PROGRESS REPORT
ON
PARAMAGNETIC RESONANCE ABSORPTION

MASTER

FROM
THE UNIVERSITY OF CHICAGO
DIVISION OF PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY

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1. Apparatus.

1.1. During this year we have moved our experimental work from the Research Institutes Building, 5640 Ellis Avenue, to the new Searle Chemistry Laboratory, 5733 Ellis Avenue. Although this move has produced some momentary delays in our research program, the end result of the move will be acceleration of our program because:

1.1.1. For the first time since the beginning of our work on paramagnetic resonance absorption we will be located in laboratories which were designed for the types of experimental work in which we are engaged. Among the facilities which have been incorporated in the new laboratories are the following:

1.1.1.1. electrical and plumbing service from overhead stations especially designed for our magnetic resonance spectrometers;

1.1.1.2. a cryogenic room containing helium liquifaction equipment, high capacity high vacuum pumping equipment, and helium boiloff return and storage equipment, all located as a permanent installation in a location with convenient direct access to and from all of our laboratories;

1.1.1.3. a special room designed for electronics construction and the assembly of microwave plumbing of the types that we use in connection with our research;

1.1.1.4. a special chemical preparations laboratory designed for the particular types of purification procedures and crystal growing procedures which we employ in our work;

1.1.1.5. a special laboratory maintained at approximately -30°C which is ideally suited for our work on the preparation of aromatic organic crystals and for our mounting of such crystal samples in our magnetic resonance equipment.

1.1.2. We have taken this occasion to redesign and reconstruct all of our magnetic resonance spectrometers and associated equipment in such a manner as to permit more efficient utilization of the relatively limited equipment which we have.

1.2. A new 23GHz superheterodyne magnetic resonance spectrometer usable for both electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) studies has been constructed. In this spectrometer in addition to the possibility of rotation of the magnetic field about the cryostat, the crystal may also be rotated in a controllable manner inside the resonant cavity during the EPR or ENDOR experiment while the sample is being maintained at temperatures

in the vicinity of 2 K. This additional degree of freedom is of very great assistance, particularly in our investigation of photoexcited states of aromatic organic molecules in single crystals. In fact our recent success with the investigation of photoexcited benzene was made possible only by the design and construction of this new spectrometer. This is not the older spectrometer mentioned in 1.7. in our Progress Report dated 1967 December; rather this is a spectrometer in which the entire cavity assembly is immersed in a liquid helium bath which is maintained below the lambda point of helium.

1.3. The new electron spin electron spin double resonance spectrometer has been completed and is being put into use. Difficult design problems connected with the construction of a suitable bimodal cavity for the investigation of rare earth type spectra were solved by an electroforming technique.

1.4. We have perfected our spectrometer which was especially designed for the study of the kinetics of chemical reactions involving organic triplet state species in single crystals.

1.5. We have constructed a modified 10 GHz electron paramagnetic resonance spectrometer for the investigation of the intensity of the U^{+4} spectrum as a function of temperature.

1.6. New sample preparation and crystal growth equipment especially designed for purifying and growing crystals of benzene has been constructed and used.

2. Research during the calendar year 1967.

2.1. Rare earth and heavy metal ions in crystals.

2.1.1. $^{147}\text{Sm}^{+3}$ and $^{149}\text{Sm}^{+3}$ in LaCl_3 single crystals.

After extensive additional experimental work, the fitting of spin hamiltonians to the ENDOR spectra of $^{147}\text{Sm}^{+3}$ and $^{149}\text{Sm}^{+3}$ in LaCl_3 single crystals has been completed. The variable metric minimization computer program developed last year was used for this purpose. The physical interpretation of the spin hamiltonian parameters has yielded values of nuclear magnetic dipole moments, of ratios of nuclear electric quadrupole moments for the 2 isotopes, of ratios of nuclear magnetic dipole moments for the 2 isotopes, and of the parameters, $\langle r^{-3} \rangle$, for the Sm^{+3} f electrons, as well as information on the sizes of core polarization effects.

One of the new spectrometers mentioned in 1.1.2. has been designed for the purpose of investigating the super-hyperfine interactions, between rare earth trivalent ions and Cl^- ions in LaCl_3 crystals, which were mentioned last year.

