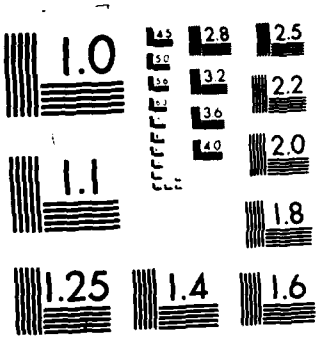
AD-A128 755 PHOTOACOUSTIC AND PHOTOTHERMAL SPECTROSCOPY OF IMPURITY 1/1
ION SYSTEMS(U) WISCONSIN UNIV-MADISON W M YEN
15 APR 83 ARO-16176.7-PH DAAG29-79-C-0040

UNCLASSIFIED F/G 20/1 NL

END
DATE FILMED
6-83
DTIC



UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

ARO 16176.7-PH (12)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A128755	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photoacoustic and Photothermal Spectroscopy of Impurity Ion Systems	5. TYPE OF REPORT & PERIOD COVERED Final - 2/79-2/83
	6. PERFORMING ORG. REPORT NUMBER -
7. AUTHOR(s) W. M. Yen	8. CONTRACT OR GRANT NUMBER(s) DAAG-29-79-C-0040
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Wisconsin-Madison	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 16176
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	12. REPORT DATE 4/15/83
	13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	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)

NA

DTIC ELECTE JUN 1 1983

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, Photothermal, Quantum Efficiencies

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The work performed under the auspices of this grant over the past four years is suumarized.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

05 31 130

AD A128755

DTIC FILE COPY

Final Report to the

U.S. Army Research Office

P.O. Box 12211

Research Triangle Park, NC 27709

on work performed on a grant entitled

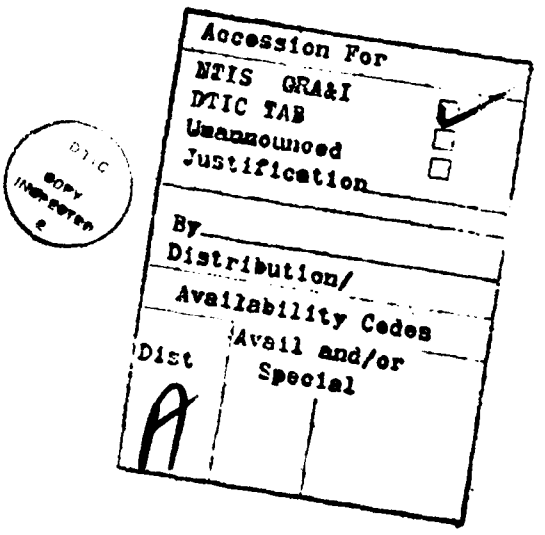
"Photoacoustic and Photothermal Effects in Impurity Ion Systems"

ARO Proposal No: 16176 Grant No: DAAG-29-79-C-0040

for the period February 1979 - February 1983

Submitted by: W.M. Yen, Principal Investigator
Department of Physics
University of Wisconsin
Madison, WI 63706

W.M. Yen, Principal Investigator



A. Progress Attained During This Grant.

The general features and theoretical framework of the photoacoustic effect have been reviewed in a comprehensive fashion recently.[2] In the case of solids, much of the theoretical understanding is based on the work of Rosencwaig and Gersho[2] which postulated that the absorbing solid behaved as a simple thermal piston on the coupling gas medium to produce the necessary pressure variation. In this theory, which is largely one dimensional, the PAS signals produced depend on a series of thermal and surface parameters of the solid sample, the solid-gas interface and to a lesser extent of the carrier gas itself.

