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Preface

For unfortunate reasons the success of vibrational (infrared and Raman spectroscopy) in industrial and university laboratories seems to fade quickly in favor of other physical techniques which aim at chemical or structural diagnosis of unknown samples. On the other hand, engineers and instrument manufacturers in the field of vibrational spectroscopy keep producing magnificent and very sophisticated new instruments and accessories which enable the recording of vibrational spectra of samples under the most awkward experimental conditions which can never be attained by the other very popular new physical techniques.

At present, infrared spectra can be obtained with fast and very fast FTIR interferometers with microscopes, in reflection and microreflection, in diffusion, at very low or very high temperature, in dilute solutions, etc. Raman scattering can span a very large energy range in the excitation lines, thus reaching off-resonance or resonance conditions; spectrometers and interferometers can be used, microsampling is common, a few scattered photons can be detected with very sensitive CCD detectors and optical fibers provide a variety of new sampling procedures.

Parallel to the technological development we watch the invasion (even on a commercial level) of theoretical and computational techniques (both *ab initio* or semiempirical) which, by simply pushing a button, provide vibrational frequencies and intensities and even show the animated wiggling of molecules on the screen of any personal computer.

In spite of the wealth of experimental and theoretical data which are easily available for the study of molecules and of their behavior, other fields of physics and chemistry seem to have the priority in the teaching at Universities. Vibrational spectroscopy is, in general, no longer taught in detail and, at most, students are quickly exposed to molecular vibrations in some courses of analytical chemistry or structural organic chemistry. It is curious to notice that molecular dynamics is considered a very complicated mathematical machinery which must be avoided by simply mentioning briefly that molecules 'wiggle' in a curious way. Then, the traditional old-fashioned structure-group frequency spectral correlations (mostly in infrared) are considered the only useful tool for the interpretation of spectra. This very limited spectroscopic culture is obviously transferred to industrial laboratories who rely on the use of vibrational spectra only for very simple chemical diagnosis and routine analytical determinations.

The conclusion of this analysis is that the ratio: (number of information)/(capa-

bility of the experimental and theoretical techniques) turns out to be very small, in spite of the great potential offered by vibrational spectroscopy.

The above analysis, shared by many spectroscopists in the field of small molecules, can be further expanded when vibrational spectroscopy is considered in the field of polymers and macromolecules in general. The wiggling of polymers adds new flavor to physics and chemistry. The translational periodicity of infinite polymers with perfect structure generates phonons and collective vibrations which give rise to absorption or Raman scattering bands that escape the interpretation based on the traditional spectroscopic correlations. The concept of collective motions forms the basis for the understanding of the vibrations of finite chain molecules which form a nonnegligible part of industrially relevant materials. On the other hand, real polymer samples never show perfect chemical, strereochemical, and conformational structure. Symmetry is broken and new bands appear which become characteristic of specific types of disorder.

If a few simple theoretical concepts of the dynamics of ordered and disordered chain molecules are taken into account it can be easily perceived that the vibrational infrared and Raman spectra contain a wealth of information essential to analytical polymer chemistry, structural chemistry, and physics.

The content of this book has been planned to rejuvenate the vibrational spectroscopy of polymers. At present, the classes of polymeric materials are very many in number and range from classical bulk polymers of great industrial and technological relevance to highly sophisticated functional polymers which reach even the interest of photonics and molecular electronics. Also, the whole world of biopolymers requires great attention from spectroscopy.

This book touches on a very few classes of polymeric materials which we consider representatives for introducing problems, spectroscopic techniques, and solutions prototypical of many other classes of polymers and plastics.

Chapters 1 and 2 introduce new experimental techniques that provide new sets of relevant data for the study of the local and overall mobility of polymer chains. In Chapter 1, the development of two-dimensional infrared spectroscopy is described with a discussion of the mathematical principles, the description of the instrumental technique, and a detailed analysis of a few cases. In Chapter 2 the success of Fourier transform infrared polarization spectroscopy is shown for the study of segmental mobility in a polymer or a liquid-crystalline polymer under the influence of an external directional perturbation such as electric, electromagnetic, or mechanical forces. Industrial research laboratories should pay much attention to the information which can be acquired with this technique for technologically relevant polymeric materials.

