

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 7/7/77

Project Title: *Relative Contributions of Scattering Equation Terms to the Resonance Spectra of Synthetic Metalloporphyrins*

Project No: *G-41-660*

Project Director: *Dr. D. C. O'Shea and Dr. J. A. Shelnut*

Sponsor: *National Science Foundation; Washington, D. C. 20550*

Agreement Period: From 6/1/77 Until 11/30/79*
**24 Months proposed period plus 6 months for flexibility*

Type Agreement: *Grant No. DMR77-05971*

Amount: *\$75,900 NSF Funds (G-41-660)*
22,348 GIT Contribution (G-41-347)
\$98,248 Total

Reports Required: *Annual Technical Letters; Summary of Completed Project; Final Technical Report.*

Sponsor Contact Person (s):

Technical Matters

Dr. Fred E. Stafford
Program Director
Solid State Chemistry Program
Division of Materials Research
National Science Foundation
Washington, D. C. 20550

Contractual Matters

(thru OCA)
Ms. Mary Frances O'Connell
Grants Administrator
National Science Foundation
Washington, D. C. 20550
(202) 632-2858

Defense Priority Rating: *None*

Assigned to: *Physics* (School/Laboratory)

COPIES TO:

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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT TERMINATION

Date: June 10, 1980

Project Title: Relative Contributions of Scattering Equation Terms to the Resonance Spectra of Synthetic Metalloporphyrins

Project No: G-41-660

Project Director: Dr. D. C. O'Shea and Dr. J. A. Shelnett

Sponsor: National Science Foundation; Washington, D. C. 20550

Effective Termination Date: 11/30/79

Clearance of Accounting Charges: 11/30/79

Grant/Contract Closeout Actions Remaining:

- Final Invoice and Closing Documents
- Final Fiscal Report
- Final Report of Inventions
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other _____

Assigned to: Physics (School/Laboratory)

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

(404) 894-8201

June 28, 1978

SCHOOL OF PHYSICS

MEMORANDUM

TO: National Science Foundation
Division of Materials Research
Washington, D. C. 20550

FROM: Georgia Institute of Technology
Atlanta, Georgia 30332
Principal Investigator: Dr. Donald C. O'Shea

SUBJECT: Grant No.: DMR-77-05971
Starting Date: 6/1/77; Completion Date: 11/30/79
Grant Title: Relative Contributions of Scattering Equation
Terms to the Resonance Raman Spectra of Syn-
thetic Metalloporphyrins.

ITEM: Yearly Technical Letter Report

Work under this grant has been concentrated in two specific areas: Understanding the excitation profiles of Copper tetraphenylporphyrins (CuTPP) and producing matrix isolated porphyrin samples. In the first area considerable work has been done by Dr. John Shelnett to modify the calculations of Raman excitation profiles to include the effects of strong vibronic coupling and coupling between vibrational modes in the excited state (Duschinsky type terms). Raman excitation profiles of CuTPP have been obtained and can be interpreted in terms of strong vibronic coupling. The Duschinsky mixing of normal modes in the excited Q electronic state has a dominant effect on the excitation profiles and the absorption spectrum. In addition to the general theoretical technique for calculating the vibronic states of molecules, analytical expressions have been obtained using a Feenberg perturbation treatment. This treatment permits a detailed physical understanding of strong coupling influences and interference effects observed in the CuTPP excitation profiles. A paper on the entire study is being submitted.

Current work is concerned with the preparation of matrix isolated porphyrin samples. In addition to modification of our Knudsen cell for subliming porphyrins, a gas flow system for low flow rates has been constructed and put into service. Initial runs of matrix-isolated samples have been made. To provide a characterization of the isolated samples, modifications in our Raman spectra scanning and analysis routine have been made to provide us with absorption spectra of the samples in situ. Raman runs of the matrix isolated samples will begin shortly.

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6/28/78

Memo To: National Science Foundation
Division of Materials Research
Washington, D. C. 20550

From: Dr. D. C. O'Shea, Georgia Tech

There have been a number of personnel changes in the project during the past year. Dr. John Shelnett, the co-principal investigator has taken a leave of absence from the School of Physics for a consultant position at Bell Labs at Murray Hill. He will continue to provide calculational expertise and advise to the project. He has been replaced by Dr. Jo-Lein Yang. Dr. Yang did her doctoral work at CCNY under Professor Robert Callendar and her experience in optical spectroscopy and computer controlled instrumentation will be most valuable for the present project.

