

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) **READ INSTRUCTIONS REPORT DOCUMENTATION PAGE** BEFORE COMPLETING FORM 2. GOVT ACCESSION NO. 3. RECIPIENT'S CATALOG NUMBER REPORT NUMBE # 15 5. TYPE OF REPORT & PERIOD COVERED TITLE (and Subtitle) FOURIER TRANSFORM PHOTOACOUSTIC SPECTROSCOPY Technical Report. AD A 053698 PERFORMING ORG. REPORT NUMBER 8. CONTRACT OR GRANT NUMBER(+) Michael M. /Farrow, Roger K. /Burnham Edward M./Eyring N00014-75-C-0796 PERFORMING ORGANIZATION NAME AND ADDRESS 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Department of Chemistry University of Utah Salt Lake City, Utah 84112 Task No. NR 051-556 11. CONTROLLING OFFICE NAME AND ADDRESS 12. REPORT DATE April 28, 1978 Office of Naval Research 13. NUMBER OF PAGES Arlington, Virginia 22217 10 14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office) 15. SECURITY CLASS. (of this report) Unclassified 25 APr 78 154. DECLASSIFICATION/DOWNGRADING SCHEDULE 16. DISTRIBUTION STATEMENT (of this Report Approved for public release; distribution unlimited. D D C 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 8 1978 18. SUPPLEMENTARY NOTES 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) visible spectroscopy neodymium(III) glass Fourier transform photoacoustic spectroscopy multiplex advantage Felgett's advantage interferometer Jacquinot's advantage Michelson interferometer monochromator ABSTRACT (Continue on reverse side if necessary and identify by block number) The feasibility of visible light Fourier transform photoacoustic spectroscopy (FTPAS) is demonstrated. The combined throughput and multiplex advantages of the interferometer significantly reduce the data collection time and/or improve the signal to noise ratio. An FTPAS interferogram and transformed spectrum of neodymium(III) doped glass are reported. DD 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE Unclassified S/N 0102-LF-014-6601 SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered) 400 730 JOR

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0796

Task No. NR 051-556

TECHNICAL REPORT NO. 15

FOURIER TRANSFORM FHOTOACOUSTIC SPECTROSCOPY

by

Michael M. Farrow, Roger K. Burnham, and Edward M. Eyring

Prepared for Publication in APPLIED PHYSICS LETTERS

University of Utah Department of Chemistry Salt Lake City, Utah 84112

April 25, 1978

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Fourier transform photoacoustic spectroscopy Michael M. Farrow, Roger K. Burnham, and Edward M. Eyring Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (Received ; accepted for publication)

(Abstract)

The feasibility of visible light Fourier transform photoacoustic spectroscopy (FTPAS) is demonstrated. The combined throughput and multiplex advantages of the interferometer significantly reduce the data collection time and/or improve the signal to noise ratio. An FTPAS interferogram and transformed spectrum of neodymium(III) doped glass are reported.

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Photoacoustic spectroscopy¹ (PAS) traces its origins to experiments reported by Alexander Graham Bell² in 1881. A periodically chopped beam of tunable, monochromatic, uv-visible light passes through a window onto a condensed phase sample in an enclosed cell. The cell also contains a transparent gas and a microphone. If the sample absorbs light of the particular incident wavelength and does not fluoresce, rapid radiationless decay processes convert the electronic energy to thermal energy that in turn heats the ambient gas at the sample-gas interface. The heating of the gas produces a sound wave of the same frequency as the chopping frequency of the incident light This audio frequency sound wave is detected by the microphone and sorted beam. out of the environmental and electronic noise by a lock-in amplifier. The stress wave may also be detected directly in the sample by attaching a piezoelectric transducer to the sample.^{3,4} Thus by varying the wavelength of the incident light it is possible⁵ to obtain a uv-visible absorbance spectrum of a light transmitting solid or liquid sample that closely resembles that obtained by a more conventional transmission spectrometer. More important, PAS permits an experimentalist to obtain uv-visible absorbance spectra of samples that are $opaque^{6}$ as well as of highly transparent samples of short optical path length.3