Chapter 3 is a guided tour of molecular dynamics and infrared and Raman frequency and intensity spectroscopy of polymethylene chains, from oligomers to polymers, in their perfect and disordered states. The reader is exposed in the easiest possible way to the basic theoretical concepts and to the numerical techniques which can be applied to such studies. Many references are provided for the spectroscopist who wants to develop his or her own independent skill and judgment.

However, theory and calculations yield concepts and data to be used also in polymer characterization, even for routine analytical work. After discussing several oligomers or polymers the reader is guided step-by-step in the practical exercise to derive the detailed scenario of the mechanism of phase transition and melting of n-alkanes.

Some of the theoretical tools laid in Chapter 3 are fully exploited in Chapter 4, which exposes the reader to the actual problems (and proposed solutions) of the chemistry and physics of modern and technologically relevant polyconjugated polymers in their intact (insulating) and in the doped (electrically conducting) states.

Chapter 5 is an up-to-date review of the spectroscopic and structural problems and solutions reached by a modern approach to the dynamics of polypeptides. A clear and comprehensive discussion is presented on the force fields necessary for a reliable structural analysis through the vibrational spectra. Tools are thus becoming available for a systematic study of the structure even of complex polypeptides.

The message we wish to send to the reader of this book is that modern machines provide beautiful infrared and Raman spectra of polymers full of specific, unique and detailed information which can be extracted, not just merely and lazily using group frequency correlations. We will be very pleased to find that this book has provided the reader with enough motivation to overcome the potential barrier of some theoretical technicalities in order to enjoy fully the wealth of information inherently contained in the vibrational spectra of ordered or disordered chain molecules.

Milan, June 1998 *Giuseppe Zerbi*

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1 Two-Dimensional Infrared (2D IR) Spectroscopy

I. Noda, A. E. Dowrey, and C. Marcott

1.1 Introduction

Two-dimensional infrared (2D IR) correlation spectroscopy [1–8] is a relatively new addition to the spectroscopic methods used for the characterization of polymers. In 2D IR, infrared spectral intensity is obtained as a function of two independent wavenumbers as shown in Figure 1-1. The well-recognized strength of IR spectroscopy arises from the specificity of an IR probe toward individual molecular vibrations which are strongly influenced by the local molecular structure and environment [9–12]. Because of such specificity toward the submolecular state of a sample, surprisingly useful information about a complex polymeric system is provided by expanding IR analysis to the second spectral dimension.

The initial idea of generating two-dimensional correlation spectra was introduced several decades ago in the field of NMR spectroscopy [13–16]. Since then, numerous successful applications of multidimensional resonance spectroscopy techniques have been reported, including many different types of studies of polymeric materials by 2D NMR [17–19]. However, until now the propagation of this powerful concept of multidimensional spectroscopy in other areas of spectroscopy, especially vibrational spectroscopies such as IR and Raman, has been surprisingly slow.

One of the reasons why the two-dimensional correlation approach as applied in NMR spectroscopy was not readily incorporated into the field of IR spectroscopy was the relatively short *characteristic times* (on the order of *picoseconds*) associated with typical molecular vibrations probed by IR. Such a time scale is many orders of magnitude shorter than the relaxation times usually encountered in NMR. Consequently, the standard approach used so successfully in 2D NMR, i.e., multiple-pulse excitations of a system followed by the detection and subsequent double Fourier transformation of a series of free induction decay signals, is not readily applicable to conventional IR experiments. A very different experimental approach, therefore, needed to be developed in order to produce 2D IR spectra useful for the characterization of polymers using an ordinary IR spectrometer.

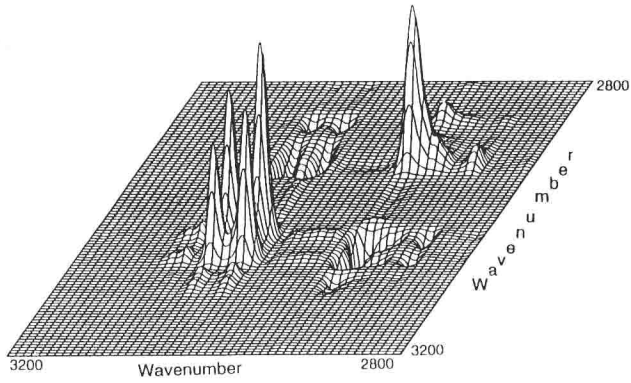

Figure 1-1. A fishnet plot of a synchronous two-dimensional infrared (2D IR) correlation spectrum of atactic polystyrene in the CH-stretching vibration region at room temperature.