DCO:ec

G-41-660

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I-PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Institute of Technology 225 North Ave., N. W. Atlanta, Georgia 30332	2. NSF Program Solid State Chemistry	3. NSF Award Number 77-05971
	4. Award Period From 6/1/77 To 11/30/79	5. Cumulative Award Amount

6. Project Title

PART II-SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

This project investigated the electronic structure of molecules of biological interest because of their similarity to the absorbing molecules that carry oxygen in the blood (hemoglobin) or convert sunlight to chemical energy in plants (chlorophyll).

The tool used to probe these molecules was resonant Raman Scattering. A small amount of the laser energy incident on a solution of these molecules will be shifted in color by the internal atomic motions of the molecules. By detecting and analyzing this shifted radiation, one can gain some knowledge of these internal motions. When the exciting laser radiation is of a color absorbed by the molecules, the light is said to be resonant with certain molecular electronic states. In resonance, there is an enormous increase in the scattered light and a change in the relative intensities of between the various shifted color bands.

This project has advanced our understanding of the electronic states of the molecules under study by providing both experimental data and theory on the variation in shifted color intensities as a function of incident laser color (resonant Raman excitation profiles). Analyses of the Raman spectra have shown that it is not possible to decouple the motions of the electrons from the motions of the atomic nuclei when describing the energy states of these molecules. One of the most important findings was that molecular vibrations of considerably different oscillation frequency contribute to the scattering by other vibrations. We have termed these vibrations "helping modes".

Work on a copper porphyrin has indicated that there is a very strong coupling between an electronic state of the molecule and the vibrational states of the molecule. This can be compared to earlier work in which the coupling was much weaker. By building up information on a series of these molecules and comparing our experimental and theoretical results on these systems we are coming to a better understanding of the significant energy paths in this important family of molecules. To further understand these molecules we are studying the copper porphyrin in a solid crystal of nitrogen at 20 degrees above absolute zero.

PART III-TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	✓				
b. Publication Citations		✓			
c. Data on Scientific Collaborators		✓			
d. Information on Inventions	✓				
e. Technical Description of Project and Results		✓			
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) Donald C. O'Shea	3. Principal Investigator/Project Director Signature 			4. Date 5/12/80	

**INSTRUCTIONS FOR FINAL PROJECT REPORT
(NSF FORM 98A)**

This report is due within 90 days after the expiration of the award. It should be submitted in two copies to:

National Science Foundation
Division of Grants and Contracts
Post-Award Projects Branch
1800 G Street, N.W.
Washington, D.C. 20550

INSTRUCTIONS FOR PART I

These identifying data items should be the same as on the award documents.

INSTRUCTIONS FOR PART II

The summary (about 200 words) must be self-contained and intelligible to a scientifically literate reader. Without restating the project title, it should begin with a topic sentence stating the project's major thesis. The summary should include, if pertinent to the project being described, the following items:

- The primary objectives and scope of the project.
- The techniques or approaches used only to the degree necessary for comprehension.
- The findings and implications stated as concisely and informatively as possible.

This summary will be published in an annual NSF report. Authors should also be aware that the summary may be used to answer inquiries by nonscientists as to the nature and significance of the research. Scientific jargon and abbreviations should be avoided.

INSTRUCTIONS FOR PART III

Items in Part III may, but need not, be submitted with this Final Project Report. Place a check mark in the appropriate block next to each item to indicate the status of your submission.

- a. Self-explanatory.
- b. For publications (published and planned) include title, journal or other reference, date, and authors. Provide two copies of any reprints as they become available.
- c. Scientific Collaborators: provide a list of co-investigators, research assistants and others associated with the project. Include title or status, e.g. associate professor, graduate student, etc.
- ✓ d. Briefly describe any inventions which resulted from the project and the status of pending patent applications, if any.
- ✓ e. Provide a technical summary of the activities and results. The information supplied in proposals for further support, updated as necessary, may be used to fulfill this requirement.
- f. Include any additional material, either specifically required in the award instrument (e.g. special technical reports or products such as films, books, studies) or which you consider would be useful to the Foundation.

