
1 Introduction

1.1 TWO-DIMENSIONAL SPECTROSCOPY

An intriguing idea was put forward in the field of NMR spectroscopy about 30 years ago that, by spreading spectral peaks over the second dimension, one can simplify the visualization of complex spectra consisting of many overlapped peaks.^{1–4} It became possible for the spectral intensity to be obtained as a function of two independent spectral variables. Following this conceptual breakthrough, an impressive amount of progress has been made in the branch of science now known as *two-dimensional (2D) spectroscopy*. While traditional field of 2D spectroscopy is still dominated by NMR and other resonance spectroscopy methods, lately a very different form of 2D spectroscopy applicable to many other types of spectroscopic techniques is also emerging. This book's focus is on this latter type of 2D spectroscopy.

The introduction of the concept of 2D spectroscopy to optical spectroscopy, such as IR and Raman, occurred much later than NMR in a very different form. The basic concept of *perturbation-based* two-dimensional spectroscopy applicable to infrared (2D IR) was proposed first by Noda in 1986.^{5–7} This new form of 2D spectroscopy has evolved to become a very versatile and broadly applicable technique,^{8,9} which gained considerable popularity among scientists in many different areas of research activities.^{10–14} So far, over several hundred scientific papers related to this topic have been published, and the technique is establishing itself as a powerful general tool for the analysis of spectroscopic data. 2D spectra appearing in this book are all based on the analysis of perturbation-induced spectral variations.

So, what does a 2D correlation spectrum look like? And what kind of information does it provide us with? Figure 1.1 shows an example of a *stacked-trace* or *fishnet* plot of a 2D IR correlation spectrum in the CH stretching region of an atactic polystyrene film under a mechanical (acoustic) perturbation.¹⁵ The IR correlation intensity is plotted as a function of two independent wavenumber axes. Figure 1.2 is the same spectrum plotted in the form of a counter map. The stacked-trace or pseudo three-dimensional representation provides the best overall view of the intensity profile of a correlation spectrum, while the contour map representation is better to observe the detailed peak shapes and positions. It should be immediately apparent that the 2D IR spectrum consists of much sharper and better resolved peaks than the corresponding 1D spectrum. This enhancement

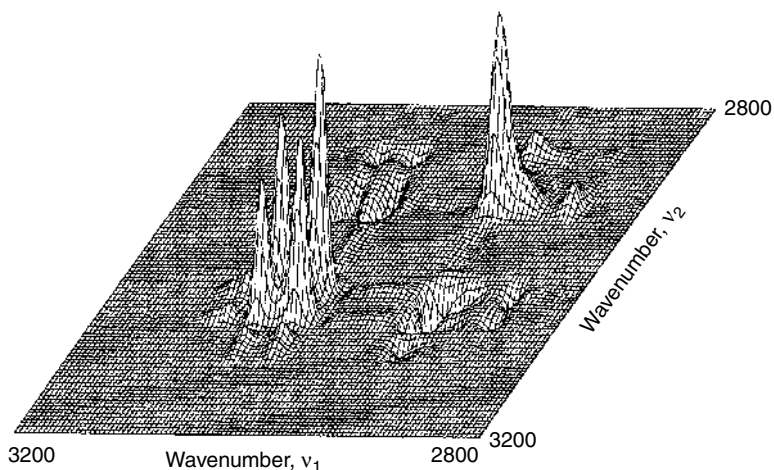


Figure 1.1 Fishnet representation of a 2D IR correlation spectrum of an atactic polystyrene film under a mechanical perturbation. (Copyright © 1990 by Chemtracts, originally published in *ChemTracts: Macromolecular Chemistry*, **1**(2): 89–105.)

