VACUUM UV SPECTRA OF MOLECULAR CRYSTALS

Final Report

C.W. Peterson, Associate Professor of Physics

The University of Connecticut

Storrs, Connecticut

February 1, 1971 to June 30, 1975

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.

Prepared for the U.S. Energy Research and Development Administration under Contract No. AF(11-1)-3142

NOTICE
This report was prepared in an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of its employees, nor any of the contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

427 attached

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FINAL REPORT: VACUUM UV SPECTRA OF MOLECULAR CRYSTALS AT(11-1)-3142

C.W. Peterson, Associate Professor of Physics, The University of Connecticut,
Storrs, Connecticut 06268

Summary

The broad goal of this work is the characterization of the optical and electronic properties of molecular crystals and biomaterials in the vacuum UV region. Work during the tenure of this contract can be summarized into two general areas:

- 1) setting up and implementing a general facility for normal incidence reflection spectroscopy in the VUV region, with accompanying computer analyses for optical constants and derived functions. Detailed results were obtained on two molecular crystals in the form of thin films of tetraphenylporphyrin and its magnesium compound MgTPP. A general program for characterizing the VUV absorption of protein and nucleic acid components was set up, and specific results were obtained for tobacco mosaic virus and its protein in polymerized and unpolymerized configurations. Data were also taken on a synthetic polypeptide, polyglutamic acid in controlled morphologies.
- 2) initiating a program to determine the VUV photoemission properties of biomaterials and thereby completely delineate their electronic structure. The requisite ultrahigh vacuum system was finalized and key components designed and fabricated; preliminary data will be taken by the end of the year on the prototype molecular crystal TPP.

PROGRESS REPORT-- FINAL YEAR

During the final year of the contract progress was made in the following areas, subject to the limitations of reduced funding:

- 1) final results were obtained on tobacco mosaic virus (TMV) thin films; additional data were taken and earlier discrepancies resolved. A complete set of normal incidence reflection spectra were taken on several samples of the unpolymerized protein (TMVP-UP) for comparison with both polymerized protein (TMVP) and assembled virus results. Both TMV and TMVP-UP final spectra were reduced via our Time Domain procedure; detailed analysis of all

three is just about complete. For comparison all derived absorption curves were normalized to the same relative-scale (as though all samples contained the same concentration of absorbing material, protein or virus, and were of uniform thickness). There are intriguing differences between all three normalized absorption curves, particularly surprising in the comparison of PMVP and PMVP-UP where effects of unraveling the tertiary structure of the assembled protein were not expected to be appreciable. (It was hoped a preprint could be included in this final report, but time has run out; the preprint will be forwarded as soon as available.)

2) the work proposed on the metal tetraphenylporphyrins Ni:TPP and Mn:TPP was not undertaken during this final year; due to severe budget limitations it was not practical to embark on this new extension of earlier results with our reduced manpower and resources. Hence although of interest in their own right and for the relation to the VUV bands for TPP and MgTPP, the absorption spectra and derived electronic energy structure of Ni and MnTPP were postponed for future work.

3) as originally proposed, work on the VUV photoemission of MgTPP and TPP was carried out during the past year. In particular construction of the analyzer was completed, a sample holder was designed and fabricated, and final plans for sample preparation worked out (we abandoned the Knudsen Cell molecular oven approach in favor of a simpler in situ evaporation scheme). We are completing final system assembly and are also fabricating the optical coupling compartment linking VUV monochromator and ultrahigh vacuum photoemission chamber. (We spent considerably time in the design of the latter compartment, since there are no beam splitters available in the vacuum UV and we require simultaneous intensity and electron emission data.) A novel calibration scheme for absolute intensities in the VUV was developed in conjunction with Professor W. Smith in our department. The technique involves measurements of noble gas collisions whose absolute cross-sections are known, using a channeltron as a secondary standard; a publication is anticipated in J. Opt. Soc. Am. or Applied Optics when final results are in. As originally proposed, the photoemission area of research was expected to be longer range than one year; we are on schedule in this work and expect our first data by the end of the year.