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA 30332

(404) 894-5201

SCHOOL OF PHYSICS

May 13, 1980

MEMORANDUM

TO: National Science Foundation
Division of Materials Research
Washington, D.C. 20550

FROM: Georgia Institute of Technology
Atlanta, GA 30332
Principal Investigator: Dr. Donald C. O'Shea

SUBJECT: Grant No.: DMR 77-05971
Starting date: 6/1/77; Completion date: 11/30/79
Grant Title: Relative Contributions of Scattering
Equation Terms to the Resonance Spectra
of Synthetic Metalloporphyrins

ITEM: Final Technical Letter Report

I. Scientific Description of Research and Results

In early work^{1,2} supported by this grant we used resonance Raman scattering to obtain electronic assignments for bands in the absorption spectra of some of the hyperporphyrins. In this investigation we obtained the first experimental verification of a "non-adiabatic" vibronic coupling contribution to RRS intensities which was predicted by an extension³ of the existing theory of RRS. We further demonstrated that totally symmetric modes in metalloporphyrins (previously thought to be vibronically inactive) were involved in vibronic coupling of non-degenerate electronic states.

This study of Mn(III) porphyrins at room temperature has shown that excitation profiles over a large range of exciting frequencies can provide valuable quantitative structural, vibrational, and electronic information not obtainable by other methods. For example, from RRS data one can obtain shifts in the equilibrium positions of the nuclei in the excited state, estimates of the vibronic coupling constants, composition of charge transfer states, and assignments of electronic absorption bands in molecules with complicated absorption spectra.^{1,2}

This investigation also pointed to deficiencies in the theoretical description of RR intensities of polyatomic molecules. In addition to the neglect of the "non-adiabatic" terms in the scattering tensor by previous authors, we noted that the effects of degenerate electronic states had been

Memorandum to the National Science Foundation
May 13, 1980
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omitted in current theoretical treatments. The importance of the theoretical studies were enhanced when the excitation profiles of nickel etioporphyrin (NiEtio) (an investigation prompted by the success of the Mn(III) etioporphyrin complex work) were obtained throughout the visible.⁴ Experimental excitation profiles of totally symmetric and Jahn-Teller active modes exhibited unexpected behavior and pointed to a theoretical answer based on the inclusion of the effects of degeneracy of the resonant excited electronic states. Further anomalies were observed in a study of chromium (III) tetraphenyl-porphyrin chloride (Cr(III)TPPCl) excitation profiles. For example, the observation of maxima in a profile of one vibration due to another "helping" mode has been reported⁴ for Cr(III)TPPCl. This behavior in an excitation profile is a manifestation of the larger distortion in the excited states of Cr(III)TPPCl than in Ni etioporphyrin.

At room temperature, the "helping" mode behavior is most easily observed when the frequencies of the vibrations differ considerably so that the helping mode maxima will be resolved. We have observed a broad helping mode maximum at $\approx 1400 \text{ cm}^{-1}$ above the 0-0 frequency in the excitation profile of the 400 cm^{-1} (p) line of Cr(III)TPPCl.

Extensive Raman excitation spectra of CuTPP in the Q band region of the absorption spectrum between 16.5 kK ($1\text{kK} = 1000 \text{ cm}^{-1}$) and 22.1 kK have been obtained and interpreted in terms of strong vibronic coupling. Strong coupling is indicated in the excitation profiles by (1) considerable vibronic state energy renormalization in the Q band, (2) strong 0-2 maxima in many totally symmetric mode excitation profiles, (3) Raman intensity borrowing among high frequency Q band vibronic states and (4) the enhancement of low frequency modes at resonance with the fundamental of the Q-state normal mode which is the symmetric mixture of the interacting high-frequency ground state normal modes. The CuTPP absorption spectrum is consistent with this interpretation.⁵

The spectroscopic data is in qualitative agreement with strong, linear vibronic coupling and weak purely electronic interaction between the 50/50 mixed MO configurations, (Q_x, Q_y) and (B_x, B_y). In addition, the data indicates that the 50/50 mixed Q transition is slightly allowed, that is, the cancellation of the dipoles in the Q state is incomplete. Both coupling between the Q and B manifolds and coupling within these manifolds give a significant contribution to the Raman scattering. Physically, the two kinds of coupling are manifested as a totally symmetric distortion of the molecule and a change in the force constants in the excited state, respectively. This might occur as a result of the delocalization of charge onto the phenyl rings in the excited (Q) state. This would be expected to change force constants and/or distort the molecule from the ground state nuclear configuration.