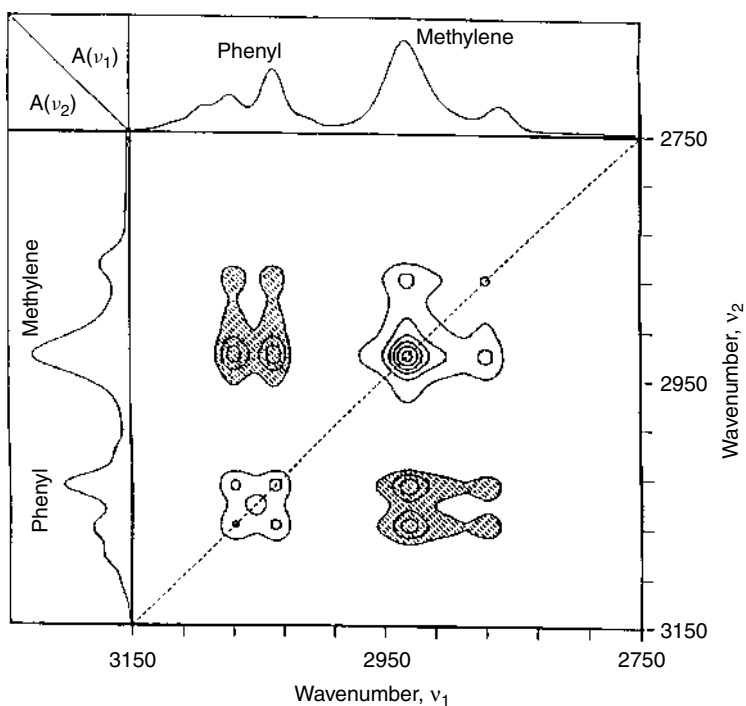


Figure 1.2 Contour map representation of a 2D IR correlation spectrum of polystyrene film. (Reproduced with permission from Ref. No. 121. Copyright (1999) Wiley-VCH.)

of the resolution is a direct consequence of spreading highly overlapped IR peaks along the second dimension. The appearance of positive and negative *cross peaks* located at the off-diagonal positions of a 2D spectrum indicates various forms of correlational features among IR bands. Correlations among bands that belong to, for example, the same chemical group, or groups interacting strongly, can be effectively investigated by 2D spectra. Basic properties of 2D spectra and a procedure to interpret their features are described in Chapter 2.

2D IR spectra, such as those shown in Figures 1.1 and 1.2, may look very different from conventional IR spectra, but in fact they are measured with a spectrometer not that different from an ordinary commercial instrument. Sometimes the spectrometer is equipped with an additional peripheral attachment designed to stimulate or perturb a sample, but quite often 2D correlation spectroscopy does not require any special attachment at all. When a certain perturbation is applied to a sample, various chemical constituents of the system are selectively excited or transformed. The perturbation-induced changes, such as excitation and subsequent relaxation toward the equilibrium, can be monitored with electromagnetic probes such as an IR beam to generate so-called *dynamic spectra*. The intensity changes, band shifts, and changes in band shapes are typical spectral variations observed under external perturbation. The monitored fluctuations of spectral signals are then transformed into 2D spectra by using a correlation method described in Chapters 2 and 3. The experimental approach, therefore, is relatively simple and broadly applicable to many aspects of spectroscopic studies. One of the important characteristic points of Noda's 2D spectroscopy lies in the fact that 2D correlation spectra consist of two orthogonal components, the synchronous and asynchronous correlation spectrum, which individually carry very distinct and useful information for the subsequent analysis.

The main advantages of the 2D correlation spectroscopy discussed in this book lie in the following points: (i) simplification of complex spectra consisting of many overlapped peaks, and enhancement of spectral resolution by spreading peaks over the second dimension; (ii) establishment of unambiguous assignments through correlation of bands; (iii) probing the specific sequential order of spectral intensity changes taking place during the measurement or the value of controlling variable affecting the spectrum through asynchronous analysis; (iv) so-called *heterospectral* correlation, i.e., the investigation of correlation among bands in two different types of spectroscopy, for example, the correlation between IR and Raman bands; and (v) truly universal applicability of the technique, which is not limited to any type of spectroscopy, or even any form of analytical technique (e.g., chromatography, microscopy, and so on).

1.2 OVERVIEW OF THE FIELD

Some historical perspective and overview of the field of 2D correlation spectroscopy should be useful for the reader. It is difficult to describe the development of optical 2D correlation spectroscopy without mentioning the significant

influence of 2D NMR on the field of multi-dimensional spectroscopy.¹⁻⁴ The direct and indirect influence of 2D NMR on the earlier development of 2D IR correlation spectroscopy was profound. The whole idea of obtaining 2D spectra had previously been totally alien to the field of IR and other vibrational spectroscopy. The success of 2D NMR motivated the desire to extend this powerful concept into general optical spectroscopy applications. A conceptual breakthrough in the development of practical optical 2D spectroscopy was realized for IR studies around 1986.⁵⁻⁷ It was developed separately from 2D NMR spectroscopy with a significantly different experimental approach, not limited by the manipulation of pulse-based signals. Most importantly, this new approach turned out to be adaptable to a vast number of conventional spectroscopic techniques.

