**GEORGIA INSTITUTE OF TECHNOLOGY**
OFFICE OF CONTRACT ADMINISTRATION
**SPONSORED PROJECT INITIATION**

Date: September 16, 1976

Project Title: Laser-Excited Raman Spectroscopy of Biopolymers

Project No: G-33-G01 (Continuation of work previously budgeted under G-33-601)

Project Director: Dr. Nai-Teng Yu

Sponsor: DHEW/PHY/NIH - National Institute of General Medical Sciences

Agreement Period: From 9/1/76 Until 8/31/78 (end current project period)

Type Agreement: Grant No. 5-R01-GM18894-06

Amount: $37,021 PHS
3,500 GIT (G-33-364)
$40,521 Total (For .06 Year only)

Reports Required:
(Annual Progress Reports with continuation applications;
Terminal Progress Report upon Grant expiration.

Sponsor Contact Person (s):

Technical Matters

Contractual Matters

Walter L. Newton, Ph.D (thru OCA)
Deputy Assoc. Dir. for Program Activities
National Institute of General Medical Sciences
DHEW/PHS/NIH
Bethesda, MD 20014
Program Administrator: Dr. Marvin Cassman (301) 496-7463

Defense Priority Rating:

Assigned to: Chemistry (School/Laboratory)

COPIES TO:

- Project Director
- Division Chief (EES)
- School/Laboratory Director
- Dean/Director-EES
- Accounting Office
- Procurement Office
- Security Coordinator (OCA)
- Reports Coordinator (OCA) ✓
- Library, Technical Reports Section
- Office of Computing Services
- Director, Physical Plant
- EES Information Office
- Project File (OCA)
- Project Code (GTRI)
- Other

CA-3 (3/76)

Posted 8/8

OHL

**GEORGIA INSTITUTE OF TECHNOLOGY**
OFFICE OF CONTRACT ADMINISTRATION

# SPONSORED PROJECT TERMINATION

Date: 9/15/77

Project Title: *Laser - Excited Raman Spectroscopy of Biopolymers*

Project No: *G-33-G01*

Project Director: *Dr. Nai-Teng Yu*

Sponsor: *DHEW/PHS/NIH - National Institute of General Medical Sciences*

Effective Termination Date: *8/31/77 (end of 06 budget period)*

Clearance of Accounting Charges: *by 8/31/77*

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
X Other *Annual Report of Expenditures due by 11/30/77.*

*NOTE: FOLLOW-ON PROJECT IS G-33-G02 (07 Year).*

Assigned to: *Chemistry* (School/Laboratory)

COPIES TO:

Project Director
Division Chief (EES)
School/Laboratory Director
Dean/Director—EES
Accounting Office
Procurement Office
Security Coordinator (OCA)
Reports Coordinator (OCA)
Library, Technical Reports Section
Office of Computing Services
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EES Information Office
Project File (OCA)
Project Code (GTRI)
Other _____

CA—4 (3/76)

APPLICANT: REPEAT GRANT NUMBER SHOWN ON PAGE 1 →

GRANT NUMBER

## SECTION IV—SUMMARY PROGRESS REPORT

GM18894-07

PRINCIPAL INVESTIGATOR OR PROGRAM DIRECTOR (Last, First, Initial)

Yu, Nai-Teng

PERIOD COVERED BY THIS REPORT

FROM: 09/01/76 THROUGH: 06/30/77

NAME OF ORGANIZATION

Georgia Institute of Technology

TITLE (Repeat title shown in Item 1 on first page)

Laser-Excited Raman Spectroscopy of Biopolymers

1. List publications: (a) published and not previously reported; (b) in press. Provide five reprints if not previously submitted.
2. List all additions and deletions in professional personnel and any changes in effort.
3. Progress Report. (See Instructions)

1. (a) (i) Nai-Teng Yu, Emily J. East, Robert C.C. Chang and J.F.R. Kuck, Jr., Raman Spectra of Bird and Reptile Lens Proteins", Exp. Eye Res. 24, 321-334 (1977).

(ii) J.F.R. Kuck, Jr., E. J. East and Nai-Teng Yu, "Prevalence of α-Helical Form in Avian Lens Proteins", Exp. Eye Res. 23, 9-4 (1976).

(iii) Nai-Teng Yu, "Raman Spectroscopy: A Conformational Probe in Biochemistry", CRC Critical Rev. in Biochemistry, 4, 229-280 (1977).

(iv) J. A. Shelnutt, L. D. Cheung, R.C.C. Chang, Nai-Teng Yu and R. H. Felton, "Resonance Raman Spectra of Metalloporphyrins. Effects of Jahn-Teller Instability and Nuclear Distortion on Excitation Profiles of Stokes Fundamentals", J. Chem. Phys. 66, 3387 (1977).

