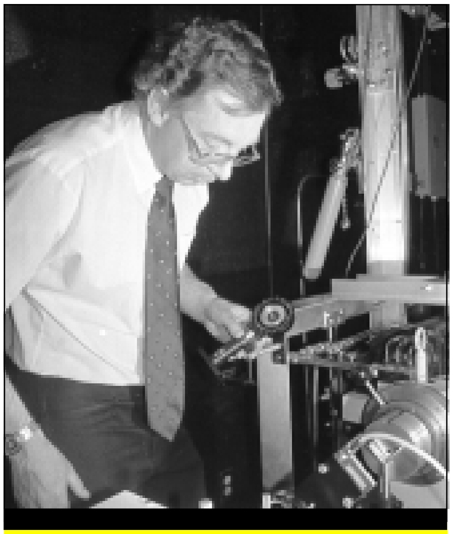
SUMMER 1995

HINDS INSTRUMENTS, INC.

PEM™ APPLICATIONS NEWS FOR USERS OF PHOTOELASTIC MODULATORS



ABOUT THE SCIENTIST

Dr. John W. Kenney, III, shown above with his MCD/absorption apparatus, is a tenured associate professor of chemistry at Eastern New Mexico University (ENMU) and director of the Chemical Physics Research Laboratory. In addition to his research, he teaches both chemistry and physics courses.

Kenney has been very active in recruiting minority students into the sciences in general and specifically into high tech research. His formula for success is to "generate enthusiasm, demand excellence, and require high standards."

"Treat people right, demand the world of them, and then support them, and they will outperform themselves beyond belief," he says. "That's what I do with all my students."

In the laboratory, Kenney is assisted by his wife Inga. "She has all the brains and beauty. I just have the title," he says. They both have been at ENMU for 13 years. "We started this whole thing as newlyweds," he

(Continued on page 3)

Simultaneous MCD & Double Beam Absorption Spectra

Dr. John Kenney, associate professor of chemistry at Eastern New Mexico University, has developed a novel experimental setup and techniques for simultaneously measuring magnetic circular dichroism (MCD) and absorption. He and his students (undergraduates at ENMU) use this for studying alkali metal atoms (Li, Na, K) embedded in solid rare gas matrices (Ne Ar, Kr, Xe).

Dr. Kenney's apparatus is based upon a Hinds PEM-90 photoelastic modulator (PEM). Use of a PEM has become the technique of choice for measurement of circular dichroism.[1,2] When set at quarter-wave peak retardation, the PEM produces alternating right and left circular polarized light. The phenomenon of circular dichroism is a differential absorption of these two senses of circular polarized light.

Simultaneous MCD and absorption data acquisition is preferred over separate scans to ensure that the two spectral data sets are acquired under identical conditions. This is crucial if the sample has any tendency to change its characteristics with the passage of time, changes in temperature or other environmental parameters, or exposure to light.

Experimental Setup

Dr. Kenney chose to build his own spectrophotometer rather than purchase a commercial instrument. Commercial designs did not lend themselves to incorporating a large electromagnet into the sample chamber. A custom design also provided the flexibility needed for his special experiments.

The experimental setup is shown in Figure 1 (page 2). The light source is an automobile quartz halogen headlamp, powered by a 12 volt power supply. The filament is focused onto the entrance slit of a 0.275 m f/3.8 monochromator (Acton SpectaPro 275) equipped with a 1200 lines/mm grating blazed in the mid visible. The monochromatic light emerging from the exit slit of the monochromator is collimated by a quartz lens. Quartz lenses and Glan-Taylor polarizers have been chosen so that measurements later may be extended into the UV by changing only the light source to a Xenon arc lamp or deuterium lamp.

It is important to maintain a constant average photomultiplier (PMT) signal for MCD measurements.[2] This is accomplished by two methods: first, by adjusting the intensity of the light passing through the system, and second, by adjusting the PMT high voltage, which changes the PMT gain.