Today, it may seem almost surprising to us that this powerful yet simple idea of obtaining a spectrum as a function of two independent spectral axes had not been practiced in vibrational spectroscopy until only several decades ago. The 2D technique had been virtually ignored in the optical spectroscopy community for a long period, due to the apparent difficulty in implementing the elegant experimental approach based on multiple pulses, which has been so successfully employed in 2D NMR using radio frequency (rf) excitations. Common optical spectroscopy techniques, such as IR, Raman, and ultraviolet-visible (UV-vis) are governed by physical phenomena having time scales which are very different from those of NMR. The characteristic time scale of molecular vibrations observed in IR absorption spectroscopy is on the order of picosecond, compared to the micro- to millisecond ranges usually encountered in NMR. In NMR, the double Fourier transformation (FT) of a set of time-domain data collected under multiple-pulse excitations generates 2D spectra.¹⁻⁴ Direct adaptations of such a procedure based on pulsed excitations to conventional vibrational spectroscopy was rather difficult several decades ago. Nowadays, it has become possible to conduct certain experiments based on ultrafast femtosecond optical pulses in a fashion analogous to pulse-based 2D NMR experiments.¹⁶⁻²¹ Chapter 7 of this book briefly discusses such ultrafast optical measurements. However, such measurements are still in their infancy and typically carried out in specialized laboratories with the access to highly sophisticated equipments. Ordinary commercial IR spectrometers cannot adequately provide rapid excitation and detection of vibrational relaxation responses to carry out such measurements. Thus, the specific experimental procedure developed adequately for 2D NMR had to be fundamentally modified before being applied to practical optical spectroscopy.

The first generation of optical 2D correlation spectra were obtained from IR experiments based on the detection of various relaxation processes, which are much slower than vibrational relaxations but closely associated with molecular-scale phenomena.⁵⁻⁷ These slow relaxation processes can be studied with a conventional IR spectrometer using a standard time-resolved technique. A simple cross-correlation analysis was applied to sinusoidally varying dynamic IR signals to obtain a set of 2D IR correlation spectra. This type of 2D IR correlation spectroscopy has been especially successful in the study of samples stimulated

by a small-amplitude mechanical or electrical perturbation. The technique was first applied to the analysis of a rheo-optical dynamic IR dichroism measurement of a polymer film perturbed with a small-amplitude oscillatory strain. Dynamic fluctuations of IR dichroism signals due to the submolecular level reorientation of polymer chain segments were analyzed by a 2D correlation scheme. In addition to such mechanically stimulated experiments, similar 2D IR investigations based on time-dependent IR signals induced by sinusoidally varying electrical or photo-acoustic perturbations have also been tried. One can find many examples of the applications of 2D IR correlation spectroscopy in the studies of polymers and liquid crystals. Chapter 8 of this book presents some of the useful applications of 2D spectra based on sinusoidal perturbations.

One of the major shortcomings of the above 2D correlation approach, however, was that the time-dependent behavior (i.e., waveform) of dynamic spectral intensity variations must be a simple sinusoid to effectively employ the original data analysis scheme. To overcome this limitation, Noda in 1993 expanded the concept of 2D vibrational correlation spectroscopy to include a much more general form of spectroscopic analysis, now known as the *generalized 2D correlation spectroscopy*.⁸ The mathematical procedure to yield 2D correlation spectra was modified to handle an arbitrary form of variable dependence much more complex than simple sinusoidally varying time-dependent spectral signals.⁸ The type of spectral signals analyzed by the newly proposed 2D correlation method became virtually limitless, ranging from IR, Raman, X-ray, UV-vis, fluorescence, and many more, even to fields outside of spectroscopy, such as chromatography.¹⁰⁻¹⁴ Most importantly, the generalized 2D correlation scheme lifted the constraint of the perturbations and excitation types. As a result, perturbations with a variety of physical origins, such as temperature, concentration, pH, pressure, or any combination thereof, have been tried successfully for 2D correlation spectroscopy applications.¹⁰⁻¹⁴ Hetero-spectral correlation among different spectroscopic techniques, such as IR-Raman and IR-NIR, has also become straightforward with the generalized 2D scheme. Such a generalized correlation idea truly revolutionized the scope of potential applications for 2D spectroscopy, especially in the field of vibrational spectroscopy.