1.2 Background

1.2.1 Perturbation-Induced Dynamic Spectra

The basic scheme adapted for generating 2D IR spectra [3, 8] is shown in Figure 1-2. In a typical optical spectroscopy experiment, an electromagnetic probe (e.g., IR, X-ray, UV or visible light) is applied to the system of interest, and physical or chemical information about the system is obtained in the form of a *spectrum* representing a characteristic transformation (e.g., absorption, retardation, and scattering) of the electromagnetic probe by the system constituents. In a 2D IR experiment, an external physical perturbation is applied to the system [2, 3] with the incident IR beam used as a probe for spectroscopic observation. Such a perturbation often induces time-dependent fluctuations of the spectral intensity, known as the *dynamic spectrum*, superposed onto the normal *static* IR spectrum.

There are, of course, many different types of physical stimuli which could induce such dynamic variations in the spectral intensities of polymeric samples. Possible sources of perturbations include electrical, thermal, magnetic, acoustic, chemical, optical, and mechanical stimuli. The waveform or specific time signature of the perturbation may also vary from a simple step function or short pulse, to more complex ones, including highly multiplexed signals and even random noises. In this chapter, dynamic spectra generated by a simple sinusoidal mechanical perturbation applied to polymers will be discussed.

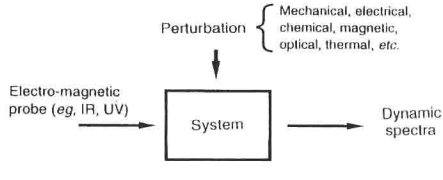

Figure 1-2. A generalized experimental scheme for 2D correlation spectroscopy based on perturbation-induced dynamic spectral signals [8].

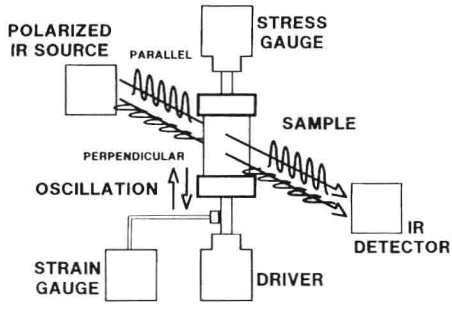

Figure 1-3. Schematic diagram of the dynamic infrared linear dichroism (DIRLD) experiment [23]. A small-amplitude sinusoidal strain is applied to a sample, and submolecular level reorientation responses of chemical moieties are monitored with a polarized IR beam.

1.2.2 Dynamic IR Linear Dichroism (DIRLD)

Figure 1-3 shows a schematic diagram of a dynamic IR linear dichroism (DIRLD) experiment [20–25] which provided the foundation for the 2D IR analysis of polymers. In DIRLD spectroscopy, a small-amplitude oscillatory strain (ca. 0.1% of the sample dimension) with an acoustic-range frequency is applied to a thin polymer film. The submolecular-level response of individual chemical constituents induced by the applied dynamic strain is then monitored by using a polarized IR probe as a function of deformation frequency and other variables such as temperature. The macroscopic stress response of the system may also be measured simultaneously. In short, a DIRLD experiment may be regarded as a combination of two well-established characterization techniques already used extensively for polymers: *dynamic mechanical analysis* (DMA) [26, 27] and *infrared dichroism* (IRD) spectroscopy [10, 11].

The optical anisotropy, as characterized by the difference between the absorption of IR light polarized in the directions parallel and perpendicular to the reference axis (i.e., the direction of applied strain), is known as the IR linear dichroism of the system. For a uniaxially oriented polymer system [10, 28–30], the *dichroic difference*, $\Delta A(\nu) \equiv A_{\parallel}(\nu) - A_{\perp}(\nu)$, is proportional to the average orientation, i.e., the second moment of the orientation distribution function, of transition dipoles (or electric-dipole transition moments) associated with the molecular vibration occurring at frequency ν. If the average orientation of the transition dipoles absorbing light at frequency ν is in the direction parallel to the applied strain, the dichroic difference ΔA takes a positive value; on the other hand, the IR dichroism becomes negative if the transition dipoles are perpendicularly oriented.

