

# Laser Techniques in Chemistry

EDITED BY ANNE B. MYERS

THOMAS R. RIZZO

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SERIES EDITOR: WILLIAM H. SAUNDERS, JR.

# TECHNIQUES OF CHEMISTRY

VOLUME XXIII

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# LASER TECHNIQUES IN CHEMISTRY

*Edited by*

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## INTRODUCTION TO THE SERIES

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Techniques of Chemistry is the successor to Technique of Organic Chemistry and its companion, Technique of Inorganic Chemistry. The newer series reflects the fact that many modern techniques are applicable over a wide area of chemical science. All of these were originated by Arnold Weissberger and edited by him for many years.

Following in Dr. Weissberger's footsteps is no easy task, but every effort will be made to uphold the high standards he set. The aim remains the same: the comprehensive presentation of important techniques. At the same time, authors will be encouraged to illustrate what can be done with a technique rather than cataloging all known applications. It is hoped in this way to keep individual volumes to a reasonable size. Readers can help with advice and comments. Suggestions of topics for new volumes will be particularly welcome.

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## PREFACE

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Thirty years ago, lasers existed mainly as *subjects* of research in the laboratories of a few physicists and engineers. Today they have become indispensable *tools* for research in chemistry, physics, biology, and a variety of other fields. In chemistry, lasers have had their greatest impact in spectroscopic applications, where the unique properties of laser radiation have both reinvigorated old spectroscopies and stimulated the invention of many new ones. In many cases, lasers have opened areas of chemical research that were previously unthinkable.

In this volume, 10 different laser spectroscopic techniques are described by one or more of their leading practitioners. We have made no attempt to cover "laser techniques in chemistry" comprehensively; this topic is far too broad for a single volume. Rather, we have chosen to focus on those techniques that are sufficiently established to be beyond the proof-of-principle stage, but have not yet become routine. Each chapter describes how the particular spectroscopy is carried out experimentally and/or interpretively, the types of systems to which it is applicable, and the type of information that can be learned from its application. Also included are some speculations about possible further developments and extensions of the techniques that one might expect to see in the near future.

The volume is targeted toward graduate students, postdoctorals, and senior scientists who are familiar with one or more types of optical spectroscopy and wish to learn about others. It is written in a sufficiently pedagogical style so as to allow someone uninitiated in a particular approach to get a start at applying it in the laboratory. We hope that our readers will come away with an increased understanding of the power and variety of laser spectroscopic techniques, an eagerness to apply some of these techniques to new problems, and, perhaps, ideas for even more novel and powerful techniques that might be developed in the future.

ANNE B. MYERS  
THOMAS R. RIZZO

*Rochester, New York*  
*Lausanne, Switzerland*  
*May, 1995*

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## Chapter I

# FOURIER-TRANSFORM NONLINEAR SPECTROSCOPIES

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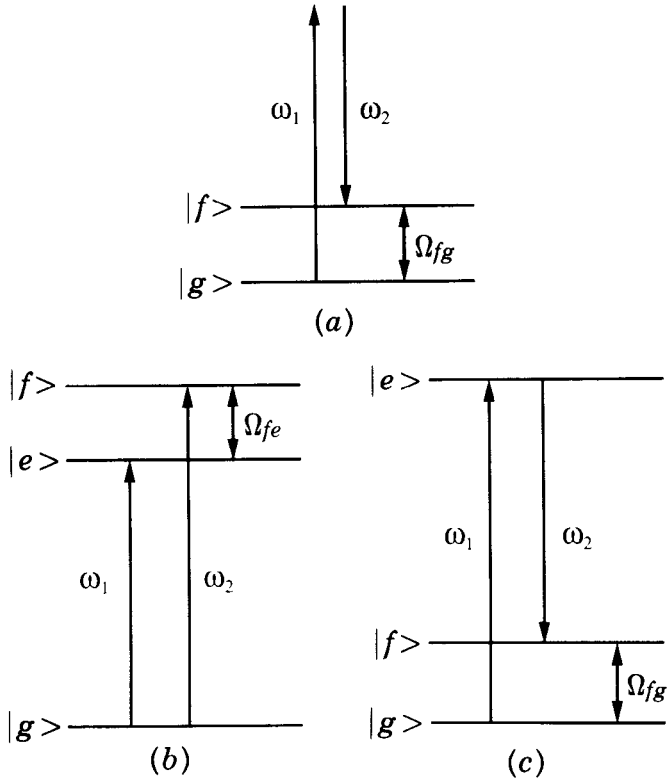
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## 1.1. INTRODUCTION