2.1.2. U doped ThO_2 single crystals.

In addition to the results reported last year, we have doped ThO_2 single crystals with ^{235}U and have obtained the $^{235}\text{U}^{+4}$ nuclear hyperfine patterns arising from the f electrons of the Γ_5 state of the U^{+4} at the Th^{+4} site. The fitting of spin hamiltonians to these spectra and to those reported last year has been completed and the physical interpretation of the spin hamiltonian parameters has yielded interesting information on the f electron states in this crystal. Moreover we have also completed an investigation of variation of intensities of the U^{+4} spectra with temperature which has permitted a determination of the $\Gamma_1 - \Gamma_5$ energy separation. This work is closely related to the previous magnetic susceptibility studies of microcrystalline $\text{UO}_2 - \text{ThO}_2$ mixtures which have been made in our laboratory.

2.1.3. NpF_6 .

One of the new spectrometers mentioned in 1.1.2. has been constructed for the investigation of the superhyperfine interaction between F nuclei and f electrons in NpF_6 molecules. The metal vacuum lines for preparation of NpF_6 and for the growth of crystals has been completed and successfully used.

2.1.4. ENDOR dynamics.

Studies of electron spin electron spin double resonance and of the dynamics of ENDOR in rare earth ions in single crystals has been begun with a view toward obtaining insight into the dynamical aspects of the processes which produce the ENDOR signals which we have been using in our laboratory as a spectroscopic tool for many years. These studies will also serve the purpose of developing new practical and generally useful spectroscopic methods.

2.2. Organic molecules in triplet states.

(We report here not only the work outlined in 1.3. of the Revised Proposed Technical Program 1968 February 12, but also, because of its close relevance, the work mentioned in 0.2. which was excluded from the proposed program support because of insufficient funds.)

2.2.1. Electron nuclear double resonance (ENDOR).

2.2.1.1. Benzene single crystals.

The investigation of the ENDOR spectra of triplet state protobenzene in deuterobenzene single crystals is nearly completed. This has permitted the determination of the types and extents of distortions of the photoexcited molecule from a planar, regular hexagonal shape in the crystal. It has also given the details of the not hexagonal distribution of spin angular momentum over the photoexcited benzene molecule.

2.2.1.2. Diphenylmethylenes in diphenylethylene single crystals.

The distant ENDOR spectra of diphenylmethylenes in diphenylethylene crystals, arising from protons on the host molecules, has been utilized to determine the precise arrangement of host molecules in the vicinity of structure sites in which a diphenylmethylenes molecule has been substituted for a host molecule. This has been a very important accomplishment in connection with our investigation by EPR methods, of the kinetics of the chemical reaction of guest molecules with the host molecules in the single crystal system.

2.2.1.3. α -naphthylmethylenes. An investigation of the ENDOR spectrum of α -naphthylmethylenes has been begun with a view toward a precise determination of the molecular structure of this ground state triplet species in a single crystal.

2.2.1.4. Phenanthrene.

An ENDOR study of triplet state phenanthrene in diphenyl single crystals is nearly completed. This study has permitted a more precise determination of the spin densities than was possible in our previous EPR studies. It has also given us detailed information concerning the orientation of the photoexcited phenanthrene guest molecules in the diphenyl crystal.

2.2.2. Electron paramagnetic resonance (EPR).

2.2.2.1. Zero field line shapes.

The theoretical discussion of the shapes of magnetic dipole absorption lines of randomly oriented triplet state aromatic molecules at low magnetic field strengths, i.e. under conditions in which the electron Zeeman interaction is small relative to the zero field splittings, has been completed and some of the necessary numerical calculations have been made.

2.2.2.2. Temperature and pressure effects.

The studies of the variation of zero field splittings, in triplet state aromatic molecules in single crystals, with temperature and pressure have been extended.

2.2.3. EPR studies of reaction kinetics in single crystals.

The EPR studies of the kinetics of the chemical reactions of diphenylmethylenes molecules, dilutely and substitutionally dispersed in a host diphenylethylene single crystal, have been completed and analyzed. The x-ray determination of the detailed structure of the host crystal is in progress.

2.2.4. Triplet state energy transfer.

We have begun the preparation and purification of benzene single crystals for the study, by EPR methods, of triplet state energy transfer processes in this crystal system.