

Two-Dimensional Infrared Spectroscopy

Isao Noda

Contribution from The Procter & Gamble Company, Miami Valley Laboratories,
P.O. Box 398707, Cincinnati, Ohio 45239-8707. Received January 22, 1988

Abstract: Two-dimensional infrared (2D IR) spectroscopy, a novel technique based on time-resolved IR spectroscopy, is introduced. In 2D IR, a system is excited by an external perturbation, which induces a dynamic fluctuation of the IR spectrum. A correlation analysis is applied to the time-dependent IR signals to yield a spectrum defined by two independent wavenumbers. By spreading IR peaks over the second dimension, a complex spectrum consisting of overlapped peaks can be substantially simplified, and spectral resolution is enhanced. Peaks located on a 2D spectral plane provide information on connectivity and interactions among functional groups associated with the IR bands. 2D IR spectra are presented for a system consisting of a mixture of atactic polystyrene (PS) and low-density polyethylene (PE) to illustrate these features. The spectroscopic evidence clearly shows PS and PE in a blend are segregated at the molecular level, allowing the components to respond to an applied external perturbation independently of each other. A substantial difference is observed in the local mobility of the backbone and side-group functionalities of PS. On the basis of this observation, it is possible to assign the 1459-cm⁻¹ component of the broad IR band centered around 1454 cm⁻¹ to the backbone CH₂ deformation in PS.

A novel analytical concept in vibrational spectroscopy called two-dimensional infrared (2D IR) spectroscopy is introduced. In 2D IR, a spectrum is obtained as a function of two independent wavenumber axes, and peaks located on the spectral plane are used to study intra- and intermolecular interactions among functional groups. The basic concept of 2D IR is somewhat analogous to the 2D correlation technique used extensively in NMR.¹⁻³ However, since vibrational relaxation rates are many orders of magnitude faster than spin relaxations, the double Fourier transform technique developed for 2D NMR based on multiple-pulse excitations is not readily applicable to IR. Instead, a different experimental procedure is proposed to generate 2D IR correlation spectra.

In the proposed approach, an external perturbation (e.g., a small-amplitude strain) is applied to the sample. Such a perturbation selectively induces time-dependent reorientations of electric dipole-transition moments associated with the individual normal modes of vibration in the system.⁴⁻⁸ The altered orientation distribution of dipole-transition moments can be detected as a variation of the directionally sensitive absorbance of the system.⁹ Interestingly, IR bands arising from molecular vibrations of different functional groups often exhibit substantially different time-dependent variations which are characteristic of the type and local environment of submolecular structures.^{6,7} Individual dipole-transition moments responding to a single external perturbation, therefore, have unique reorientation rates which can be used as a convenient spectroscopic label to differentiate highly overlapped IR bands.

To accentuate the differences among the reorientation rates of electric dipole-transition moments, a simple correlation analysis is applied. For a pair of time-dependent variations of IR signals measured at two different wavenumbers, $\tilde{A}(\nu_1, t)$ and $\tilde{A}(\nu_2, t)$, the absorptive-intensity cross-correlation function $X(\tau)$ is defined as

$$X(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} \tilde{A}(\nu_1, t) \cdot \tilde{A}(\nu_2, t + \tau) dt \quad (1)$$

For a given system at a correlation time τ , this function is uniquely specified by the two independent wavenumbers, ν_1 and ν_2 . While $X(\tau)$ can in principle be evaluated for a time-dependent signal pair of any arbitrary functional form, it is convenient to restrict the discussion to a system described by a simple sinusoidal function.¹⁰ Suppose an external sinusoidal perturbation with a fixed angular frequency ω ,

$$\xi(t) = \xi \sin \omega t \quad (2)$$

is applied to the system. As long as this perturbation is capable of inducing molecular-level changes in the system which alter the IR spectrum and the system responds linearly to the perturbation, the dynamic variation of IR intensity is expected to take the form^{7,8}

$$\tilde{A}(\nu, t) = A'(\nu) \sin \omega t + A''(\nu) \cos \omega t \quad (3)$$

By substituting eq 3 into eq 1, the cross-correlation function reduces to

$$X(\tau) = \Phi(\nu_1, \nu_2) \cos \omega \tau + \Psi(\nu_1, \nu_2) \sin \omega \tau \quad (4)$$

