

**Adventures in
CHEMICAL PHYSICS
ADVANCES IN CHEMICAL PHYSICS
VOLUME 132**

Edited by

R. STEPHEN BERRY and JOSHUA JORTNER

Series Editor

STUART A. RICE

Department of Chemistry
and
The James Franck Institute
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ADVENTURES IN CHEMICAL PHYSICS

A SPECIAL VOLUME OF ADVANCES IN CHEMICAL PHYSICS

VOLUME 132

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

STUART ALAN RICE: SCIENTIST WITHOUT BOUNDS

We, the editors of this volume, have had the remarkably good fortune to be close friends and scientific associates of Stuart Rice almost “from the days when dinosaurs roamed the earth.” One of us met Stuart in 1952 on the first day of graduate school at Harvard. The other began working with Stuart ten years later in 1962, five years after Stuart had joined the faculty of the University of Chicago. Stuart came to Harvard from Bronx Science High School and then Brooklyn College. In 1952, when he arrived as a graduate student at Harvard, he joined the research group of Paul Doty, working on biopolymers, including the unwinding of the strands of the DNA helix. Characteristically, that work did not keep him completely occupied, so he simultaneously worked on several other problems such as polyelectrolytes and the folding of proteins, among other things. He became a Junior Fellow at Harvard and switched to doing high-temperature infrared spectroscopy of gaseous molecules, in collaboration with William Klemperer. After a year he moved to Yale, where he spent his second year of the Fellowship in the group of John Kirkwood.

Stuart came to the University of Chicago in 1957, and has been a major figure in physical chemistry and other areas of science for almost 50 years. He made central contributions to the intellectual environment, to the highest-quality scientific endeavor, to the remarkable interdisciplinary scientific collaboration, and to the intense focus on excellence at the University of Chicago. In an admirable way he promoted and perpetuated the unique culture of the University. In 2005, the University of Chicago Alumni Association awarded him its Faculty Achievement Medal, in recognition of what his teaching and guidance meant to many, many students over the years.

Stuart’s contributions to science have ranged across virtually the entire domain of modern physical chemistry. His research uses state-of-the-art experimental methods and fundamental theoretical approaches, spanning from isolated molecules to the condensed phase. His work has consistently been pioneering, often constituting the first attack on a new subject

and, most characteristically, always addressing an important research area. Stuart as a scientist is universal, deep and demanding of the highest intellectual standards. His work has had, and continues to have, great influence on the development of chemistry and other related areas of science.

Stuart has taught us new fundamental concepts in fields ranging from the nature of liquids through the puzzling subject of liquid metal surfaces to coherent quantum control of chemical reactions. His studies of active control of molecular dynamics can be seen as evolving through a long series of contributions to predecessor forefront areas of physical chemistry. He made seminal advances to the theory of electronic states of molecular solids, polymers, and liquids, including theoretical studies of singlet and triplet exciton band structure, exciton–exciton annihilation reactions, hole and electron mobility and band structure, and exciton states in liquids. Although now 40 years old, these calculations have not been superseded, and recent experimental data testify to their accuracy. The studies of condensed matter electronic structure led to theoretical and experimental studies of radiationless transitions, including landmark experimental and theoretical studies of the vibrational state dependence of the decay of optically excited molecules under collision-free conditions and the generalization of the theory to describe unimolecular reactions. In turn, these studies led to the examination of vibrational energy flow in polyatomic molecules. He was a pioneer in the study of the influence of deterministic classical mechanical chaos on the classical theory of the unimolecular reaction rate, and he has published seminal studies of quantum chaos and its relevance to chemical reactions. These diverse studies laid the foundation for Stuart’s development of the theory of optical control of molecular dynamics as applied to controlling product selection in a chemical reaction, introducing the concepts of multiple pulse timing control. Stuart studied the conditions for the existence of the optimal control field for a system with a spectrum that is typical of a reacting molecule. Recently, Stuart has focused his attention on adiabatic transfer processes that can be used to control molecular dynamics and has started to develop the theory of control of molecular dynamics in a liquid, the medium in which the vast majority of chemical reactions take place.

Stuart’s studies of the structure of the liquid–vapor interfaces of metals and alloys can also be related to his previous research. He developed the first theory of transport in dense simple fluids that explicitly recognizes, and accounts for, the different dynamics associated with short-range repulsion and longer-ranged attraction. He has contributed to the theory of the three-molecule distribution function in a liquid and the theory of melting, and he developed the Random Network Model of water and the first consistent

description of the amorphous solid phase of water. His work provided the first evidence for the existence of a high-density form of amorphous solid water, opening the study of polymorphism in disordered phases. Concurrently, he initiated studies of the structures of the liquid–vapor interfaces of metals and alloys. This work showed that the character of the interaction between the atoms in a liquid metal (e.g., a “pool of mercury”) is fundamentally different from that between the atoms in a dielectric liquid. Consequently, it is reasonable to expect that their respective interfaces have different structures. The theoretical challenge is that in the inhomogeneous region the various length scales associated with the width, the depth over which the excess concentration of a segregated component is distributed, the range of positional correlations, the range of the effective ion–ion interactions, and the distances over which the electrons undergo a transition from delocalized states (in the bulk liquid) to localized states (e.g., in the vapor) are all of comparable magnitude. He developed the modern theoretical description of the liquid–vapor interfaces of pure metals and alloys that correctly accounts for the electronic structure of the metal and its dependence on the atomic distribution and composition across the interface, and he advanced the first prediction that the liquid–vapor interface of a metal is stratified and that in a dilute alloy the solute segregates to form a complete monolayer at the interface. These predictions have now been multiply verified in experimental studies. Some recent, fascinating experimental work led to the discovery that some solutes can form a crystalline monolayer in the liquid–vapor interface, a finding that was not anticipated by theory and which does not yet have a theoretical interpretation.