In Dr. Kenney's setup, the light intensity is controlled in an ingenious manner. A dual Glan-Taylor polarizer setup is used before the light enters the PEM (Model I/FS50). The second (stationary) polarizer is aligned at 45° with respect to the PEM axis. The first polarizer is mounted on a computer-controlled rotator. By varying the angle between the polarizer axes

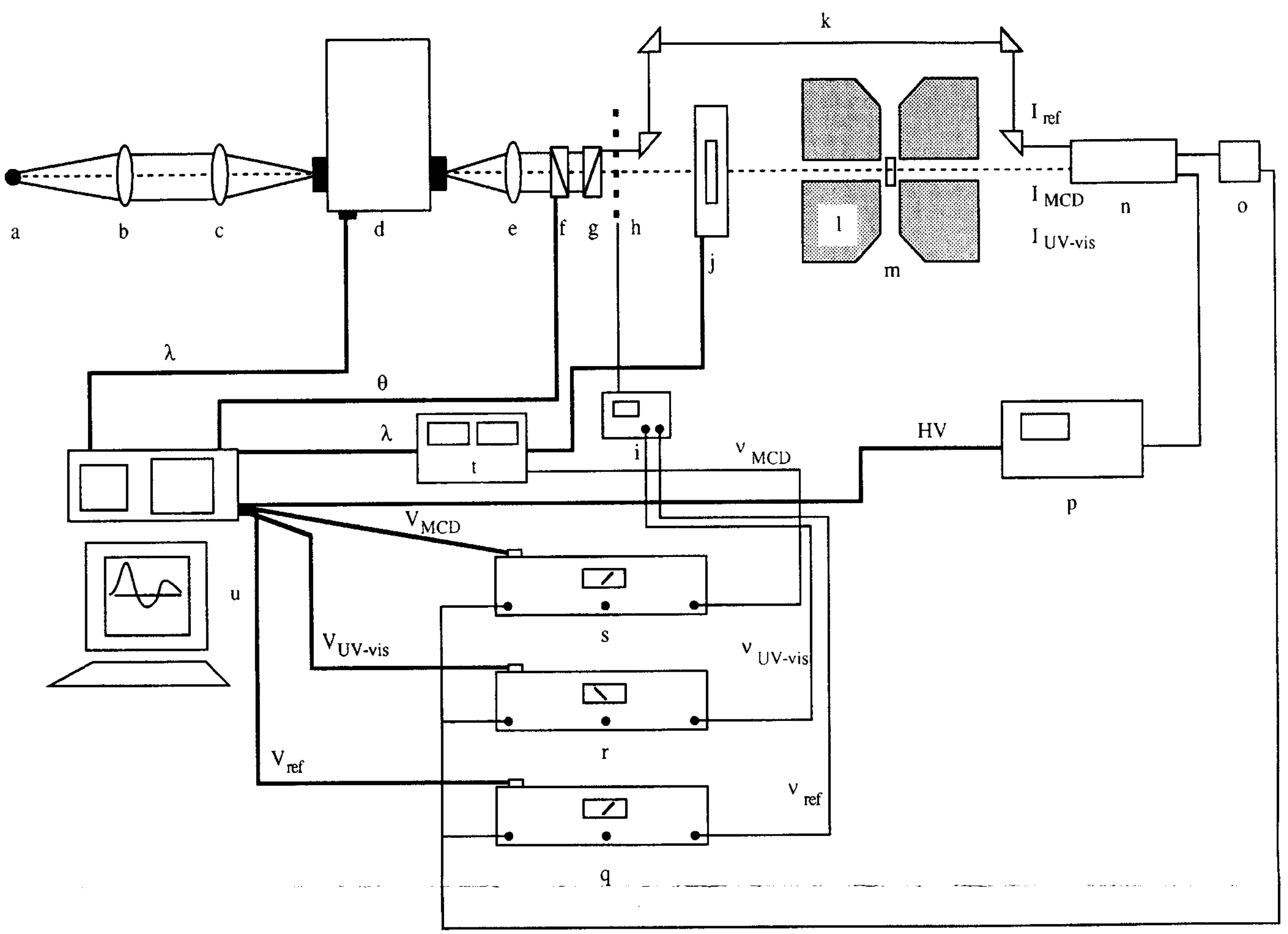


Figure 1. MCD/Absorption Spectrophotometer: (a) 100 W quartz halogen lamp; (b) and (c) quartz lenses; (d) monochromator, Acton SpectraPro275; (e) quartz collimating lens; (f) Glan-Taylor polarizer, rotating; (g) Glan-Taylor polarizer, fixed; (h) 2-ring mechanical chopper, SRS;(i) chopper controller; (j) Hinds PEM-90, I/FS50; (k) reference beam; (l) electromagnet; (m) sample; (n) PMT, Hamamatsu; (p) PMT high voltage controller, SRS; (q) reference lock-in amplifier, SRS 510; (r) UV-visible lock-in amplifier, SRS 510; (s) MCD lock-in amplifier, SRS 530; (t) PEM-90 controller; and (u) computer and data acquisition/instrument controller, Hewlett Packard 3497A, 9816. Note: dark lines represent IEEE-488 computer cables; light lines represent standard BNC-type cables.

the output light intensity may be varied over a range of about 10^3.