The significance of the photoemission research is severalfold:

i) the determination of occupied and unoccupied band states in these materials, interpreted in terms of the latest available theoretical band schemes for the materials

ii) in particular, what is the change in optical density of states upon insertion of the monometal M_2

iii) deduction of the selection rules for the relevant transitions and quantitative evaluation of electron excitation and scattering processes when applicable.

4) Concerning the earlier proposed polypeptide work, we have concentrated on a single polypeptide (synthetic), polyglutamic acid (PGA) in controlled morphologies for our initial investigation; related work with other simple polypeptides such as polytyrosine will follow. Samples of PGA were purified and brought to requisite morphologies using pH of the liquid film as a parameter. New techniques were developed to maintain these configuration under the special conditions produced in drying the thin films for vacuum UV measurements, as well as verify the final configurations. Preliminary results were obtained for PGA in helix and coil geometries and the data are being processed at present; the resulting paper will be forwarded at a later time.

Some of the questions we are addressing in this work include

i) what features are common to PGA and TMV protein in respective conformations?

ii) are PGA hypochromic effects analogous to those in the near UV band observed between the two configurations?

iii) can one identify effects due to burying or exposing absorbing chromophores in the two morphologies, analogous to the effects seen for polymerized and unpolymerized TMV protein?

iv) can we establish a new criterion for estimating the helical content of a protein (in earlier work related to the single near UV band extinction coefficient in the restricted cases where it is appropriate)?

v) how do the results compare with predictions of higher transitions of the relevant chromophores, including possible exciton splittings?

vi) is identification possible of collective effects analogous to those seen in earlier determinations of energy loss functions of DNA in the vacuum UV, as opposed to essentially single electron excitations?

Concerning the financial picture for the final year, out of a total spendable of \$7000 (\$9000 awarded less \$2000 for overhead and fringe benefits), the major items were about \$4000 for salaries, \$1700 for supplies, \$400 contractual, and in the category of equipment, \$1000 towards a grating and grating holder (for greater intensities at the far UV end of our spectrum) and part payment for the requisite X-Y recorder for photoemission output, as budgeted in our original proposal. (This represents a change from our revised budget, submitted in the summer of 1974; the photoemission work could not proceed without this recorder and since the contribution towards its purchase was in the spirit of the original proposal, it was felt justified at this time.)

One graduate student was supported half time as planned, and funds were expended for student labor to assist with data analyses, computer work, and shop fabrication of parts for the ultrahigh vacuum apparatus. A portion of the salary figure was the partial support of Dr. R. Scheele for a number of weeks. As outlined in our original proposal, Dr. Scheele has been indispensable to our work with virus, protein and polypeptide sample preparation; this collaboration has been most effective. While not specifically called for in our revised budget, we did feel this partial expenditure of our terminal year support was most justified. Dr. Scheele is a co-author on both our papers on FMV and its protein, and in the PGA work. As in our letter of November 17, 1975, we therefore seek part of this amount (\$839.63) to be transferred from the category of equipment to salaries and wages.

CONTRACT PERIOD: EPILOGUE

Over the three years of full funding plus our terminal year, we have accomplished the following objectives:

1. established a working laboratory in reflection spectroscopy in the Vacuum UV region; we are now one of the few such installations in the country. (When the contract began, the laboratory was not yet operational and much of the first two years were spent in refining of sample alignment procedures, making the system operational and debugging of data protocols.)

