Contents

Part I  Advances in the Generation of Ultrashort Light Pulses

Moving from the Picosecond to the Femtosecond Time Regime
By C.V. Shank, R.L. Fork, and R.T. Yen ......................... 2

Femtosecond Optical Pulses: Towards Tunability at the Gigawatt Level
By A. Migus, J.L. Martin, R. Astier, A. Antonetti, and A. Orszag .. 6

Femtosecond Continuum Generation. By R.L. Fork, C.V. Shank, R.T. Yen,
C. Hirlimann, and W.J. Tomlinson ................................ 10

New Picosecond Sources and Techniques
By A.E. Siegman and H. Vanherzeele ......................... 14

Generation of Coherent Tunable Picosecond Pulses in the XUV
By T. Srinivasan, K. Boyer, H. Egger, T.S. Luk, D.F. Muller,
H. Pummer, and C.K. Rhodes ................................. 19

New Infrared Dyes for Synchronously Pumped Picosecond Lasers
By A. Seilmeier, B. Kopainsky, W. Kranitzky, W. Kaiser, and
K.H. Drexhage ........................................... 23

Acousto-Optic Stabilization of Mode-Locked Pulsed Nd:YAG Laser
By H.P. Kortz ............................................. 27

Active Mode Stabilization of Synchronously Pumped Dye Lasers
By A.I. Ferguson and R.A. Taylor .......................... 31

Spectral Hole Burning in the Saturation Region of Mode-Locked Nd-Glass
Lasers. By A. Penzofer and N. Weinhardt ..................... 36

Single and Double Mode-Locked Ring Dye Lasers; Theory and Experiment
By K.K. Li, G. Arjavalgingam, A. Dienes, and J.R. Whinnery .... 40

Theoretical and Experimental Investigations of Colliding Pulse
Mode-Locking (CPM). By W. Dietel, D. Kühike, W. Rudolph, and
B. Wilhelmi .............................................. 45

Picosecond Carrier Dynamics and Laser Action in Optically Pumped
Buried Heterostructure Lasers
By T.L. Koch, L.C. Chiu, Ch. Harder, and A. Yariv ............... 49

Optically Pumped Semiconductor Platelet Lasers in External Cavities
By M.M. Salour ........................................... 53

The Pulse Duration of a Distributed Feedback Dye Laser Under Single Pulse Conditions. By Z. Bor, B. Rácz, G. Szabó, and A. Müller ..... 62


Modelocking of a Wavelength Tunable High-Pressure CO2-Laser by Synchronous Modulation of a Broadband Intracavity Saturable Absorber. By J.K. Ajo, Y. Hefetz, and A.V. Nurmikko ......................... 68

The Non-Mode-Locked Picosecond Laser
By F. Armani, F. DeMartini, and P. Mataloni .................................. 71


Optical Dephasing in Inorganic Glasses
By R.M. Shelby and R.M. MacFarlane ........................................... 78

Part II Ultrashort Measuring Techniques

Picosecond Holographic Grating Experiments in Molecular Condensed Phases. By M.D. Fayer ...................................................... 82


A Picosecond Raman Technique with Resolution Four Times Better than Obtained by Spontaneous Raman Spectroscopy
By W. Zinth, M.C. Nuss, and W. Kaiser .................................. 91

Broadband CARS Probe Using the Picosecond Continuum
By L.S. Goldberg ................................................................. 94

Jitter-Free Streak Camera System
By W. Knox, T.M. Nordlund, and G. Mourou ................................ 98

Electrical Transient Sampling System with Two Picosecond Resolution
By J.A. Valdmanis, G. Mourou, and C.W. Gabel .......................... 101

High-Resolution Picosecond Modulation Spectroscopy of Near Interband Resonances in Semiconductors
By S. Sugai, J.H. Harris, and A.V. Nurmikko ............................. 103


