ABOUT THE SCIENTIST

Robert Corn, Ph.D., is a professor and chair of the analytical division of the chemistry department at the University of Wisconsin. He uses polarization modulation FTIR spectroscopy in order to characterize the chemical structure of surfaces and thin films.

His interest in chemistry developed as an undergraduate at UC San Diego. "I participated in a couple of research projects with wonderful professors. That's where I learned about scientific research and that I enjoyed doing it," he says. "I still strongly encourage and support undergraduate research for this reason." Regarding his area of specialty he adds, "From the beginning, I always enjoyed the combination of spectroscopy and physical chemistry. I think that it's the right mixture of theory and experiment for my tastes."

Dr. Corn did his graduate work at UC Berkeley on the application of Fourier transform infrared spectroscopy to the study of motion in molecular solids. He worked as a visiting scientist at the IBM Research Laboratory in San Jose where he ap-

Rapid-scan Polarization-modulated Fourier-transform Infra-red Reflection Absorption Spectroscopy

Infra-red reflection absorption spectroscopy (IRRAS) is a technique for studying the IR absorption in very thin layers of molecules adsorbed on a specular reflective metal surface.[1]

Dr. Robert Corn and his group at the Chemistry Department of the University of Wisconsin have developed a technique for polarization-modulated Fourier-transform IRRAS (PM-FTIRRAS) using a rapid-scanning Fourier transform spectrometer. A photoelastic modulator (PEM) provides the polarization modulation. Demodulation is accomplished using a unique real-time sampling circuit. A significant advantage of this method is that measurement of a separate reference scan on the bare metal surface is not required.

Traditional PM-IRRAS Methods

Most IRRAS experiments utilize a high angle of incidence of the light on the sample/reflector, as shown in Figure 1. For this geometry, s-polarized light (parallel to the reflective surface) is virtually unabsorbed. The p-polarized light (in the plane of incidence) is absorbed by the molecular layer, with the absorption being significantly enhanced by the near-grazing angle of the incident light. Molecules not near the reflecting surface (e.g., gas molecules) absorb s and p polarized light equally. The parameter of interest is (Is - Ip)/(Is + Ip), proportional to the difference signal divided by the average signal. Photoelastic modulators (PEMs) have gained wide acceptance as the technique of polarization modulation (PM) in IRRAS measurements.

Early PM-IRRAS setups used dispersive spectrometers. Recently, however, the emphasis has switched to FT-IR spectrometers because of a number of advantages they offer over dispersive systems.[1]

Figure 1 shows a traditional PM-FTIRRAS optical setup following the interferometer. A lock-in amplifier is used to demodulate the PM signal. For a continuous-scan interferometer, the requirement for a large separation between the PM frequencies and the Fourier frequencies limits the scanning speed of the mirror. Requirements for the shortest possible lock-in time constant presently dictate the use of high-quality (and expensive) analog lock-in amplifiers.
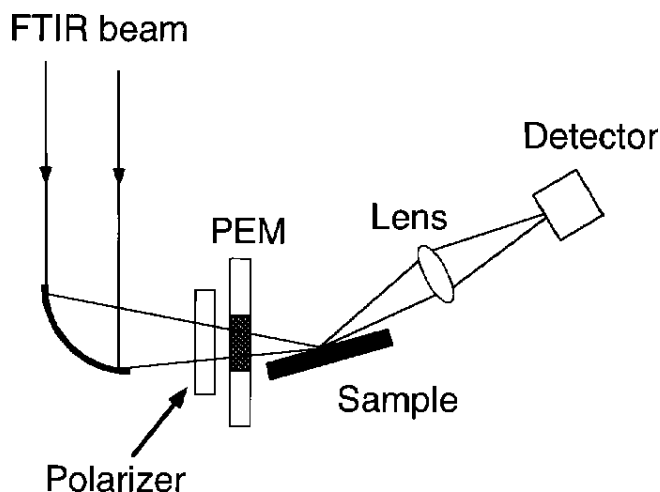
Rapid-Scan PM-FTIRRAS

Dr. Robert Corn and his group have developed a technique for PM-FTIRRAS which uses a rapid scanning spectrometer (Mattson Cygnus 100) and a 37 kHz zinc selenide PEM (Model II/ZS37) manufactured by Hinds Instruments. The optical setup is similar to traditional PM-FTIRRAS setups (Figure 1).

The key to this system is a unique demodulation circuit which samples each cycle of the modulated waveform to determine directly values of I_p and I_s.

Figure 1. Optical layout for a double-modulation experiment using a scanning FT-IR spectrometer and a PEM to modulate the polarization. (Reference 2, Figure 1b)

The demodulation circuit uses high-quality video sample-and-hold amplifiers as described in Green, et. al.[2] and Barner, et. al.[3]

In Figure 1, the PEM is oriented at 45 degrees from the plane of incidence of the beam. The PEM is operated at half-wave retardation, and the polarizer is oriented so that s-polarized linear light is produced at the retardation maxima, while p-polarized linear light occurs at times of zero PEM retardation.[4] These two states occur twice with each PEM oscillation cycle. The sampling frequency is, therefore, 74 kHz.