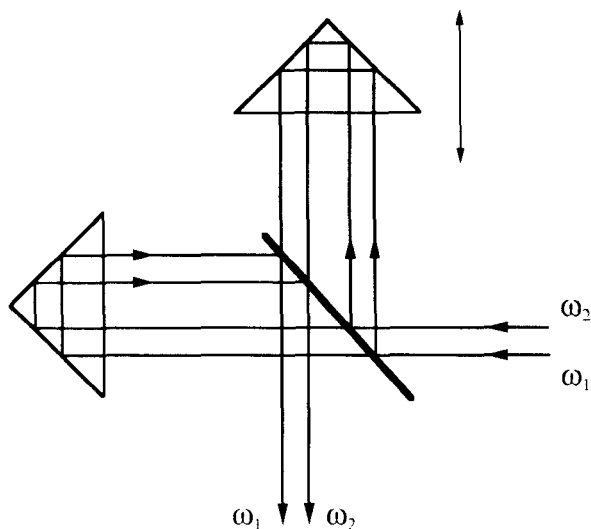
Fourier-transform (FT) spectroscopies (1) have proved to be very powerful methods in the study of chemical systems. The most prominent example, of course, is FT-infrared (IR) spectroscopy (2), which has developed into an indispensable tool for chemical analysis. Other techniques are also becoming more and more important. These include FT versions of optical absorption and emission (3), Raman spectroscopy (4), as well as methodological advances that have greatly facilitated the study of pulse-generated transient species (e.g., photolysis products, radicals, and ions) by FT techniques (5). These methods all have one thing in common—they are FT implementations of *linear* spectroscopies. An interferometer is used as the spectrum analyzer of photons involved in single-photon transitions.

In recent years, the development of FT versions of *nonlinear* spectroscopies has also been an area of active research (6–11). In these schemes an interferometer is used as the spectrum analyzer of the resonant *difference frequencies* characterizing two-photon resonant processes. The two-photon processes involved in these schemes are of two types. There are those that rely on stimulated Raman transitions [Fig. 1.1(a)] and those whose two-photon processes are the consequence of two single-photon resonant transitions in sequence [Fig. 1.1(b) and (c)]. In either case, the  $\omega_1$  and  $\omega_2$  excitation fields involved in the process pass through a Michelson interferometer prior to interacting with the sample (Fig. 1.2). The output of the interferometer then impinges on the sample, and an observable dependent on the pertinent two-photon process is measured as a function of interferometer delay. The



**Figure 1.1.** The two classes of two-photon processes involved in the FT nonlinear spectroscopies discussed in this chapter. (a) Stimulated Raman scattering. A two-color pulse ( $\omega_1$ ,  $\omega_2$ ) drives a rovibrational transition from  $|g\rangle$  to  $|f\rangle$ , characterized by angular frequency  $\Omega_{fg}$ . (b) and (c) Sequential one-photon resonant processes. The level diagram in (b) corresponds to ground-state hole burning. The  $\omega_1$  field depletes the population of  $|g\rangle$  and the  $\omega_2$  field samples that depletion. The two-photon resonance frequency  $\Omega_{fe}$  corresponds to the splitting between the excited states involved in the process. The level diagram in (c) corresponds to stimulated emission spectroscopy. The  $\omega_1$  field puts population into  $|e\rangle$ . The  $\omega_2$  field depletes that population by stimulated emission into ground-state  $|f\rangle$ . The two-photon resonance is at frequency  $\Omega_{fg}$ .

“interferogram” that results from such an experiment is modulated by terms whose frequencies are resonances of the sample. In the case of the stimulated Raman schemes, the modulation frequencies are those ground-state rovibrational intervals associated with the energy differences between the initial and final states involved in the Raman transitions [ $\Omega_{fg}$  in Fig. 1.1(a)]. Fourier transformation of such an interferogram yields a portion of the stimulated Raman spectrum of the sample. In the second kind of process the modulation frequencies in the interferogram correspond to the energy differences between those pairs of excited-state rovibronic levels connected to a single ground-state level [ $\Omega_{fe}$  in Fig. 1.1(b)] or those pairs of ground-state levels connected to a single excited-state level [ $\Omega_{fg}$  in Fig. 1.1(c)].



**Figure 1.2.** The interferometer arrangement employed for all of the FT nonlinear spectroscopies implemented in this laboratory. The  $\omega_1$  and  $\omega_2$  fields propagate through the interferometer parallel to one another (or colinear), such that they both experience the same delay. At the output the  $\omega_1$  fields from the two arms are combined colinearly, as are the  $\omega_2$  fields.

Fourier transformation of this type of interferogram produces a spectrum of these excited- or ground-state rovibronic frequencies.