Regardless of whether one uses a microphone or piezoelectric transducer as the detector in a PAS experiment, the measurement is detector noise limited.⁷ This is in contrast to the photon detectors used in transmission spectroscopy in the visible and ultraviolet wavelength ranges. In the latter case, the photomultipliers used are among the quietest detectors and amplifiers used in any system; the noise in these systems comes from the radiation source not the detector. Of course, if the noise is indeed random in the photoacoustic

system, an improved S/N may be obtained by integrating the signal longer, that is, increasing the detection time constant and lowering the spectral scan rate. This accounts for the long time presently required to obtain a photoacoustic spectrum (up to ~1 hour).

A Michelson interferometer allows collection of data from all spectral frequencies simultaneously throughout the duration of the measurement. The resulting interferogram can then be numerically transformed via the Fourier transform back to a conventional spectrum. The improvement in S/N achieved by multiplexing the spectral information and measuring the variations in the much higher intensity is known as Fellgett's advantage. The magnitude of this advantage is determined by the number of spectral resolution elements, M, to be measured. This is given by⁸

$$M = v_{\rm R} / \Delta v_{\rm T} \tag{1}$$

where v_R is the wavenumber range of the measurement and Δv_I , the instrumental resolution, in cm⁻¹. For spectra measured in equal times with identical sources, detectors, optical throughput, and sample, the interferometer will theoretically have a S/N which is \sqrt{M} times better. Alternately, if the two spectra are measured with equal S/N, the FT spectrum can theoretically be measured M times faster. Fellgett's advantage applies only to the time necessary to collect the data and not the time necessary to compute and plot the spectrum from the interferogram (~ 2 to ~ 10 seconds depending on the available minicomputer.)

The second fundamental advantage of a Fourier transform spectrometer over a grating (dispersive) spectrometer is Jacquinot's advantage and derives from the increased throughput of an interferometer compared to a grating spectrometer. This advantage is given by⁸

$$\vartheta^{I}/\vartheta^{G} = (A^{I} f a \vartheta^{2} 2)/(A^{G} h \vartheta_{max} \Delta \vartheta)$$
 (2)

where θ is the maximum optical throughput of an interferometer (superscript I) or grating spectrometer (superscript G); A is the area of the mirrors in the interferometer (I) or the area of the grating (G); f is the focal length of the collimator; a is the spacing of the lines on the grating; v is the spectral wavenumber; h is the slit height on the monochromator; v_{max} is the highest wavenumber in the spectrum and Δv is the spectral resolution.

Application of FTS to visible wavelengths is not carried out routinely since the broad band noise from the source will be added to each spectral component by the interferometer rather than just the noise from the source at that wavelength which is observed with monochromators. Thus if the spectral information to be gathered is a line source, such as atomic emission spectra, the multiplex advantage will improve the S/N of the spectrum even if the detector is source noise limited.⁹ Since the noise in photoacoustic detectors is fixed by the detector itself and the associated electronics and is independent of the signal intensity⁵ the optimum means of collecting broadband uv-visible photoacoustic spectra should be a Fourier transform system if the optical and mechanical requirements can be met.

At least two commercial PAS instruments are available (from Princeton Applied Research Corporation and Gilford Instrument Laboratories) and both have dispersive elements (monochromators). The optical components in these systems are similar to those we have used in our dispersive PAS system,⁴ and so for an illustration of the improvements which are theoretically attainable by using FT optics we will use the specifications for our monochromator (Bausch and Lomb model 33-86-40) in Eqs. 1 and 2.

Fellgett's advantage (Eq. 1) is computed to be 168 for the 300 to 800 nm spectrum with 8 nm resolution. $(v_R = 20833 \text{ cm}^{-1}, \Delta v = 66 \text{ cm}^{-1} = 8 \text{ nm})$ @ 550 nm.) This means applying only Fellgett's advantage, it should be possible to obtain exactly the same spectrum (using the same detector, source and electronics) in 1/168 the amount of time (~18 seconds vs. 50 <u>minutes</u>). Alternately, if 50 minutes are used to collect the interferogram, the S/N will be ~13 times better ($\sqrt{168}$). This is indeed a significant improvement, but an additional advantage appears possible due to the increased throughput of the interferometer.