Our original goal was polarized spectra of single crystals. Despite repeated attempts, the requisite large single crystals could not be grown, so we have concentrated at first on work with thin films. We have characteri-

zed the VUV optical properties (relative complex index of refraction and dielectric constant and energy loss function) for the following compounds of biological significance: IPP and MgIPP, DNA and its associated protein in polymerized and unpolymerized form, with partial results available on PGA in helix and coil morphologies. Two papers are about to be submitted for publication and the PGA one is in progress. Rather than enclosing the figures or reporting on detailed results at this time, reprints of the relevant papers will be forwarded as soon as available. One talk on preliminary results was given at the 27th Symposium on Molecular Structure and Spectroscopy at the Ohio State University, Columbus, Ohio, June 1973. ¹

The experimental procedures proved satisfactory, but we plan to extend the work to single crystals on different compounds (more amenable to growth of large single crystals) by next year, for detailed results on polarization and transition moments. Although single crystal work is desirable, it is felt our preliminary work with thin films has added much to the fundamental knowledge of the positions and relative intensities of energy bands in the VUV region, unavailable by any other means. In particular, in the case of protein and virus results, it is doubtful that large single crystals will ever be available, hence the present results represent the only approach to spectroscopy in this important energy range. Additionally, crystals are far from the active biological morphology of these virus and protein compounds, and application of crystalline results to vivo conditions, e.g., tissue, is questionable. In short, thin films are nearer the biologically significant state.

Each spectrum alone is of interest in its own right, in identifying component absorptions in the various configurations. Concerning the more recent virus and protein work, although detailed sequencing of protein and RNA have been worked out, the gross morphology is still a matter of dispute. The unfolding of the difference spectra between intact virus and reassembled protein rod illuminates, for example, the influence of the RNA in situ and is complementary to the relevant ORD findings in the visible. The corresponding difference curve for protein, polymerized and unpolymerized, sheds light on the problem of the conformational free energy of a folded natural protein and the relative importance of peptide backbone interactions versus amino acid side chains in stabilizing the ordered

structures. Our spectroscopic measurements extend the vast data of protein difference spectroscopy, previously used to obtain binding energies, solvent and other environmental effects, and spectrophotometric titration applications, into the vacuum UV region, the fundamental region of absorption for these biochemical entities. These results are related in important ways to existing X-ray, visual and electron microscopic studies on the one hand, and chemical probe and activation work on the other.

The program in these laboratories is ongoing, and partial support by the A.E.C. in its inauguration and subsequent first few years is gratefully acknowledged.

2. established an ultra-high vacuum facility for the determination of external photoelectric yield and energy distributions of emitted photoelectrons. During the time period of A.E.C. support this facility was designed and partially completed, mostly with outside funding. During the last year of A.E.C. support, the component parts were finalized and experiments are now about to begin. While there are several VUV photoemission laboratories in this country, ours is the only one devoted to work with biomaterials. By determining properties such as the electronic energy levels, optical densities of states, mechanisms of energy transport within the materials and the ways in which these prototype biological compounds interact with external radiation, we have taken the fundamental first step in the understanding of the biological processes which depend on these molecules. (It is worth reiterating that absorption due to the fundamental biological entities such as proteins and polynucleotides is available only in the VUV range.) Although the action of near UV light has been studied extensively, the problem of radiation damage in biological materials remains one of the unsolved problems; direct application of photoemission results to the problem of radiation damage is anticipated.

In conclusion we feel that we have established and carried out a significant program in the determination of the VUV optical and electronic properties of thin films of bio-materials; we plan to continue with this important work and extend it into other areas with different compounds as available. We are also in the process of setting up an exploratory program

to measure and interpret the external photoelectric emission from molecular crystals in evaporated samples, and we look forward to preliminary results in the next year.

1. During the course of the support, two papers relevant to the supported work have been published with copies forwarded to the A.E.C. at that time:

BeO as a window in the vacuum UV (with G.E. Palma), J. Opt.Soc.Am. 61, 387 (1973)

Causality Calculations in the time domain: An efficient alternative to the Kramers-Kronig method (with B.W. Knight), J. Optic. Soc.Am. 61, 1238 (1973).

2. During the course of the support, one student (Barry Peterson) obtained a Master's degree working on the initial stages of setting up the VUV reflection spectrometer, and a second student (Bee Sun-Wei) is in the final stages of Ph.D. thesis research and is expected to complete the Ph.D. work during 1976.