COO-3435-27

MASTER

MICROWAVE-OPTICAL DOUBLE RESONANCE SPECTROSCOPY

Progress Report
for the period
February 1, 1976 - January 31, 1977

D. W. Pratt
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

November 1, 1976

Prepared for
THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. E-(11-1)-3435

DISCLAIMER

ABSTRACT

Zero-field and high-field optical detection of magnetic resonance (ODMR), electron paramagnetic resonance (EPR), and optical spectroscopy experiments have been performed on several systems in order to further basic knowledge of the structure, reactions, and response to radiation of atoms, molecules, and ions in their ground and/or excited electronic states. Particularly noteworthy results for the present contract year include the determination of the complete magnetic and optical properties of the lowest triplet states of 1-chloro, 1-bromo, and 1-iodonaphthalene, the development of a microscopic model for the intramolecular heavy-atom effect in the $^3(\pi,\pi^*)$ states of aromatic molecules, a detailed analysis of the angular dependence of the hyperfine and quadrupole structure in triplet 1-bromonaphthalene, observation of proton hyperfine structure in the hf ODMR spectra of short-lived triplet states, a definitive paper on the relative importance of spin delocalization and second-order spin-orbit coupling effects in $^3(n,\pi^*)$ benzophenone (a phototype photochemical system), a detailed analysis of the level-anticrossing spectra of several triplet state benzophenones which exhibit hyperfine structure in the cross-relaxation region (thus permitting the determination of key magnetic parameters in the complete absence of perturbing microwave or radiofrequency fields), optical detection of ground-state NQR transitions in host crystal molecules, the observation of strong radiofrequency transitions near avoided crossing points in Zeeman energy level diagrams of photoexcited triplet states, the construction of zero-field ODMR, ODENDOR, and hf ODENDOR spectrometers, measurements of the activation parameters for ring interconversions of several free radicals containing five- and six-membered rings, and experimental proof that the triplet state of trimethylenemethane (a key reactive intermediate in organic chemistry) is the ground state.

ANNUAL PROGRESS REPORT, 1976

A. Summary

The principal objective of this research project is to develop basic knowledge about the structure of matter and its interaction with radiation fields through the exploration of new physical and chemical phenomena. As indicated in the enclosed report, the primary emphasis of this year's contract work has been on short-lived chemical species which are produced by irradiation of organic solids with high energy X-rays and ultraviolet light. These species include electronically-excited molecules with lifetimes in the range of 1 μsec to 10 sec and ground state organic free radicals with lifetimes in the range of minutes to days. Because of their short lifetimes, new techniques and methods of sample preparation have been utilized to study their structure and kinetic behavior. These techniques include electron paramagnetic resonance (EPR) spectroscopy, optical spectroscopy, optical detection of magnetic resonance (ODMR) spectroscopy both in the presence and absence of external magnetic fields, microwave-induced delayed phosphorescence (MIDP) spectroscopy and level anticrossing (LAC) spectroscopy.

Reported herein are the results of several such spectroscopic studies of a wide variety of systems, from biological molecules containing transition metal ions to small free radicals containing only three or four atoms. We have shown how the ODMR method can be used to obtain an extremely detailed picture of the electronic distributions and structures of molecules which "live" for only a few milliseconds, and which, in spite of their short lifetimes, are key intermediates in photochemical reactions, *i.e.*, chemical reactions initiated with light. We have

demonstrated that EPR spectroscopy, together with powerful computer programs, can be used to analyze the nature of changes in the geometry of molecules which occur in the microsecond time range. We have developed methods for obtaining the optical spectra of reactive free radicals at room temperature using an "everyday" experimental setup. We have also extended treatments of the fundamental equations of quantum mechanics which govern the behavior of paramagnetic systems in the solid state, studied the motion of mobile excitations in organic crystals at low temperatures, and developed a "paramagnetic resonance without microwaves" technique for obtaining information about cross-relaxation behavior involving two different spin systems in contact with the same thermal reservoir. It is anticipated that these results will find application in a wide variety of fields ranging from synthetic organic chemistry, where photochemical methods are finding increased use in natural product construction, to energy conversion, where storage of energy at low temperatures is becoming an increasingly attractive alternative to more conventional methods.

B. Detailed Report

1. Structural Studies on Phosphorescent Triplet States.

a. Halogenated benzenes.

Since initiation of this contract, several reports describing various features of the ODMR spectra and structure of the lowest triplet states of halogenated benzenes have been submitted (COO-3435-4,8,10, and 13). Highlights of these papers include (1) the development of variable temperature methods for the determination of the absolute signs of the zero-field (zf) parameters, (2) the first observation of well-resolved hyperfine structure in the ODMR spectrum of a triplet-state molecule, and (3) the definitive assignment of the orbital symmetry of the lowest triplet states of *p*-dihalobenzenes as B_{1u}. However, a number of important questions about these species remain unanswered, most notably those having to do with the effect of second-order spin-orbit (SO) coupling on their optical and magnetic properties. These were described in detail in last year's proposal. It was hoped that these problems could be resolved in the present contract year. Unfortunately, due to a considerable reduction in the proposed budget ($73,881 → $40,000), funds for the necessary personnel were not available and no further work on this problem has been carried out. This will be rectified in the coming year if the proposed budget is approved.

b. Halogenated naphthalenes.