Fourier transform nonlinear spectroscopies have several features that make them useful as spectroscopic tools. First, the spectral resolution available with the methods is independent of the properties of the light source employed. Instead, resolution depends on the range over which the interferometer is scanned in an experiment. This feature permits one to use convenient, high-power, short-pulsed laser sources to drive the relevant nonlinear processes without requiring any compromise on spectral resolution. Second, the frequency scale in interferometric FT spectroscopies can be made to be very accurate without a great deal of effort (1). This is because that scale is determined by the interferometer scan range, a distance that can be measured easily and accurately. Thus, when one is interested in absolute transition frequencies and/or small shifts in such frequencies from one species to another, a FT experiment is very well suited for obtaining the desired information. Third, the information content of the FT nonlinear spectroscopies that rely on sequential one-photon resonant transitions is different from that of their frequency-domain counterparts (11). When implemented in the frequency domain the spectroscopies measure single-photon vibronic spectra of labeled species. In contrast, the FT versions of these spectroscopies give the two-photon resonances directly. The upshot is that characteristics like rotational structure and Doppler broadening are not the same in the FT and frequency-domain versions. Depending on the experiment at hand and the information desired, these differences can render the

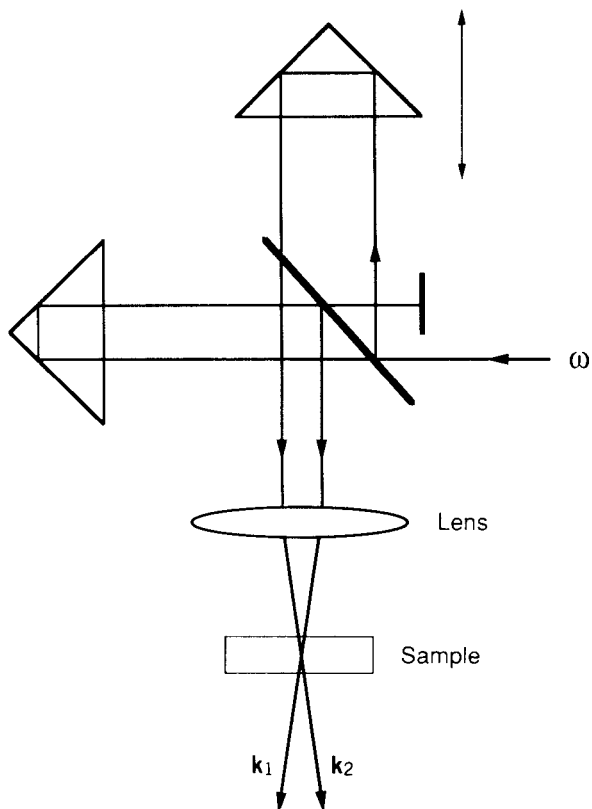
FT version the better alternative. Finally, in some circumstances there is information that is more readily obtained directly from an interferogram than from a spectrum. In particular, the spectroscopic manifestation of free rotation in a very large species is a large number of resonances in the frequency domain, whereas in the Fourier-conjugate domain (the interferogram) rotation is manifest as a small number of time localized, equally spaced transients (12) whose positions depend directly on the species' rotational constants. In these cases the measurement of such transients and their interpretation can be considerably easier than obtaining frequency-domain results of suitable quality and interpreting such results.

Our laboratory has developed a number of different methods of FT nonlinear spectroscopies. These are FT methods based on coherent Raman scattering (CRS) (6,10), ionization-detected stimulated Raman spectroscopy (IDSRS) (8,10), stimulated emission spectroscopy (SES), and hole-burning spectroscopy (HBS) (7,11). We have also demonstrated a variant of such schemes (down-shifting), which shifts high-frequency modulations in interferograms down to much lower frequency and thus facilitates their measurement (9). This chapter intends to provide a review of these techniques and the results obtained from them. The following section starts with a brief historical account of work relevant to this area. Then, Section 1.3 presents a pedagogical treatment to show how the two-photon resonances produce modulations in the interferograms whose frequencies are just the resonant difference frequencies. Section 1.4 outlines each of the methods, their information content, and their implementation in our laboratory. Following this, Section 1.5 presents representative results from these methods and discusses some of their implications. Finally, Section 1.6 closes with a brief discussion of the future in regard to the application of FT nonlinear spectroscopies.

## 1.2. HISTORICAL PERSPECTIVE

The first experiments involving the use of long pulses of incoherent light to achieve subpicosecond time resolution in dynamical studies were reported in the mid-1980s by several groups (13–17). Each of these experiments was an interferometric implementation of a resonant four-wave mixing scheme. The experimental arrangements are represented schematically by the diagram in Fig. 1.3. The output of a broadband laser source was split into two by a beamsplitter. One of the two parts was optically delayed with respect to the other. The two parallel beams were then focused at an angle into the sample. The intensity of a coherent beam generated by resonant degenerate, or nearly degenerate four-wave mixing in the sample was then detected as a function of the optical delay. The detected beam was the one propagating with wavevector  $2\mathbf{k}_2 - \mathbf{k}_1$ , where  $\mathbf{k}_1$  represents the wavevector of the undelayed beam and  $\mathbf{k}_2$  that of the delayed beam.

