GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. ____

Project No. G33-G07 (NIH) DATE 9-21-82

Project Director: NAI-TENG YU School/~~Lab~~ Chemistry

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

Type Agreement: Grant No. 2-R01-GM18894-12

Award Period: From 9-1-82 To 8-31-83 (Performance) 11-30-83 (Reports)

Sponsor Amount: $92,722 Contracted through:

Cost Sharing: $4,880 (G33-338) ~~GTRI~~/GIT

Title: Laser-excited Raman Spectroscopy of Biopolymers

ADMINISTRATIVE DATA OCA Contact Don Hasty

1) Sponsor Technical Contact:

Dr. Marvin Cassman
Grants Program Administrator
National Institute of General Medical Sciences
Bethesda, MD 20014

Phone (301) 496-7463

Defense Priority Rating: N/A

2) Sponsor Admin/Contractual Matters:

R. Monaghan or L.V. Allen
Grants Management Specialist
National Institute of General Medical Sciences
Bethesda, MD 20014

Phone (301) 496-7746

Security Classification: N/A

RESTRICTIONS

See Attached NIH Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with G.I.T. We are accountable for all equipment purchased.

COMMENTS: Follow on to G33-G06

COPIES TO:

~~Administrative Coordinator~~ RAN
Research Property Management
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FORM OCA 4:781

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

2-sr 306 360

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 10/12/83

Project No. G-33-G07 School ~~xxx~~ Chemistry

Includes Subproject No.(s) NONE

Project Director(s) Dr. Nai-Teng Yu ~~xxxx~~GIT

Sponsor HHS/PHS/NIH - National Institute of General Medical Sciences.

Title: Laser-excited Raman Spectroscopy of Biopolymers

Effective Completion Date: 8/31/83 (Performance) _____ (Reports)

Grant/Contract Closeout Actions Remaining:

- [X] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Continues Project No. G-33-G06

Continued by Project No. G-33-G08

COPIES TO:

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Project File
Other _____

Form OCA 83-1004

G-33-60

SECTION IV PROGRESS REPORT SUMMARY	GRANT NUMBER GM18894-13	
PRINCIPAL INVESTIGATOR OR PROGRAM DIRECTOR Yu, Nai-Teng	PERIOD COVERED BY THIS REPORT FROM 09/01/82	THROUGH 05/21/83
NAME OF ORGANIZATION Georgia Institute of Technology		

TITLE *(Repeat title shown in item 1 on first page)*

Laser-excited Raman Spectroscopy of Biopolymers

(SEE INSTRUCTIONS)

Publications:

1. Tsubaki, M., Srivastava, R. B. and Yu, N.-T. "Resonance Raman Investigation of Carbon Monoxide Bonding in (Carbonmonoxy) hemoglobin and -myoglobin: Detection of Fe-CO Stretching and Fe-C-O Bending Vibrations and Influence of the Quaternary Structure Change". Biochemistry 21, 1132-1140 (1982).
2. Tsubaki, M. and Yu, N.-T. "Resonance Raman Investigation of Nitric Oxide Bonding in Nitrosylhemoglobin A and -myoglobin: Detection of Bound N-O Stretching and Fe-NO Stretching Vibrations from Hexacoordinated NO-Heme Complex" Biochemistry, 21, 1140-1144 (1982).
3. Mackin, H. C., Tsubaki, M. and Yu, N.-T. "Resonance Raman Studies of Co-O_2 and O-O Stretching Vibrations in Oxy-Cobalt Hemes" Biophys. J. 41, 349-357 (1983).
4. Yu, N.-T., Kerr, E. A., Ward, B. and Chang, C. K. (1983) "Resonance Raman Detection of Fe-CO Stretching and Fe-C-O Bending Vibrations in Sterically Hindered Carbonmonoxy Strapped Hemes. A Structural Probe of Fe-C-O Distortion" Biochemistry (submitted).
5. Kerr, E. A., Mackin, H. C. and Yu, N.-T. "Resonance Raman Studies of Carbon Monoxide Binding to Iron "Picket Fence" Porphyrin with Unhindered and Hindered Axial Bases. An Inverse Relationship Between Binding Affinity and the Strength of Iron-Carbon Bond" Biochemistry (submitted).