Since the radiative and non-radiative decay constants, intersystem crossing rates, and $\underset{\sim}{g}$ tensor anisotropy of a triplet state molecule depend on the intramolecular SO interaction, one expects that a correlation may exist among these parameters for a given system. In addition, it is well known that the SO interaction can influence the principal values and directions of the fine structure tensor, $\underset{\sim}{D}$. To date, the task of correlating these parameters has proven difficult, especially since there is no single system for which all of the necessary optical and magnetic parameters have been determined. For this reason, we have undertaken such a study of a series of halonaphthalenes, and the work on 1-halonaphthalenes (1XN, X = Cl, Br, I) is now essentially complete. This research has been done largely by Dr. Kothandaraman.

The results of ODMR experiments on triplet 1BN in high-field (hf) and triplet 1IN in both zf and hf have been submitted previously (COO-3435-12,17, and 22). In this work, it was shown that (1) both the absolute signs and magnitudes of each of the zf parameters as well as the principal values and directions of the $\underset{\sim}{g}$, quadrupole, and hyperfine tensors of emitting triplet states could be determined using ODMR techniques, (2) the zf parameters of the lowest triplet states of the heavier halogenated naphthalenes are considerably perturbed from those of $^3B_{2u}$ naphthalene, and (3) these effects could only be explained if SO coupling between triplet states was taken into account. In addition, the first measurement of an asymmetry parameter of a halogen atom field gradient tensor in an excited state molecule was reported and the principal values of the hyperfine tensor of an iodine atom attached to an sp^2-hybridized carbon atom were determined for the first time.

In a summary paper which is now in the final stages of preparation, we will report the observation and analysis of the zf ODMR and EPR spectra of the $^3(\pi,\pi^*)$ states of 1CN and 1BN, their halogen atom quadrupole and hyperfine parameters, their $\underset{\sim}{g}$ tensors, a tentative analysis of the phosphorescence spectra of 1CN, 1BN, and 1IN in a durene host single crystal using AM-PMDR techniques, and the total decay rates, relative radiative decay rates, relative populating rates, and steady-state populations of each of the spin sublevels of each of the three species using MIDP and microwave fast passage techniques. Comparison of the data for the different molecules provides, for the first time, a microscopic picture of the intramolecular heavy atom effect on both the optical and magnetic properties of a prototype $^3(\pi,\pi^*)$ state. In related work, we are presently carrying out both zf and hf ODMR experiments on perdeutero-1-bromonaphthalene in normal and perdeutero/durene host crystals in an effort to gain information about the radiationless processes in excited triplet states in molecular crystals. These same crystals will be used to confirm results already obtained on the angular dependence of the bromine nuclear quadrupole and hyperfine interactions, which form the nucleus of a second paper already in preparation, to be submitted to the Journal of Chemical Physics by the end of the contract year.

A particularly noteworthy finding made by Kothandaraman is that extremely high resolution hf ODMR spectra can be obtained by operating the spectrometer at low power and utilizing field modulation. For example, the hf ODMR spectrum of 1-bromonaphthalene in durene with $\underline{H}||\underline{x}$ exhibits proton hyperfine structure from the three magnetically-equivalent α protons and ^{79,81}Br hyperfine structure from the αbromine. The significance of this particular result is that it shows that the spin density distribution in $^3B_{2u}$ naphthalene is not seriously affected by the substitution of bromine in the 1-position; clearly, application of this method to other systems will now provide as detailed a description of the electronic structure of short-lived excited states as is presently available for ground states via ordinary EPR.

In separate experiments, Grandy has examined the EPR spectra of triplet 2-chloronaphthalene in several host crystals (COO-3435-26). A biphenyl host was found to give high-quality spectra, and proton hyperfine structure is easily resolved with $\underline{H}||\underline{x}$ in triplet 2-chloronaphthalene ($\tau \sim$ 0.45 sec). Further experiments on this system, as well as on other 2-halonaphthalenes, using the new zero-field instrument are in progress. The principal goal of these experiments is to determine the effects of the position of substitution and neighboring atom spin densities on the SO contributions to $\underset{\sim}{D}$ and $\underset{\sim}{g}$.

c. Excimers and intermolecular heavy-atom effects.

No further work on this project has been carried out in the present contract year, again because of a lack of funds.

d. Aromatic carbonyls.