Stuart has held many responsible administrative posts at the University of Chicago, ranging from the Director of the James Franck Institute to the Chairman of the Chemistry Department. Subsequently he became the longest-serving Dean of Physical Sciences in the Division’s history. Through all that, Stuart’s research continued at full speed and productivity. He served on the National Science Board and received the Presidential Medal of Science of the United States. And he still continues his research program, working closely with his students and postdoctorals, even when he changed roles to Professor Emeritus at Chicago and became Special Advisor to the Director at Argonne National Laboratory.

Stuart has been a major contributor to building and maintaining the strength of the Chemical Sciences in Chicago, in the United States, and throughout the world. The more than 100 Ph.D. research students and many postdoctoral fellows who worked with him have become important figures in the field of physical chemistry and in other areas of science. Stuart has been an advocate for chemistry and for science generally, both nationally

and internationally, and has helped to shape the direction of science for the future.

We both want to take this opportunity to express the great pleasure and honor it has been and still is to be Stuart's colleagues and collaborators, and we look forward to many new explorations with him into the mysteries that science can unravel.

R. STEPHEN BERRY
JOSHUA JORTNER

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DYNAMICAL MODELS FOR TWO-DIMENSIONAL INFRARED SPECTROSCOPY OF PEPTIDES[†]

ROBIN M. HOCHSTRASSER

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[†]In recognition of his amazing impact on chemical physics, this survey is dedicated to Stuart Rice on the occasion of his 70th birthday.

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I. INTRODUCTION

The development of methods that can determine the time dependence of structural changes in complex systems, particularly biological systems, represents an exciting challenge for chemical physics. The new multidimensional infrared spectroscopies, 2D- and 3D-IR [1–19], which have essentially unlimited time resolution on the scale of large structural changes, can be expected to contribute significantly to this goal. Such approaches are expected to complement the vast knowledge of average structures obtained by the established methods of structural biology and their time dependent variants.

Decades of theoretical and experimental research on nonlinear optical and infrared spectroscopy have established the concepts underlying the operational aspects of multidimensional infrared experiments. However, the principles now used for the manipulation of the multidimensional IR data sets in time or frequency domains, phase manipulation, properties of multidimensional Fourier transforms, and many other procedures, often of significant complexity, are closely related to textbook material in NMR [20] even though the practical aspects of the two types of experiment are quite different. Analogous to NMR, the signal generation in 2D-IR is based on the interaction of successive phase-locked pulses with a sample followed by detection of the field generated after the last pulse. For experiments in the IR or the optical regime, which are at much higher frequencies than most detectors can respond, heterodyne methods must be used to obtain the generated *field*. Heterodyning, which permits the measurement of optical electric fields by mixing on a slow square law detector, has been employed since the earliest days of optical nonlinear spectroscopy [21]. In the higher-frequency regimes of optical and IR fields, in contrast to radio and microwaves, the detected field is generally in the weak signal limit and therefore chosen from a particular order of nonlinearity. On the other hand, NMR and EPR are generally conducted near the saturation limit. The optical and IR approaches have mainly been third-order susceptibility measurements with the exception of some recent Raman spectroscopy experiments on liquids which were in the fifth order [22].

The earliest 2D-IR experiments used a versatile pump-probe technique [1], but the first 2D-IR photon-echo results were reported soon after that [3]. The spectral line narrowing or optimization aspect of 2D-IR arises from the contribution of the *photon echo* to the signal. These echoes are part of the pump-probe signal also, but they can be examined free from other influences by means of photon-echo spectroscopic methods. Since the announcement of the first photon-echo experiment with two incident visible light pulses on ruby crystals [23], it has been well known that the echo signal separates inhomogeneous and homogeneous contributions to the spectral line width in the optical spectrum in analogy with what already had been clear for radio-frequency and microwave spin echoes of two-level systems. However, the work of Mukamel and co-workers [24] has shown that the dynamics of optically prepared states cannot generally be considered in terms of Bloch parameters, so the echo responses in the optical and IR spectral regions are indeed considerably different and often more difficult to model than those in NMR. The first high-frequency two-pulse photon echoes on individual molecules, rather than solid-state materials, were actually carried out in the *infrared* around 10.6 μm on SF_6 by Patel and co-workers [25] and at 3 μm by Brewer and Shoemaker [26] who demonstrated that most of the pulsed RF responses could be reproduced in the infrared with vibrational modes of methyl fluoride acting as the two-level systems. This work was a landmark achievement in quantum optics and led to many other infrared photon echo studies of the dephasing of vibrational transitions. In 1974 Wiersma and Aartsma reported two-pulse photon echoes of two-level electronic transitions of molecules in mixed molecular crystals at low temperatures on nanosecond time scales, in work that gave birth to a new dimension in the field of time-dependent spectroscopy of molecular solids [27]. With the advent of reliable, shorter, laser pulses these optical measurements were naturally extended to the available pulse time scales and to a range of media such as liquids and glasses in which the motions were faster, matching the available time resolution. For example, in 1991, Shank and co-workers [28] reported two-pulse photon echoes in the optical spectrum with 6-fs time resolution, the then shortest available pulses. Many variants of the photon echo at a variety of time scales including heterodyning, gating, three-pulse methods (see, for example, Ref. 29), and more recent two-dimensional techniques [30] were developed for optical pulse experiments along with methods for deducing the time correlation functions of the frequency fluctuations [31]. On the theoretical side, predictions of the form and possible importance of multidimensional optical spectroscopies had been predicted already in 1993 [32]. Although various femtosecond-time-scale IR experiments had been carried out on a variety of proteins and aqueous systems in this early period [33–38], suitably short, sufficiently stable, and tunable pulses were not so readily available in the infrared region until the titanium sapphire laser and modern nonlinear optical materials for infrared