If a sinusoidally varying small-amplitude dynamic strain is applied to a polymeric system, a similar sinusoidal change in IR dichroic difference, as shown in Figure 1-4, is usually observed [3, 23]. The dynamic variation of IR dichroism arises from the time-dependent reorientation of transition dipoles induced by the applied strain. Interestingly, however, the dichroism signal often is not fully in phase with the strain. There is a finite phase difference between the two sinusoidal signals representing the externally applied macroscopic perturbation and the resulting dynamic molecular-level response of the system. This phase difference is due obviously to

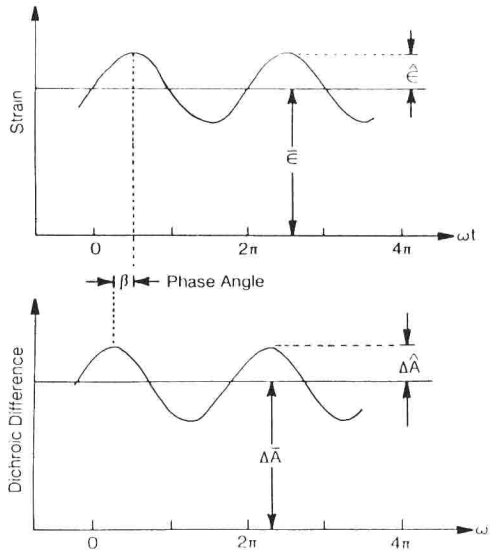

Figure 1-4. A small-amplitude sinusoidal strain applied to a sample and resulting dynamic IR dichroism (DIRLD) response induced by the strain. The two sinusoidal signals are not always in phase with each other.

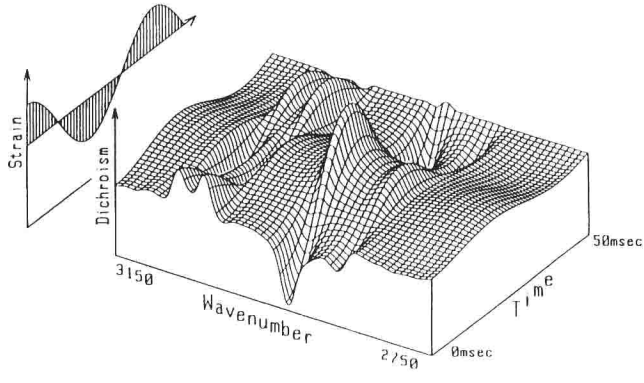

Figure 1-5. A time-resolved dynamic IR dichroism (DIRLD) spectrum of an atactic polystyrene film under a small-amplitude (ca. 0.1%) sinusoidal (23-Hz) dynamic strain at room temperature.

the rate-dependent nature of the reorientation processes of various submolecular constituents.

The advantage of using IR spectroscopy in dynamic studies of polymers is that such a measurement can be used to examine individual submolecular constituents or chemical functional groups by simply changing the wavelength of the IR probe. The variation of IR dichroism, depicted as a simple sinusoidal signal in Figure 1-4, can actually be measured as a function of not only time but also IR wavenumber. In other words, dynamic IR dichroism is obtained as a time-resolved spectrum representing the molecular level response of polymers, as shown in Figure 1-5.

For a given sinusoidal dynamic strain $\tilde{\varepsilon}(t)$ with a small amplitude $\hat{\varepsilon}$ and fre-

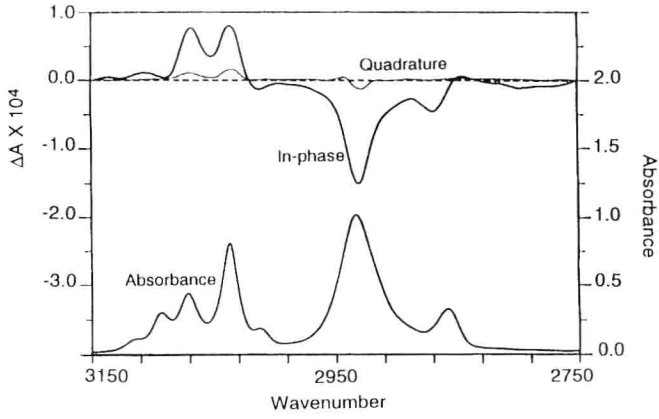

Figure 1-6. The *in-phase* and *quadrature* components of the DIRLD spectrum shown in Figure 1-5. A normal static absorbance spectrum of the sample is also provided for reference.