Preliminary reports of hf ODMR experiments on the lowest triplet state of benzophenone and several of its derivatives have been submitted previously (COO-3435-19 and 23). Accompanying this report are copies of a manuscript entitled "Optically-Detected Magnetic Resonance Spectra of the Lowest Triplet States of Benzophenone, ^{13}C-Benzophenone, and Three 4,4'-Dihalobenzophenones" which has been submitted to the Journal of Chemical Physics. A summary of the principal conclusions of this paper is given below.

An analysis of the orientational dependence of the optically-detected magnetic resonance spectra of $^3(n,\pi^*)$ benzophenone, carbonyl-^{13}C-benzophenone, and three of its halogenated derivatives in 4,4'-dibromodiphenylether host crystals is presented. By using the experimentally-measured g values to evaluate spin-orbit contributions arising from coupling with triplet states, and *ab initio* estimates to correct for spin-orbit effects involving singlet states, a "dipolar-only" zero-field scheme of triplet benzophenone has been constructed. Based on a comparison of this scheme with the spin-spin contributions to $\underset{\sim}{D}$ in $^3A_2$ formaldehyde, we have argued that a significant fraction of the total spin density in the lowest triplet state of benzophenone resides on the aromatic rings, as originally suggested by Hochstrasser and Lin. This view is supported by the additional findings that (a) the 2s and π-orbital spin densities at the carbonyl carbon are much smaller (0.008 and $\leq$ 0.14) than those estimated for $^3(n,\pi^*)$ H_2CO (0.036 and 0.34), (b) the C_1-C(O)-C_1' fragment in $^3(n,\pi^*)$ benzophenone is most likely planar, unlike the corresponding atoms in the lowest triplet state of formaldehyde, (c) the $\underset{\sim}{D}$ tensor in triplet benzophenone has its $\underline{x}'$ and $\underline{y}'$ axes rotated by 20°

relative to the x and y symmetry axes of the C_1-C(O)-C_1' fragment, (d) both the principal values and directions of $\underset{\sim}{D}$ are affected significantly by substituents in the para ring position, and (e) ring atom hyperfine structure has been observed in triplet 4,4'-DFBP and 4,4'-DBBP which suggests that $\rho_{2p_\pi}^{C4} \geq 0.10$ in the lowest triplet state of benzophenone itself. A spin-orbit coupling model involving one-center terms on the halogen atoms has been proposed which accounts for most of the observed substituent effects.

These findings are of great chemical significance since $^3(n,\pi^*)$ benzophenone is widely regarded as the most representative example of a broad class of photochemically-important molecules. For this reason, Brode is presently carrying out further experiments which are designed to determine the complete spin density distribution and angle of ring twist in the lowest triplet state of benzophenone. This work is progressing rapidly; we have just finished a complete analysis of the carbonyl-^{13}C hyperfine tensor by studying the angular dependence of the ^{13}C-hyperfine splitting exhibited by a perdeutero-^{13}C-benzophenone guest triplet and have designed an ODENDOR helix and cavity for use in the study of ^{17}O and ^{19}F-labelled molecules in both zf and hf.

In related work, we have initiated zf ODMR experiments on several of the isotopically-labelled benzophenones (^{12}C-BP-$\underline{h}_{10}$, ^{12}C-BP-$\underline{d}_{10}$, ^{13}C-BP-$\underline{h}_{10}$, ^{13}C-BP-$\underline{d}_{10}$, and ^{17}O-BP-$\underline{h}_{10}$) in order to examine some interesting and unexpected effects, namely the dependence of the zf parameters and sublevel radiative properties on isotopic substitution.

e. Aromatic azines.

No further work on this project has been carried out during the present contract year.

2. Solid State Effects.

a. Level anticrossing and cross relaxation.

In a recent communication (COO-3435-16), we have described the direct observation of level anticrossing (LAC) and mixing effects between a pair of Zeeman sublevels of a phosphorescent triplet state using ODMR methods. These experiments were performed by examining the frequency dependence of the separations and relative intensities of the "$\Delta m_S = \pm 1$" and "$\Delta m_S = \pm 2$" microwave transitions of an excited triplet state molecule with a magnetic field directed along a principal axis of the fine-structure tensor in oriented single crystals at 1.6°K. At these temperatures, the populations of the Zeeman sublevels are governed primarily by independent radiative and (non-radiative) processes which connect the triplet state to the singlet state manifold. Consequently, because of the mixing of the sublevel wavefunctions, one expects and indeed observes changes in the steady-state phosphorescence intensity in the vicinity of the avoided crossing region. The observation and analysis of these changes in several $^3(n,\pi^*)$ benzophenones, which occur in response to time-independent perturbations (*i.e.*, without coherent optical, microwave, or radiofrequency excitation), constitute the subject of a second paper which has been submitted to the *Journal of Chemical Physics* ~~(preprint enclosed)~~.