(v) J. A. Shelnutt, Nai-Teng Yu, R.C.C. Chang, L. D. Cheung, and R. H. Felton, "Effects of Jahn-Teller Instability and Excited State Metalloporphyrins: Theory and Experiment", in "Proceedings of the Fifth International Conference on Raman Spectroscopy" (Eds. E. Schmid, J. Brandmuller, W. Kiefer, B. Schrader, H. Schrotter), Freiburg, 1976, p. 336-337, Schulz Publ., Freiburg.

(b) R. H. Felton and Nai-Teng Yu, "Resonance Raman Spectra of Metalloporphyrins" in The Porphyrins (D. Dolphin ed.) Academic Press. (in press).

2. (1) Dr. E. J. East, after working in this research group for 3 years, will terminate her position on June 30, 1977. A new postdoctoral associate, Dr. H.K. Hong will join our research group in Aug. 1977.

(2) Our laser Raman system has been converted into a pulsed laser operation with a wavelength range of 217-750 nm without gaps. Georgia Tech has invested a total of ~$30,000 for a Molectron UV-1000 nitrogen pumped pulsed dye laser and accessories. Our capabilities for studying a wide range of biological problems have been greatly enhanced.

3. Summary Progress Report:

(1) Objectives

a. The overall objectives of the total project are: (a) to develop the techniques and procedures necessary to obtain and interpret the Raman spectra of biopolymers; (b) to derive significant structural information not obtainable by other research techniques; and (c) to correlate the structure-function relationship of biomolecules.

b. Goals set for the current year: (a) to develop pulsed laser Raman spectroscopy using boxcars integration technique; (b) to continue studies on



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3. Summary Progress Report (Continue)

fibroblast, using CARS technique; (c) to investigate the resonance Raman spectra of fluorescent age-dependent pigments in human lens by CARS technique; and (d) to continue studies of hemeproteins and metalloporphyrins.

2. Main Specific Findings and Their Significance:

a. We have developed a pulse laser Raman system, employing 180° scattering geometry. The technique allows one to obtain the excitation profile of strongly absorbing samples without "saturation" effect. In the usual 90° scattering geometry the resonance Raman intensities relative to the solvent line (internal reference, non-resonance signal) were found dependent on the intensity of the exciting line due to the fact that the number of photons in the very short pulse (~10 nesc) is far greater than the number of solute molecules in the scattering volume and the relaxation of the molecules to the ground state is often not fast enough. This "saturation" effect always causes spurious excitation profiles in the 217-750 nm region.

b. Interpretations of the detailed resonance Raman excitation profiles of Ni(II)Etio and Cr(III)TPPCl are given (J. Chem. Phys. 66, 3387 (1977). Within the crude Born-Oppenheimer approximation, a theoretical model is presented which explains the 0-0 enhancements of depolarized modes as arising from interference of intermanifold (Q-B) and intramanifold (Q-Q) vibronic coupling. Comparison of computed and observed excitation profiles shows that a weak Jahn-Teller distortion is present in the Q state. Evidence of increased vibronic coupling of both 400 and 1365 $cm^{-1}$ polarized vibrations ($a_{1g}$) is found in chromium tetraphenylporphyrin with the appearance of a supernumerary peak at 1400 $cm^{-1}$ in the excitation profile of the 400 $cm^{-1}$ vibration. Excitation profiles of $a_{2g}$ modes in the chromium complex exhibit an apparent decrease in excited state vibrational frequencies due to increased coupling. Estimates of vibronic coupling strengths for the Q state are given for the nickel and chromium porphyrins The results of model studies here ehnance the understanding of the complex intensity behavior in the resonance Raman spectra of hemeproteins.

c. Recently in collaboration with Prof. L. A. Carreira of the University of Georgia we have demonstrated that the so-called "CARS" technique is capable of generating Raman spectra of highly fluorescent biological molecules. β-Carboline, a fluorescent pigment in human lens, is the focus of our CARS studies. A high quality pre-resonance CARS (Coherent Anti-Stokes Raman Scattering) spectrum is presented in Figure 1. This means that it is possible to obtain in situ fingerprint information of fluorescent pigments in an intact human lens. The chemical identities of these pigments are important for finding the mechanism of their formation.

d. The excitation profile of the polariged line at 352 $cm^{-1}$ has been obtained (see Figure 2). It shows a maximum near 18,000 $cm^{-1}$ (555.6 nm) where the Z-polarized spectrum also exhibit an absorption maximum. However, evidence is not sufficient to establish that this line is a Fe(III)-S stretching

2. Main Specific Findings and Their Significance (Continue)

vibration, although it is tentatively assigned to a Fe-N ring vibration mode (P. M. Champion and I. C. Gunsalus (1977) JACS, 99, 200). Excitation profile in the 300-450 nm region will be obtained using our recently developed pulsed laser Raman system. It should allow us to pinpoint the origin of this 352 $cm^{-1}$ line.

