000-294-10

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000-294-10

Technical Progress Report

Special Research Support Agreement

The University of Chicago

Contract No. AT(11-1)-294

For the Period 1970 March 1 through 1971 February 28

Studies of (1) Actinide and Lanthanide Ions and
(2) Organic Molecules in Triplet States by
Magnetic Resonance Methods.

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1970 December 16

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Technical Progress Report

Studies of (1) Actinide and Lanthanide Ions and
(2) Organic Molecules in Triplet States by
Magnetic Resonance Methods.

1. Apparatus.

1.1. In our previous Technical Progress Report dated 1969 December 4, we reported (a) the moving of all of our laboratory equipment to, and (b) its complete reconstruction in, the new Searle Chemistry Laboratory building. During the present year all of the plumbing, electrical cabling, new vacuum pump installation, etc., associated with this move, and with the utilization of the cryogenics facility (liquid helium production plant; high vacuum, high speed helium return systems, etc.) located contiguously to our laboratories, has been completed in permanent form.

1.2. Our zero field magnetic resonance spectrometer, described in 1.1. of the 1969 December 4 Report, has been rebuilt in a manner which permits us to operate it at levels of power, incident on the sample cavity, in the nanowatt range. This modification has been made possible by the relatively recent development of very low noise traveling wave tubes which will operate at low power levels. This development of our spectrometer has made it possible for us to study various types of

systems, particularly some involving aromatic organic molecules in photoexcited triplet states, which are very easily saturatable at very low temperatures, and which we have never previously been able to investigate.

A new resonant cavity system for this zero field magnetic resonance spectrometer has been developed and put into operation. This permits its use for the investigation of the NpF_6 in UF_6 system which was described in 2.1.2. of the 1969 December 4 Report, and which we had not previously been able to study at zero external field.

1.3. Two new cavity assemblies with provision for irradiation of samples with UV light and for rotation of samples, at 1.5°K , have been constructed for use in our K band spectrometers. These assemblies may be used for work on either the f electron systems or the triplet state systems which we are currently studying.

1.4. We have developed and constructed a light modulation system, using a mechanical light chopper, for detection of light sensitive magnetic resonance signals. This system may be employed to advantage in certain phases of our work on organic triplet state systems at zero external field, as well as in connection with our studies of photoexcited states of f electron ions, where previously we employed either magnetic field modulation or frequency modulation schemes for signal detection.

1.5. Other Apparatus Developments Have Included:

1.5.1. The design and construction of a new unified 2 klystron power supply system particularly adapted for use on both our K band and our X band superheterodyne magnetic resonance systems.

1.5.2. A new low frequency (800 Hz) magnetic field modulation and phase sensitive detection system.

1.5.3. Several new optical systems, specially constructed for mounting on our spectrometer assemblies, and including new lamp housings, filter systems, and flexible optical bench systems, for the irradiation of either aromatic organic crystals, or f electron crystals, at low temperatures.

2. Research During the Calendar Year, 1970.

2.1. f Electron Systems in Single Crystals.

2.1.1. We have achieved considerable success in the interpretation of the electron nuclear double resonance (ENDOR) data on the hyperfine interactions between the $^{147}\text{Sm}^{+3}$ and $^{149}\text{Sm}^{+3}$ ions and the Cl^- ions in single crystals of LaCl_3 which were described in 2.1.1. of the 1969 December 4 Report. Both La and Cl distant ENDOR lines are observed in these spectra. Additional data have been obtained, subsequent to preliminary line assignments, and the analysis of these very complicated spectra is still in progress.

2.1.2. Most of the ENDOR data, at high magnetic fields, for the NpF_6 in UF_6 crystals, described in 2.1.2. of last year's Report, have now been collected. As a result of work on line assignments and interpretation of these spectra, the need for measurements in zero external magnetic fields has become apparent. Such measurements will permit us to arrive more easily and reliably at values of some of the spin hamiltonian parameters and this will greatly facilitate the completion of the analyses of the high field spectra. It is for this reason that the apparatus for this type of work, described in 1.2., has been developed. Our first NpF_6 spectra have just been obtained with this system.

2.1.3. In the 1969 December 4 Report we mentioned the preparation of crystal samples, and the construction of cavity assemblies and related apparatus, for the study of photoexcited states of rare earth ions in single crystals. A number of systems have now been investigated. The most successful of these investigations has been concerned with the Nd^{+3} ions in LaCl_3 single crystals. We have found that we may obtain sufficiently high concentrations of photoexcited Nd^{+3} ions in LaCl_3 for investigation of their excited states by conventional high field EPR methods, by incorporating U^{+3} ions in the same crystal. The U^{+3} ions absorb strongly in the region of the spectrum in which our light sources have intense emissions, particularly in the visible. They apparently transfer their energy of optical excitation with relatively high efficiency to the

Nd^{+3} ions. Three different photoexcited states of Nd^{+3} have now been investigated by this method.