The terms, $\Phi(\nu_1, \nu_2)$ and $\Psi(\nu_1, \nu_2)$, which may be regarded as the real and imaginary (i.e. in-phase and quadrature) components of the cross-correlation function, are referred to as the synchronous and asynchronous 2D IR correlation intensities, respectively. They are related to the dynamic fluctuations of IR absorbance by

$$\Phi(\nu_1, \nu_2) = \frac{1}{2}[A'(\nu_1)A'(\nu_2) + A''(\nu_1)A''(\nu_2)] \quad (5)$$

and

$$\Psi(\nu_1, \nu_2) = \frac{1}{2}[A''(\nu_1)A'(\nu_2) - A'(\nu_1)A''(\nu_2)] \quad (6)$$

The synchronous correlation intensity $\Phi(\nu_1, \nu_2)$ characterizes the degree of coherence between the dynamic fluctuations of IR signals measured at two different wavenumbers. The magnitude of $\Phi(\nu_1, \nu_2)$ becomes significant (i.e., nonvanishing) only if the time-dependent variations of the two IR signals are similar to each other. The asynchronous correlation intensity $\Psi(\nu_1, \nu_2)$, on the other hand, characterizes the independent and uncoordinated fluctuations of IR signals. Unlike the synchronous correlation, the magnitude of $\Psi(\nu_1, \nu_2)$ becomes nonvanishing only if the time-dependent variations are *not* synchronized. It becomes maximum if the variations of signals $\tilde{A}(\nu_1, t)$ and $\tilde{A}(\nu_2, t)$ are 90° out of phase with each other. 2D IR spectra are constructed by

- (1) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
- (2) Bax, A. *Two Dimensional Nuclear Magnetic Resonance in Liquids*; Reidel: Boston, 1982.
- (3) Turner, D. L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1985**, *17*, 281.
- (4) Noda, I.; Dowrey, A. E.; Marcott, C. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 99.
- (5) Nomura, S.; Nakamachi, M.; Morikawa, M.; Kurokawa, M.; Soen, T. *Rep. Prog. Polym. Phys. Japan* **1983**, *26*, 495.
- (6) Noda, I.; Dowrey, A. E.; Marcott, C. *SPIE* **1985**, *553* (Fourier and Computerized Infrared Spectroscopy), 56.
- (7) Noda, I.; Dowrey, A. E.; Marcott, C. In *FT-IR Characterization of Polymers*; Ishida, H., Ed.; Plenum: New York, 1987; p 33.
- (8) Noda, I.; Dowrey, A. E.; Marcott, C. *Appl. Spectrosc.* **1988**, *48*, 203.
- (9) While the reorientation of dipole-transition moments is usually studied with a linearly polarized IR beam, a simple absorbance measurement with unpolarized light can also be used to detect the effect of reorientation with respect to the axis parallel to the propagation direction of the light.

- (10) In general, two-dimensional correlation analysis of time-dependent signals having more complicated functional forms can be carried out by using a complex Fourier transformation.

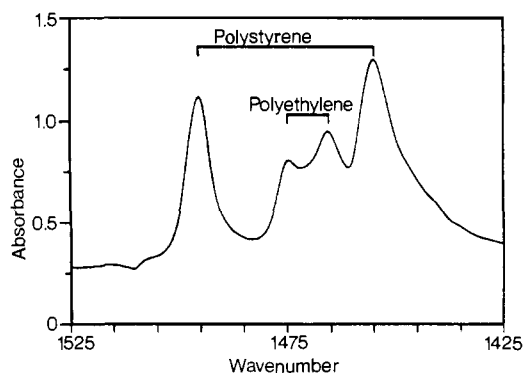


Figure 1. Conventional IR absorbance spectrum of a mixture of atactic polystyrene (PS) and low-density polyethylene (PE) obtained at 4-cm⁻¹ resolution.

plotting these correlation intensities over a spectral plane defined by the two independent (orthogonal) wavenumber axes, ν_1 and ν_2 . Some of the useful properties of 2D IR correlation spectra are highlighted below.