During the past grant period, we have investigated the validity of various aspects of the theoretical modeling of the photoacoustic effect. In an early paper,[3] we were successful in illustrating three dimensional heat flow effects in the PAS of solids and showed that they are present whenever the thermal diffusion length of the carrier gas becomes of the same order as the dimensions of the photoacoustic cell. These effects are specially pronounced at low chopping frequencies where diffusion lengths are greatest. In subsequent work, we have been able to establish the limits of applicability of the RG theory and have shown that even if heat flow occurs three dimensionally, one dimensional theories remain good approximations provided thermal diffusion lengths in the gas are less than the radius of the sample chamber.[4]

Also, in a recent paper, Cesar and co-workers[5] pointed out that the thermal contact resistance between two interfacings had not been taken into account in the various PAS theories (RG,[2] composite piston[6] etc.) dealing with condensed phases and that when this effect is included significant modifications in the frequency dependence of the PA signal result. We have been able to show that the above authors made a fundamental error concerning the appropriate

mechanism for heat transport across a solid/gas interface and that when the correct treatment is introduced thermal contact resistance produces negligible corrections to the interpretation of PAS signal in most conditions of experimental interest.[7]

Generally then, these theoretical developments we have participated in, as well as earlier work which allowed the identification of coherent noise sources in PAS sample chambers have served to establish a more solid foundation on the interpretation of PA phenomena in solids and have lent confidence in obtaining a more analytical and quantitative description of spectra and signals obtained through these techniques.

A great deal of the work carried out in PAS of solids, has in fact concentrated in obtaining static spectroscopic features of materials which could not be obtained through normal spectroscopic methods. The principal focus in this type of spectroscopy has been to obtain, for example, absorption bands energy positions with no attempt at obtaining absolute numbers in the spectra.[8] The reason for this has been precisely because PAS in solids still suffers from the lack of theoretical and empirical quantification. The general aim of our efforts, both theoretical and experimental, has been in the direction of rectifying this situation.

For example, during the present grant period we have developed simple new techniques which allow us to measure absolute radiative quantum efficiencies of fluorescing transitions of ions in insulators through PAS techniques. In the past, various methods have been used to measure the quantum efficiencies (QE) of radiative transitions in solids. The QE is the ratio of radiated to pump power and is of significant technical importance to the design of lasers. Measurements of this quantity using conventional means are empirically difficult because they entail absolute determinations of absorbed

and radiated radiation levels. PAS provides us with an alternate way of measuring QE's through measuring the amount of light which is converted into low grade heat directly. Murphy and Aamodt[9] conducted the first such PAS measurement in ruby and were able to demonstrate quenching effects with increasing Cr^{3+} concentration but did not obtain QE values for ruby.

In a previous grant (DAAG-29-76-G0100), we had conducted measurements of QE in various laser hosts using a black film reference technique to provide a calibration of the experimental system. According to theory, the final PAS signal is proportional to $\eta\beta\mu_s$ where η is related to the QE, β is the absorption coefficient and μ_s is the thermal diffusion length of the sample material. By evaporating a gold black film on the sample surface which provides 100% light to heat conversion efficiency, i.e. QE = 0, and comparing vector PAS signals obtained from coated vs. uncoated samples, the absolute value of the QE of a given transition may be obtained. A number of auxiliary measurements are still required in the extraction procedures such as determination of β and μ_s which sometimes produce complications.

In order to circumvent the necessity for auxiliary measurements and enlarge the applicability of PAS methods to QE determinations, we have developed two additional ways to conduct these experiments. The first is a technique relevant to systems such as Nd^{3+} in which fluorescence concentration quenching occurs through ion-ion cross relaxation;[10] in a recent publication, we have shown that the PAS signal in these cases is simply related to the QE at zero concentration (no quenching) and the fluorescence lifetime of the quenched state. The second method we have developed comprises systems which have a simple decay scheme and moderately long fluorescence lifetimes.[11] A system that falls into this category is ruby, for example. In this method, one