frequency generation became more established. Nevertheless, the two-pulse echo technique with infrared radiation was extended to the picosecond regime in experiments of Fayer and co-workers, who used an infrared free electron laser source to determine the two-level system dynamics of vibrators in solutions and glasses [39]. Femtosecond-time-scale three-pulse echoes of vibrations in the infrared were first accomplished in 1998 for ions in liquid water [40] and later for peptides [41] and proteins [41, 42]. In 2000, three-pulse phase-locked echo experiments with heterodyne detection on peptides [3] finally enabled the assembly of multidimensional vibrational spectra in the mid-infrared. The 2D-IR spectra had also been constructed from pump-probe experiments on peptides and proteins [1]: the spectra obtained in this approach are closely related to the real part of the heterodyned 2D-IR experiment [43]. The theory of two-dimensional vibrational spectroscopy is also in place [44]. The field of multidimensional IR spectroscopy of vibrators is now very active and is replete with recent important technical and scientific advances from many different laboratories and diverse areas of application [43, 45, 46], including liquids [47, 48], which attests to the outstanding potential of such methods for the study of structure and molecular dynamics in liquids, glasses, and biological systems.

The backbones of protein structures are the polypeptides whose amide units, $-\text{NHCH(R)CO}-$, have infrared spectra that are ultrasensitive to the details of the many possible secondary structures that exist in proteins. The 2D-IR method exposes much more information regarding the potential surfaces of polypeptides than conventional FTIR spectroscopy because it accesses anharmonic contributions directly, but the interpretation of the results depends on having a deeper understanding of the dynamics of vibrational states than can be obtained from pump-probe experiments. Already a few nonlinear IR spectroscopic investigations have been carried out on the amide-I and amide-II transitions of polypeptides and peptides: These transitions involve mainly the carbonyl stretching mode and in-plane CNH bending modes. Another structure sensitive vibration of the peptide group is the amide-A mode that is mainly the N-H stretching motion. Recently the first series of experiments using dual frequencies in 2D-IR were used to examine the coupling between the amide-I and amide-A modes [18].

Nonlinear infrared spectroscopy can in principle provide knowledge of all the relaxation processes of oscillators, including those that do not manifest themselves in the linear spectral line shapes. The $\nu = 0 \rightarrow \nu = 1$ transition line shape is determined by the overall rotation of the molecule, population relaxation time T_1 and by the vibrational frequency correlation function. The experimental line-shape is not a very useful determinant of this correlation function [40, 49] because it provides experimental data only along one axis, either frequency or time, and the line-shape function is usually too complex to

be described by a few parameters. The third-order nonlinear IR experiments provide data along three axes in principle, and even 2D-IR obtains a square grid of data points. These factors result in the correlation function being much better determined than by linear methods simply because of the increase in the number of observables dependent on the same set of parameters. The nonlinear experiments probe levels beyond $v = 0$ and $v = 1$ and so generate relaxation properties that are not part of the IR line shape. Furthermore, by judicious choice of phase-matching conditions and pulse sequences, the nonlinear signal can be chosen to emphasize different characteristics of the dynamics and of the correlation function by means of the pump-probe, transient grating and two- or three-pulse photon echo experimental arrangements [6, 40, 42, 47, 50–54]. Furthermore, the methods allow the determination of key parameters of the anharmonic potential surfaces of peptides and hence provide important tests of theoretical calculations of molecular structure and dynamics. These coherent nonlinear infrared techniques permit experimental determination of the coupling and angular relations of vibrators using experimental protocols that are analogous to those developed for NMR. The first such experiments concerned the amide-I modes of peptides, which are mainly C=O vibrators. In that case all the relevant frequencies of an interacting ensemble of modes could readily be bracketed by the spectral bandwidth of 120-fs infrared laser pulses. The response of such a system to sequences of three pulses, each with the same center frequency in the amide-I region, gave rise to coherent signals whose two- and three-dimensional correlation spectra yielded the relevant structural and dynamical information. We have recently carried out dual-frequency phase-locked 2D-IR experiments in which the coupling of different modes can be examined, free from the contributions of the fundamentals themselves [15, 16, 18].

