



2DCOS and I. Three decades of two-dimensional correlation spectroscopy



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ABSTRACT

Historical and personal accounts of the development of two-dimensional correlation spectroscopy (2DCOS) in the last 30 years are presented. 2DCOS originally started as a data sorting technique developed specifically for dynamic IR linear dichroism (DIRLD) spectra of polymers observed under a small amplitude sinusoidal strain. The concept was later generalized to provide a surprisingly versatile analytical tool to study many different types of samples under the influence of not only dynamic but also various static perturbations. Introduction of the efficient computational method based on discrete Hilbert transform and availability of software, as well as the comprehensive textbook in the field, have made the widespread and continuously growing use of 2DCOS technique possible. Evolution of the technique to incorporate new and variant forms of 2DCOS is also noted.

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30 years have passed since the introduction of two-dimensional correlation spectroscopy (2DCOS) to the field of analytical science. During this time I have been fortunate enough to observe the expanding applications of this technique to numerous types of spectroscopic analyses. A number of exemplary researchers who have become close friends and collaborators have contributed to these developments. This paper traces my own personal journey with 2DCOS.

Encounter with spectroscopy

I came to the United States from Japan in 1969 and studied at Columbia University in New York for almost a decade. After completing my doctorate in chemical engineering in 1979, I started working for the Procter & Gamble Company in Cincinnati. While I was reasonably well-equipped with the background in polymer science (my thesis topic was on diffusion of small molecules in a polymeric membrane), I had received essentially no formal advanced training in spectroscopy during my university days. Fortunately, I met my colleague and lifelong friend Curtis Marcott, who joined P&G several months after me and happened to reside in the same apartment complex that I lived. During the carpool commute to work every day, Curt taught me so much about the newly emerging Fourier transform IR spectroscopy and time-resolved IR measurement.

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Dynamic IR dichroism

I was actively involved in the polymer design and characterization program at P&G. In November 1981, I was attending the Second Users' Group Meeting for the SAXS/SANS facilities at Oakridge National Laboratory. There I heard an intriguing lecture by Richard Stein of U. Mass., Amherst describing the variation of x-ray scattering patterns of polymer films under dynamic deformation. In fact, that was the only topic I could recall from the day, as I was suffering from a terrible hangover from the boilermakers (shots of Jack Daniels chased with beer) wickedly introduced to me the night before by Hyuk Yu of University of Wisconsin. Anyway, upon my return to Cincinnati I proposed to Curt that we explore the potential of a similar experiment with IR for plastic films under dynamic deformation. Tony Dowrey and Gloria Story also joined the effort. It was the beginning of the dynamic IR linear dichroism (DIRLD) spectroscopy project at P&G.

Fig. 1 shows the experimental set up in earlier days of DIRLD measurement using an old dispersive Perkin–Elmer 521 IR spectrometer coupled with a dynamic polymer film stretcher [1]. Improvements of instrumentation, including the use of a step-scan FT IR spectrometer, followed [2,3]. In DIRLD spectroscopy, a small amplitude deformation is applied to a film sample, which induces microscopic reorganization of constituents. For a sinusoidal deformation, one observes sinusoidal change in IR dichroism, i.e., difference in the absorption of light aligned parallel vs. perpendicular to the axis of deformation, which in turn is proportional to the average orientation of electric dipole transition moments

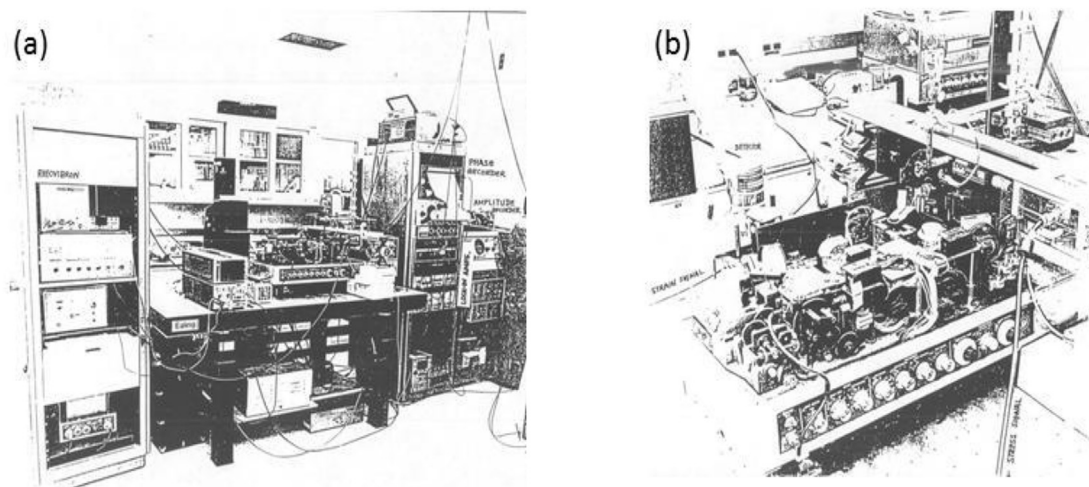


Fig. 1. Dynamic infrared linear dichroism (DIRLD) spectrometer: (a) overall set up; (b) close-up view of the mechanical stretcher coupled with a dispersive IR spectrometer.

