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**SPECTROSCOPIC INVESTIGATIONS OF ORGANIC MOLECULES
ON GRAPHITE SURFACES**

FINAL REPORT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The final report describes work on the spectroscopy of organic aromatic molecules boud to the surface of graphite. The experiments performed include' raman, ODMR, surface emission and reflectancespectroscopy.		

ARO FINAL REPORT

Introduction:

The research program conducted over the past three years under ARO sponsorship focused on the spectroscopic investigation of polycyclic aromatic molecules adsorbed onto the surface of graphite. The overall aim of the investigation was to characterize the structural features of the adsorbed complex and to identify the nature of the interactions which stabilize them. Our approach was to examine a series of prototypical aromatic molecules bound to highly oriented pyrolytic graphite by optical, magnetic resonance, and raman spectroscopy.

Summary of Important Research Results:

Results in several areas of significance were obtained in the course of the research program. In summary, these were:

- ① observance of optical and ODMR spectra of photoexcited quinoline and quinoxaline on graphite;
- ② observance of resonance raman scattering from chlorophyll on graphite
- ③ observance of ODMR from chlorophyll on graphite;
- ④ determination of the chlorophyll geometry on the graphite surface;
- ⑤ demonstration of the feasibility of raman-detected ODMR on surfaces.

The ability to prepare and detect at the monolayer level the spectroscopic properties of organic molecules on a surface, one of the principal goals of the program, is clearly demonstrated in each of these research results.

In detail, we have shown for the first time that photoexcited triplet state zero-field magnetic resonance transition may be observed using the raman peak intensities to monitor the microwave induced population changes effected in the triplet state. This approach allows a complex molecular system, such as can occur on a metal surface in which molecules may be found at a variety of binding sites or in aggregated domains distributed on the surface, to be sorted out on the basis of its raman spectrum; then only the molecules of interest identified by their characteristic raman bands are monitored for their triplet state features. We have employed this approach to investigate the chlorophyll-graphite system and have been able to separate monomeric and aggregate features of the chlorophylls bound to the graphite surface.

In addition to the chlorophyll ODMR experiments we sought to confirm the orientational features on graphite by performing polarized raman experiments with the laser field polarization fixed parallel and perpendicular to the graphite surface. The variation of polarization ratios over the raman bands over the totally symmetric modes made the determination of orientation angle less specific than in the ODMR case, but the two results - from quite different experimental approaches - were consistent.

In contrast to the chlorophyll case, our experiments with quinoline and quinoxaline indicated that a preferred orientation on the graphite surface is not maintained for all molecular systems. In fact, a series of careful experiments to deposit the molecules under differing conditions (vapor deposition, evaporation, spinning droplets on the surface) indicated that sample preparation conditions may be the dominant influence on the surface spectroscopic properties observed from the smaller adsorbed molecules.

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Publications resulting from the present research:

- R. H. Clarke and E. B. Hanlon
ODMR and Resonance Raman Spectroscopy of Chlorophyll B
on Graphite
J. Chem. Phys., 82, 5275 (1985)
- R. H. Clarke, D. J. Graham, and E. B. Hanlon
Triplet State ODMR of Molecules Adsorbed to the Surfaces
of Bulk Metals
Photochemistry and Photobiology (A. Zewail, ed.), 2, 1011 (1983)
- R. H. Clarke, D. J. Graham, E. B. Hanlon, and P. Mitra
Resonance Raman Detected Triplet State Magnetic Resonance
J. Chem. Phys., 79, 1549 (1983).

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