In the present chapter we discuss the signal processing of heterodyned three-pulse echo experiments in the infrared using single and dual frequencies. The basic approaches to understanding these experiments have long been part of nonlinear spectroscopy on which subject there have been many reviews [8, 11, 43, 55–62] and textbooks [21]; the underlying theory of nonlinear spectroscopic experiments with special focus on pulsed laser responses is unified in the recent book by Mukamel [29]. An important part of all nonlinear experiments, including 2D-IR, is the processing and engineering of the signals. All of the procedures used are common in other fields such as radio-frequency communications, acoustics, and nuclear magnetic resonance. However, until recently, such approaches have not been widely used for high-frequency signals as in the optical and mid-IR regimes. Therefore a very brief review is given of elementary properties of electromagnetic fields and the way they enter into nonlinear experiments. Different types of interferometry are then briefly introduced with reference to model pulses. There are a number of recent, useful

accounts of the technical aspects of nonlinear spectroscopy using short pulses that focus on multidimensional methods. But the current activity in multidimensional methods derives from basic nonlinear optical spectroscopy developed for molecules mainly in the 1970s and 1980s, the vast literature on signal processing and spectral analysis (see, for example, the Prentice-Hall Signal Processing Series), and gradual enlightenments on the relationships between nonlinear spectroscopy and NMR [63].

In the 2D-IR experiments there exists a useful simplification of the description of the spectra when the vibrational dynamics is in the separation of time-scales limit of the so-called Bloch dynamics. Then the correlations of the fluctuations of the various quasi-degenerate amide modes dominate the signals and the interpretations are quite straightforward and analytic. On the basis of experimental determinations of the correlation functions, we explore some of the sensitivities of the 2D-IR signals to the dynamic approximations. In addition, we discuss some of the important possible manipulations of the 2D-IR spectra that permit the display of essentially all possible third-order nonlinear responses from a single data set.

II. RELEVANT ASPECTS OF THE GENERATED FIELDS AND LINEAR RESPONSE

In order to introduce some notation, we first recall a few of the well-known properties of the interaction of light pulses with molecules in the linear approximation. Frequently, the signals in nonlinear optical experiments are expressed in terms of the polarization induced in the medium by the incident pulses. The complex linear polarization $P(t)$ vector for a distribution of identical two-level systems is obtained from an elementary calculation of the density matrix using the Liouville equation of a system perturbed by an electric field and proceeding as follows:

$$P(t) = \mu_{10}\rho_{01}(t) = -\left(\frac{i}{2\hbar}\right)\mu_{10}\mu_{01} \cdot \hat{\mathbf{e}} \int_0^\infty dT E(t-T)e^{-(i\omega_{01}+\gamma)T} \quad (1)$$

where $\hbar\omega_{01} = \hbar(\omega_0 - \omega_1)$, $\rho_{01}(t)$ is the coherence in the two-level system, $E(t)$ is the applied field in the rotating wave approximation (i.e., the envelope times $\exp(-i\omega t)$), μ_{10} is the $1 \rightarrow 0$ transition moment dipole vector, $\hat{\mathbf{e}}$ is the field polarization vector, and γ is the relaxation rate of the coherent state. More generally, the dynamics is not representable by a distribution of homogeneously broadened transitions but requires more elaborate types of frequency correlation functions. However, this so-called Bloch model is useful to demonstrate the character of the interaction of light and molecules.

A delta-pulse field of unit area and angular frequency ω is obtained from a Gaussian pulse by tending its time width to 0:

$$E(t - T) = \text{Lim}_{\sigma \rightarrow 0} \left(\frac{1}{\sigma\sqrt{\pi}} \right) e^{-(t-T)^2/\sigma^2 + i\omega(t-T)} = \delta(t - T) e^{i\omega(t-T)} \quad (2)$$

The complex polarization [Eq. (1)] becomes

$$P_\delta(t) = - \left(\frac{i}{2\hbar} \right) \mu_{10} \mu_{01} \cdot \hat{\mathbf{e}} e^{-(i\omega_{01} + \gamma)t} = R(\omega_{01}, t) \quad (3)$$

which defines a linear response function for a single oscillator from a distribution of oscillators undergoing spontaneous decay with rate γ . In a very weakly absorbing medium where the probability distribution of frequencies is $G(\omega_{01})$, the corresponding ensemble polarization is obtained as

$$\langle R(\omega_{01}, t) \rangle = \int R(\omega_{01}, t) G(\omega_{01}) d\omega_{01} \quad (4)$$

If the deviation from the mean frequency, $\bar{\omega}_{01}$, is Gaussian with standard deviation σ , the complex polarization response to a delta function excitation becomes

$$- \left(\frac{i}{2\hbar} \right) \mu_{10} \mu_{01} \cdot \hat{\mathbf{e}} e^{-(i\bar{\omega}_{01} + \gamma)t - \sigma^2 t^2 / 2} \quad (5)$$

This polarization generates the so-called free decay field of the sample which, when dominated by the inhomogeneous contribution, exhibits a Gaussian decay of the oscillations at $\bar{\omega}_{01}$. This emission trails behind the excitation pulse and its peak amplitude is related to the absorption coefficient of the sample. The Fourier transform of this signal is the Voigt profile. In a conventional linear experiment, this free induction decay (FID) of the sample is collinear with the driving field, as specified by Maxwell's equations. In the next paragraph we imagine that the FID is measured independently of the driving field, which can be arranged in a variety of different experimental arrangements, one of which is by combining the signal on the detector with a variably delayed ultra-short pulse excitation.