A two-section mechanical chopper follows the polarizers, with a part of the beam (chopped at 390 Hz) used as a reference beam and the center part of the beam going to the sample. The center beam, chopped at 325 Hz, passes through the PEM where it is modulated at quarter-wave peak retardation at a nominal frequency of 50 kHz. This beam impinges on the sample, located in a cryogenic refrigerator between the poles of a large electromagnet. Small holes drilled through the pole pieces of the electromagnet allow the beam to reach the sample, traveling in a direction which is parallel to the magnetic field. The beam then continues through the second pole piece of the electromagnet to the PMT.

Both the reference beam and the center beam are detected simultaneously by the PMT tube, which gives an output signal modulated at 325 Hz, 390 Hz, and 50 kHz. The three resulting signals are referred to as V_{ref}(390 Hz), $V_{UV\text{-}vis}$(325 Hz) and V_{MCD}(50 kHz). Three lock-in amplifiers are used to detect these three signals.

A computer controls the entire operation, including setting the monochromator wavelength, the light intensity after the polarizers, the wavelength setting of the PEM controller and the high voltage for the PMT. The computer is also connected to each lock-in amplifier from which it received the digitized output signal. The computer analyzes and displays the resulting data.

The absorbance is given at a specific wavelength as

$$A = K\log_{10}(V_{ref} / V_{UV\text{-}vis})$$

where K is a constant of proportionality related to the relative intensities of the reference beam and the central beam through the sample.

The MCD is given, as a function of wavelength, as

$$\Delta A' / A' = (A'_{LCP} - A'_{RCP}) / A'$$

ΔA' can be obtained directly from the measurement of the 50 kHz modulated V_{MCD} signal. The prime in A' indicates that the sample is being observed under the influence of a magnetic field. However, A' = A for almost all systems which Dr. Kenney and his group investigate (i.e. the average absorbance does not change under the influence of the magnetic field).

Experiment Objectives

Dr. Kenney is investigating alkali metal atoms (Li, Na, K) embedded in solid rare gas matrices (Ne, Ar, Kr, Xe) deposited on a sapphire substrate.[3] Temperatures of 15 - 20 K are maintained in a cryogenic sample chamber. The sapphire substrate is selected so that the optic axis is normal to the substrate surfaces, so there is no net birefringence which may give false CD signals. The alkali metal atoms are deposited in the matrix by striking an alkali metal target with a UV laser beam. This is called laser ablation.

MCD serves as a very effective probe for investigating the environment of the alkali metal atoms in the rare gas matrices.[4,5] The spectra observed are directly related to the atomic absorption lines in alkali metal vapor, but perturbed by the presence of the matrix atoms. An example of the spectrum obtained is shown in Figure 2. This shows the MCD and transmission spectra of Li deposited in solid Ar.

This work is being funded by the High Energy Density Materials Program of the Air Force Office of Scientific Research and by the Research Corporation. The motivation is improvement in rocket propellants by doping them with alkali metals. The propellants are typically liquid hydrogen and oxygen. This research is directed toward understanding of the chemical and physical characteristics of these alkali metals in the propellant matrix. Dr. Kenney's research will soon be investigating alkali metals in solid hydrogen matrices.

Student Involvement in Research

A unique aspect of Dr. Kenney's research projects is the high level of involvement of undergraduate physics, chemistry, and mathematics students. Only students who maintain grades of A or B in every class are eligible to participate. Each participant is required to be familiar with all aspects of the project, but is expected to be the "expert" on a particular phase of the project, such as high vacuum, computer programming, spectroscopy, etc. Students spend 10 to 20 hours per week in the laboratory, in addition to carrying a full academic load.

The program seeks to prepare participants for graduate school, and most go on to graduate school, for which they are exceptionally well prepared.

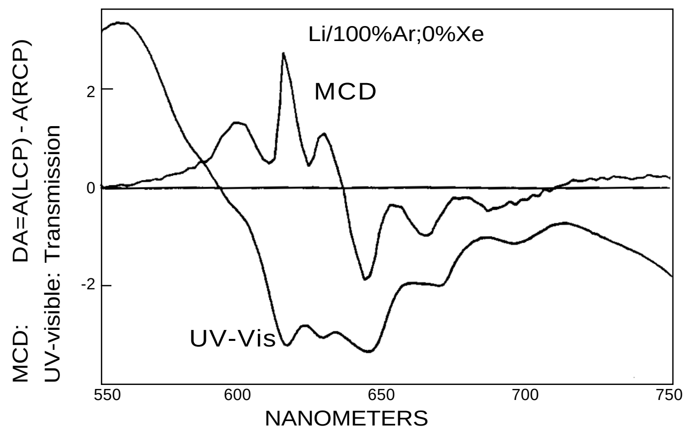


Figure 2. MCD and transmission spectra for Lithium in solid Argon. The 671 nm $^2S \rightarrow {}^2P$ resonance line has been split into three bands and shifted toward the blue due to the presence of argon matrix atoms.