VIII
Picosecond Time-Resolved Photoacoustic Spectroscopy
By M. Bernstein, L.J. Rothberg, and K.S. Peters ................. 112

Subpicosecond Pulse Shape Measurement and Modeling of Passively Mode-Locked Dye Lasers Including Saturation and Spatial Hole Burning
By J.-C. Diels, I.C. McMichael, J.J. Fontaine, and C.Y. Wang ...... 116

Experimental Demonstration of a New Technique to Measure Ultrashort Dephasing Times
By J.C. Diels, W.C. Wang, P. Kumar, and R.K. Jain ................... 120

Optical Pulse Compression with Reduced Wings
By D. Grischkowsky and A.C. Balant ................................ 123

Polarization-Induced Compensation of Picosecond Pulse Broadening in Optical Fibers. By G.W. Fehrenbach and M.M. Salour ........... 126

Part III Advances in Optoelectronics


Addressing and Control of High-Speed GaAs FET Logic Circuits with Picosecond Light Pulses
By R.K. Jain, J.E. Brown, and D.E. Snyder ............................ 134

Surface Metal-Oxide-Silicon-Oxide-Metal Picosecond Photodetector
By S. Thaniyavarn and T.K. Gustafson ................................. 137

Solid-State Detector for Single-Photon Measurements of Fluorescence Decays with 100 Picosecond FWHM Resolution
By A. Andreoni, S. Cova, R. Cubeddu, and A. Longoni ............... 141

Picosecond Optoelectric Modulation of Millimeter-Waves in GaAs Waveguide
By M.G. Li, V.K. Mathur, Wei-Lou Cao, and Chi H. Lee ............... 145

Synchronscan Streak Camera Measurements of Mode-Propagation in Optical Fibers. By J.P. Willson, W. Sibbett, and P.G. May ............... 149

Part IV Relaxation Phenomena in Molecular Physics

Picosecond Lifetimes and Efficient Decay Channels of Vibrational Models of Polyatomic Molecules in Liquids
By C. Kolmeder, W. Zinth, and W. Kaiser ............................... 154

Vibrational Population Decay and Dephasing of Small and Large Polyatomic Molecules in Liquids
By H. Graener, D. Reiser, H.R. Telle, and A. Laubereau .............. 159

Mechanisms for Ultrafast Vibrational Energy Relaxation of Polyatomic Molecules. By S.F. Fischer ................................. 164
Studies of the Generation and Energy Relaxation in Chemical Intermediates-Divalent Carbon Molecules and Singlet Oxygen
By E.V. Sitzmann, C. Dupuy, Y. Wang, and K.B. Eisenthal ............ 168

New Developments in Picosecond Time-Resolved Fluorescence Spectroscopy: Vibrational Relaxation Phenomena
By B.P. Boczar and M.R. Topp ........................................... 174

Picosecond Photon Echo and Coherent Raman Scattering Studies of Dephasing in Mixed Molecular Crystals
By K. Duppen, D.P. Weitekamp, and D.A. Wiersma .................... 179

Picosecond Laser Spectroscopy of Molecules in Supersonic Jets: Vibrational Energy Redistribution and Quantum Beats
By A.H. Zewail ............................................................... 184


Direct Picosecond Resolving of Hot Luminescence Spectrum
By J. Aaviksoo, A. Anijalg, A. Freiberg, M. Lepik, P. Saari, T. Tamm, and K. Timpmann ............................................. 192

The Temperature Dependence of Homogeneous and Inhomogeneous Vibrational Linewidth Broadening Studies Using Coherent Picosecond Stokes Scattering. By S.M. George, A.L. Harris, M. Berg, and C.B. Harris 196


Picosecond Studies of Intramolecular Charge Transfer Processes in Excited $\alpha$-D Molecules
By H. Staerk, R. Mitzkus, W. Kühnle, and A. Weller .................. 205

Femtosecond Transient Birefringence in CS$_2$
By B.I. Greene and R.C. Farrow .......................................... 209