This paper reports the observation and analysis of magnetically-induced changes in the phosphorescence intensities of triplet state benzophenone, carbonyl-^{13}C-benzophenone, and three 4,4'-dihalobenzophenones in single crystals of 4,4'-dibromodiphenylether at 1.6°K. The results can be interpreted in terms of two effects; (1) anticrossings of two different electron-nuclear spin manifolds of the guest molecule and (2) cross relaxation between the spin system of the guest and that of the host. At fields where anticrossings occur, the mixing between the spin states is strong and no hyperfine structure is observed. However, by comparing the results for the different molecules, it is shown that the hyperfine interaction plays a key role in determining the minimum spectral width of the "transitions". At fields where cross relaxation predominates, the mixing between the spin states is weak and hyperfine and quadrupole splittings of both the guest and host can be resolved. The magnetic parameters obtained by fitting the "spectra" are in excellent agreement with those determined by ODMR techniques. Thus, experiments of this type can be utilized to provide information about the fine-structure, $\underset{\sim}{g}$, hyperfine, and quadrupole tensors of emitting paramagnetic species in the complete absence of perturbing radiofrequency or microwave fields.

The existence of strong cross relaxation effects involving both the guest and host spin in these crystals suggests a wide variety of new experiments. For example, we have recently discovered that one can make use of the contact between the two spin systems to <u>optically-detect</u> transitions in the nuclear spin manifold of the host bromine atoms; <u>i.e.</u> do NQR spectroscopy on ground-state molecules <u>via</u> optical detection. A short paper describing these results is in preparation. Furthermore, it is conceivable that systems of this type may be ideal spin refrigerators for use in energy conversion processes. Several approaches towards understanding the mechanisms and rates of spin relaxation in these systems are described in the accompanying proposal.

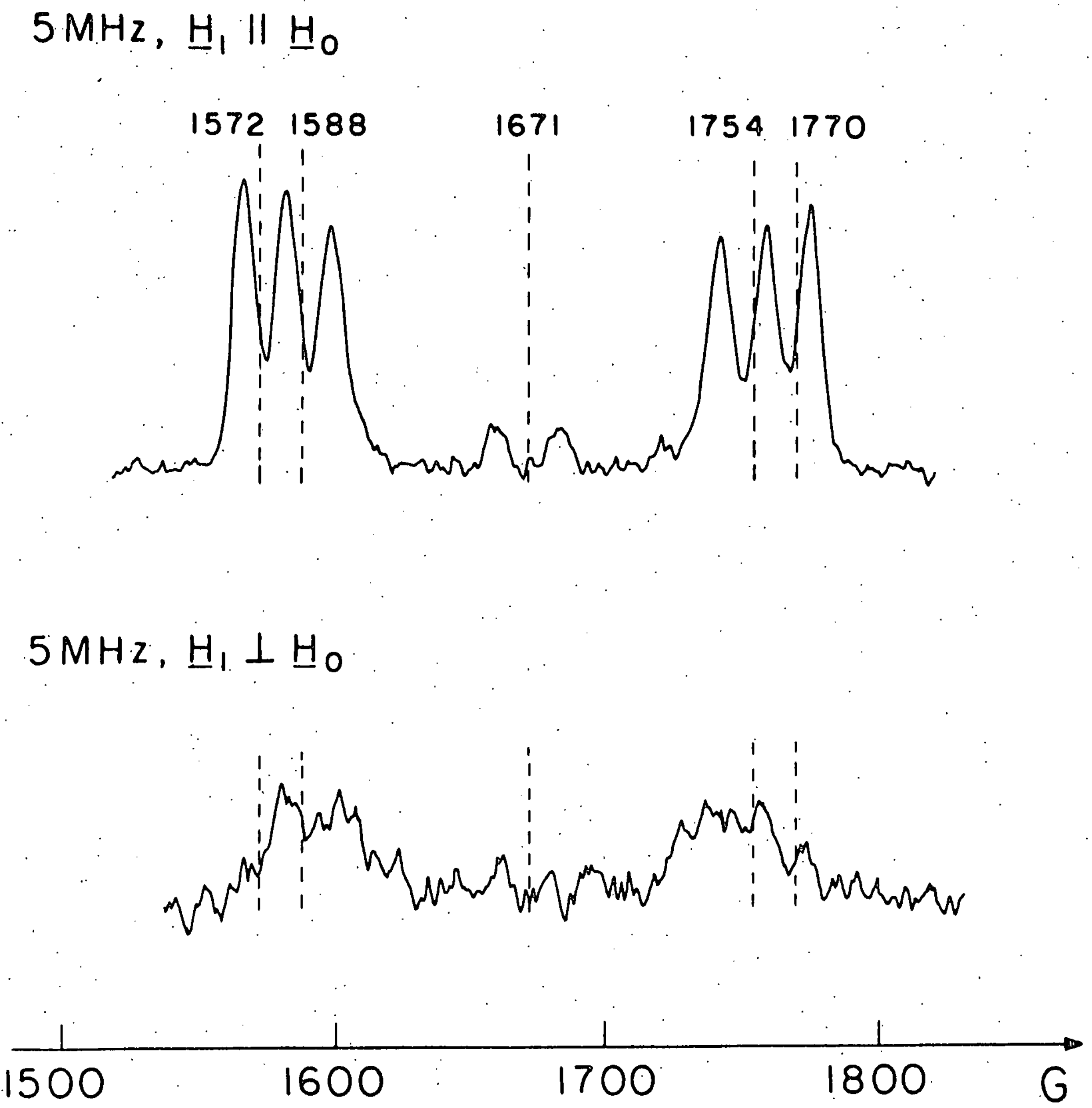
Examination of the Figures in the LAC manuscript (particularly Fig. 7) shows that the detailed behavior of the combined electron-nuclear spin states of the guest is extremely complex in the avoided crossing region. For this reason, we were curious to see whether we could gain more insight into this process by carrying out the following experiment. A crystal of 4,4'-dibromodiphenylether containing a small amount of oriented benzophenone-$\underline{d}_{10}$ was mounted in the TE012 microwave cavity of the hf ODMR spectrometer together with a small loop of wire which would support a radiofrequency (RF) field. A combined ODMR/LAC experiment was then carried out to orient the crystal so that the field was exactly parallel to the $\underline{z}'$-axis of the fine-structure tensor. Then, with the microwaves turned off, the "static" magnetic field was swept from 1500-1800 G while monitoring the AC component of the phosphorescence intensity in the presence of a weak (< 1 mW) amplitude - modulated RF field. The resulting optically-detected radiofrequency spectra are shown in the accompanying Figures, with ν_{RF} = 5 and 85 MHz and with the RF field vector either parallel or perpendicular to the static field vector. Quite to our surprise, several strong transitions displaced symmetrically about the LAC field of 1671 G are observed. Furthermore, the transitions are clearly polarized, and exhibit a strong dependence on field and frequency. This kind of experiment has been done over the frequency range 0.1 - 200 MHz for several different guest molecules, and promises much in the way of new information about both LAC and CR processes in molecular crystals, as a paper now in preparation will show.