The correlation intensity at the diagonal position ($\nu_1 = \nu_2$) of a synchronous 2D spectrum corresponds to the autocorrelation of perturbation-induced dynamic fluctuations of IR signals. Local intensity maxima along the diagonal are thus referred to as *autopeaks*. They indicate the susceptibility of corresponding absorbance bands to a given external perturbation. More specifically, if the dynamic variation of the IR spectrum reflects the reorientation of electric dipole-transition moments, autopeaks in a synchronous 2D IR spectrum represent the ease of reorientation, and consequently the local mobility, of chemical groups contributing to the transition moments. This concept is much easier to visualize for well-established group frequencies where the transition moments are associated with specific functional groups in the system.

Peaks located at off-diagonal positions of a 2D spectral plane are called *cross peaks*. Cross peaks appear when the dynamic variations of the IR spectrum at two different wavenumbers are correlated or anticorrelated (i.e., opposite sign) to each other. For a synchronous spectrum, this occurs when the two IR signals are fluctuating in phase with each other. The synchronized variation of IR absorbance intensities can result from the simultaneous reorientation of a pair of dipole-transition moments responsible for the absorption bands. Coordinated local motions of functional groups, for example, can lead to simultaneous reorientations. Highly correlated local reorientational responses of functional groups to a common external stimulus, in turn, imply the possible existence of chemical interactions or connectivity which restrict the independent reorientational motions of the submolecular structures. Functional groups which are not strongly interacting, on the other hand, can move independently of each other. The transition moments associated with molecular vibrations of these

groups may then reorient at different rates, resulting in a much weaker or nonexistent synchronous correlation intensity. Thus, as long as the normal modes of vibration correspond to reasonably pure group frequencies, one can use the cross peaks in a synchronous 2D IR spectrum to map out the degree of intra- and intermolecular interactions of various functional groups.

Asynchronous 2D IR correlation spectra provide information complementary to synchronous spectra; cross peaks appear in asynchronous spectra if the fluctuations of IR signals induced by a common external stimulus are not completely synchronized. This feature is particularly useful since bands arising from molecular vibrations of different functional groups or of similar groups in different local environments may exhibit substantially different time-dependent intensity fluctuations. Thus, asynchronous 2D correlation spectra can be used to differentiate highly overlapped IR bands, as well-defined cross peaks often develop among these bands.

2D IR Spectra of Polyethylene/Polystyrene Blend. A simple example is presented to illustrate the unique features of 2D IR spectra. The system studied is a film made of a mixture of atactic polystyrene (PS) and low-density polyethylene (PE). A conventional IR spectrum for this film is shown in Figure 1. Absorption peaks associated with the semicircle-stretching modes of the PS phenyl ring and CH₂ deformations of the PE and PS backbone are observed. From this spectrum alone, it is difficult to determine the state of mixing between PS and PE. The corresponding 2D spectra (Figures 2–4) were obtained with the time-resolved IR spectrometer described in ref 8. The dynamic IR measurement was carried out by mechanically perturbing the system at the room temperature with a 23-Hz small-amplitude oscillatory tensile strain (ca. 0.1%) and recording the time-dependent fluctuations of IR absorbance induced by the perturbation at a spectral resolution of 4 cm⁻¹.

Figure 2 shows a fishnet representation of the synchronous 2D IR spectrum. The spectral resolution is clearly enhanced by spreading the peaks over the second dimension. While the relative magnitudes of correlation intensities are best represented by a fishnet plot, it is usually more convenient to use contour map representation (Figure 3 and 4) to determine the location of peaks in 2D IR spectra. Autopeaks observed on the diagonal near 1454 and 1495 cm⁻¹ in the synchronous 2D spectrum (Figures 2 and 3) represent the perturbation-induced local reorientation of PS phenyl ring. The 1454-cm⁻¹ band may also contain a contribution from CH₂ deformation in the backbone of PS. A pair of intense cross peaks appearing at the off-diagonal positions of the spectral plane near 1454 and 1495 cm⁻¹ indicate the existence of a strong synchronous correlation between the two PS bands. Similarly, autopeaks corresponding to the dynamic intensity fluctuation of IR bands associated with CH₂ deformations in the PE are located near 1466 and 1475 cm⁻¹. These autopeaks arise predominantly from the reorientation of molecular chains in the amorphous and crystalline regions of PE. A pair of cross peaks clearly correlate the IR bands originating from the PE component. There is little