In any experiment the generated signal *after the sample* is actually a real field that is generated by the oscillating polarization *in the sample* over the path length l . This complex electric field is $(2\pi i \omega l / c) P(t)$, so that the envelope of the cosine part of the polarization is the envelope of the sine part of the electric field, and vice versa. If we carry out a heterodyne measurement on this field with a very short pulse, we measure a real signal $S(t)$ which is proportional to $\text{Re}\{iP(t)\}$, so that for the homogeneous system the signal is

$S(t) = e^{-\gamma t} \cos \omega_{01} t$. The half-Fourier transform (HFT) of this signal is the complex spectrum. We take the HFT because there is no signal prior to the excitation time $t = 0$:

$$\mathbf{S}(\omega) = \int_0^{\infty} dt S(t) e^{-i\omega t} = \frac{(\gamma + i\omega)}{(\gamma + i\omega)^2 + \omega_{01}^2} \quad (6)$$

There are identical spectra at positive and negative frequency in this cosine transform. If we assume the delta pulse probing time to be shifted by an amount τ , we get a phase shift $\phi = \omega_{01} \tau$ and the real and imaginary parts of the spectrum become mixed illustrating how important is the choice of time zero in experiments. It is also important to avoid timing fluctuations $\delta\tau$ in such experiments since they give rise to phase fluctuations $\omega_{01} \delta\tau$. A brief discussion of some elementary aspects of signal processing that need to be considered in IR experiments is presented in Section III.

The polarization induced in a molecule by n successive interactions with a field $E(t)$ is termed the n th order polarization. Each interaction involves the field coupling to a transition dipole μ . The 2D IR involves a calculation of the third order polarization, $Tr\{\rho^{(3)}(t)\mu\}$, which requires a quantum dynamics derivation of the third order term, $\rho^{(3)}(t)$, in the expansion of the density operator as a function of the field. The quantum dynamics is accomplished by solving the Liouville equation for the density matrix: $\dot{\rho}(t) = i/\hbar[\mu(t) \cdot E(t), \rho(t)]$, which is often done by some type of iterative procedure. In the experimental methods described herein the field $E(t)$ is composed of up to three light pulses that can be separated in time and direction by the experimenter. But always there will be three interactions: either all interactions from one pulse; two from one and one from the other; or one from each of three pulses. Mukamel's book [29] contains a full account of the theoretical methods of nonlinear spectroscopy which will not be dealt with further in this article.

III. TIME-DEPENDENT AND SPECTRAL PHASE

The subject of phase and phase retrieval with pulsed optical signals, although it is textbook material and involves well-known signal processing concepts [64, 65], has impacted on molecular spectroscopy only recently [66] through consideration of optical control experiments. As we shall see the phase is a consideration in heterodyne laser experiments because it influences the mixing of fields incident on a square-law detector. It is well known that a quadratic phase alters the spectrum, the time envelope and the time–frequency bandwidth of a pulse. Consider a pulse:

$$E(t) = e^{-at^2} e^{i(\omega_0 t + bt^2)} = \varepsilon(t) e^{i\phi(t)} \quad (7)$$

and its Fourier transform:

$$\mathbf{E}(\omega) = \int_{-\infty}^{\infty} E(t)e^{-i\omega t} dt = (\pi/(a - ib))^{1/2} e^{-(\omega_0 - \omega)^2/4(a - ib)} = \varepsilon(\omega)e^{i\varphi(\omega)} \quad (8)$$

with $\phi(t)$ the *time-dependent phase*, a real spectrum amplitude $\varepsilon(\omega)$, and a *spectral phase* $\varphi(\omega)$ which includes a constant part. The power spectrum $\mathbf{E}(\omega)\mathbf{E}^*(\omega)$ of the field is $\varepsilon^2(\omega)$ whose time–frequency bandwidth is $0.44\sqrt{1 + (b/a)^2}$. All signal fields representing input or output fields of nonlinear optical experiments can be written in the equivalent forms in the last steps of Eqs. (7) and (8), and we can discuss them either in terms of the time-dependent or spectral phase. Although $\phi(t)$ and $\varphi(\omega)$ are often awkwardly related, there is an exact connecting relationship between them [67]:

$$\int t\phi'(t)\varepsilon^2(t) dt = \int \omega\varphi'(\omega)\varepsilon^2(\omega) d\omega \quad (9)$$