Time-Resolved Observation of Molecular Dynamics in Liquids by Femtosecond Interferometry. By C.L. Tang and J.M. Halbout .............. 212


Viscosity-Dependent Internal Rotation in Polymethine Dyes Measured by Picosecond Fluorescence Spectroscopy
By A.C. Winkworth, A.D. Osborne, and G. Porter ....................... 228

Investigation of Level Kinetics and Reorientation by Means of Double Pulse Excited Fluorescence
By D. Schubert, J. Schwarz, H. Wabnitz, and B. Wilhelmi .............. 235

Dynamics of Photoisomerization
By G.R. Fleming, S.P. Velsko, and D.H. Waldeck ......................... 238

Evidence for the Existence of a Short-Lived Twisted Electronic State in Triphenylmethane Dyes
By V. Sundström, T. Gillbro, and H. Bergström .......................... 242


Picosecond Resolution Studies of Ground State Quantum Beats and Rapid Collisional Relaxation Processes in Sodium Vapor
By R.K. Jain, H.W.K. Tom, and J.C. Diels ................................. 250

Part V Picosecond Chemical Processes

Unimolecular Processes and Vibrational Energy Randomization
By R.A. Marcus ................................................................. 254


Vibrational Predissociation of S-Tetrazine-Ar van der Waals-Molecules
By J.J.F. Ramaekers, J. Langelaar, and R.P.H. Rettschnick ................ 264

Picosecond Laser Induced Fluorescence Probing of NO₂ Photofragments
By P.E. Schoen, M.J. Marrone, and L.S. Goldberg ......................... 269

Excited State Proton Transfer in 2-(2'-Hydroxyphenyl)-Benzoxazole
By G.J. Woolfe, M. Melzig, S. Schneider, and F. Dörr .................... 273

Picosecond Dynamics of Unimolecular Ion Pair Formation
By K.G. Spears, T.H. Gray, and D. Huang .................................. 278

Effect of Polymerization on the Fluorescence Lifetime of Eosin in Water
By Wei-Zhu Lin, Yong-Lian Zhang, and Xin-Dong Fang ...................... 282

Part VI Ultrashort Processes in Biology

Picosecond Processes Involving CO, O₂, and NO Derivatives of Hemeproteins. By P.A. Cornelius and R.M. Hochstrasser .................. 288

Femtosecond and Picosecond Transient Processes After Photolysis of Liganded Hemeproteins. By J.L. Martin, C. Poyart, A. Migus, Y. Lecarpentier, R. Astier, and J.P. Chambaret ...................... 294

Picosecond Fluorescence Spectroscopy of Hematoporphyrin Derivative and Related Porphyrins


Multiple Photon Processes in Molecules Induced by Picosecond UV Laser Pulses. By V.S. Antonov, E.V. Khoroshilova, N.P. Kuzmina, V.S. Letokhov, Yu.A. Matveetz, A.N. Shibanov, and S.E. Yegorov 310

P-BR and Its Role in the Photocycle of Bacteriorhodopsin
By T. Gillbro and V. Sundström 315

Picosecond Linear Dichroism Spectroscopy of Retinal. By M.E. Lippitsch, M. Riegler, F.R. Aussenegg, L. Margulies, and Y. Mazur 319

Picosecond Absorption Spectroscopy of Biliverdin
By M.E. Lippitsch, M. Riegler, A. Leitner, and F.R. Aussenegg 323

Picosecond Time-Resolved Resonance Raman Spectroscopy of the Photolysis Product of Oxy-Hemoglobin
By J. Terner, T.G. Spiro, D.F. Voss, C. Paddock, and R.B. Miles 327

Part VII Applications in Solid-State Physics

Picosecond Time-Resolved Detection of Plasma Formation and Phase Transition in Silicon
By J.M. Liu, H. Kurz, and N. Bloembergen 332