The results of these experiments displayed two notable features. First, transients evolving on timescales much faster than the pulse width of the light source used were observed (13,14,16). Second, when more than a single transition was spanned by the bandwidth of the excitation source, modulations having a frequency match-



**Figure 1.3.** The general experimental arrangement employed in the interferometric spectroscopies of Refs. 13–17. The broadband field ( $\omega$ ) used to drive the resonant, degenerate (or near-degenerate) four-wave mixing process is split into two parts by a beam splitter. One part is optically delayed with respect to the other. The two, noncolinear beams are focused into the sample, where they intersect with different wavevectors ( $k_1$  and  $k_2$ ) and generate the four-wave mixing signal.

ing the frequency difference between the transitions appeared in the observable, despite the fact that the modulation period was much shorter than the excitation source pulse width (15,17). These results were explained (14,15) by noting that the pulses produced by an incoherent, or partially incoherent light source are actually comprised of a randomly phased series of very short, subpulses. Splitting the output of such a light source in two produces two pulses having the same pulse substructure—that is, two correlated series of ultrafast noise spikes. When a four-wave mixing process is driven by these two pulses in sequence, the pairs of correlated noise spikes between the pulses build up an accumulated photon echo, which is just the four-wave mixing signal in the experiment. The accumulated echo amplitude depends on the evolution of the sample during the time between correlated spikes. Thus, the four-wave mixing signal versus pulse delay can reflect sam-



ple dynamics on a timescale that is limited only by the duration of the noise spikes, not the overall pulse width of the light source.

In 1986 DeBeer et al. (18) reported an important extension to the experiments described above. In a near-degenerate four-wave mixing experiment on the  $D$  lines in Na, they used two, narrow-band dye-laser sources (5-GHz bandwidth, 7-ns pulses) to excite the two  $D$ -line transitions, respectively. The two laser beams were combined colinearly. Then the resulting two-color pulse was split in two. Next, the experiment proceeded in the same way as above: The undelayed ( $\mathbf{k}_1$ ) and delayed ( $\mathbf{k}_2$ ) pulses were focused at an angle into the sample and the beam generated at  $2\mathbf{k}_2 - \mathbf{k}_1$  was detected as a function of delay. The interesting result was the observation of well-modulated beats having a period of 1.9-ps, beats corresponding to the energy splitting between the two upper states associated with the  $D$ -line transitions. Notably, these beats were not only much faster than the laser pulses, they were also much faster than the evolution of the noise substructure within those pulses. These experiments showed that very fast modulations reflecting energy differences between the states of a species (Bohr-frequency beats) could be observed in a nonlinear interferometric experiment employing two *narrow-band* light sources. Neither short nor very broadband pulses were required. This “ultrafast modulation spectroscopy” (UMS) (18) suggested a new, powerful approach for characterizing otherwise difficult-to-characterize energy splittings.

The work of DeBeer et al. (18) stimulated us to try to extend the interferometric UMS approach to four-wave mixing processes other than fully resonant ones. We subsequently demonstrated an interferometric version of coherent Raman scattering. This Fourier transform coherent Raman scattering (FTCRS) (6) has one procedural difference from UMS, aside from the fact that different four-wave mixing processes are involved in each. In FTCRS, just as in UMS, the outputs of two lasers are both split in two, and one split pair is delayed with respect to the other split pair. However, in FTCRS the two pulses of a given color from the two arms of the interferometer are recombined colinearly (see Fig. 1.2), unlike in UMS.

The analysis of FTCRS showed us that a fruitful way of viewing interferometric versions of nonlinear spectroscopies was as FT techniques analogous to linear methods (1) like FT-IR spectroscopy. This analysis also suggested that *any nonlinear spectroscopy involving a resonance condition of the form  $\omega_1 - \omega_2 \approx \Omega_j$* , should be susceptible to implementation interferometrically as a FT spectroscopy. The general recipe for such implementation is to direct the  $\omega_1$  and  $\omega_2$  light beams parallel (or colinearly) through a Michelson interferometer, colinearly recombine the two  $\omega_1$  beams from the two interferometer arms and the two  $\omega_2$  beams from the two arms, direct the output of the interferometer to the sample, along with any other probe beams required, and measure the pertinent signal as a function of interferometer delay. In doing such an experiment one will obtain a signal versus delay trace (interferogram) that is modulated by the resonant difference frequencies  $\Omega_j$ . Fourier transformation produces the desired spectrum. Realizing this, we then conceived of and demonstrated the other FT nonlinear spectroscopies that are the subject of this chapter.

Finally, in 1988 a different class of interferometric four-wave mixing methods