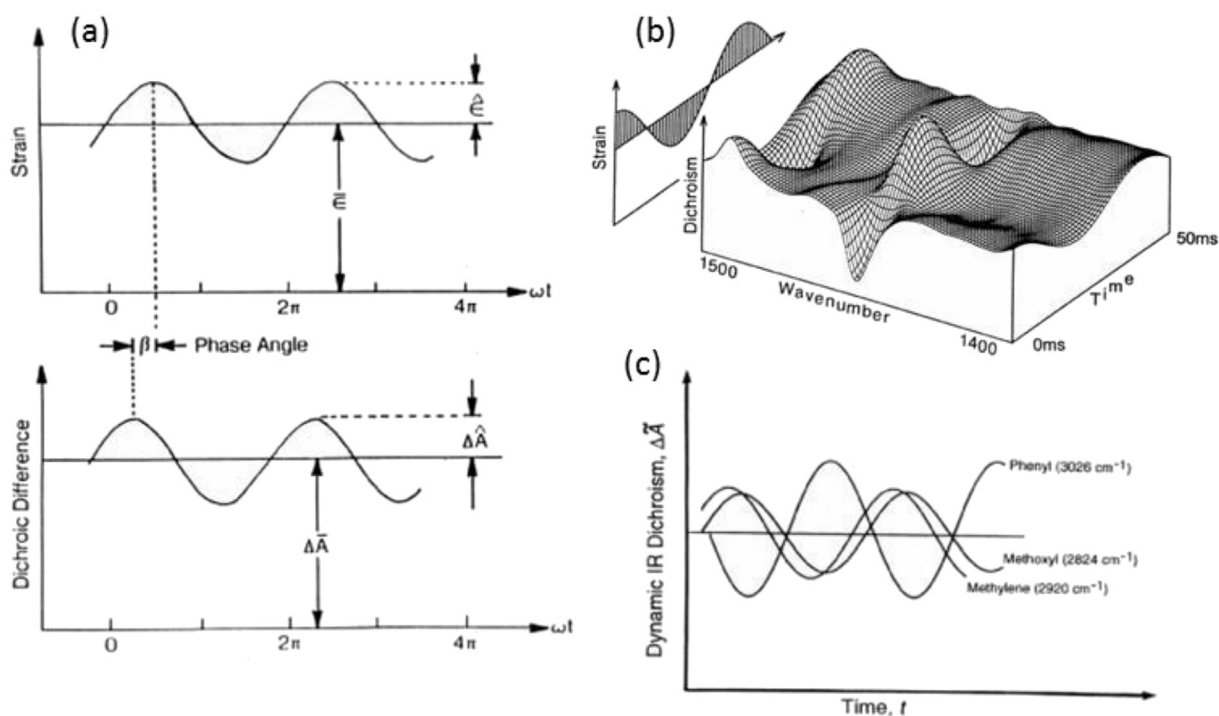


Fig. 2. DIRLD spectroscopy: (a) IR dichroism induced by a small sinusoidal strain; (b) time-resolved DIRLD spectrum; and (c) asynchronous reorientations of individual molecular constituent groups.

associated with individual molecular constituent groups (Fig. 2a). By changing the wavenumber of the polarized IR probe, reorientations of different constituents of the sample, e.g., crystalline vs. amorphous components, may be monitored (Fig. 2b).

However, we were totally surprised by the unexpected observation that different parts of the same molecule within even a seemingly homogeneous sample, such as amorphous polystyrene film, can individually reorient at very different rates under the dynamic deformation (Fig. 2c). Interpretation of DIRLD data with multiple responses with many different rates suddenly became a very complicated task. I had to find a way to sort out such complex and often highly overlapped spectral responses, which are reflecting the individual responses of molecular constituents to the macroscopic deformation (perturbation) in a manner out-of-phase with each other. Then the revelation came.

Dynamic 2D IR spectroscopy

It was around 3:00 a.m. in the morning of September 14, 1985, an idea suddenly occurred to me, still in a half-awakened state of mind: how about mapping cross correlation intensities among dynamically varying IR signals on a two-dimensional spectral plane. Fig. 3 shows the copy of pages from a notebook I happened to keep with me at the bedside. Mental images of plotting coupled synchronous variations vs. decoupled asynchronous behaviors, which have become the signature hallmark of 2D correlation spectroscopy, were unmistakably recorded in the original note. I must confess, however, that it still remains a mystery to me how this idea actually came to me that morning.

It became obvious that various DIRLD spectra we had already collected could be readily converted to 2D correlation IR dichroism

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