Most recently, the matrix isolation system constructed during the present grant period has begun to yield additional information of the porphyrins and the effects of their environment. The technique has been used to study CuTPP

Memorandum to the National Science Foundation
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at low temperatures and with (possibly) reduced coupling of the molecule with its surroundings. To our knowledge this is the first resonance Raman spectroscopy of large molecules using matrix isolation techniques. Prior to this most investigations have been carried out on small molecules such as I_2 and molecular ions.

The absorption spectrum of CuTPP in a nitrogen matrix shows stronger relative absorption at the Q(0-0) transition, the lower energy electronic state with no vibrational quanta excited, than at the B (or Soret) transition compared to this same ratio, Q(0-0)/B, for CuTPP in CS₂ solution at room temperature. Raman excitation profiles for the matrix isolated samples generated from the resonance Raman spectra of a number of vibrational lines appear to show an enhanced peak at the Q(0-0) wavelength over the spectra in the CS₂ solution. These results also show evidence of reduced vibronic coupling in the nitrogen matrix. (Figure 1)

At this time we are unable to explain the inverse correlation between the strength of the Q(0-0) absorption relative to the Soret band absorption and the occurrence of strong vibronic coupling phenomena in Raman excitation spectra. NiEtio which has a strong Q(0-0) transition but weak vibrational side band shows almost no evidence of strong coupling effects. The absorption spectrum of CrTPPCl has about equal Q(0-0) and Q(0-1) bands and some strong coupling behavior was observed in the Raman data. The Raman profiles of CuTPP in CS₂ at room temperature which exhibit a very weak Q(0-0) absorption, are dominated by strong coupling behavior, whereas the same molecule in a N₂ matrix at low temperature shows an increased Q(0-0)/B and reduced strong coupling. These latter studies give yet another indication of the importance of environmental effects on the electronic states of porphyrins.

Besides presenting the first qualitative description of extensive excitation profiles of typical metalloporphyrins, through the use of computer programs for calculating the RRS intensity we have been able to obtain quantitative information about vibronic parameters for these metalloporphyrins. Furthermore, predictions for the excitation frequency dependence of depolarization ratios, the intensity of overtone and combination modes, the resonance Rayleigh intensity, and the electronic absorption spectrum are easily obtained. The computer programs, already constructed, will greatly aid in future investigations.

Within the past year we have perfected our matrix isolation techniques to produce porphyrin-doped crystals reliably. Now that we have achieved this facility we intend to proceed with measurements on a range of porphyrin samples via a number of frozen gas matrices, particularly N₂, Ar and CH₄.