needs only to measure relative quantities to obtain an absolute value of the QE and requires no auxiliary experiments. The technique requires simply a measurement of the phase of the PAS signal as a function of chopping frequency; in view of our better understanding of PAS theory, it has been possible to relate the phase difference produced when the system is excited by two distinct light frequencies directly to the quantum efficiency of the radiating level. In both of the above measurements conducted on ED-2 Nd^{3+} laser glass and ruby, respectively, we have demonstrated that absolute QE's may be obtained with accuracies which are comparable or better than the best measurements made through other means. In this regard, it has been pointed out recently that our measurement in Nd^{3+} glass produced a value of QE which was too small (70% vs expected 90%) and that this is due to the weakness of the absorption and to surface effects in the glassine host;[12] we shall return to this point later. Be that as it may, the interpretation in this specific case rather than the measurement is in question and we do not believe that there can be any doubt that PAS provides us with a unique tool to measure these properties.

The quantum efficiency of a given transition is but one of many properties of ions in insulators which manifest the results of phonon-ion interactions in these systems. In order to study these effects in depth, we have recently built a PAS cavity modelled after that of Pichon et al.[13] which allows us to cool the sample down to ~20K. In the course of the past year or so, we have calibrated this new cavity and undertaken a measurement of the temperature dependence of the QE of the R_1 line in ruby which has allowed us to identify the phonon induced non-radiative mechanisms which affect this particular state.[14]

We have also considered the case in which ion-ion interactions lead to the transfer of energy in insulators and produce spatial diffusion of the optical excitation.[15] Since the PAS signal depends not only on the location at which the energy is originally deposited but also on the position within the sample it eventually is converted into low grade heat, the diffusion of the energy must thus play a role in determining the ultimate nature of the signal. In all theoretical work on PAS spatial energy migration in the sample has been assumed to be negligible i.e. that the light absorbed and the heat generated are produced on the same location. This is a valid assumption for many luminescent materials; for ruby, for example, recent laser spectroscopic measurements have shown no migration over macroscopic distances. There are however other systems of technical importance in which these effects are measurable, again, recent optical measurements indicate motion over many sites in the stoichiometric materials of the NdP_5O_{14} class.[16] In order to investigate systems in which transfer occurs using PAS methods, the theory needs to be modified to include this possibility. We have recently expanded the PAS theory in this direction and have suggested a way in which the relevant diffusion of energy parameters may be extracted from the frequency and phase dependence of the PAS signal. These results still await experimental verification.

Finally we have been able to adapt recent developments in photothermal deflection spectroscopy[17] to an intra laser cavity configuration and have demonstrated that one can modulate the laser by inducing an absorption in the sample and hence misaligning the intra cavity laser beam.[18] We have also demonstrated that this is a very sensitive method to detect both very strong and very weak absorptions. These results will be published shortly and will be pursued further under other auspices.

References

1. For a comprehensive review, see for example, Optoacoustic Spectroscopy and Detection, Yoh-han Pao, editor (Academic Press, New York, 1977).
2. A. Rosencwaig and A. Gersho, J. Appl. Phys. 47, 64 (1976).
3. R. S. Quimby and W. M. Yen, Appl. Phys. Letters 35, 43 (1979).
4. R. S. Quimby and W. M. Yen, J. Appl. Phys. 51, 1252 (1980).
5. C. L. Cesar, H. Vargas, J. A. Meyer, and L. C. M. Miranda, Phys. Rev. Letters 42, 1570 (1979).
6. F. A. McDonald and G. C. Wetsel, Jr., J. Appl. Phys. 49, 2313 (1978).
7. R. S. Quimby and W. M. Yen, J. Appl. Phys. 52, 500 (1981).
8. For examples see the Technical Digest for Topical Meeting on PAS, Ames, Iowa, August 1-3, 1979 (Optical Society of America, 1979).
9. L. C. Aamodt and J. C. Murphy, J. Appl. Phys. 48, 3502 (1977).
10. R. S. Quimby and W. M. Yen, Opt. Letters 3, 183 (1978).
11. R. S. Quimby and W. M. Yen, J. Appl. Phys. 51, 1780 (1980).
12. A. Rosencwaig and E. A. Hildum, Phys. Rev. 23, 3301 (1981).
13. C. Pichon, M. Lelibaux, D. Fournier and A. C. Boccara, Appl. Phys. Letters 35, 435 (1979).
14. M. Gallmaier, E. Strauss, R. Germer, W. Schubert, R. T. Brundage and W. M. Yen, J. Phys. (to be published).
15. R. S. Quimby and W. M. Yen, J.Appl. Phys. 51, 4985 (1980).
16. See for example: H. G. Danielmeyer, J. Lumines 12/13, 179 (1976).
17. W. Jackson, N. M. Ames, A. C. Boccara and D. Fournier, Appl. Opt. 20, 1333 (1981).
18. C. Johnson, R. T. Brundage, T. J. Glynn and W. M. Yen, J. Phys. (to be published).