b. Excitons.

In separate experiments on neat 4,4'-dichlorobenzophenone (COO-3435-19 and in preparation) we have also discovered excitonic behavior in the ODMR spectra of the lowest triplet state in high field. These results have not been published earlier because we wished to further study the detailed line-shape exhibited by the exciton in zero field; these experiments are now essentially complete. An interesting aspect of this problem is that the observation

Radiofrequency Experiments

^{12}C-BP-$\underline{d}_{10}$ / DDE , $\underline{H}_0 \parallel \underline{z}$

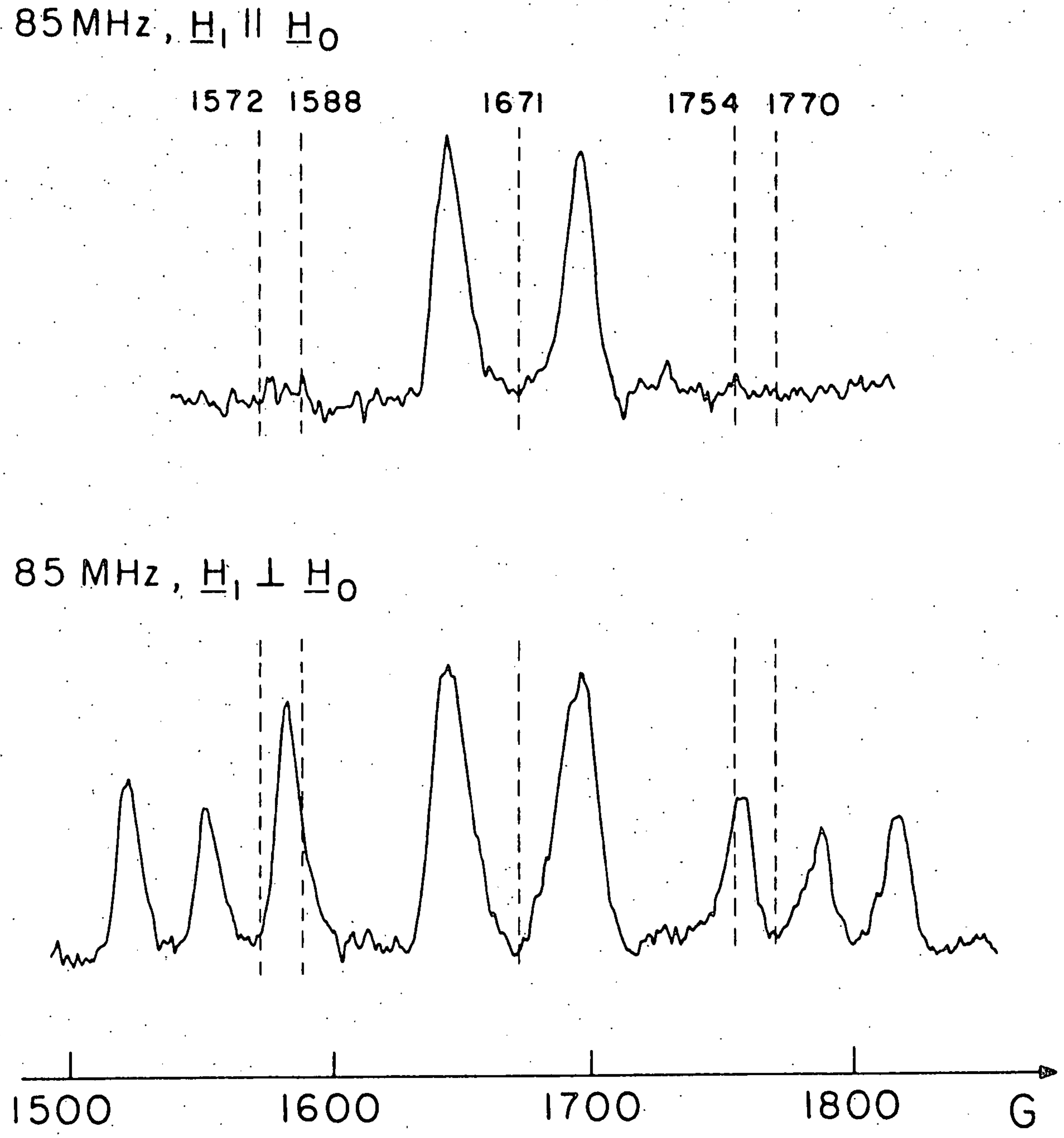


5 MHz, $\underline{H}_1 \parallel \underline{H}_0$

5 MHz, $\underline{H}_1 \perp \underline{H}_0$

Radiofrequency Experiments

^{12}C-BP-$\underline{d}_{10}$/DDE, $\underline{H}_0 \parallel \underline{z}$



85 MHz, $\underline{H}_1 \parallel \underline{H}_0$

85 MHz, $\underline{H}_1 \perp \underline{H}_0$

of such behavior is inconsistent with the concept of a localized excitation in triplet benzophenone itself; i.e., that it appears that both the spin density and excitation "density" are delocalized in the lowest triplet state of this molecule.

c. Plastic crystals and molecular freedom.

The idea of rotation inside a crystal is incompatible with the ordinary definition of a crystal lattice which is considered to be made up of atoms, molecules, or ions whose positions are fixed. However, there are some crystals which are composed of almost spherical molecules which possess unusual mobility and are called "plastic" crystals. Adamantane is a good example. The fact that it is possible to isolate a free radical in a matrix of adamantane, and that the EPR spectrum of a free radical is extremely sensitive to its motion, suggests that it should be possible to use the radical as a label to provide information about the nature of the motion (translational as well as rotational) in plastic crystals.

In preliminary experiments of this type, Edelheit has shown that the overall rotation and/or translation of the cyclohexyl radical in adamantane becomes restricted at temperatures near 100°K. A computer simulation of the EPR spectrum of this radical at different temperatures is in progress, and further experiments on simpler radical probes are anticipated. A report on this work was given in an invited paper at the first Gordon Conference on Plastic Crystals and Molecular Freedom in January 1976.