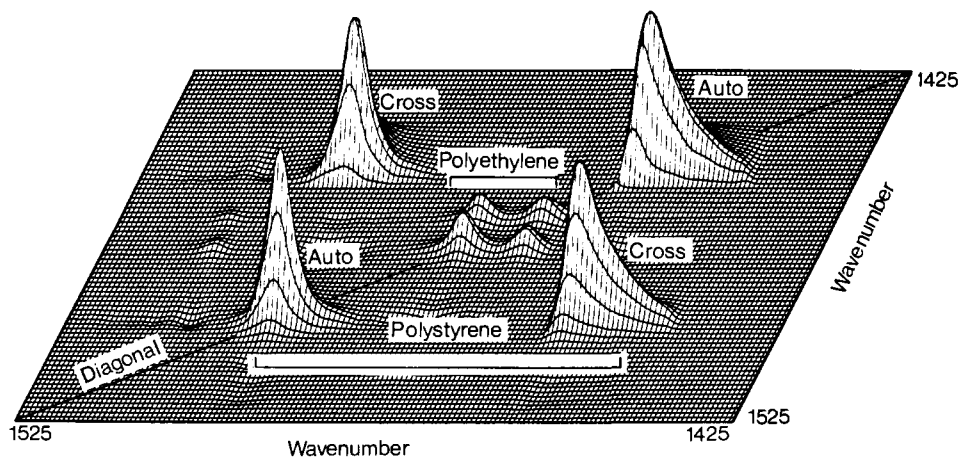


Figure 2. Fishnet representation of the synchronous 2D IR correlation spectrum $\Phi(\nu_1, \nu_2)$ of a mixture of PS and PE.

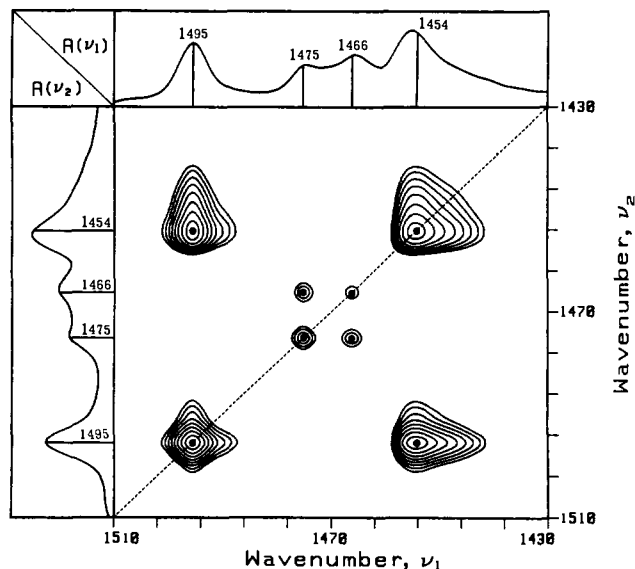


Figure 3. Contour map representation of the synchronous 2D IR correlation spectrum $\Phi(\nu_1, \nu_2)$ of a mixture of PS and PE. Conventional absorbance spectra are provided at the top and side of the map for reference purposes.