where $\varphi'(\omega) = d\varphi(\omega)/d\omega$ and $\phi'(t) = d\phi(t)/dt$ is the instantaneous frequency. The interpretation of $\phi(t)$ is straightforward: The phase gives the variations of frequency across the pulse. Changes in the spectrum enter through $\varphi(\omega)$, which may cause shifts in the mean frequency of the field. These definitions are easily illustrated for a Gaussian pulse having both quadratic and cubic phase, which would be approximately the situation if the phase were determined by passing the beam through standard optical materials [68] as occurs in our 2D-IR experiments:

$$E(t) = e^{-at^2/2} e^{i\varphi(t)} = e^{-at^2/2} e^{i(\omega_0 t + bt^2/2 + ct^3/3)} \quad (10)$$

for which $\phi'(t)$ is $\omega_0 + bt + ct^2$, manifesting both *linear* and *quadratic* chirp. Its mean frequency of $(\omega_0 + c/2a)$ is calculated from the average over the envelope squared as $\int_{-\infty}^{\infty} \phi'(t)e^{-at^2} dt$, illustrating that the cubic phase shifts the mean frequency. The frequency bandwidth is computed from $\langle \phi'(t)^2 \rangle - \langle \phi'(t) \rangle^2$, and only if there is no chirp do we get the expected variance of $a/2$. The complex spectrum of a linearly chirped pulse ($c = 0$) is readily obtained analytically from Eq. (10) to illustrate some important aspects. Apart from constant phase and amplitude terms, it is

$$\mathbf{E}(\omega) = e^{-a(\omega - \omega_0)^2/2(a^2 + b^2)} e^{-ib(\omega - \omega_0)^2/2(a^2 + b^2)} \quad (11)$$

from which it is seen that the spectral phase is also Gaussian and it can cause the real part of the field to change its sign at certain frequencies, depending on the magnitudes of the factors a and b . The spectral phase at the $1/e$ points of the power spectrum of the pulse is $b/2a$. Although well known from conventional signal theory, these are important considerations for spectroscopies such as

2D-IR where the complex field is measured and where representations of the real and imaginary parts of a spectrum might be desired. A comparison of the result (11) to the time-dependent phase through expressions (10) and (9) is a useful exercise. In nonlinear spectroscopy the generated field may have a time-dependent frequency that manifests itself in much the same manner as these simple examples of chirp.

IV. THE EFFECT OF OPTICAL DENSITY

In many of the nonlinear IR experiments the samples might have to be optically dense. This presents challenges to the interpretation of multi dimensional spectroscopy as the following example describing the propagation of a Gaussian pulse through an absorbing medium shows. This question was treated sometime ago [69] for an input Gaussian pulse spectrum with spectral width σ :

$$\mathbf{E}(\omega, 0) = \left(\frac{1}{2\pi\sigma^2} \right)^{1/2} e^{-(\omega-\omega_0)^2/2\sigma^2} \quad (12)$$

The output pulse after distance z is

$$\mathbf{E}(\omega, z) = \mathbf{E}(\omega, 0) e^{i\omega z n(\omega)/c} \quad (13)$$

where $n(\omega)$ is the complex refractive index through the resonance given by

$$n(\omega) = n_\infty - \frac{c\gamma\alpha(\omega_0)}{2\omega(\omega - \omega_0 + i\gamma)} \quad (14)$$

where ω_0 is the resonance frequency and γ is the resonance half-width (i.e., $1/T_2$, in angular frequency units). We assume that no other resonances need to be considered, which would be good approximation for an isolated vibrational transition. The field suffers loss with absorption coefficient $\alpha(\omega)/2$ as a result of the imaginary part of $n(\omega)$. The outgoing pulse in the time domain is then given by

$$\begin{aligned} E(z, t) &= \left(\frac{1}{2\pi\sigma^2} \right)^{1/2} \int_{-\infty}^{\infty} d\omega e^{i\omega t} \left\{ e^{-(\omega-\omega_0)^2/2s^2} e^{-\alpha(\omega)z/2} \right\} e^{i\left\{ \omega n_\infty z/c - \frac{\gamma(\omega-\omega_0)\alpha(\omega_0)z/2}{(\omega-\omega_0)^2 + \gamma^2} \right\}} \\ &\equiv \int_{-\infty}^{\infty} d\omega e^{i\omega t} \varepsilon(\omega) e^{i\varphi(\omega)} = \int_{-\infty}^{\infty} d\omega e^{i\omega t} \mathbf{E}(\omega, z) \end{aligned} \quad (15)$$

where we have used the curly brackets to clarify our definition of the field amplitude $\varepsilon(\omega)$ and the spectral phase $\varphi(\omega)$, where both ε and φ are real and t is now a reduced time ($t - n_\infty z/c$). In this case the spectral phase is a Lorentzian having a different sign on either side of the resonance. An important point about the integral in Eq. (15), according to Garrett and McCumber, is that a correct description is not obtained by expanding the Lorentzian phase and absorption

factors about ω_0 up to quadratic or cubic terms *except when the spectral width of the light pulse is much less than the resonance width*. This limit is not useful when we use femtosecond pulses and vibrational resonances having dephasing times comparable or longer than the pulse widths—which are the only cases of much modern interest. Thus the integral must be evaluated numerically. When the optical density of the sample at the peak, given by $\alpha(\omega_0)z/2.303$, is large and the peak is relatively narrow compared with the bandwidth of the pulse, the integrand only has value on either side of the pulse. $E(z, t)$, as shown in Fig. 1(b). The Wigner spectrogram, $W(\omega, t)$, offers a useful representation of the time-dependent frequency of this signal. It is convenient to use the frequency