3. Experiments Involving Time Resolution.

a. Spin-lattice relaxation.

No further work on this problem has been carried out during the present contract year.

b. Population and depopulation rate constants.

A zero-field ODMR spectrometer has been constructed with the expert technical help of Kothandaraman and with the financial support of the Commonwealth of Pennsylvania. The spectrometer consists of an evacuable liquid helium cryostat, a source of microwaves (0.1-18 GHz), a helix in which the sample is placed, coupling of the helix to the microwave source via a coaxial adapter, an optical excitation source, a 3/4 meter Spex monochromator with computer drive capability, photomultiplier and photon-counting detection circuits, a lock-in amplifier, various electronic delay and trigger units, an XY recorder, and a signal averager/digital computer (Nicolet LAB-80).

This spectrometer can be used for several different types of experiments, including high resolution optical spectroscopy, zero-field ODMR spectroscopy, and microwave-induced delay phosphorescence (MIDP) spectroscopy. In a typical zf ODMR experiment, the microwave frequency is scanned and changes in the intensity of isolated phosphorescence bands are detected. The signal-to-noise ratio in such experiments is poor unless the percent change in intensity is large (> 10%). Phase-sensitive detection techniques improve the sensitivity considerably; in this method, the microwave power is 100% amplitude modulated at a desired frequency by applying the output of a square wave generator to the microwave oscillator. The same square wave is used as a reference input for the lock-in amplifier. Since only those signals modulated at the reference frequency are detected, the output of the amplifier corresponds to the microwave modulation of the phosphorescence emission; hence, the output of the amplifier as a function of microwave frequency yields the zf ODMR spectrum of the sample.