Parallel to the development of generalized 2D correlation spectroscopy by Noda, some other variants of 2D correlation methods have been proposed. For example, in 1989 Frasiniski *et al.*²² developed the 2D covariance mapping and applied it to time-of-flight mass spectroscopy using a picosecond laser pulse ionization technique. Barton II *et al.*^{23,24} proposed a 2D correlation based on statistical correlation coefficient mapping. Chapter 7 of this book discusses more on this approach. 2D correlation maps generated from the idea of Barton II *et al.* display correlation coefficients between two series of spectra, for example, between IR and NIR spectra of a sample, respectively. The main aim of their approach lies in investigating relations between spectral bands in IR and NIR regions. The 2D correlation analysis by Barton II *et al.* set an important direction for the eventual development of the generalized 2D correlation spectroscopy. The

idea by Barton II *et al.* was closely followed by Windig *et al.*,²⁵ who employed a 2D correlation coefficient map to define the purest available variables in the IR–NIR system of spectra. These variables are subsequently used for chemometric alternating least-squares regression to extract pure IR and NIR spectra of components. In 2001, Šašić and Ozaki²⁶ expanded statistical 2D correlation spectroscopy originally proposed by Barton II *et al.* to incorporate several improvements concerned with objects and targets of correlation analysis, as well as a relatively simple matrix algebra representation that the methodology utilizes. See Chapter 7 for a further description of their work. Ekgasit and Ishida²⁷ proposed to refine the 2D correlation method through the normalization of spectral intensities and phase calculation. Their method seems to work for synthetic spectra, but the robust applicability to real-world spectra, especially those with substantial noise, has yet to be determined.

One of the interesting recent developments in generalized 2D correlation spectroscopy was the introduction of sample–sample 2D correlation spectroscopy by Šašić *et al.*^{28,29} An in-depth discussion on this subject is found in Chapter 5. Usually 2D maps have spectral variables (wavelengths, wavenumbers) on their axes and depict the correlations between spectral features (variable–variable correlation maps). One can also produce 2D maps that have samples (observed at different time, temperature, concentration, etc.) on their axes and provide information about the correlations among, for example, the concentration vectors of species present (sample–sample correlation maps). Information obtained by variable–variable and sample–sample 2D correlation spectroscopy is often complementary, and general features of variable–variable correlation maps are expected to be equally applicable to the sample–sample correlation maps. Recently, Wu *et al.*³⁰ proposed hybrid 2D correlation spectroscopy to further expand the concept. Chapter 5 describes the basic concept of this approach.

Meanwhile, studies on ultrafast laser pulse-based optical analogues of 2D NMR have also been getting very active.^{16–21} For example, the recent conceptual development of 2D Raman experiments based on pulsed excitations is creating a possible link for vibrational spectroscopy and 2D NMR. The detailed discussion on nonlinear optical 2D spectroscopy, which is rapidly establishing itself as an independent branch of physical science, is beyond the scope of this book. The content of this volume is mainly concerned with 2D correlation spectroscopy proposed by Noda, but in Chapters 5–7 different types of 2D correlation methods will also be discussed.

1.3 GENERALIZED TWO-DIMENSIONAL CORRELATION

The concept of *generalized two-dimensional (2D) correlation* is the central theme of this book. It is a formal but very versatile approach to the analysis of a set of spectroscopic data collected for a system under some type of external perturbation.⁸ The introduction of the generalized 2D correlation scheme

has opened up the possibility of utilizing a powerful and versatile analytical capability for a wide range of spectroscopic applications. Recognition of the general applicability of the 2D correlation technique to the investigation of a set of ordinary spectra obtained not only for time-dependent phenomena but also from a static or stationary measurement was clearly a major conceptual departure from the previous approach. The unrestricted selection of different spectroscopic probes, perturbation methods and forms, and the combination of multiple analytical methods provided the astonishing breadth and versatility of application areas for generalized 2D correlation spectroscopy.