2.1.4. The electron electron double resonance (EEDOR) spectroscopic studies, which have been discussed in preceding reports, have been extended over a wider temperature range. Also more detailed and quantitative measurements for a much larger number of hyperfine line pairs, for the $^{235}\text{U}^{+3}$ ion on LaCl_3 single crystals, have been completed.

2.2. Organic Molecules in Triplet States.

2.2.1. The system, anthracene in phenazine, (See publications, 3.1., 3.2., 3.3., below.) was described and discussed in 2.2.1.1. of our 1969 December 4 Report. Two studies of quite different types, which have now been completed, are the following.

2.2.1.1. (See publication, 3.1., below.) The electron paramagnetic resonance and proton electron nuclear double resonance spectra of anthracene molecules in their lowest energy photoexcited states in a single crystal of phenazine, have been studied. The values of the fine structure parameters and of the components of the proton electron hyperfine interaction tensors, in the fine structure principal axis system, have been determined and tabulated. The values of spin densities and of anisotropic and isotropic proton hyperfine interactions per unit spin density on the adjacent carbon, which best describe the experimental results, have been determined and compared

with similar values for other systems. The geometry of the anthracene molecule in the phenazine host crystal, and its orientation in the host structure, have been elucidated by means of these studies.

2.2.1.2. (See publications, 3.2., 3.3., below.) The fact that the lowest energy triplet state of the anthracene molecule is populated, in the phenazine crystal, by transfer, to the anthracene, of triplet excitation from the host, and not by an internal conversion process in the guest (the latter is the case for most of the triplet state molecules which have previously been investigated in this laboratory), leads to very interesting EPR spectra for the anthracene molecule in this system. Among these interesting features is the fact that the conservations of spin during the transfer leads to unequal populating rates for different ones of the 3 triplet levels. As a result, non Boltzmann populations of the triplet levels occur, and emissive as well as absorptive lines are observed in the EPR spectrum, i.e. very marked optical spin polarizations are observed. By means of studies of rates of decay of these signals and of changes in the absorptive or emissive characters of these signals, after cessation of illumination and concomitant cessation of pumping of the 3 triplet levels, very detailed information on the rates of populating, and rates of depopulating, of individual triplet levels, have been obtained. These studies have made very significant contributions to the understanding of the dynamics of triplet state populating

and depopulating, and of the energy transfer processes, in these systems.

2.2.2. Our continued investigations of the EPR spectra of benzene single crystals, in which the triplet excitation is relatively firmly trapped on perprotobenzene molecules at low temperatures ($\sim 1.5^\circ\text{K}$) by the device of adding concentrations of perprotobenzene in the range from 0.1 to 10. mole per cent to perdeuterobenzene crystals, have revealed extraordinarily interesting spectral features. A relatively complicated spectrum has been observed, which results from exchange interactions, magnetic dipole dipole interactions, and energy transfer processes in the crystals which have high concentrations of the perprotonated species. Detailed analysis of these spectra, and further studies of such spectra at other concentrations in the same range, are currently in progress.

2.2.3. Our zero field electron paramagnetic resonance studies of aromatic organic molecules in triplet states in single crystals (See publications, 3.4., 3.5., below.) have met with considerable success during the present year with respect to both (a) experimental results and (b) the theoretical understanding of such results, as described below.

2.2.3.1. The experimental results (See publications, 3.4., 3.5., below.) have included precise measurements of the effects of temperature, of pressure, and of deuteration, on the triplet state spin hamiltonian parameters of naphthalene in various

host crystals. In addition, line structures which result from multiple orientations of guest molecules substituted for host molecules at otherwise crystallographically equivalent host molecule sites, have been observed and studied in detail. Resolution of hyperfine structures due to proton electron intramolecular interactions at exactly zero external magnetic fields, has been increased, beyond that described previously, by means of our new much lower power system described in 1.2. above. We have observed X-trap spectra, which result from the trapping of triplet excitation, not on chemical or isotopic impurities whose triplet states lie lower in energy than the lowest triplet states of the host molecules, but rather on host molecules which have been distorted or disturbed in some manner by the insertion of the impurity, and whose lowest triplet states are sufficiently lower in energy than those of the rest of the host crystal that they can trap the excitation. These X-trap species have been identified and investigated in detail by means of their zero field spectra. The observed zero field proton hyperfine structure has been a very useful tool in this connection.

2.2.3.2. Our theoretical understanding (See publications, 3.4., 3.5., below.) of the various features of zero field magnetic resonance spectra described in 2.2.3.1., above, has been greatly increased during this year. Not only have we developed and considerably extended the approximate methods for treating the very complicated problem of obtaining the eigenstates and

eigenvalues of triplet state aromatic organic molecules in various external magnetic field ranges, and for relating conventional high field results to our zero field results, but we have also made many additional exact calculations for the zero field limit for the particular case of the naphthalene molecule, and have confirmed such exact results by means of appropriate experimental studies. In addition we have completed an interpretation of the variation of the spin hamiltonian parameters with temperature, in which the variation arises from vibrational excitation, the different vibrational states having different electronic magnetic dipole dipole interactions. The fitting of the resulting expressions for the spin hamiltonian parameters, as functions of temperature, to our experimental data, yields vibrational frequencies of eminently reasonable magnitudes. Two ranges of frequencies are required for fitting of our model. One of them turns out to be in very good agreement with known values of the out of plane bending frequencies for the naphthalene molecule, and the other approximates the expected size of phonon modes or librational modes of the crystal.