In the MIDP experiment, the sample is irradiated with the exciting light for a period which is sufficient to establish steady-state conditions.

At this time, an electronically-controlled shutter closes and a pulse from the shutter control unit triggers a delay box. The delay unit is capable of time delays of 10^{-6} to 10^{2} sec which can be preset to the value desired. At the end of this delay, a trigger pulse is applied to the microwave source, the oscilloscope, and the signal averager. The output of the phototube is fed to the oscilloscope or to the averager, and shows directly the effect of applying a microwave pulse after the system has had some time to decay. Such information can then be used to provide a detailed description of the kinetic behavior of the system.

Successful phosphorescence, zf ODMR, and MIDP experiments using this new spectrometer have been carried out in the present contract year, especially on the 1-halonaphthalenes (vide supra), and extension of this work to several other systems is in progress. The spectrometer can also be easily adapted for several other types of experiments; of particular importance here is the Nicolet LAB-80 system which allows one to rapidly accumulate and analyze the data.

4. ODMR Experiments on Doublet States.

For several years now we have been interested in the extension of ODMR techniques to electronically-excited states of free radicals. Some progress on this problem has been made in the past year. Specifically, Edelheit has assembled the necessary instrumentation for electron-spin echo experiments using the high-field ODMR spectrometer, Biomation 805 transient recorder, and LAB-80 system. Our first experiments of this type will be performed in the very near future on excited triplet states, and if the echoes are successfully observed, we will apply the technique to the lowest excited doublet state of the benzyl radical before the end of the contract year. It is hoped that this new method will avoid the short lifetime problem associated with spin-allowed optical transitions, and be extremely useful in time-resolved studies of transient paramagnetic species.

5. Trapped-radical Spectroscopy.

a. Free radicals containing five-membered rings.

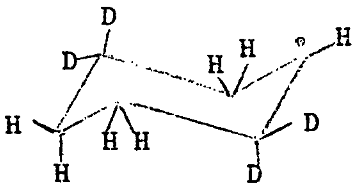
Parise and Baer have complete their studies of the conformational properties of several radicals derived from cyclopentanone and cyclopentene. Somewhat to our surprise, we have discovered that many of these species show temperature dependent hyperfine splittings in their EPR spectra, and we are in the process of analyzing the data to obtain information about the nature of conformational change in these systems. This analysis requires further experiments to obtain well-defined low-temperature limits for some of the β protons hfs; this work is being done by Baseman using the new DISPLEX liquid helium refrigerator.

b. Free radicals containing six-membered rings.

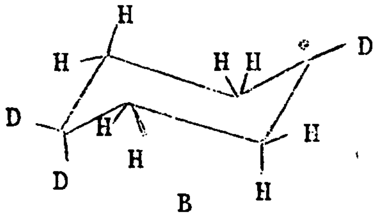
EPR spectra have been obtained for radicals produced by X-irradiation of cyclohexanone and various alkyl-substituted cyclohexanones trapped in an adamantane matrix by Walter (COO-3435-21). Temperature variations of these spectra permit determination of the enthalpy and entropy of activation for interconversion between the two half-chair conformations. In those cases where the two conformations have intrinsically different energies, the enthalpy and entropy differences between conformations are determined. For 2-cyclohexanonyl radical, the enthalpy of activation is 3.90 ± 0.07 kcal/mole and the entropy of activation is -2.3 ± 0.3 e.u. Methyl substitution on C_3 or C_5 gives a radical with activation parameters similar to the parent radicals; indicating only moderate realignment of atoms during the conformational change. Methyl substitution on C4 gives a radical with lower activation parameters, which are interpreted to indicate that the conformational change occurs by a folding along the diagonal through the radical site. Larger groups attached to C_3 influence enthalpy and entropy differences between conformations much less than when they are attached to C_5. Very large groups attached to C_5 apparently flatten the ring; it is not known whether this is a matrix effect. Deuteration seems to cause a slight reduction in the activation parameters for 2-cyclohexanonyl radical.

EPR spectra have also been obtained for radicals produced by X-irradiation of cyclohexene and various alkyl-substituted cyclohexenes trapped in adamantane matrix by de Tannoux (COO-3435-24). These have been analyzed using the programs developed by Walter in this laboratory. For cyclohexenyl radical itself, the enthalpy of activation is 6.81 ± 0.58 kcal/mole and the entropy of activation is -0.04 ± 2.38 e.u. Methyl substitution on C_1 gives a radical with activation parameters similar to the parent radical. Methyl groups attached to C_5 increase the activation parameters significantly. On the basis of these observations, it is suggested that cyclohexenyl radicals exist in two conformations of the same energy which are of the "envelope" type, with C_1, C_2, C_3, C_4, and C_6 coplanar. A model involving a planar transition state for the interconversion process is proposed which accounts for most of the experimental results. This work is being prepared for publication.

