MASTER

FOURIER TRANSFORM PHOTOACOUSTIC
KINETIC SPECTROSCOPY OF SOLID SURFACES

Annual Progress Report
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Abstract

A description of visible Fourier transform photoacoustic spectroscopy (PAS) has been published in two places. Application of PAS to a zirconium phosphate inorganic system has also been described. The use of visible synchrotron radiation in quantitative high frequency PAS has been attempted, and a theoretical modeling of such experiments is nearing completion. A Nicolet FTIR spectrometer is being used to perform mid-infrared PA spectroscopy on carbon samples with a view to determining the best means of ratioing out variations with wavelength in infrared source intensity.

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The scope of this unclassified contract consists of a study of Fourier transform photoacoustic spectroscopy (FTPAS) by applying it to analytical problems on solid surfaces and the application of infrared FTPAS to opaque uncolored surfaces. Specific objectives for the year beginning April 1, 1980 were the dissemination of a sufficiently simple yet complete description of FTPAS instrumentation and programming so that other laboratories would try the technique; the elimination of phase errors in FTPAS interferograms; the discovery of the useful properties of synchrotron radiation as an ultraviolet-visible and infrared light source for FTPAS; and the production of seminal visible and infrared FTPA spectra.

Work Completed

A description of Fourier transform photoacoustic spectroscopy at visible wavelengths was revised, accepted for publication by the editor of Analytical Chemistry on June 20, 1980, and appeared in print in September.¹ Another manuscript giving greater emphasis to the details of Michelson interferometer construction and minicomputer programming was accepted by Review of Scientific Instruments on July 20, 1980, and scheduled for publication in November, 1980.² In each of these reports visible photoacoustic spectra are presented of solids that show good wavelength agreement with dispersive PA spectra. While we have not eliminated all the phase errors inherent in FTPA spectral measurements, this agreement indicates we have carried the process as far as is presently profitable.

In a recently completed manuscript³ we have used visible photoacoustic spectroscopy as an analytical tool in an inorganic synthesis problem. The preparation of a crystalline zirconium phosphate containing apparent monolayers of tris(2,2'-bipyridine) ruthenium(II) is described, and its expanded lattice is characterized by X-ray powder pattern diffraction. Electron spin resonance and photoacoustic spectral data are shown to indicate the ruthenium

complex retains its octahedral symmetry in this new host environment. Electron spin resonance data also indicate that under visible illumination triethylamine transfers an electron to the ruthenium complex to form a free radical amine cation.

Work in Progress

In mid-August, dispersive PAS instrumentation was hauled in a university van to the Synchrotron Radiation Center, University of Wisconsin-Madison (located in a cornfield in Stoughton a few miles out of Madison.) The facility director, Ed Rowe, permitted us to use a port of the smaller of the two synchrotrons at Stoughton (the Tantalus) that emits visible radiation and is therefore little used. (The major value of synchrotrons from the spectroscopist's point of view is their ability to produce comparatively intense, wavelength tunable X-ray and vacuum ultraviolet radiation. With its 32 MHz amplitude modulation visually undiscernible, the output of the Tantalus looks like that from a small flashlight.) Inadequate shielding of our RF amplifier and sample-piezoelectric detector sandwich from the intense RF background noise near the Tantalus precluded the detection of the expected weak PA signal. A new RF amplifier has been thoroughly remodeled in our electronics shop to make it capable of detecting RF PA signals. It will be tested successfully with an 83 MHz, mode locked, CW, dye laser in our building before further experiments are attempted at a synchrotron.

The motivation for high frequency PA spectral measurements is primarily the achievement of a truly quantitative PAS. As matters presently stand dispersive and interferometric PAS both yield spectra that permit the qualitative analysis of opaque samples but often do not produce PA spectral peak areas that permit reliable quantitative analysis. Signal saturation, occurring at low (submegahertz) chopping frequencies in materials with high absorptivities is a problem.⁴ The question is whether the very weak PA signal from a sample/piezo-

electric detector sandwich excited at megahertz frequencies can be reliably converted into a quantitative PA spectrum. Testing this concept with an already available, tunable laser is much more cost effective than the use of a synchrotron. Synchrotrons will certainly be used for photoacoustic surface chemical analysis at vacuum ultraviolet wavelengths and audio chopping frequencies.⁵ Whether the high frequency modulation characteristic of synchrotron radiation will ever play a useful role in photoacoustic experiments will depend on the properties of high frequency detectors and the theoretical modeling of high frequency photoacoustic systems both presently under investigation in this laboratory.