Spectroscopy of Picosecond Relaxation Processes in Semiconductors
By D. von der Linde, N. Fabricius, J. Kuhl, and E. Rosengart 336

Picosecond Spectroscopy of Excitonic Molecules and High Density Electron-Hole Plasma in Direct-Gap Semiconductors. By S. Shionoya 341

Picosecond Time-Resolved Study of Highly Excited CuCl. By D. Hulin, A. Antonetti, L.L. Chase, G. Hamoniaux, A. Migus, and A. Mysyrowicz 345

Picosecond Dynamics of Excitonic Polariton in CuCl
By Y. Aoyagi, Y. Segawa, and S. Namba 349

Picosecond Spectroscopy of Highly Excited GaAs and CdS
By H. Saito, W. Graudszus, and E.O. Göbel 353

Non-Linear Attenuation of Excitonic Polariton Pulses in CdSe
By P. Lavallard and P.H. Duong 357

Time-Resolved Photoluminescence Study of n Type CdS and CdSe Photoelectrode
By D. Huppert, Z. Harzion, N. Croitoru, and S. Gottesfeld 360

Time-Resolved Spatial Expansion of the Electron-Hole Plasma in Polar Semiconductors
By A. Cornet, T. Amand, M. Pugnet, and M. Brousseau 364
Weak-Wave Retardation and Phase-Conjugate Self-Defocusing in Si

Ultrafast Relaxations of Photoinduced Carriers in Amorphous
Semiconductors. By Z. Vardeny, J. Strait, and J. Tauc .............. 372

Periodic Ripple Structures on Semiconductors Under Picosecond Pulse
Illumination. By P.M. Fauchet, Zhou Guosheng, and A.E. Siegman .... 376

Transmission of Picosecond Laser-Excited Germanium at Various
Wavelengths. By C.Y. Leung and T.W. Nee .......................... 380

Nonlinear Interactions in Indium Antimonide
By M. Hasselbeck and H.S. Kwok .................................. 384

Picosecond Relaxation Kinetics of Highly Photogenerated Carriers in
Semiconductors
By S.S. Yao, M.R. Junnarkar, and R.R. Alfano ...................... 389

Picosecond Radiative and Nonradiative Recombination in Amorphous As2S3
By T.E. Orlowski, B.A. Weinstein, W.H. Knox, T.M. Nordlung, and
G. Mourou ............................................................ 395

Index of Contributors .................................................. 399
A Picosecond Raman Technique with Resolution Four Times Better than Obtained by Spontaneous Raman Spectroscopy

W. Zinth, M.C. Nuss, and W. Kaiser

Physik Department der Technischen Universität München

A new Raman technique is presented which allows to observe a Raman transition with a bandwidth smaller than the common spontaneous Raman line-width.

This technique is based on short excitation and prolonged interrogation (SEPI) of molecular states /1,2/. During the short and transient excitation process the molecules are driven at the difference frequency \( \nu_D = \nu_1 - \nu_2 \) by two pulses of frequency \( \nu_1 \) and \( \nu_2 \). Raman transitions which are close to the frequency \( \nu_D \) become coherently excited with amplitudes \( Q_i \). This material excitation persists when the two pumping pulses have left the sample. After the excitation the molecules vibrate with their individual resonance frequencies and the coherent amplitudes \( Q_i \) decay exponentially with the time constants \( T_{2i} \). A third delayed probe pulse interacts with the coherently vibrating molecules and generates a Stokes spectrum of the freely relaxing material excitation.

The crucial point of the transient excited Raman spectroscopy discussed here is the narrow Stokes spectrum produced by the long third pulse. Only molecules vibrating in phase contribute to the coherent Stokes light. Molecules which have suffered collisions are out of phase and are not observed subsequently. For Gaussian shaped probing pulses the spectral width of the observed Stokes bands equals the width \( \Delta \nu_P \) of the interrogating third pulse /1,2/. With long probing pulses of duration \( t_P > 1.4 T_{2i} \) the SEPI resolution will be better than the resolution of spontaneous Raman scattering.