3. Research goals in the coming year:

a. To further develop the pulsed laser Raman spectroscopy for biological applications.

b. To explore the potential of the so-called "rippled RIKES" technique, recently introduced by Professor M. D. Levenson of the University of Southern California. It employs a CW laser (probe beam) and a pulsed laser (pumped beam).

c. To continue studies on hemeproteins and metalloporphyrins using the UV pulsed technique.

The undersigned agree to accept responsibility for the scientific and technical conduct of the project and for provision of required progress reports if a grant is awarded as the result of this application.

6/23/77
Date

Tai-Tong Yue
Principal Investigator

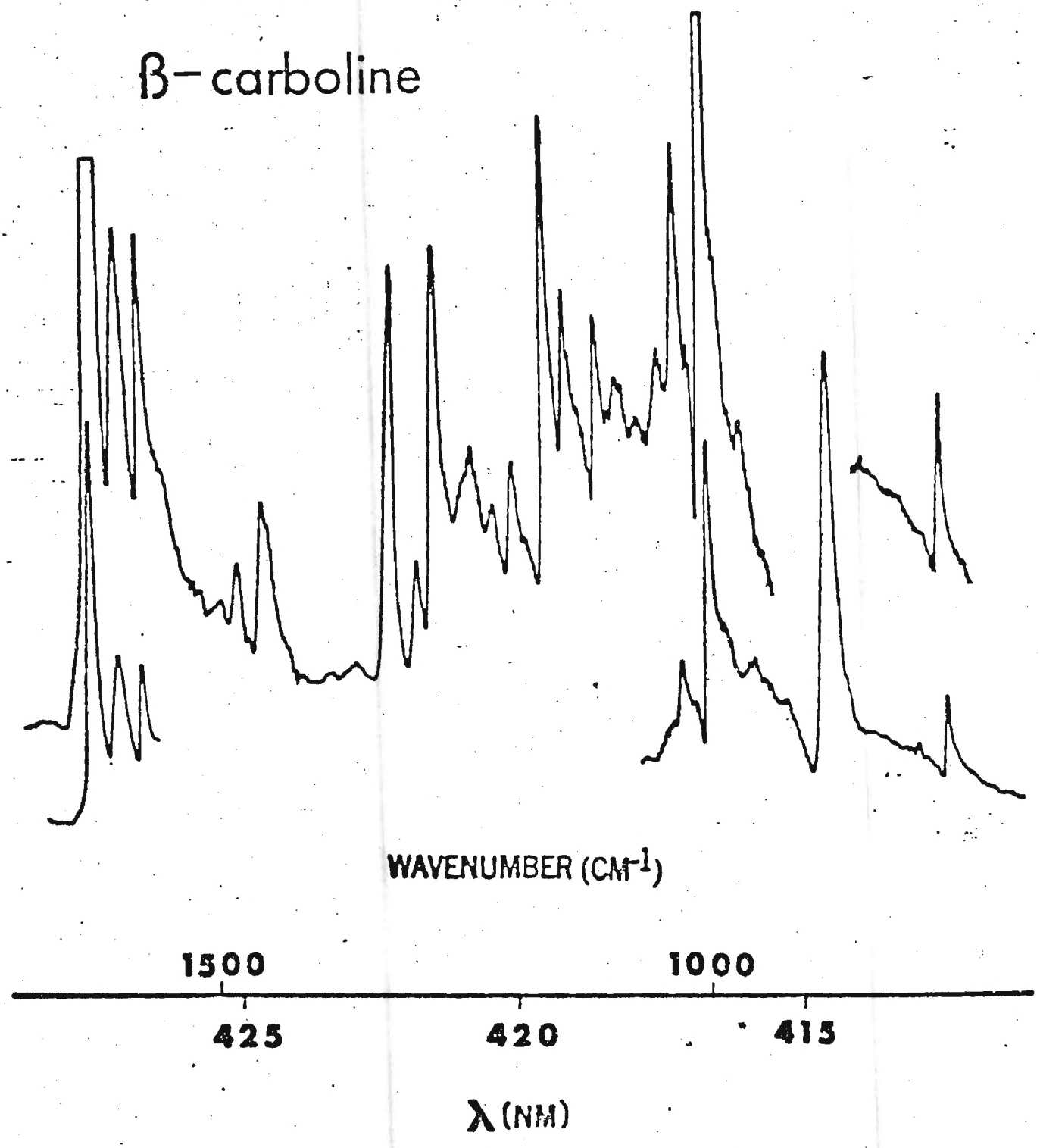


Fig. 1

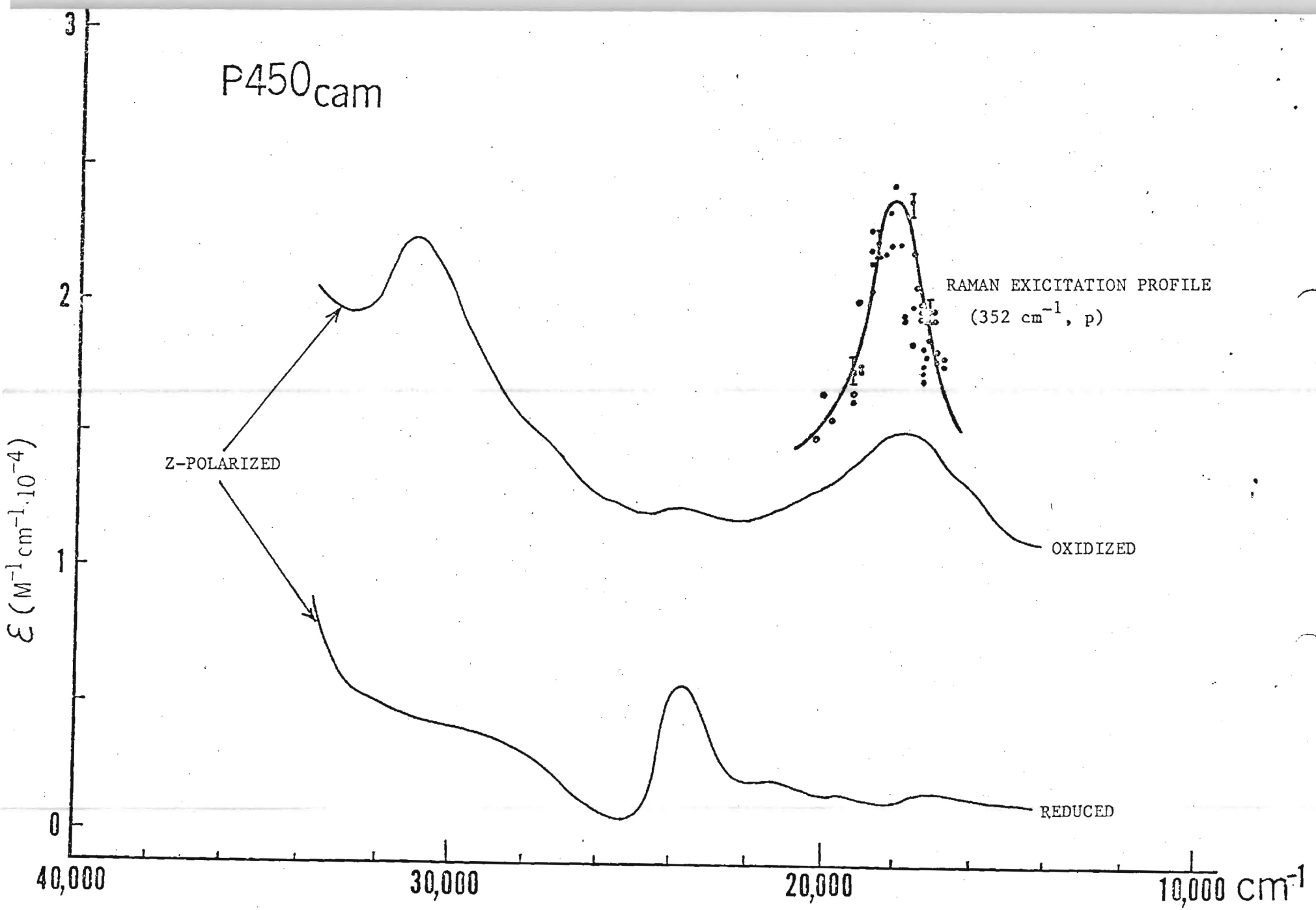
P450cam
RAMAN EXICITATION PROFILE
(352 cm$^{-1}$, p)
Z-POLARIZED
OXIDIZED
REDUCED
$\varepsilon$ ($M^{-1}cm^{-1}.10^{-4}$)
3
2
1
0
40,000
30,000
20,000
10,000 cm$^{-1}$

Fig. 2