References:

1. Hipps, K.W.; Crosby, G.A., "Applications of the Photoelastic Modulator to Polarization Spectroscopy," *J. Phys, Chem.* **83**, 555-562 (1979).
2. Drake, A.F., "Polarization modulation – the measurement of linear and circular dichroism," *J. Phys. E; Sci, Instrum.* **19**, 170-181 (1986).
3. Fajardo, M.E.; Carrick, P.G.; Kenney, J.W., III, "Matrix isolation spectroscopy of metal atoms generated by laser ablation. I. The Li/ Ar, Li/ Kr, and Li/ Xe systems," *J. Chem. Phys.* **94**, 5812-5824 (1991).
4. Ball, D.W., "An Introduction to Magnetic Circular Dichroism Spectroscopy; General Theory and Applications," *Spectroscopy* **6**, 18-24 (1991).
5. Rose, J.; Smith, D.; Williamson, B.E.; Schatz, P.N.; O'Brien, M.C.M., "Magnetic Circular Dichroism and the Jahn - Teller Effect in the $^2S \rightarrow {}^2P$ Transition of Sodium and Lithium Atoms Isolated in Xenon Matrices," *J. Phys. Chem.* **90**, 2608-2615 (1986).

Scientist *(continued from page 1)*

adds. Mrs. Kenney spends more time at home now that they have two young children, but she still teaches and participates in the research. She did much of the key computer programming for the MCD project.

In addition to his work with MCD, Dr. Kenney is a research collaborator in the high pressure spectroscopy program at Los Alamos National Laboratory's Chemical Sciences and Technology Division 14. "We literally squeeze molecules together at the molecular and atomic level and create new states of matter and new ways for light to interact with matter," Kenney says. "There are a number of practical implications in terms of friction, compression, explosions, but I'm also pursuing it for the pure fundamental science love of it."

Kenney did his post-doctoral research on the molecular electronic spectroscopy of transition metal complexes at Washington State University, his doctoral research at the University of Utah, and he received a B.S. in chemistry from the University of Nevada.

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INSIDE PEM

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NOTES OF INTEREST

New PEM-90 Controllers

In response to PEM user suggestions, a new model controller, known as the **PEM-90-D**, is now available as a direct replacement for the older PEM-90C. It incorporates several important new features and corrects a number of limitations in earlier models.

Significant among the improvements are improved f and 2f reference signals, with duty cycles now extremely close to 50 percent over the entire range of operation.

Another area of major improvement is the new RS-232 computer interface. The communication rate is now 9600 baud, resulting in much faster operation. In addition, the controller can now accept full command strings sent to its RS-232 interface port. The new model also enables enhanced low level modulation.

In addition to these features, the new PEM-90-D controller is also available in a reduced price "non-display" version (PEM-90-ND) which is operated solely through the RS-232 or the remote connector interface.

A factory upgrade option is available for PEM-90C users who wish to add the RS-232 improvements to their existing unit. Contact Hinds for further information.

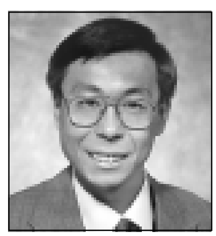
In a related product change, the Hinds IEEE-488 (GPIB) interface is no longer available. In its place, we recommend the National Instruments Model GPIB-232CV-A converter, which uses the RS-232 interface of the new PEM-90-D, -ND, or upgraded PEM-90C controller. We can provide assistance in obtaining the National Instruments IEEE-488 converter for those who are interested.

Trade Shows

The new PEM-90 controller will be on display at these upcoming conferences:

- Laser '95 in Munich, Germany, June 19-23, Hall 2, Stand 2D18.
- Optical Society of America Exhibit in Portland, Oregon, September 10-15.

New Applications Engineer



Hinds welcomes Baoliang (Bob) Wang as a new PEM applications engineer. Wang recently completed a post-doctoral appointment at the University of Illinois in Chicago. He completed his PhD there in physical chemistry under Prof. Tim Keiderling, a long-time PEM user. Wang's job will focus on customer technical support, laboratory investigations, and technical writing.

For Further Information

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