Since our August visit to the Wisconsin synchrotron we have performed a computer modeling of a photoacoustic signal produced by high frequency light pulses incident either singly or successively on a condensed phase sample. The numerical work has been carried out on a DEC 20 midicomputer and will be ready for publication by the end of December, 1980. The following sketch of the problem will suggest the motivation of this theoretical modeling and its potential utility.

In a typical PA experiment intensity modulated radiation is incident on the sample which is either enclosed in a cell with a microphone or attached directly to a piezoelectric transducer (PZT). When the sample is not too strongly absorbing, and sinusoidal modulation of less than ~ 10 KHz is employed, the measured amplitude and phase of the PA signal can be fitted to relatively simple mathematical expressions to yield optical absorption coefficients. In general, the functional form of the expected signal depends on the incident energy, chopping frequency, and thermal and elastic constants of the sample.

From an examination of the sample/detector response to an impulse of radiation it is clear that the energy is transported in two distinct ways. Imagine the sample to be at thermal equilibrium and then allow a submicrosecond

pulse of radiation to impinge on one surface. That fraction of the absorbed energy not lost by fluorescence or phosphorescence produces a non-uniform heating of the solid. The resulting expansion of the sample due to a non-zero thermal expansion coefficient can propagate energy away from the heated region at the velocity of sound. For solids this is on the order of 10^6 cm/sec. Qualitatively, the production of acoustic energy will be enhanced by larger temperature gradients in the sample caused either by a high sample absorptivity or by chopping the light at a high enough frequency. Energy also flows as heat during the subsequent thermal equilibration of the solid. However, thermal diffusivities of most non-metallic solids ensure that heat only flows on time scales on the order of milliseconds or longer. Thus, there are in general two different modes of energy transport taking place which are well separated in time.

In the Rosencwaig-Gersho (RG) theory⁶ of microphonic PAS the presumed source of the measured signal is the periodic heat flow from the sample to the surrounding gas in the enclosed cell as the sample is cyclically heated by the absorption of suitably modulated monochromatic light. In the RG theory this cyclic flow of heat from the surface warms a thin layer of adjacent gas which in turn acts as a piston on the remaining volume. These pressure fluctuations are then detected by the enclosed microphone. A number of authors⁷⁻¹⁵ have incorporated improvements into the RG theory so that the basic principles of microphonic solid state PAS are now well understood. Two general results are worth noting: the predicted signal is inversely proportional to the chopping frequency and is directly proportional to the amount of heat deposited within one diffusion length of the surface. If all of the light is absorbed within this layer the measured signal will be independent of the optical properties of the sample and instead dependent on the incident power. This saturation effect

can be remedied by either diluting the sample with a nonabsorber of light or by decreasing the thermal diffusion length by increasing the modulation frequency.

If a highly absorbing sample cannot conveniently be diluted, there is a fundamental limit to the magnitude of absorption coefficients that can be measured by microphonic detectors. As the chopping frequency is increased both the PA signal and the detector sensitivity decrease, and it becomes increasingly difficult to distinguish the signal from the noise.

Recently, a quantitative theory of piezoelectric detection of photoacoustic signals has been developed¹⁶ for sinusoidal modulation frequencies below ~ 10 kHz. In this model the periodic flow of heat within the sample causes the periodic deformation of the sample surface due to the thermal expansion of the heated region. The resulting displacements of the surface is converted into an electrical voltage by an attached piezoelectric transducer. Because of the thermal nature of the signal this method of PA detection suffers from the saturation effect discussed above. This theoretical model does not allow for the acoustic mode of energy propagation which for highly absorbing materials can begin to predominate at frequencies greater than several tens of kilohertz.

Successful theories of high frequency (piezoelectric) PAS are divided among those which deal with very highly absorbing material^{17,18} and those treating materials that are almost completely transparent.¹⁹ Due to the very complicated nature of the governing differential equations, analytic expressions for the expected signal obtained in these high frequency models depend on the sample being of infinite extent for the low absorption case and semi-infinite when large absorptions are considered. In practice these restrictions mean that the transducer must be placed well away from the heated region of the sample if the theory is going to apply to experiment.

One defect of the existing high frequency theories is that they allow for only one type of elastic wave motion, while in general there can be two different

types. In the longitudinal waves the particle motion is in the direction the wave is propagating, while a transverse wave results in oscillations in a plane perpendicular to the direction of propagation. In our pulsed PAS experiment, the initial acoustic waves launched from the heated region are exclusively of the longitudinal type. However, the boundary conditions that exist on the surface of the sample cause the reflected wave to have components of both types. Only in the case of very low absorptivities is it possible to show that the transverse components remain negligible.¹⁹ Thus at present PAS cannot offer a technique for the reliable determination of absolute absorption coefficients for samples which would be in saturation at modulation frequencies lower than ~ 10 kHz.

