FINAL TECHNICAL REPORT

Molecular Nonlinear Optical Susceptibilities in Condensed Phases
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Nonlinear Optical Susceptibilities of Conjugated Polymers

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A unified microscopic theoretical framework for the calculation of optical excitations in molecular and semiconductor materials was developed. The hierarchy of many-body density matrices for a pair-conserving many-electron model and the Frenkel exciton model was rigorously truncated to a given order in the radiation field. Closed equations of motion were derived for five generating functions representing the dynamics up to third order in the laser field including phonon degrees of freedom as well as all direct and exchange-type contributions to the Coulomb interaction. By eliminating the phonons perturbatively we obtained equations that, in the case of the many-electron system, generalize the semiconductor Bloch equations, are particularly suited for the analysis of the interplay between coherent and incoherent dynamics including many-body correlations, and lead to thermalized exciton (rather than single-particle) distributions at long times. A complete structural equivalence with the Frenkel exciton model of molecular materials was established.

Molecular, Semiconductor, Frenkel Exciton, Coulomb

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STATUS OF EFFORT

Optical spectroscopy of conjugated molecules was described by using collective electronic coordinates, which represent the joint dynamics of electron-hole pairs. The approach relates the optical signals directly to the dynamics of charges and bond orders (electronic coherences) induced by the radiation field and uses only ground-state information, thus avoiding the explicit calculation of excited molecular states. The resulting real-space picture is reminiscent of the normal-mode analysis of molecular vibrations and offers a unified framework for the treatment of other types of systems including semiconductor nanostructures and biological complexes. Collective-oscillator representation of electronic excitations in large molecules was developed. Direct calculation of dominant oscillators was carried out using the DSMA (Density Matrix Spectral Moment Algorithm). Using this approach real-space analysis of electronic coherence sizes underlying the optical response was performed. Applications were made to collective optical excitations of poly(p-phenylenevinylene) (PPV) oligomers, stilbenoid aggregates, and acceptor-substituted carotenoids. Origin, scaling, and saturation of second order polarizabilities in donor/acceptor polyenes was studied. Vibrational and solvent effects in resonant and off-resonant optical spectroscopy were investigated. Electronically resonant and off-resonant polarizabilities were calculated. Optical response femtosecond spectroscopies and localized electronic excitations in phenylacetylene dendimers were studied.

ACCOMPLISHMENTS/NEW FINDINGS

The grant resulted in 83 publications which are listed below.

Nonlinear Optics of Molecular and Semiconductor Nanostructures: A Common Perspective

A unified microscopic theoretical framework for the calculation of optical excitations in molecular and semiconductor materials was developed. The hierarchy of many-body density matrices for a pair-conserving many-electron model and the Frenkel exciton model was rigorously truncated to a given order in the radiation field. Closed equations of motion were derived for five generating functions representing the dynamics up to third order in the laser field including phonon degrees of freedom as well as all direct and exchange-type contributions to the Coulomb interaction. By eliminating the phonons perturbatively we obtained equations that, in the case of the many-electron system, generalize the semiconductor Bloch equations, are particularly suited for the analysis of the interplay between coherent and incoherent dynamics including many-body correlations, and lead to thermalized exciton (rather than single-particle) distributions at long times. A complete structural equivalence with the Frenkel exciton model of molecular materials was established.
Multiple Exciton Coherence Sizes in Biological Antenna Complexes