The experiments on SEPI spectroscopy are performed using a picosecond Nd-glass laser system /2/. The second harmonic frequency \( \nu_2 \) is used for one pumping and the probing pulse. The second pump frequency \( \nu_2 \) is generated via transient stimulated Raman scattering in a generator cell.

Experimental results on liquid cyclohexane in the frequency range 2850 cm\(^{-1}\) to 2940 cm\(^{-1}\) are shown in Fig.1. Fig.1a shows the emission band-widths of the liquids employed to generate pulses at \( \nu_2 \). The spontaneous polarized Raman spectrum of \( \text{C}_6\text{H}_{12} \) is shown in Fig.1b. Between the three strong CH-stretching modes one encounters a diffuse spectrum due to overlapping overtones or combination bands. Transition frequencies found in SEPI spectroscopy are marked with the vertical lines.
Fig. 1 Experimental results of SEPI spectroscopy of C\textsubscript{6}H\textsubscript{12}.
(a) Frequency ranges of the various Raman generators liquids used in the experiment. (b) Polarized spontaneous Raman spectrum of C\textsubscript{6}H\textsubscript{12} recorded with a resolution of 1 cm\textsuperscript{-1}. The frequency positions of the resonances found in SEPI spectra are marked with vertical lines. (c) Three SEPI spectra taken with different generator liquids. New Raman lines are detected and the spectral resolution is improved. (Note, the frequency scale of (c) is 3.7 times larger than the one of (b).)

In Fig. 1c we show three SEPI spectra on an expanded scale (factor 3.7). Each spectrum was obtained by a single laser shot. On the r.h.s. we present the sharp SEPI band corresponding to the CH-stretching mode at 2923 cm\textsuperscript{-1}. We note that the SEPI band is considerably narrower than the corresponding band in the spontaneous Raman spectrum. The SEPI spectrum in the center shows four Raman transitions between 2905 cm\textsuperscript{-1} and 2916 cm\textsuperscript{-1}. Lines as close as 2.5 cm\textsuperscript{-1} are clearly resolved. In spontaneous Raman spectra the four transitions are hidden under the wing of the strong Raman band at 2923 cm\textsuperscript{-1} and cannot be detected. Fig. 1c, l.h.s., shows a SEPI spectrum of the frequency range 2875 cm\textsuperscript{-1} to 2890 cm\textsuperscript{-1}. We find two distinct Raman bands at 2877.5 cm\textsuperscript{-1} and 2887 cm\textsuperscript{-1}. The band at 2877.5 cm\textsuperscript{-1} has never been reported on previously. It is buried in the diffuse part of the conventional Raman spectrum.

The following points are relevant for the application of the SEPI technique: (i) The frequency positions of the observed Raman lines are independent of the excitation conditions since we observe freely relaxing molecules. (ii) In SEPI experiments the exciting and interrogating pulses should not overlap temporarily in order to avoid the generation of a coherent signal via
the non-resonant four-photon parametric process. (iii) SEPI spectra taken for different delay times allow an estimate of the dephasing times $T_{2i}$. (iv) The frequency precision of the generated Stokes spectrum depends upon the frequency stability of the interrogating pulse. For highest accuracy the frequency $\nu_1$ has to be measured simultaneously with the SEPI spectrum. (v) The scattering process may also be performed on the anti-Stokes part of the spectrum. The disturbing interference found in stationary CARS spectroscopy does not occur for the delayed probing used with SEPI spectroscopy.

The data presented here give convincing evidence of the potentiality of the short excitation and prolonged interrogation spectroscopy; new Raman lines are readily observed and vibrational energies are determined with improved accuracy.

References

1 W. Zinth, Optics Commun. 34 (1980) 479