A resulting interferogram is shown in Figure 2, showing the signal from the detector, with the PM modulation superimposed on the signal resulting from the interferometer operation. The envelope of the curve (s-polarization) corresponds to the average signal ($I_s + I_p$) while the amplitude of the small negative spikes corresponds to the difference signal ($I_s - I_p$).
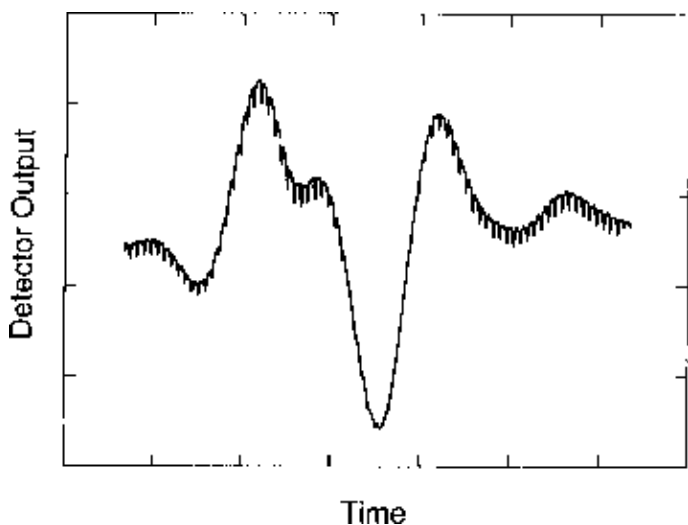

Figure 2. Portion of an experimental PM-FTIR interferogram signal prior to the real-time sampling electronics. (Reference 3, Figure 5)

This signal is split, one branch going to a low-pass filter whose output is an analog average signal. The other branch goes to the difference signal circuit. A detailed description of the difference signal demodulation scheme is beyond the scope of this article, but a complete description is given in Green, et. al.[2] A simplified overview, however, will be given here.

The difference signal is typically much smaller than the average signal, so the first step is to electronically "subtract out" the average signal so that the PM signal can be amplified. The resulting signal is split again, with one branch being used to sample the p-polarization magnitude and the second branch to sample the s-polarization magnitude. For the computation of the difference signal for each half-cycle, the s-polarization is evaluated twice, once at the beginning of each cycle and once at the end. Each of these signals is amplified/attenuated by the appropriate factor then sent to a sum-difference amplifier. The output is sampled and the result sent to a low-pass filter, whose output is an analog difference signal.

The average signal and difference signal are then digitized and transformed using the system computer to give the IRRAS spectrum of the sample. An example of the IRRAS spectrum of a polyimide thin film on a polycrystalline chromium substrate is shown in Figure 3.[3]

Advantages

There are a number of advantages which this method has over a traditional experiment setup using a lock-in amplifer. The setup described above does not require obtaining a reference scan with a bare mirror in place. This reduces the time required for the experiment. It also eliminates the potential difficulties arising from any contamination on the "bare" mirror. The mirror can be scanned 2 to 3 times faster than with a traditional setup, which can reduce instabilities in some interferometers. Finally, problems with overloading the lock-in amplifiers (which have plagued some investigators) are eliminated.
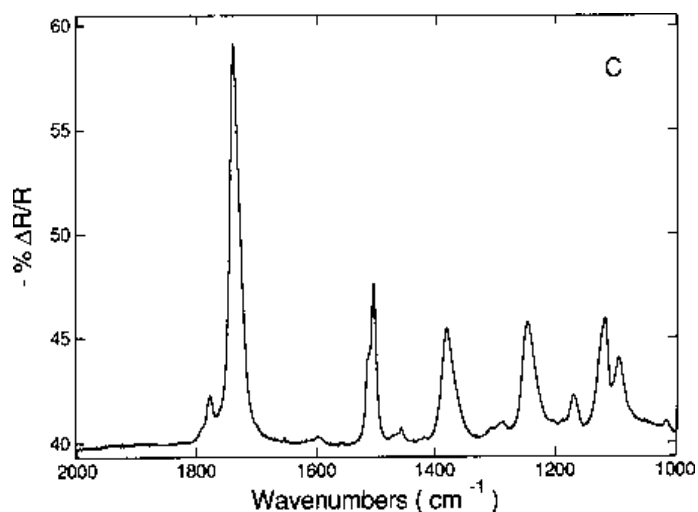
Figure 3. IRRAS spectrum of a 15 nm polyimide thin film on a chromium substrate. (Reference 3, Figure 8c)

References:

1. Baoliang Wang, "Infrared reflection-absorption spectroscopy using the photoelastic modulator," Hinds Instruments application note, March, 1996.
2. Michael J. Green, Barbara J. Barner, and Robert M. Corn, "Real time sampling electronics for double modulation experiments with Fourier transform spectrometers," Rev. Sci. Instrum. **62** (6), June, 1991.
3. Barbara J. Barner, Michael J. Green, Edna I. Saez, and Robert M. Corn, "Polarization modulation Fourier transform infrared reflectance measurements of thin films and monolayers at metal surfaces utilizing real-time sampling electronics," Anal. Chem. **63**, 55, 1991.
4. "PEM-90™ Photoelastic Modulators," Hinds Instruments brochure, Hillsboro, OR, 1995. (Figure 5b, page 7)
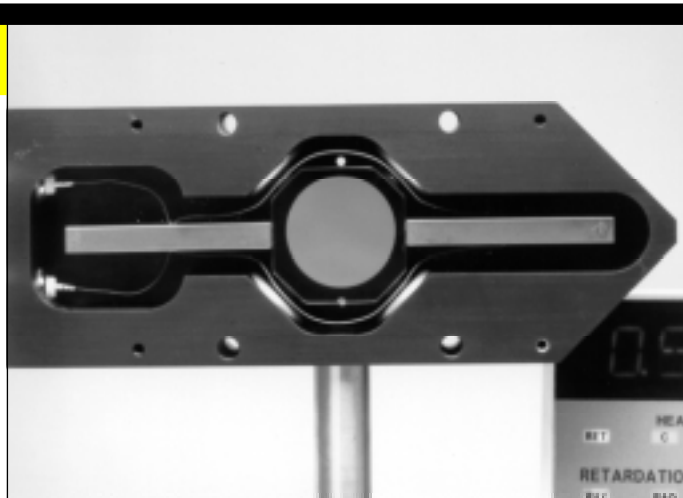
PEM-90™ MODEL II/ZS50

Hinds PEM-90 ZnSe modulators are routinely specified for polarization modulation IRRAS (PM-IRRAS) spectrometers. The model II/ZS37 (37 kHz) PEM has been commonly used for the mid-IR polarization modulation experiments. Recently Hinds Instruments has added a new ZnSe model to the PEM-90 series.

Designated the II/ZS50, this PEM employs a symmetrical ZnSe optical element and provides a nominal resonant frequency at 50 kHz. When compared with the PEM II/ZS37, the II/ZS50 has a more compact design that makes this model preferred for installation in a space-limited compartment. This model is also capable of providing more efficient modulation in the long wavelength IR region. Furthermore, due to its reduced size, the II/ZS50 offers price advantages.

The specifications for this new model are summarized in the table at the right.

Like all other Hinds PEMs, the II/ZS50 provides the unique benefits of a wide acceptance angle (>±20 degrees), a good transmission wavelength range, and a high sensitivity (10^{-6} and more). These features make the PEM-90s especially well-suited to the basic characteristics of polarization modulation IR spectroscopy, including both FT- and dispersive-based vibrational circular dichroism , vibrational linear dichroism, and IRRAS.

Finally, it is worth noting that the PEM-90 II/ZS37 offers a larger optical aperture than the II/ZS50 does. These two ZnSe models, complementing each other, provide the user more choices for setting up the instrument customized according to their particular needs.

PEM-90 II/ZS50 Specifications

Nominal 1f Frequency	50 kHz
Spectral Range[1]	550 nm-18 μ[1]
Range of $\lambda/4$ Retardation	550 nm-18 μ[1]
Range of $\lambda/2$ Retardation	550 nm-10 μ[2]
Useful Aperture	14 mm[3]

[1]Spectral limits defined by transmission less than 50 percent of maximum transmission. Contact Hinds Instruments for details of performance beyond these limits.

[2]Contact Hinds Instruments if retardation greater than half-wave at 10μ is required.

[3]In many FTIR-related polarization modulation experiments, a larger aperture may be used.

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- CLEO '96, Anaheim, CA, June 2-7

- SPIE Polarization Conference, Yokohama, Japan, June 12-14

- AIRS II, Duke University, Durham, NC, June 17-19

Additional Information

For further information, contact:
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plied the techniques of plasmon-enhanced Raman scattering and optical second harmonic generation to electrochemical surfaces. Following IBM, he spent a year as visiting assistant professor in the area of physical chemistry at Swarthmore College in Pennsylvania. Since 1985 he has been at the University of Wisconsin.

"Science and scientific research are changing rapidly," Dr. Corn says. "My first set of goals was to become a professor, to set up an active research program in spectroscopy at surfaces, and to help graduate students become scientists. Now that I've accomplished these, I find that scientists need to do more for the general public.

"We need to convince people that 'chemistry' is not a bad word, and that understanding nature is something that enhances our world and is worth spending time and money on. I feel that all scientists will spend more time educating and interacting with the general public, who, after all, are paying for this research and rightfully want to know what they're getting."

Dr. Corn feels strongly about the practical applications of his own research: "A great number of the chemical processes and transformations that control energy supply and storage, biological functioning, and environmental chemistry happen to occur at surfaces. We have ongoing projects in the study of electrochemical surfaces for better batteries, liquid/liquid surfaces that mimic the behavior of biological membranes, semiconductor/liquid surfaces for the removal of PCBs and organic contaminants from natural ground waters, and oligonucleotide-coated surfaces for DNA computing."

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