The pump-probe signal from the light-harvesting antenna LH2 of purple bacteria was analyzed using a Green function expression derived by solving the nonlinear exciton-oscillator equations of motion (NEE). A microscopic definition of the exciton mean free path ($L_q$) and localization size ($L_p$) was given in terms of the off-diagonal elements of the exciton Green function and density matrix, respectively. Using phonon-induced (homogeneous) and disorder-induced (inhomogeneous) line widths compatible with superradiance measurements, we find that at 4.2 K the localization size is $L_p$ and that the shift •• between the positive and negative peaks in the differential absorption is determined by a different effective size $L_q/2 = 5.6$ associated with the exciton mean free path. Our model further predicts the recently observed superradiance coherence size determined by $L_p$. A real-space formulation of time-resolved fluorescence of molecular aggregates was developed using the one-exciton density matrix $\rho(t)$ of the optically-driven system. A direct relationship was established between the superradiance enhancement factor $L_s$ and the exciton coherence size $L_p$ associated with the off-diagonal density matrix elements in the molecular representation. Various factors which affect the latter, including finite temperature, energetic disorder, coupling with phonons, and polaron formation were explored. The theory was applied for the interpretation of recent measurements in the B850 systems of the LH2 photosynthetic complexes. Femtosecond spectroscopies of chlorophyll dimers and the LH2 antenna complex were calculated using a theory that incorporates the effect of two-exciton states, static disorder and coupling of excitons to phonons with an arbitrary spectral density. Applications were made to pump-probe and echo peak-shift measurements in the B820 dimers, and to fluorescence depolarization in the B850 system of the LH2 antenna of purple bacteria.

Two-pulse four-wave-mixing signals from molecular aggregates, including effects of two-exciton states, static disorder, and exciton-phonon interaction represented by arbitrary spectral densities were calculated. Three types of contributions to the signal were identified. The first, reflecting exciton self-correlation, is similar to the photon echo from disordered two-level systems and dominates the signal for long time-delays. The second is related to correlations of one-exciton states, whereas the third reflects correlations between one- and two-exciton states. The information gained by completely resolving the signal field (both amplitude and phase) was analyzed using Wigner spectrograms.

Two-Dimensional Real-Space Analysis of Optical Excitations in Acceptor-Substituted Carotenoids

Absorption spectra of substituted carotenoids with varying acceptor strength were analyzed using collective electronic normal modes obtained using the time-dependent Hartree—Fock (TDHF) technique combined with the INDO/S semiempirical Hamiltonian. Two-dimensional plots of the collective excitations in real-space show an off-diagonal size associated with relative motion of electron-hole pairs created upon optical excitation and a diagonal size representing the pair’s center of mass motion. By
varying the polyene chain length we show that the response of symmetric molecules is controlled by “bulk delocalized excitations with coherence size ~12 double bonds, whereas the response of short polar molecules is dominated by a localized “charge-transfer” excitation created at the acceptor end with coherence and diagonal lengths ~12 and ~17 double bonds, respectively.

**Origin, Scaling, and Saturation of Second Order Polarizabilities in Donor/Acceptor Polyenes**

Spatial coherence displayed in two-dimensional plots of the five electronic normal modes that dominate the optical response of poly (p-phenylene vinylene) oligomers with up to 50 repeat units (398 carbon atoms) in the 1.5- to 8-electronvolt frequency range suggests a saturation to bulk behavior at about five repeat units. Two-dimensional plots representing the changes in charge and bond-order distributions induced by the optical field were used to investigate the size-scaling of polarizabilities of donor/acceptor substituted elongated polyenes. The second order polarizability was shown to originate from localized regions at the donor/acceptor ends and therefore saturates to a constant value, independent on polyene size $n$, for large $n$. In contrast, the linear and cubic polarizabilites have coherence sizes that control the optical response and should be most valuable in the design of new optical materials.

**Solvent Reorganization in Long-Range Electron Transfer: Density Matrix Approach**

The dynamics of charge transfer from a photoexcited donor to an acceptor coupled through a bridge was investigated by using a correlation-function approach in Liouville space that takes into account solvent dynamics with an arbitrary distribution of time scales. The time- and frequency-resolved fluorescence spectrum from the acceptor was used to probe the scaling of the ET rate with bridge size. The crossover between the coherent tunneling (transfer) and the incoherent sequential (transport) regimes and its implications on the nature of ET process in DNA were discussed.