The Bausch and Lomb monochromator has a 5.2 cm square grating with groove spacing of 1.6 x 10^{-4} cm, slit height of 1.2 cm and accepts a 25 cm focal length collimator. For comparison, we choose an interferometer with 5.1 cm diameter mirrors. The application of Eq. 2 using $\Delta v = 50$ cm⁻¹, $v_{max} = 33333$ cm⁻¹ (300 nm), indicates that Jacquinot's advantage should be as large as 590 at 300 nm and still be 50% of Fellgett's advantage at 800 nm. Thus dividing the shorter scan time necessary made possible by Fellgett's advantage, one arrives at a minimum time required to collect a 300 to 800 nm spectrum of 50.22 seconds. It should be reiterated that the resulting FTPAS spectrum will have the same signal to noise ratio as the spectrum collected in 50 minutes using a monochromator.

Although not mentioned in the foregoing, other techniques of multiplexing spectral information are available, but the only other under development which appears to offer similar advantages for PAS is the Hadamard technique.¹⁰ Bard suggested ⁷ that this technique might improve the S/N of photoacoustic spectra, although the cost may be prohibitive. Commercial Fourier transform

spectrometers for IR are also costly, but Horlick and Yuen¹¹ point out that, exclusive of computer, an effective interferometer can be constructed for less than \$3,000.

Lately, there has been some discussion¹² of the size of Fellgett's advantage for interferometers but the actual magnitude of the S/N improvements achieved by Fourier Transform instruments in the IR have been confirmed and do generally correspond to those expected based on Eqs. 1 and 2.

Figure 1 shows a block diagram of our Michelson interferometer for FTPAS. Modulation of the output light from the interferometer is achieved by driving one of the mirrors sinusoidally at the lock-in reference frequency in lieu of mechanical chopping with a rotating sector as in ordinary PAS. This results in a phase modulated¹³ interferogram thus eliminating the large D.C. offset in the detected signal.

For this demonstration of the feasibility of FTPAS, the scan is accomplished by a total of 11.5 μ m change (two times the actual mechanical travel) in one arm of the interferometer. This is the maximum motion possible using the Burleigh PZAT-90 while it also provides the phase modulation. For these experiments, no simultaneous fringe referencing system was used and voltagemotion linearity of the PZAT-90 was assumed.

Figure 2a shows the unreferenced FTPAS interferogram obtained with a sample of Owens-Illinois neodymium(III) doped laser glass. Fig. 2b shows the transformed FTPAS spectrum (not source intensity normalized) which agrees in its broad features with published^{4,14} absorption spectra of neodymium(III) doped glass. Although no signal to noise comparison has been made, it should be noted that our previous PAS spectrum of Nd:glass required a 450 watt xenon arc lamp as a source and 90 minutes to collect whereas Fig. 2b was collected and transformed in under 4 minutes using a 100 watt tungsten-iodide lamp.

Discussions with Joel M. Harris, D. J. Baker, and Alan Steed and partial financial support from the Chemical Directorate, Air Force Office of Scientific Research (Grant AFOSR-77-3255), the Office of Naval Research, and Biomedical Sciences Support Grant RR 07092 from the NIH are gratefully acknowledged.

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Figure Captions:

- FIG. 1. Schematic of Fourier transform-visible-photoacoustic spectrometer. A Michelson interferometer is depicted schematically in the top right hand corner. A He-Ne laser reference system is depicted that has not been implemented in the present study.
- FIG. 2. Photoacoustic interferogram (above) and absorption spectrum calculated from the interferogram (below) for a neodymium(III) doped laser glass sample. The spectrum has not been source normalized (i.e. signal has not been divided by light source intensity at each wavelength.) The interferogram was based on samples taken at 256 equally spaced mirror positions. The spectral resolution is \sim 850 cm⁻¹ or \sim 20 nm @ λ = 500 nm.