1.3.1 TYPES OF SPECTROSCOPIC PROBES

The basic idea of generalized 2D correlation is so flexible and general that its application is not limited to any particular field of spectroscopy confined to a specific electromagnetic probe. Thus far, generalized 2D correlation spectroscopy has been applied to IR,^{15,26,27,29-75} NIR,^{23,24,29,76-97} Raman,⁹⁸⁻¹⁰⁶ ultraviolet-visible (UV-vis),¹⁰⁷⁻¹⁰⁹ fluorescence,¹¹⁰⁻¹¹² circular dichroism (CD),^{46,47} and vibrational circular dichroism (VCD)¹¹³ spectroscopy. Furthermore, the application of 2D correlation spectroscopy is not even restricted to optical spectroscopy. It has, for example, been applied to X-ray^{15,114} and mass spectrometry.¹¹⁵ An interesting testimony of the versatility of generalized 2D correlation was demonstrated by Izawa *et al.*,¹¹⁶⁻¹¹⁸ where the basic idea of 2D correlation is applied to time-resolved gel permeation chromatography, which is totally outside of conventional spectroscopic applications.

1.3.2 EXTERNAL PERTURBATIONS

The generalized 2D correlation scheme enables one to use numerous types of external perturbations and physical stimuli that can induce spectral variations.^{10,13,14} The perturbations utilized in the 2D correlation analysis may be classified into two major types. One type yields the spectral data set as a direct function of the perturbation variable itself (e.g., temperature, concentration, or pressure), and the second type gives it as a function of the secondary consequence caused by the perturbation, such as a time-dependent progression of spectral variations caused by the application of a stimulus.

Temperature^{29,37,38,76-79,81,82,87,100} and concentration^{43,50,56,80,83-86,101,102,104-106} are the most commonly used static perturbations for generalized 2D correlation spectroscopy. Typical examples of temperature-induced spectral variations studied by 2D correlation analysis involve dissociation of hydrogen-bonded systems in alcohols,^{29,76,79,81,82} and amides,^{77-79,87,100} the denaturation of proteins,^{57,59,60} and the melting and premelting behavior of polymers.^{61,78} Alcohols such as oleyl alcohol and butanol and *N*-methylacetamide show complex temperature-dependent spectral variations due to the dissociation

of hydrogen bonds, and resulting spectral changes were analyzed by 2D correlation spectroscopy. Šašić *et al.*²⁹ utilized sample–sample 2D NIR correlation spectroscopy to explore the dissociation of associated oleic acids in the pure liquid state. Thermal denaturation of proteins has long been a matter of keen interest. 2D correlation spectroscopy has provided new insight into the denaturation process of proteins.^{57,59,60,80,86} For example, a 2D NIR correlation spectroscopy study of the thermal denaturation of ovalbumin revealed an interesting relationship between the temperature-induced secondary structural changes and changes in the extent of hydration.⁸⁰ Although most thermal studies are concerned with the static effect of temperature itself on the spectra, one can also apply 2D correlation analysis to a dynamic experiment where the time dependent response caused by a temperature shift (e.g., T-jump or thermal modulation) induces dynamic spectral variations.

A number of 2D correlation spectroscopy studies have been carried out for concentration- or composition-dependent spectral modifications of simple molecules, proteins,^{43,56,80,86,106} polymers,^{50,83,84,101,102,104,105} and multicomponent mixtures.^{23,24,31,85} For example, systematic studies of polymer blends and copolymers exhibiting specific interactions of components using 2D IR, 2D NIR, 2D Raman, and hetero-correlation analysis have been reported.^{50,83,84,101,102,104,105} Concentration changes often induce nonlinear structural perturbations for a variety of molecules. 2D correlation analysis may be uniquely suited for finding such changes, because if the systems yield nonlinear responses of spectral intensities to concentration changes (i.e., apparent deviation from the classical Beer–Lambert law), some new features not readily analyzable by conventional techniques may be extracted from 2D correlation analysis. The first example of a 2D correlation study of multicomponent mixtures was carried out for complex liquid detergent formulations comprising a number of ingredients by use of a simple 2D covariance analysis.³¹

2D correlation spectroscopy of pressure-dependent spectral variations is also becoming popular.^{26,48,49,65} Several research groups have reported 2D IR studies of pressure-induced protein denaturation.^{48,65} For example, pressure-induced spectral changes of polymer films were also subjected to 2D correlation analysis to investigate the morphologically influenced deformation mechanism of polyethylene under compression.⁴⁹ Magtoto *et al.*⁵³ reported IR reflection–absorption measurement of pressure-induced chemisorption of nitric oxide on Pt (100). Noda *et al.*⁴⁹ investigated combined effects of pressure and temperature by means of 2D IR spectroscopy.

