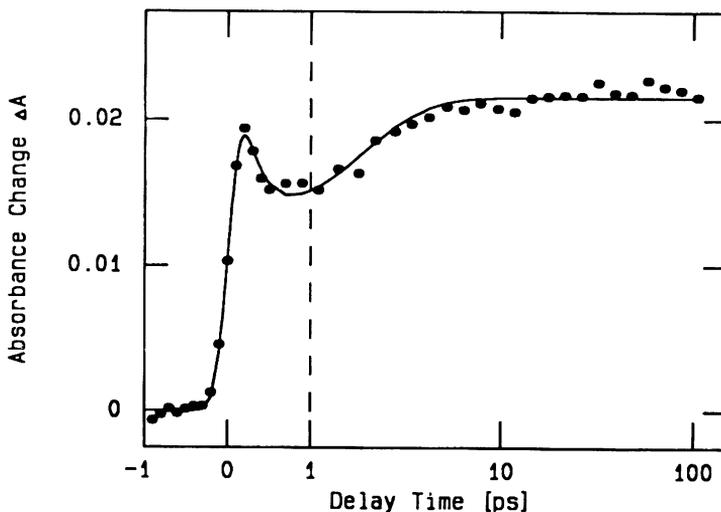


Figure 3: Transient absorption data on RC from *Rb. sphaeroides* at 25 K. The absorbance change is plotted on a linear scale for delay times $t_D < 1$ ps and on a logarithmic scale for longer delay times. Probing wavelength 794 nm. The transient data show a complex time dependence which can be fitted by a sum of exponential functions with time constants of 0.3 ps and 1.4 ps.

length of 794 nm at a temperature of 25 K. The absorption change rises quickly during the first 100 fs to the pronounced peak. Subsequently an additional fast decay leads to a minimum at $t_D = 700$ fs. A subsequent slower rise of the absorbance leads to a plateau which is reached after approximately 2 ps. The complex time dependence of the absorbance change excludes the possibility that there is only one, namely the 1.4 ps kinetic component. There must be an additional faster kinetic process which is responsible for the first decay of the absorbance change. From a series of experiments the time constant of this additional kinetic component was determined to be 0.3 ± 0.15 ps. In a set of measurements we have recorded the temperature dependence of the fast kinetic component. These experimental results are summarized in Figure 4: At high temperatures around 300 K the time constant is around 1 ps i. e. we observe a rate of $1 \cdot 10^{12} \text{ s}^{-1}$. At lower temperatures a slow rise of the rate constant occurs which accelerates below 100 K. At 25 K a rate constant of $3.3 \cdot 10^{12} \text{ s}^{-1}$ is reached. In Figure 4 the points represent the experimental data; the solid line reflects the results of conventional electron transfer theory [13, 17]. The whole set of experimental results can be summarized as follows: (i) at all temperatures between 300 K and 25 K two time constants are required to explain the experimental data during the first 10 ps. (ii) Qualitatively similar transient absorption features occur at all temperatures (iii) The time constant of the fast kinetic component becomes shorter with decreasing temperature reaching a very small value of $t = 0.3$ ps at $T = 25$ K.

5. DISCUSSION

The three reaction models of Figure 1 will now be discussed in the context of the new experimental data. We start with the branched reaction model of Figure 1c. In this model the energy level of state P^+B^- should be of the order of 100 cm^{-1} above the level of P^* [12]. At very low temperatures this energy difference prevents the population of state P^+B^- . As a consequence the

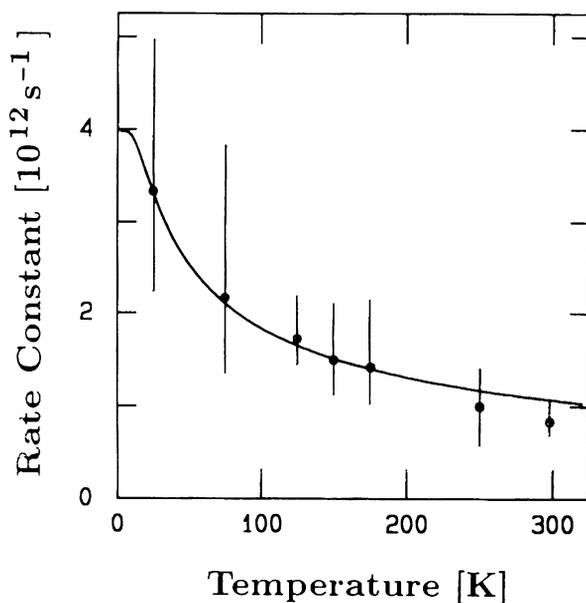


Figure 4: Temperature dependence of the fast rate constant. Points with error bars give the experimental data. The solid line represents the result of conventional electron transfer theory with parameters listed in /13/.

reaction path via P^+B^- is closed and the lifetime of state P^* should become longer. In addition the amplitude of the fast kinetic component related to the decay of state P^+B^- should strongly decrease. Both phenomena are not observed experimentally. Therefore the branched reaction model is quite unlikely. In the superexchange model of Figure 1b the fast kinetic component is related to an S_1 vibrational relaxation. It is well known from a number of publications that vibrational relaxation slows down considerably at low temperatures /15, 16/. Experimentally, however, the fast process (which is related in the superexchange model with a vibrational relaxation) accelerates continuously when lowering the temperature. This is in clear contradiction to the interpretation of the fast step being vibrational relaxation. On the other hand the evaluation of the temperature dependent transient absorption data according to the stepwise model of Figure 1a leads to a fully consistent picture.

In conclusion, we have found that the dynamics of the primary electron transfer in reaction centers of *Rb. sphaeroides* shows transient absorption changes with two picosecond time constants throughout the whole investigated temperature range from 300 K to 25 K. The existence of the two kinetic processes in this temperature range as well as the temperature dependence of time constants and amplitudes strongly support the idea that the primary electron transfer in reaction centers is a stepwise process via the monomeric bacteriochlorophyll molecule.

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