

AD-A066 063

WISCONSIN UNIV-MADISON DEPT OF PHYSICS  
PHOTOACOUSTIC AND PHOTOTHERMAL SPECTROSCOPY OF IONS IN SOLIDS.(U)  
NOV 78 W M YEN

F/6 20/1

DAAG29-76-G-0100

ARO-13462.4-P

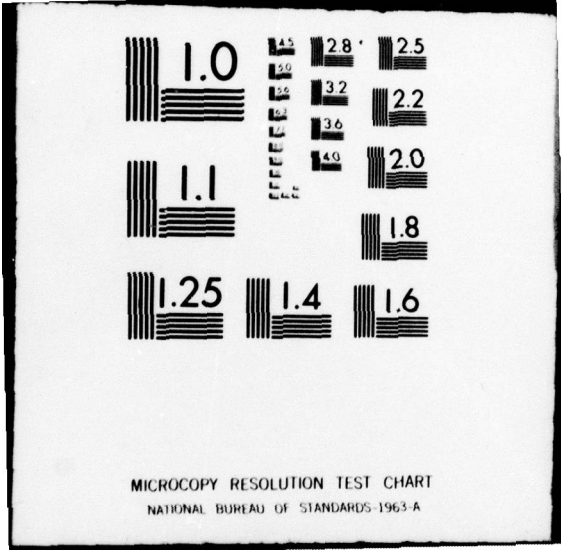
NL

UNCLASSIFIED

|OF|  
AD  
A066063  
1



END  
DATE  
FILMED  
5 -79  
DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

ARO 462.4-P

12

LEVEL II

SC

DDC FILE COPY AD A0 66063

Final Report  
to

The United States Department of the Army  
US Army Research Office  
Research Triangle Park, N.C. 27709

on a grant entitled  
"Photoacoustic and Photothermal Spectroscopy  
of Ions in Solids"  
DAAG 29-76-G-0100

See 1079  
in  
back

For Period: 15 November 1975 - 14 November 1978

submitted by

William M. Yen, Principal Investigator  
Department of Physics, University of Wisconsin  
1150 University Avenue  
Madison, WI 53706

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION _____	
BY _____	
DISTRIBUTION STATEMENT A	
Dist. _____	
A	

**DISTRIBUTION STATEMENT A**  
Approved for public release;  
Distribution Unlimited

DDC  
RECEIVED  
MAR 20 1979  
E

79 03 01 041

## I. Introduction

Our efforts under the auspices of this grant have been directed along two main lines. First, we found that the photoacoustic cell design was an important consideration in any attempt to obtain quantitative photoacoustic information, and so considerable time and effort were spent during the first part of the grant constructing and evaluating the performance of various photoacoustic cells. After settling on the best cell design, in which coherent background signals were minimized, we were able to pursue the second line of investigation, that of quantitatively characterizing the nonradiative relaxation of excited electronic states in solids. It is worth stressing at the outset that in order to be successful in this second endeavor, one must be able to eliminate coherent background signals and have a means of verifying that they have been eliminated. In the following report, then, we first discuss the most important cell design considerations and secondly describe our progress toward the quantitative application of photoacoustic spectroscopy to nonradiative decay processes.

## II. Photoacoustic cell design

In our earliest photoacoustic cells, constructed from aluminum, we encountered large coherent signals which were independent of the sample under investigation. These spurious signals were in large part due to scattered light striking the microphone diaphragm, for upon shielding the microphone from scattered light the effect was reduced

79 03 01 041

considerably. The remaining spurious signals could be due either to a small amount of multiply-scattered light still reaching the microphone diaphragm, or to the absorption of scattered light at the cell walls. To reduce both of these effects, a cell patterned after McClelland<sup>1</sup> was constructed, in which the geometry largely prevents scattered light from striking the microphone diaphragm, and which is made of clear plexiglas in order to reduce absorption and reflection at the cell walls. We still saw some spurious signals in this cell, but we were able to distinguish between the two sources of background signals by observing the time development of the background signal in response to a short laser pulse.<sup>2</sup> In order to further reduce the scattered light (and for other reasons to be discussed later) we modified the cell design such that the sample itself forms the exit window of the cell. This results in much less scattered light because the incident laser beam passes through only two materials, the entrance window (clear glass) and the exit window (the sample), both of which are of high optical quality. In this way we have been able to eliminate coherent background signals for many samples of interest.

For some samples, however (especially those with very small optical absorption coefficients), coherent background signals still remain. It is important, therefore, to have a technique for determining whether and to what extent coherent background signals are present. We have developed such a technique, and it is quite simple: one simply monitors the phase of the photoacoustic signal. The coherent background

due to scattered light enters at a different phase than the "real" photoacoustic signal from the sample of interest, so the two signals, real and spurious, must be added vectorally to obtain the resultant magnitude and phase that is actually measured on the lockin detector. It is clear then that the deviation in phase will be greater as the relative amount of coherent background is increased. In fact it is possible using vectoral subtraction to determine the magnitude of the "real" signal even when a coherent background exists, simply by noting the deviation in phase from that of a "real" signal.