Other perturbations that yield a series of sequentially recorded spectral data are, for example, pH, position, angle, and excitation wavelength. Murayama *et al.*⁶⁶ reported a 2D IR correlation spectroscopy study of pH-induced structural changes of human serum albumin (HSA). They investigated protonation of carboxylic groups of amino acid residues as well as secondary structural alternations of HSA. Nagasaki *et al.*⁵⁵ applied 2D correlation analysis to polarization angle-dependent IR band intensity changes to investigate the molecular orientation and

structure of a ferroelectric liquid crystal with a naphthalene ring in the chiral smectic- C^* phase. Spectroscopic analysis of various chemical reactions is also a popular area. The application of reaction-based 2D IR includes complex reaction kinetics, electrochemistry, and photochemistry.^{32–34}

Mechanical deformation,^{5–7,15,36,0,41,67–69} an electric field,^{35,45} and chemical reactions^{32–34} are representative examples of stimuli that may give rise to spectral changes that we describe as producing secondary effects as a consequence of the perturbation. A simple but interesting example of this type of application is the time-dependent compositional change of a mixture by physical or chemical reactions. Noda *et al.*¹¹ analyzed transient IR spectra of a polystyrene/methyl ethyl ketone/toluene solution mixture during an evaporation process. An example of chemical reactions studied by 2D correlation analysis is an H to D exchange reaction to probe the secondary structure of a protein.^{44,63} Šašić *et al.*⁶⁴ applied sample–sample correlation spectroscopy to analyze IR spectra of chemical reactions.

Dynamic 2D IR and 2D NIR spectroscopy based on small-amplitude oscillatory mechanical perturbation is well established in polymer science and engineering. An Electric field is another stimulus frequently used for 2D correlation spectroscopy. It is particularly useful for exploring the mechanism of the reorientation of liquid crystals. Ataka and Osawa³³ first applied 2D IR spectroscopy to electrochemical systems. IR spectra near the electrode surface were collected as a function of applied potential.

1.4 HETEROSPECTRAL CORRELATION

One very intriguing possibility of 2D correlation spectroscopy is *2D heterospectral correlation* analysis,^{15,23,24,97,100,104–106,114,119,120} where two completely different types of spectra obtained for a system under the same perturbation using multiple spectroscopic probes are compared. Chapter 14 of the book provides actual examples of this approach. 2D hetero-spectral correlation may be divided into two types. The first type is concerned with the comparison between closely related spectroscopies, such as IR/NIR and Raman/NIR spectroscopy. In this case, the correlation between bands in two kinds of spectroscopy can be investigated. Therefore, it becomes possible to make band assignments and resolution enhancements by 2D heterospectral correlation. The second type of heterospectral correlation is heterocorrelation between completely different types of spectroscopy or physical techniques such as IR and X-ray scattering. This type of heterospectral correlation is useful for investigating the structural and physical properties of materials under a particular external perturbation.

Heterospectral correlation analysis provides especially rich insight and clarification into the in-depth study of vibrational spectra. For example, the investigation of the correlation between IR and Raman spectra of a molecule by heterospectral correlation is very attractive from the point of better understanding

of its complementary vibration spectra. Likewise, the correlation between NIR and IR spectroscopy is very interesting, because, by correlating NIR bands with IR bands for which the band assignments are better established, one may be able to investigate the less-understood band assignments in the NIR region.

1.5 UNIVERSAL APPLICABILITY

We have already alluded to the fact that the generalized 2D correlation spectroscopy described in this book may utilize a number of different spectroscopic probes, e.g., IR, Raman, NIR, fluorescence, UV, and X-ray, in a surprisingly flexible manner by combining the spectroscopic measurement with various physical perturbations, e.g., mechanical, thermal, chemical, optical, and electrical stimuli, to explore a very broad area of applications, ranging from the study of basic small molecules to characterization of polymers and liquid crystals, as well as complex biomolecules. This technique is truly a generally applicable versatile tool in spectroscopy.

It is also useful to point out that the fundamental concept of generalized 2D correlation analysis may be applied to any analytical problems, not at all limited to spectroscopy. Thus, any branch of analytical sciences, such as chromatography, scattering, spectrometry, and microscopy, as well as any other field of scientific research, including molecular dynamics simulations, life science and biology, medicine and pharmacology, or even topics traditionally dealt in social science, can benefit by adopting this scheme. The possibility of extending the 2D correlation method beyond the boundary of optical spectroscopy techniques will be explored in Chapter 15.

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