While it may be impossible to solve exactly the equations of elasticity,²⁰ it is possible to utilize high speed digital computers to numerically approximate the solution. To our knowledge no other attempt has been made to solve by numerical methods the full equations of elasticity for a sample of realistic size and boundary and initial conditions consistent with an impulse of heat.

The sample is taken to be a cylindrical disc of arbitrary thickness and a cylindrically symmetric focused impulse of radiation is incident at the center of one face of the sample. In order to make the solution tractable two further assumptions have been made. During the time of the measurement it is assumed that no heat flows from where it was initially deposited, a very good approximation for times less than ~ 100 μ s. It is also assumed that on the boundary the sample is perfectly rigid. While this is not an easy condition to impose in the laboratory, it can be approximated; just knowing the effects of imposing a boundary surface will be instructive.

The problem is solved with what is known as Galerkin's method.²¹ First the time dependent solution is expanded in a set of known spatial functions which automatically satisfy the boundary conditions of the differential equation. The time dependent coefficients which appear in this expansion are determined by

minimizing the residual formed from the differential equation. This leads to a constant coefficient linear second order system of differential equations which can be solved by very well developed techniques of linear algebra.

Galerkin's method has the advantage of producing the results in very compact form as well as giving a good estimate of the actual error. In this manner it is possible to systematically investigate the dependence of the acoustic signal on all of the relevant parameters of the experiment, as well as to determine the conditions under which the transverse type of wave motion becomes important. With this theoretical model it is possible to identify the optimum site for a piezoelectric detector on a sample exposed to a high frequency pulse. This is a critically important factor in our synchrotron experiments when the PA signal is so weak.

We will round out this description of work in progress by describing our experimental PAS studies at infrared wavelengths. Nicolet, Digilab, and other commercial FTIR spectrometers can be adapted^{22,23} to the speedy acquisition of mid-infrared photoacoustic spectra much more readily than the homemade Michelson interferometer (with its short moving mirror motion and small memory minicomputer) described^{1,2} in our recent visible FTPAS work. We have therefore carried out a number of infrared FTPAS experiments with one of the two Nicolet 6000 series FTIR spectrometers delivered in mid-summer, 1980, to the University of Utah Chemistry Department. (Primary users of these two instruments are Professors Josef Michl, W. A. Guillory, and Franz Rosenberger (Physics), but there is still ample time for infrared photoacoustic experiments carried out by students willing to work through the night.) Since even with a very sensitive Brüel and Kjaer 4165 microphone the PA signal at infrared wavelengths is very weak compared to that obtained by photosensitive semiconductors in transmissive FTIR, the infrared FTPAS

measurements on opaque samples require 10 to 100 times as long to execute as the corresponding FTIR spectral measurements on transmissive samples. A premium is thus placed on achieving a truly gas tight infrared FTPAS sample cell to enhance signal intensity. As is true at visible wavelengths, one would like to ratio the infrared FTPA signal against that of an ideally absorbing black material to compensate for variations in infrared source intensity with varying wavelength. Just as others have found²⁴ that there are reproducible differences in the visible PA spectra of various forms of carbon we have observed substantial differences in the mid-infrared FTPA spectra of a broad range of carbon samples. These results will be the basis of our first mid-IR FTPAS publication.²⁵

Personnel

The mid-infrared PAS studies are being performed by a fourth year graduate student, Steven M. Riseman, who will incorporate this work into a Ph.D. thesis. The high frequency experimental work has been carried out by an exceptionally gifted senior majoring in physics, Roger K. Burnham, in collaboration with Dr. Jerry Mitchell of the Chemistry Department electronics shop and Dr. Michael M. Farrow of IBM, Boulder. The theoretical modeling has been done by Roger Burnham with a little help in the early stages from Gothard Grey, now a first year physics graduate student at Cal. Tech., and from members of the mathematics faculty at Utah. Randy Yeates, a senior majoring in Chemistry, and Dr. S. M. Kuznicki carried out most of the zirconium phosphate studies with some help from a graduate student, Lindsay Lloyd, on the PA measurements.

Persons drawing salary or wages from this DOE contract at some time during the period April 1, 1980 - Dec. 10, 1980 were: R. K. Burnham, Dr. E. M. Eyring, Dr. M. M. Farrow, Dr. V. J. Jiamsakul (who returned to Thailand in midsummer), Dr. S. M. Kuznicki (who went to work for Air Products, Allentown, PA in midsummer), G. R. Phillips, S. M. Riseman, and R. Yeates.

The principal investigator continues to devote 5.7% or more of his time to this contract during the nine month academic year.

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