B. Technical Reports Appearing under DAAG-29-79-C-0040.

I. Refereed Articles

1. W. M. Yen, Time resolved fluorescence line narrowing in solids, J. Lumin. 18/19, 639 (1979).

2. R. S. Quimby and W. M. Yen, Three dimensional heat flow effects in PAS in solids, App. Phys. Lett. 35, 43 (1979).

3. R. S. Quimby and W. M. Yen, on the adequacy of one dimensional treatment of the photoacoustic effect, J. Appl. Phys. 51, 1252 (1980).

4. R. S. Quimby and W. M. Yen, PAS measurement of the ruby quantum effeciency, J. Appl. Phys. 51, 1780 (1980).

5. R. S. Quimby and W. M. Yen, PAS theory including energy migration, J. Appl. Phys. 51, 4985 (1980).

6. R. S. Quimby and W. M. Yen, The effects of thermal contact resistance on the photoacoustic signal, J. Appl. Phys. 52, 500 (1981).

7. R. T. Brundage, T. J. Glynn, W. M. Yen, R. A. Logan and J. Hegarty, PAS measurement of the quantum efficiency of GaAs epitaxial layer, Appl. Phys. Lett. (to be published, 1983).

8. M. Gallmeier, E. Strauss, R. Germer, W. Schubert, R. T. Brundage and W. M. Yen, PAS investigation of the relaxation of the ^2E state of ruby, J. Phys. (France) to be published 1983.

9. C. Johnson, R. T. Brundage, T. J. Glynn and W. M. Yen, Laser modulation induced by intracavity photothermal deflection, J. Phys. (France) to be published 1983.

10. W. M. Yen, Spatial and spectral diffusion in solids, J. Phys. (France) to be published (1983).

II. Thesis

R. S. Quimby, Photoacoustic Investigation of Non-radiative Processes in Solids, Ph.D. December, 1979.

III. Other technical contributions

W. M. Yen served on the organizing and program committees of the IInd and IIIrd International Conferences on Photoacoustic and Photothermal Spectroscopy, Berkeley and Paris respectively.

C. Personnel

W. M. Yen - Principal Investigator, Professor of Physics

S. T. Lai - Research Associate, 1979-81

T. J. Glynn - Research Associate, 1982-

R. S. Quimby - Research Assistant, 1979-80

R. T. Brundage- Research Assistant, 1980-83

M. Shulevitz - Research Assistant, 1982-

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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 Impurity Ion Systems		5. TYPE OF REPORT & PERIOD COVERED Final - 2/79-2/83 6. PERFORMING ORG. REPORT NUMBER -
7. AUTHOR(s) W. M. Yen		8. CONTRACT OR GRANT NUMBER(s) DAAG-29-79-C-0040
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Wisconsin-Madison		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 16176
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 4/15/83 13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		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)

NA

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, Photothermal, Quantum Efficiencies

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The work performed under the auspices of this grant over the past four years is suumarized.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)


MEI
8