2.2.4. The chief development in connection with our investigations, mentioned in 2.2.3. of our 1969 December 4 Report, of the transfer of triplet excitation from one molecule site to another in an organic crystal, has been the utilization of the optical spin polarization effects, of the type described in 2.2.1.2. above, as a tool for investigating such energy

transfer processes. The well known model, previously developed in our laboratory, of the transfer of energy by vibrational excitation of the donor and transmission via the triplet exciton band of the host, leads to populating of the triplet states of the acceptor by a mechanism very similar to that discussed in 2.2.1.2. above. Thus one may expect anomalous intensities of the EPR lines of the acceptor. Such effects have been observed by us and are being used in the cases of various organic crystal systems to study both the thermally activated transfer, mentioned just above, and also the very low temperature energy transfer mentioned in 2.2.3. of our 1969 December 4 Report.

2.2.5. During this year we have completed a very detailed analysis (See publication, 3.6., below.) of the kinetics of the photolysis of dilute single crystal solutions of diphenyldiazomethane in 1,1-diphenylethylene and of the thermally activated reactions of diphenylmethylenes with 1,1-diphenylethylene and with diphenyldiazomethane in the same single crystal system. All of these reactions proceed without any serious disruption of the 1,1-diphenylethylene host crystal structure. This system has been investigated in our laboratory by means of electron paramagnetic resonance, electron nuclear double resonance, polarized optical absorption, and x-ray diffraction. All of these methods and techniques have nicely supplemented each other to give a detailed picture of this single crystal system. The magnetic resonance methods have

served to give a most detailed account of the local structure at the reaction site in the vicinity of the chemical impurity, diphenylmethylene. They have served to define precisely the initial state of the reaction of the methylene with the ethylene to form a cyclopropane, and also to define clearly the reaction path. This has been made possible by the ability of the distant ENDOR signals to give precise locations of molecules which are neighbors of the paramagnetic methylene. The thermally activated processes mentioned just above have been analyzed in detail as resulting from triplet triplet and triplet singlet radiationless transitions at the reactive sites.

continued on the next page...

3. Publications.

3.1. Richard H. Clarke and Clyde A. Hutchison Jr., Electron Nuclear Double Resonance of Photoexcited Anthracene Molecules in Their Lowest Triplet State in Phenazine Single Crystals.

J. Chem. Phys. 00, 000 (1971). Preprint attached.

3.2. Richard H. Clarke, Magnetic Resonance Studies of Optical Spin Polarization in Triplet State Anthracene. Chem. Phys. Letters. 6, 413 (1970). Reprint attached.

3.3. Richard H. Clarke, EPR Studies of Optical Spin Polarizations of Triplet State Anthracene. 5th Molecular Crystals Symposium. The University of Pennsylvania. 1970 June 11. Preprint attached.

3.4. Clyde A. Hutchison Jr., John V. Nicholas, and Gary W. Scott, Magnetic Resonance Absorption by Triplet State Naphthalene in Zero Magnetic Field. 5th Molecular Crystals Symposium. The University of Pennsylvania. 1970 June 11. Preprint attached.

3.5. Clyde A. Hutchison Jr., John V. Nicholas, and Gary W. Scott, Magnetic Resonance Spectroscopy of Triplet State Organic Molecules in Zero External Magnetic Field. J. Chem. Phys. 53, 1906 (1970). Reprint attached.

3.6. Clyde A. Hutchison Jr., Electron Paramagnetic Resonance and Electron Nuclear Double Resonance of Chemically Reacting

Triplet State Species in Single Organic Crystals. Proceedings of the International Union of Pure and Applied Chemistry. 00, 000 (1971). Preprint attached.

3.7. Clyde A. Hutchison Jr. and Bryan E. Kohler, Electron Nuclear Double Resonance in an Organic Molecule in a Triplet Ground State. Spin Densities and Shape of Diphenylmethylenes in Diphenylethylene Single Crystals. J. Chem. Phys. 51, 3327 (1969). Reprint attached.

3.8. Nicholas A. Ashford and Clyde A. Hutchison Jr., Paramagnetic Resonance Absorption and Triplet State Energy Transfer of Photoexcited β -Methylnaphthalene Molecules in Naphthalene Single Crystals. J. Chem. Phys. 54, 000 (1971). Preprint attached.

3.9. Clyde A. Hutchison and Donald E. O'Reilly, Viscosities of Solutions of Potassium in Liquid Ammonia and Deutero-Ammonia. J. Chem. Phys. 52, 4400 (1970). Reprint attached.