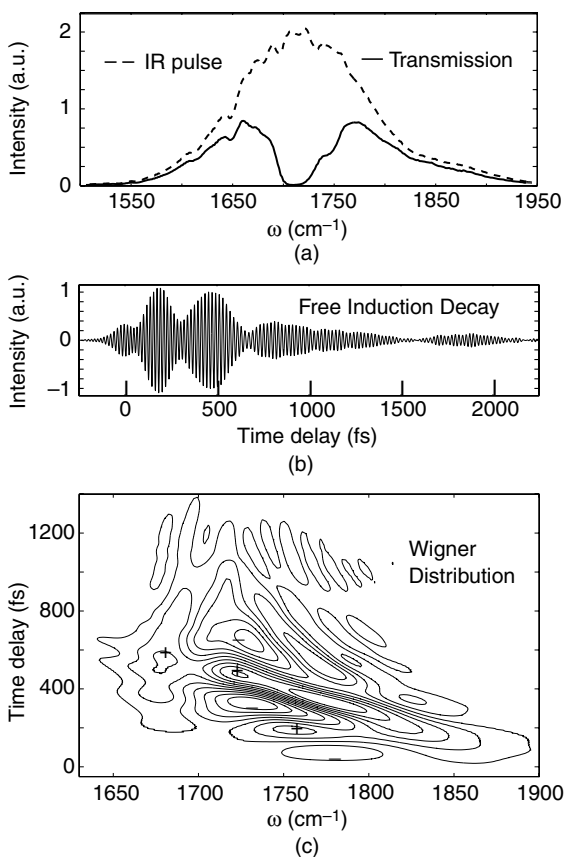


Figure 1. The effect of coherent excitation on light transmission. (a) The incident and transmitted pulses through a sample having an optical density of 1.0. (b) The free induction decay created by the coherent excitations by the pulse in (a). (c) The Wigner distribution (see text) of the FID shown in (b).

definition of the spectrogram:

$$W(\omega, t) = \int_{-\infty}^{\infty} d\theta \mathbf{E}^* \left(\omega + \frac{\theta}{2}, z \right) \mathbf{E} \left(\omega - \frac{\theta}{2}, z \right) e^{-i\theta t} \quad (16)$$

which is shown in Fig. 1(c) for a pulse passing through a sample with an optical density of 1.0. These are results for liquid acetone, illustrating the pulse reshaping that occurs because the sample has finite optical density. Of course this effect is related to continued reemissions of the type illustrated at first order in Eq. (5). The generated field measured by heterodyne detection is shown in Fig. 1(b). The effects of high optical density on heterodyned 2D spectroscopy have recently been discussed [70, 71].

V. HETERODYNE SPECTROSCOPY

In order to obtain multidimensional spectra, it is necessary to measure the amplitude and the phase of the signal generated by a sample in response to some incident fields. Directing the generated field to a square law detector such as a photomultiplier or photodiode measures only the amplitude squared of the generated field. However, if the generated field is combined collinearly with a reference field and both are incident on the detector, the current in the detector circuit has a component that depends on the product of the two fields and it determines the signal field if the reference is known. This procedure is termed *heterodyning* and the principle has been employed in nonlinear spectroscopy, particularly in Kerr effect measurements [21]. There are two principal methods of obtaining heterodyned spectra in the IR region: time domain and spectral interferometry.

VI. SPECTRAL INTERFEROMETRY

In spectral interferometry, two IR pulses separated by time τ are sent to a monochromator and the total spectrum is measured. By definition the two fields are the Fourier transforms:

$$\begin{aligned} \mathbf{E}_1(\omega) &= \int_{-\infty}^{\infty} \varepsilon_1(t) e^{i\phi_1(t) - i\omega t} dt \quad \text{and} \\ \mathbf{E}_2(\omega) &= e^{-i\omega\tau} \int_{-\infty}^{\infty} \varepsilon_2(t - \tau) e^{i\phi_2(t - \tau) - i\omega(t - \tau)} d(t - \tau) \end{aligned} \quad (17)$$

so that $\mathbf{E}_1(\omega) = \varepsilon_1(\omega) e^{i\phi(\omega)}$ and $\mathbf{E}_2(\omega) = \varepsilon_2(\omega) e^{i\phi_2(\omega) - i\omega\tau}$. The latter form is a general way of expressing a field in the frequency domain having a particular time shift. The total field incident on a detector at setting ω of the monochromator is the sum of these two fields, and the current in the detector

circuit $S(\omega)$ is proportional to the absolute square of that sum:

$$\begin{aligned} S(\omega) &= \left| \varepsilon_1(\omega)e^{i\varphi_1(\omega)} + \varepsilon_2(\omega)e^{i\varphi_2(\omega)-i\omega\tau} \right|^2 \\ &= \varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2 + 2\varepsilon_1(\omega)\varepsilon_2(\omega)\cos[\varphi_{21}(\omega) - \omega\tau] \end{aligned} \quad (18)$$