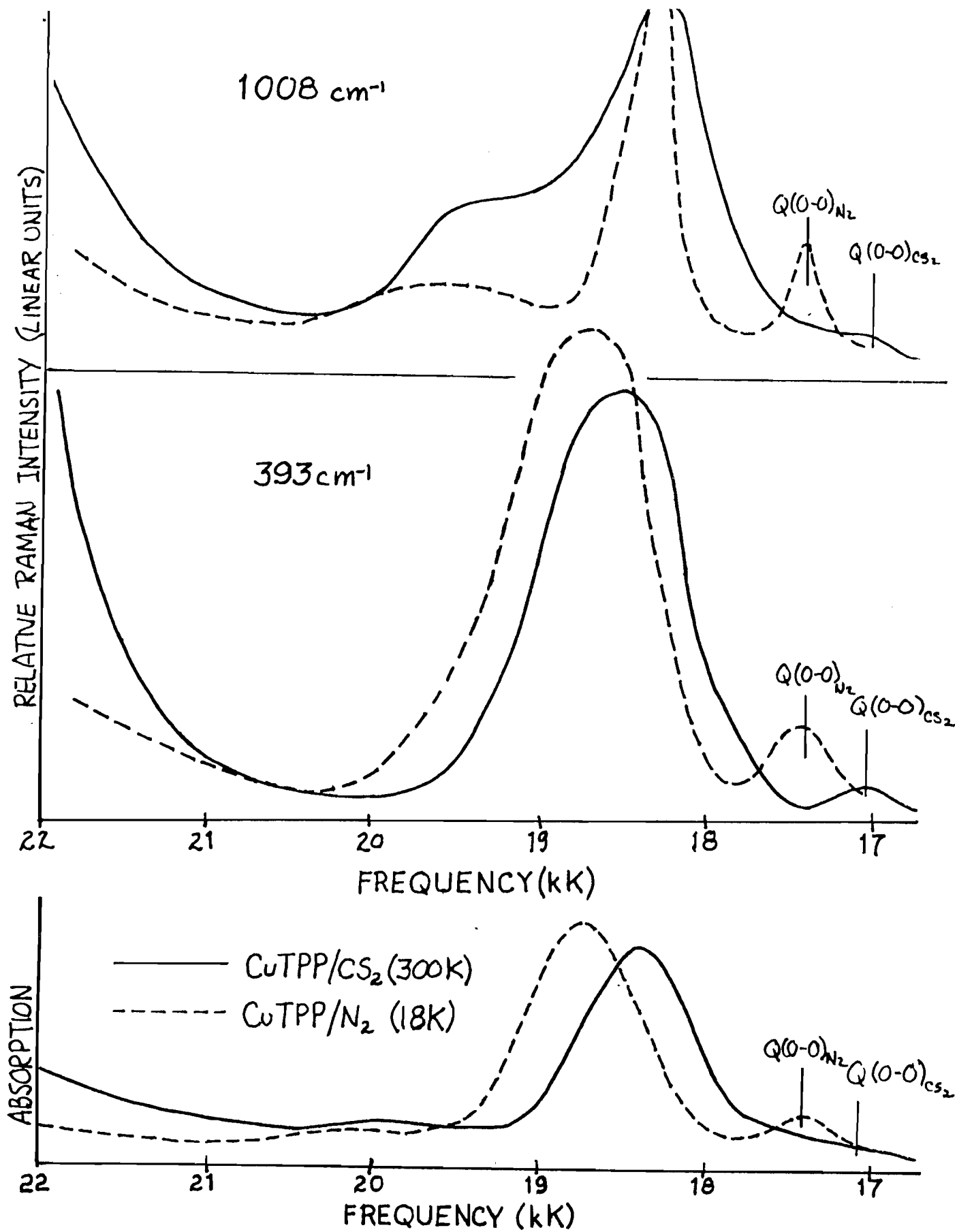


Figure 1. Preliminary Excitation Profiles and Absorption Curve of N_2 matrix isolated CuTPP compared to room temperature curves of CuTPP in CS_2 .

Bibliography

1. J. A. Shelnut, D. C. O'Shea, N. -T. Yu, L. D. Cheung, and R. H. Felton, J. Chem. Phys. 64, 1156 (1976).
2. J. A. Shelnut, thesis, Georgia Institute of Technology, 1975.
3. M. Mingardi and W. Siebrand, J. Chem. Phys. 62, 1974 (1975).
4. J. A. Shelnut, et al., J. Chem. Phys. 66, 3387-98 (1977).
5. J. A. Shelnut and D. C. O'Shea, to be published in J. Chem. Phys. (see Appendix A).

II. Publications

"Resonance Raman Spectra of copper tetraphenylporphyrin: Effects of strong vibronic coupling on excitation profiles and the absorption spectrum," by J. A. Shelnut and D. C. O'Shea, Journal of Chemical Physics 69, 5361 (1978).

III. Theses. None.

IV. Scientific Collaborators

Dr. John Allen Shelnut, Research Scientist and Co-Principal Investigator. On leave from Georgia Institute of Technology. At Bell Telephone Labs., Murray Hill, NJ.

Dr. Jo Lien Yang, Research Scientist

Mr. Patrick O'Rourke, Research Assistant. Graduate Student working on matrix isolation studies of porphyrins.

V. Comments

The project continued by this grant has been renewed. Work has begun on a picosecond pulse, mode locked system.

Respectfully submitted,

Donald C. O'Shea
Assistant Professor of Physics
Principal Investigator