Report:

1. General Scientific Goals: No change
2. Concise Description of the Studies Conducted during the Budget Year, the Results Obtained and their Significance.

   (i) We have conducted a study of the distal steric effect on the Fe-CO stretching vibrations. Four synthetic hemes (with N-methyl-imidazole) were employed. A simple iron porphyrin (heme-5) without groups to hinder the CO binding and three "strapped hemes" which have a 13, 14, or 15-atom hydrocarbon strap across the CO binding site. It was found that by decreasing the chain length (hence increasing the steric hindrance or decreasing the CO binding affinity) the Fe-CO stretching frequency increases, but the C-O stretching frequency decreases. We demonstrated that while the Fe-C-O bending mode is not detectable in heme-5, its intensity relative to that of the Fe-CO stretching mode increases in the order FeSP-15 < FeSP-14 < FeSP-13; the CO distortion causes the enhancement of the Fe-C-O bending mode. These spectral features are interpreted in terms of increased interactions between the CO ligand and the N-atom(s) of pyrrole ring(s) in both ground and excited states. To estimate the Fe-C-O bond angles, we have developed a simple equation which requires only two stretching frequencies for two different isotopes without a prior knowledge of force constants.

   (ii) We have studied resonance Raman spectra of carbonmonoxy iron "picket fence" porphyrin with unhindered and hindered axial bases. A seemingly paradoxial

relatonship was found: a weak CO binding to the heme iron can mean a strong iron-carbon bond. The explanation was given in terms of the free energy distribution/compensation upon CO binding. This is an important principle in metalloporphyrin chemistry and is crucial in the interpretation of resonance Raman data from carbonmonoxy hemoproteins. More specifically the two examples which exhibit an inverse relationship between binding affinity and the strength of iron-carbon bond are: (a) Fe(II)TpivPP(1,2-Me_2Im) vs. Fe(II)TpivPP(N-MeIm), and (b) Fe(II)TpivPP (THF) vs. Fe(II)TpivPP(N-MeIm). In both cases the ν(Fe-CO) frequency is higher (hence the Fe-C bond is shorter and stronger) for the weaker CO binding.

(iii) We have carefully studied oxy cobalt "picket fence" porphyrin, in an attempt to better understand the interaction between the ν(O-O) stretching vibration and accidentally degenerate ring modes. Strong evidence has been obtained suggesting that the ν(O-O) mode can be perturbed by an accidentally degenerate porphyrin ring mode, resulting in two split frequencies. In the Co(II)(TpivPP)(Pyridine) $^{18}O_2$ complex, we demonstrated that the $\nu(^{18}O\text{-}^{18}O)$, after being shifted from its $\nu(^{16}O\text{-}^{16}O)$ value at 1156 cm^{-1}, undergoes a resonance interaction with the 1080 cm^{-1} porphyrin mode, giving rise to two lines at 1067 and 1089 cm^{-1}. A third example of paradoxical relationship was found: a decrease in O_2 binding affinity, caused by the proximal base tension, corresponds to an increase in the CO-O_2 stretching frequency. However, in the corredponding iron complexes, the normal relationship was observed i.e., the ν(Fe-O_2) frequency decreases for the (1,2-Me_2Im) compelx.

3. Specific Objectives for the Coming Years.

(i) To develop a simple scheme for estimating the iron-carbon bond lengths in carbonmonoxy and cyanomet complexes of monomeric insect hemoglobins from Chironomus thummi thummi (in collaboration with Prof. Klaus Gersonde, RWTH Aachen, West Germany).

(ii) To study the nature of bonding interactions between Fe(III) and NO in hemoproteins and heme model compounds.

(iii) To analyze resonance Raman spectra of oxy, carbonmonoxy and dexoy elephant myoglobin - in collaboration with Prof. H. Mizukami, Wayne State Univ.

(iv) To develop a microscopic Raman technique for time-resolved resonance Raman studies of ligand binding.