quency ω,

$$\tilde{\varepsilon}(t) = \hat{\varepsilon} \sin \omega t \tag{1-1}$$

a time-resolved DIRLD spectrum may be represented by

$$\Delta\tilde{A}(\nu, t) = \Delta\hat{A}(\nu) \sin[\omega t + \beta(\nu)] \tag{1-2}$$

where $\Delta\hat{A}(\nu)$ and $\beta(\nu)$ are, respectively, the *magnitude* and *phase (loss) angle* of the dynamic IR dichroism [23]. By using a simple trigonometric identity, the above expression can also be rewritten in the form

$$\Delta\tilde{A}(\nu, t) = \Delta A'(\nu) \sin \omega t + \Delta A''(\nu) \cos \omega t. \tag{1-3}$$

The wavenumber-dependent terms, $\Delta A'(\nu)$ and $\Delta A''(\nu)$, are known respectively as the *in-phase spectrum* and *quadrature spectrum* of the dynamic dichroism of the system. They represent the *real* (storage) and *imaginary* (loss) components of the time-dependent fluctuations of dichroism. Figure 1-6 shows an example of the in-phase and quadrature spectral pair extracted from the continuous time-resolved spectrum shown in Figure 1-5. These two ways of representing a DIRLD spectrum contain equivalent information about the reorientation dynamics of transition dipoles. However, the orthogonal representation of the time-resolved spectrum using the in-phase and quadrature spectra is obviously more compact and easier to interpret than the stacked-trace plot of the time-resolved spectrum.

1.2.3 IR Dichroism and Molecular Orientation

In a traditional characterization study of polymeric materials, the IR dichroism technique is most often employed for the determination of the degree of orientation

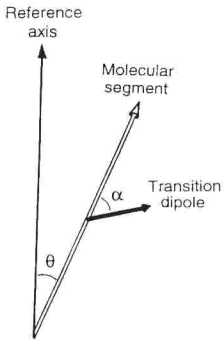

Figure 1-7. Uniaxial orientation of a polymer chain segment with respect to a reference axis and corresponding alignment of a transition dipole.

of molecular chain segments [10, 28–30]. For a uniaxially oriented polymer system (Figure 1-7), the *orientation factor* $P_2(\theta)$, i.e., the second moment of the orientation distribution function of polymer chain segments, is given by

$$P_2(\theta) = (3\langle\cos^2\theta\rangle - 1)/2 \tag{1-4}$$

where θ is the *orientation angle* between each polymer chain segment and the optical reference axis of the system. The notation $\langle\cos^2\theta\rangle$ indicates that the squared-cosine of orientation angles for individual segments are averaged over the entire space.

The orientation factor $P_2(\theta)$ is a convenient measure of the average degree of orientation of polymer chains in the system. Under an ideal orientation state where all polymer chains are aligned perfectly in the direction parallel to the reference axis, the value of $P_2(\theta)$ becomes unity. On the other hand, if polymer chain segments are all perpendicularly aligned, $P_2(\theta)$ becomes $-1/2$. An optically isotropic system gives the $P_2(\theta)$ value of zero.

According to the classical theory of the IR dichroism of polymers [10, 28, 29], the *dichroic ratio*, $D(\nu) \equiv A_{\parallel}(\nu)/A_{\perp}(\nu)$, of the system is directly related to the orientation of polymer chain segments by

$$P_2(\theta) = \frac{D(\nu) - 1}{D(\nu) + 2} \cdot \frac{D_{\infty}(\nu) + 2}{D_{\infty}(\nu) - 1} \tag{1-5}$$

The *ultimate dichroic ratio* $D_{\infty}(\nu)$ is the value of dichroic ratio if the polymer chain segments are all perfectly aligned in the direction of the reference axis, i.e., $P_2(\theta) = 1$. Given the local orientation angle α between the polymer chain segment and transition dipole probed at the IR wavenumber ν (Figure 1-7), the ultimate dichroic ratio is given by

$$D_{\infty}(\nu) = 2\cot^2\alpha. \tag{1-6}$$

It can be easily shown that Eq. (1-5) simplifies to the form

$$P_2(\theta) = \Delta A(\nu)/\Delta A_{\infty}(\nu) \tag{1-7}$$