Often in an experiment it is possible to eliminate the contributions from the two power spectra leaving only the interference term. It is only this interference term that is dependent on phase and phase fluctuations. Note that for two identical pulses the signal is simply proportional to $2\cos^2[\omega\tau/2]$, which is a series of peaks in the frequency domain separated by $2/c\tau \text{ cm}^{-1}$. Thus a $\tau = 1 \text{ ps}$ delay yields a peak separation of 67 cm^{-1} . In general the peak separations in the frequency domain are not independent of frequency and instead depend on the spectral phase difference at each frequency. Therefore spectral interferometry presents a method by which to determine the phase differences of two pulses. When the pulses are the same, we can use spectral interferometry to determine their time separations. The inverse Fourier transforms of the first two contributions to the spectrogram in Eq. (18) peak at $t = 0$ whereas the cross term peaks at $t = \pm\tau$. Therefore Fourier transformation of $S(\omega)$ can permit a separation of the cross term from the power spectra of the signal and reference fields [72].

VII. TIME-DOMAIN INTERFEROMETRY

In time-domain interferometry the two pulses are sent collinearly to a square law detector which responds equally to all the frequencies in the pulses. The current in the slow detector circuit $S(\tau)$ is measured as a function of the delay, τ , between the two pulses. A common but not necessary situation in heterodyning is that one field, $E_1(t')$ is very weak so that its square can be neglected while the other, the local oscillator field, $E_2(t' - t)$ is much larger. The signal is time integrated by the slow detector:

$$S(t) = \int_{-\infty}^{\infty} dt' |E_1(t') + E_2(t' - t)|^2 \quad (19)$$

By intermittent chopping of the beams, the constant local oscillator background signal can be eliminated and a Fourier transform along t yields a spectrum that by the convolution theorem is the product of the spectra of the local oscillator and the signal:

$$S(\omega_t) = \varepsilon_2(\omega_t)\varepsilon_1(\omega_t)\cos\varphi_{21}(\omega_t) \quad (20)$$

which is the same as the result, Eq. (18), obtained by spectral interferometry at $\tau = 0$. Thus the two methods of spectral and time-domain interferometry are equally suitable for obtaining the spectra of pulsed fields.

VIII. THE PHOTON ECHO EXPERIMENT

Traditionally the two-pulse photon-echo of a two-level system is described in terms of dynamics where there is a separation of the frequency fluctuations into two widely separated time scales, one of which is much faster and the other much slower than the time that characterizes the inhomogeneous distribution of frequencies. This gives rise to a fixed distribution of homogeneously broadened transitions for each spectral transition of the solute. The echo electric field generated from two very short pulses interacting with a molecule but separated by an interval τ is, apart from constant factors, given by

$$e^{(i\omega_{10}-\gamma)\tau} e^{(-i\omega_{10}-\gamma)t} \quad (21)$$

where γ is the homogeneous width, t is the time between the excitation and detected fields, and $\hbar\omega_{10}$ is the energy of the molecular transition. The radiating polarization is induced by a single interaction with the field of the first pulse and two field interactions with the second, coherence transferring pulse. In relationship (21) the generated signal field is presented as a complex function. The real field generated in the laboratory is the real part of this function, apart from multiplicative factors. The conventional echo signal from an ensemble is detected on a square law detector and therefore involves the integral over the detection time t of the squared average over the distribution of frequencies, namely,

$$\int_0^\infty dt \left| \left\langle e^{i\omega_{10}(\tau-t)} e^{-\gamma(\tau+t)} \right\rangle \right|^2 \quad (22)$$

By assuming a Gaussian frequency distribution with fluctuations δ about a mean, along with standard deviation σ , the echo signal becomes

$$\begin{aligned} & \int_0^\infty dt e^{-2\gamma(\tau+t)} \left| \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^\infty d\delta e^{i\delta(\tau-t)} e^{-\delta^2/2\sigma^2} \right|^2 \\ &= \int_0^\infty dt e^{-2\gamma(\tau+t)-\sigma^2(t-\tau)^2} = \sqrt{\pi}/2\sigma e^{\gamma(\gamma/\sigma^2-4\tau)} \left(\operatorname{erf}\left(\frac{\gamma}{\sigma} - \sigma\tau\right) - 1 \right) \quad (23) \end{aligned}$$

As is well known, when the fixed inhomogeneous distribution is very large compared with the homogeneous width, this echo signal occurs around $t = \tau$ and decays with a time constant $\frac{1}{4}\gamma$. However, as σ approaches zero the time constant becomes $\frac{1}{2}\gamma$ and the signal then peaks at $t = 0$. The limits are most readily seen from the second integral in (23) since $\exp[-\sigma^2(t-\tau)^2]$ only exists for $t \approx \tau$ in the limit of large σ , while for very small σ/γ the integral is an exponential decay with time constant $\frac{1}{2}\gamma$. For many vibrational systems the dynamics are more complex than assumed in this simple example as discussed later. The spectrum of the conventional echo is obtained by recording the absolute square of each frequency component in the frequency average of (21), obtained by Fourier