**Multidimensional Femtosecond Spectroscopies of Vibrational Motions in Liquids: Semiclassical Expansion**

Fifth and seventh order electronically off-resonant Raman spectroscopies in molecular liquids were investigated using a new semiclassical expansion of the optical response which applies for weak anharmonicites and low temperatures. The leading contribution can be calculated using classical equations of motion for nuclear wave packets, even when the system itself may be highly nonclassical. Two sources of nonlinearities which generate the
signal—the nonlinear dependence of the polarizability on nuclear coordinates and vibrational anharmonicities—are identified. Formal analogy between the present equations and the time-dependent Hartree-Fock equations used in electronic nonlinear spectroscopy suggest specific experimental signatures of the various nonlinearities.

Stilbenoid Dimers: Dissection of a Paracyclophe Chromophore

A series of paracyclophane derivatives that hold chromophores of varying conjugation lengths has been synthesized. These molecules mimic solid-state interactions in main-chain polychromophores and conjugated emissive polymers such as poly(\(p\)-phenylenevinylene) (PPV). Their optical properties give insight into the energetics of photoexcitations localized in a discrete chromophore relative to a state containing the through-space delocalized paracyclophe core. The observed trends in absorption, fluorescence and radiative lifetime of these compounds were reported and analyzed using collective electronic oscillators (CEO) representing the changes induced in the reduced single-electron density matrix upon optical excitation. Comparison of the CEO of the aggregates with the corresponding monomers using the two-dimensional plots provides an efficient method for tracing the origin of the various optical transition by identifying the underlying changes in the charge densities and bond orders. For some derivatives the emission is red-shifted from the “monomeric” compound and featureless, reminiscent of excimer qualities. The emissions of other molecules are similar to the “monomer” and display vibronic structure. Thus, for the smaller chromophores, emission occurs from a state containing the through-space delocalized paracyclophe core. In the situation where extended chromophores, with more stable excited states, are held together with the paracyclophe core, the photophysics of the individual chromophores dominates. The present analysis is relevant to the design and synthesis of organic molecules with desired optical properties.

Localized Electronic Excitations in Phenylacetylene Dendrimers

Electron-hole pairs created upon optical excitation of conjugated dendrimers (fractal antenna macromolecules) were shown to be localized within segments connected by benzene rings substituted at the meta-position. The absorption spectra of two families of dendrimers were analyzed using collective electronic normal modes representing the changes in charge and bond-order distributions induced by the optical field. The present approach may be used in the design of artificial light-harvesting antennae with controlled energy-funneling pathways.

Collective Coordinates for Semiclassical Femtosecond Dissipative Dynamics in Liouville Space

A semiclassical path-integral algorithm for propagating the reduced density matrix of a quantum-particle coupled to a harmonic bath with an arbitrary temperature and distribution in timescales was developed. Using a canonical transformation of the action in Liouville space, a unique prescription was provided for constructing collective bath
coordinates for a given nuclear spectral density. The number of relevant collective coordinates depends on the structure of the spectral density and increases at lower temperatures.

PUBLICATIONS

Published


PERSONNEL SUPPORTED

Research Associates:

Dr. A. Okada, Institute of Molecular Science Okazaki
Dr. E. Poliakov, University of New Mexico
Dr. E. Tsiper, University of Utah
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Dr. L. Bellegue, Institut fuer Theoretische Physik II, Germany
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Dr. T. Meier, Phillips University, Germany
Dr. O. Kuhn, Deutscher Akademischer Austauschdienst, Germany,
Dr. V. M. Axt, Institut fuer Theoretische Physik II, Germany
Dr. S. Yokojima, University of Hong Kong
Dr. Y. Zhao, University of Hong Kong
Dr. A. Piryatinski, University of Rochester
Dr. M. Schulz, University of Freiburg, Germany

Visiting Scientists:

Dr. V. Chernyak, Ph. D., USSR Academy of Sciences
Dr. O. Somsen, Free University of Amsterdam, The Netherlands

Graduate Students Supported:

Mr. S. Tretiak, Department of Chemistry, University of Rochester
Mr. W. M. Zhang, Department of Chemistry, University of Rochester
Mr. Y. Maruyama, Visiting student from the Institute of Molecular Science Okazaki
Mr. N. Wang, Department of Chemistry, University of Rochester
Mr. C. Ciordas-Ciurdario, Department of Chemistry, University of Rochester
Mr. M. Toutounji, Visiting student from Northwestern University
Mr. P. Rott, Department of Chemistry, University of Rochester

Undergraduate Students:

None

In addition, we are continuing to collaborate with these former Postdoctoral Fellows: Dr. Martin Axt, who currently holds a faculty position at the Institut fuer Theoretische Physik II Westfälische Wilhelms-Universitaet Muenster; Dr. Torsten Meier, Phillips University, Marburg; Dr. Guanhua Chen, Hong Kong University of Science
& Technology.

INTERACTIONS/TRANSITIONS

a. Participation/Presentation at Meetings, Conferences, Seminars, etc.

INVITED PRESENTATIONS


Condensed Matter Seminar on "Oscillator, Quasiparticle Representation of Femtosecond Nonlinear Spectroscopy in Condensed Phases," Department of Physics, University of California, Berkeley, April 1996.

Physical Chemistry Seminar on "Electronic Coherence and Multidimensional Optical Spectroscopy of Conjugated and Nonconjugated Molecular Materials," Department of Chemistry, University of California, Berkeley, April 1996.

Seminar on "Collective Electronic Oscillators and Nonlinear Optical Spectroscopy of Conjugated Polyenes and Molecular Aggregates," Department of Chemistry, Stanford University, Stanford, CA, April 1996.

Seminar on "Femtosecond Spectroscopy of Molecular Aggregates, conjugated Polyenes and Liquids; Molecular Dynamics in Liouville Space," Department of Chemistry, California Institute of Technology, April 1996.


Tutorial Course at the XVth International Conference on Raman Spectroscopy, (ICORS 96), University of Pittsburgh, Pennsylvania, August 1996.


Universität Würzburg, Department of Physics, Germany, "Multidimensional Femtosecond-Spectroscopy of Nuclear Dynamics in Liquids," October 1997.

Universität Ulm, Department of Physics, Germany, "Collective Excitations in Nonlinear Spectroscopy of Conjugated and Aggregated Molecules," October 1997.


University of Utrecht Institute of Theoretical Physics, Netherlands, Physics Colloquium, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.


University of Groningen, Netherlands, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.


European Laboratory for Non-Linear Spectroscopy, (LENS), University of Firenze, Italy, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.

Dipartimento di Chimica Industriale e Ingegneria Chimica "Giulio Natta" Politecnico di Milano, Italy, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.


University of Toronto, Department of Physics, Toronto, Canada, "Collective Electronic Excitations in Femtosecond Spectroscopy of Conjugated Molecules and Biological Complexes", November, 1998


b. Consultative and advisory functions
Advisory panel for DESY, workshop on “x-ray scattering from electron systems in the field of coherent radiation” to be held in Hamburg, September 17 and 18, 1996.

c. Transitions. Cases where knowledge resulting from your effort is used, or will be used

We started a collaboration with Dr. Ruth Pacher’s group at Wright Patterson to combine our oscillator procedure to ab initio calculations. We also discussed the possibilities of calculating resonant saturation effects in $\chi^{(3)}$ of conjugated polyenes.

NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

None at this time

HONORS/AWARDS

Fellow of the American Physical Society (elected 1987)

Fellow of the Optical Society of America (elected 1989)


Advisory Editorial Board of Chemical Physics Letters (1996-98)

Miller Fellowship at the Departments of Chemistry and Physics, University of California, Berkeley (1996)

Advisory board of the Ultrafast Phenomena Tenth International Meeting (1996)

Guggenheim Fellow (1996)

The Raymond and Beverly Sackler Lectureship, Tel Aviv University (1997)

Alexander von Humboldt Research Award for Senior US Scientists (1997)

Nominating Committee for the Division of Chemical Physics APS (1997)


General Co-Chair, Ultrafast Phenomena XII (2000)