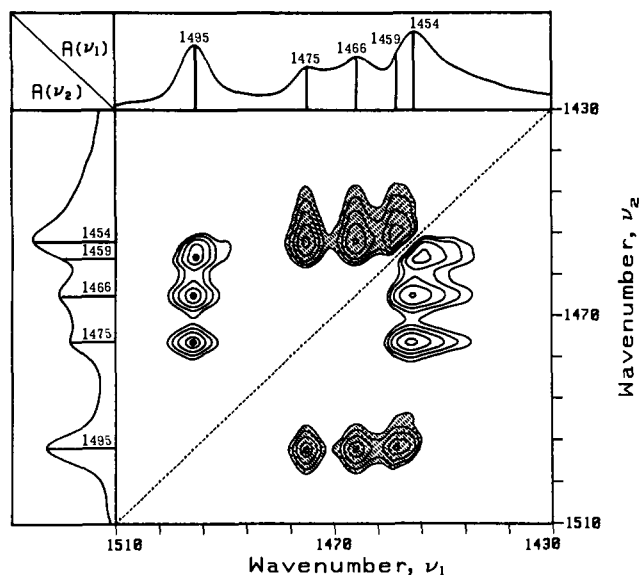


Figure 4. Contour map representation of the asynchronous 2D IR correlation spectrum $\Psi(\nu_1, \nu_2)$ of a mixture of PS and PE. Shaded areas represent negative intensity regions.

development of synchronous cross peaks correlating PS and PE bands.¹¹

The asynchronous 2D spectrum (Figure 4) shows the development of cross peaks differentiating PS and PE bands. The development of such cross peaks indicates that, even under an

(11) Even though the fluctuation rates of IR signals from PS and PE bands are substantially different, small synchronous cross peaks may develop if the signals are not completely out of phase with each other.

identical macroscopic perturbation, the time-dependent behavior of the IR intensity fluctuation for the PS component of the sample is substantially different from that for PE. Obviously, PS and PE are reorienting independently of each other at the molecular level. This result is not surprising for a pair of essentially immiscible polymers such as PS and PE,¹² where the molecular-level interaction between the components is not strong enough to coordinate their reorientational responses.

Another notable observation in Figure 4 is the development of cross peaks correlating the 1459-cm⁻¹ band to the 1454- and 1495-cm⁻¹ bands. Interestingly, these bands all belong to PS. The asynchronous correlation reveals the existence of different types of reorientational motions occurring at slightly different rates within the same polymer. Bands at 1495 and 1454 cm⁻¹ arise from semicircle-stretching vibrations of the phenyl ring side group,¹³⁻¹⁵ while the 1459-cm⁻¹ band is attributed to the CH₂ deformation modes of the PS main chain.¹⁶ The asynchronicity among IR signals from these bands must, therefore, reflect a difference in the mobilities of backbone and side-group functionalities of the polymer. This powerful feature of 2D IR spectroscopy, the deconvolution of highly overlapped bands arising from different molecular vibrations, will be further explored in a future publication.¹⁷

Conclusions

2D IR spectroscopy, a new concept in vibrational spectroscopy based on a correlation analysis of perturbation-induced dynamic fluctuation of IR signals, has been formulated. The application of this technique to the study of a mixture of atactic polystyrene (PS) and low-density polyethylene (PE) demonstrates several advantages of 2D spectroscopy over the conventional one-dimensional approach. Some notable features are as follows: simplification of complex IR spectra consisting of overlapped peaks; enhancement of spectral resolution by spreading peaks over the second dimension; and detection of the existence (or lack) of interactions among functional groups as probed through their molecular vibrations. The spectroscopic evidence clearly shows PS and PE in a blend are segregated at the molecular level, allowing the components to respond to an applied external perturbation independently of each other. A substantial difference is observed in the local mobility of the backbone and side group functionalities of PS. On the basis of this observation, it is possible to assign the 1459-cm⁻¹ component of the broad IR band centered around 1454 cm⁻¹ to the backbone CH₂ deformation in polystyrene.

Acknowledgment. I thank C. Marcott and A. E. Dowrey for helpful discussions, measurement of dynamic IR spectra, and their encouragement during the course of this work.

Registry No. PS, 9003-53-6; LDPE, 9002-88-4.

- (12) Barentsen, W. M.; Heikens D. *Polymer* **1973**, *14*, 579.
 (13) Liang, C. Y.; Krimm, S. *J. Polym. Sci.* **1958**, *27*, 241.
 (14) Painter, P. C.; Koenig, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1885.
 (15) Snyder, R. W.; Painter, P. C. *Polymer* **1981**, *22*, 1633.
 (16) The fact that the synchronous correlation cross peak maximum (Figure 3) is between 1495 and 1454 cm⁻¹, rather than 1495 and 1459 cm⁻¹, also supports this assignment.
 (17) Submitted to *Appl. Spectrosc.*