Once the coherent background problem is solved, one is still faced with the problem of incoherent background which limits the signal to noise ratio (S/N); in photoacoustic spectroscopy the noise is generally due to electronic noise in the pre-amp or building vibrations coupling to the microphone. One way of increasing the S/N is by utilizing an acoustical resonance. Of the two types of acoustical resonances (cavity resonances and Helmholtz resonances), we focused on the Helmholtz resonance since it has the lowest resonance frequencies, where the non-resonant S/N is highest. We constructed several resonant cells of various dimensions, and found resonant-enhancement factors (Q's) approaching an order of magnitude in some cells.<sup>2</sup> Thus, as long as one is not interested in measuring the dependence of the photoacoustic signal on chopping frequency, an acoustical resonance can be used to increase the S/N ratio.

### III. Nonradiative decay processes

With the problem of coherent background signals adequately understood and controlled, we could finally proceed with the quantitative investigation of nonradiative relaxation processes. Some attempts have been made by other researchers<sup>3</sup> at the quantitative characterization of nonradiative decay processes in solids. All these investigations involve taking a spectrum of the photoacoustic signal vs. the wavelength of exciting light, and then taking the ratio of peak heights to obtain quantitative information. The S/N is often quite poor for such a procedure, however, due to the limited optical power obtainable from lamp-monochrometer combinations. We have employed an entirely different technique for obtaining quantitative photoacoustic information. Due to our special cell design, it is possible to accurately compare signals from different samples at the same wavelength. This enables us to use a high power laser as the source, with the resulting increase in S/N. We will here describe two techniques we have developed for measuring radiative quantum efficiencies (QE) in solids which take advantage of this procedure.

The first technique for measuring QE in solids is what we have called the Black Film Reference technique (BFR). A preliminary account has already appeared,<sup>4</sup> and a full description and evaluation of the technique will be published shortly. Briefly, the procedure is to

compare two photoacoustic signals, one from the sample itself and the other from a thin layer of gold black deposited on the same sample. Most of the thermal properties and cell dimensions are the same in the two measurements, and therefore cancel out when the ratio of the two signals is taken. The only exception is that the thermal diffusivity of the sample must be known. In this way one can determine  $\eta$ , the thermal conversion efficiency, which is the fraction of the absorbed light energy that is converted into heat. In some systems (such as the  $\text{Nd}^{3+}$  ion doped into various solids) there is a simple relationship between the quantity  $\eta$  and the QE of a particular transition. If all other parameters describing relaxation are known, such as energy levels and branching ratios, then the QE can be determined directly by a measurement of  $\eta$ .

The second technique for measuring QE in solids, the Concentration Quenching technique (CQ), is more restricted in the range of systems to which it is applicable, but it has the advantage that one need not know the sample's thermal diffusivity. This technique is applicable to those systems in which the fluorescence is quenched as the concentration of optically active ions increases, a fairly common occurrence in rare earth systems. The procedure is simple, involving only the measurement of relative photoacoustic signals, relative fluorescent lifetimes, and relative concentrations. Although only relative measurements are required, one is able to obtain by the CQ technique the absolute QE of a fluorescing transition. We have demonstrated the utility of the CQ technique by measuring the QE of  $\text{Nd}^{3+}$  in ED2 glass, an important commercial laser glass, and we



obtained values of the QE ranging from .65 to .75 depending on the excitation wavelength. These results, along with an interpretation of the results involving site selection by the spectrally narrow laser lines, have been published.<sup>5</sup> The CQ technique seems to us to be an especially useful and convenient tool, and we are employing it in the course of our present investigation of the system  $\text{Nd}^{3+}, \text{Cr}^{3+}$ : Fluoro-phosphate glass.<sup>6</sup>

#### IV. Conclusion

In sum, we have made significant progress during the period of this grant, first in the understanding and improvement of photoacoustic cell performance, and secondly in utilizing the photoacoustic effect in the quantitative characterization of nonradiative relaxation processes in solids. Our present work is concentrated on this second endeavor, and we feel that photoacoustic spectroscopy will continue to be a useful tool in the investigation of nonradiative relaxation processes in solids.

### References

1. J. F. McClelland and R. N. Knieley, *App. Opt.* 15, 2967 (1977)
2. R. S. Quimby, P. M. Selzer and W. M. Yen, *App. Optics* 16, 2630 (1977)
3. J. C. Murphy and C. Aamodt, *J. App. Phys.* 48, 3502 (1977)
4. R. S. Quimby and W. M. Yen, *Bull. Am. Phys. Soc.* II-23, 388 (1978)
5. R. S. Quimby and W. M. Yen, *Optics Letters* 3, 181, (1978)
6. R. S. Quimby and W. M. Yen, talk to be given at the March meeting of the APS (1979)

Personnel on this Grant:

- |                 |                                  |
|-----------------|----------------------------------|
| 1. W. M. Yen    | Principal Investigator           |
| 2. P. M. Selzer | Assistant Scientist 11/75 - 6/77 |
| 3. R. S. Quimby | Research Assistant 11/75 - 11/78 |
| 4. E. Strauss   | Research Associate 7/77 - 11/78  |

Theses - NONE

Publications - as previously submitted

18 ARO 13462.4-P 19

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photoacoustic and Photothermal Spectroscopy of Solids Ions in Solids		5. TYPE OF REPORT & PERIOD COVERED Final Report 15 Nov 75-14 Nov 78 11/75-11/78
7. AUTHOR(s) W. M. Yen 10 William M. Yen		8. CONTRACT OR GRANT NUMBER(s) 15 DAAG 29-76-G-0100
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Wisconsin-Madison Department of Physics Madison, WI 53706		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 11 14 Nov 78
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 12 10p
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photoacoustic Spectroscopy; Cell Design; Quantum Efficiency		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Progress attained during grant period is reported.		

404 429

JOB