We have also made significant progress on a most interesting problem involving the cyclohexyl radical. High-resolution EPR spectra of this species exhibit an 0.9 G hyperfine triplet due to two equivalent protons at temperatures between 100-350°K. The question which arises is this; are the coupling protons which are responsible for this splitting two of the four γ-protons or the two δ-protons? If the latter, then it is reasonable that they remain equivalent at temperatures below and above the coalescence temperature for ring interconversion (∿200°K), i.e., in the "slow" and "fast" exchange limit for the β-protons. On the other hand, if these splittings are produced by two of the γ-protons, then the observation of only two (rather than four) of these protons suggests that the interconversion process which averages the β-proton hyperfine splitting involves the flipping of only one side of the ring! To resolve this problem, we have designed and executed a synthesis of 1,1,4,4-tetradeuterocyclohexane. On γ-irradiation in adamantane, two radicals will be produced:



A



B

The overall width of the EPR spectrum of radical B will exceed that of radical A; the presence or absence of the 0.9 G triplet in the spectrum of B will make possible the assignment of the triplet to the γ- or δ-protons. If the former is correct, it will be necessary to revise our current understanding of the conformational motions in radicals containing six-membered rings.

c. Trimethylenemethane.

In a paper which has just been published in the Journal of the American Chemical Society (reprints enclosed), we report a study of the relative intensity of the EPR spectrum of triplet trimethylenemethane over the temperature range 20-80°K. Curie law behavior was observed, thus demonstrating unequivocally that the triplet state of this fundamental species is the ground state. We also discovered in the course of these experiments that the zf parameters of trimethylenemethane exhibit a striking temperature dependence, varying by 25% from 20-80°K. A model to explain this unexpected behavior is being devised. In addition, we are presently carrying out studies of the optical spectrum of this molecule using the Displex refrigerator and the Beckman M VI spectrophotometer, and plan EPR experiments on trimethylenemethane oriented in host single crystals in the near future.

d. Optical studies of free radicals.

Jordan has described experiments which for the first time provide a method for obtaining and analyzing the optical absorption spectra of reactive free radicals at room temperature (COO-3435-20). Classes of free radicals studied by this method include alkyl, aminoalkyl, alkylimino, 2-alkanonyl, allyl, cyclohexadienyl, benzyl, and azabenzyl radicals. He also showed that certain free radicals exhibit strong, visible fluorescence when irradiated with uv light, and discovered that the absorption intensity of multiplicity-forbidden transitions in singlet and doublet state species is enhanced relative to spin-allowed transitions by at least three orders of magnitude. An analysis of these results in terms of MO theory is given, and experiments designed to obtain the EPR spectra of electronically-excited states of free radicals are described in his thesis. This work is being prepared for publication.

6. Other experiments.

In addition to the work described above, several other experiments on totally-unrelated systems have been performed in our laboratories and supported (in part) by this contract. Most of these are collaborative efforts involving other principal investigators in the Pittsburgh area. The following is a partial list of these projects:

a. Spin-label studies of E.-coli membrane vesicles, with C. Ho, Department of Biophysics.

b. Magnetic resonance study of energy-coupled active transport in E.-coli membrane vesicles, with C. Ho, Department of Biophysics.

c. Intermediate states of spin-labeled HbA, with C. Ho, Department of Biophysics.

d. Magnetic resonance studies of hemoglobins and their implications in the structure-function relationships in human normal and abnormal hemoglobin, with C. Ho, Department of Biophysics.

e. An EPR study of maganese(II) binding to 5'-ATP, hemoglobin, and hemocyanin, with N. Li, Department of Chemistry, Duquesne University (COO-3435-15).

f. An EPR study of spin exchange in spin-labeled fatty-acids, with D. Evans, Department of Chemical Engineering, Carnegie-Mellon University.

g. EPR studies of lunar samples, with B. Hapke, Department of Earth and Planetary Sciences.

h. Ring closure in trimethylenemethane, with P. Dowd, Department of Chemistry.

i. Study of the emission spectra of Al_2O_3 powders, with W. Kehl, Gulf Research and Development.

j. EPR studies of color centers in transition metal oxides, with J. W. Rabalais, Department of Chemistry.

k. Biochemical applications of EPR, with O. Gowron, Duquesne University, and F. deRubertis, Veterans Administration Hospital. The latter experiments involve detection of free radicals in chemical carcinogenisis.

C. Supporting Information

1. Personnel.

a. Principal Investigator.

Dr. D. W. Pratt; A. B., Princeton University, 1959; Ph.D., University of California, Berkeley, 1967. Associate Professor of Chemistry. Has devoted approximately 6 months to this project.

b. Research Associate.

Dr. G. Kothandaraman; B.S., University of Madras, 1966; Ph.D., University of California, Davis, 1973. Supported by USERDA Contract No. E-(11-1)-3435.

c. Research Assistants.

Ms. H. J. Barrows, B.A., Otterbein College, 1975. Teaching Assistant in Chemistry. Entered medical school in July, 1976.

Mr. P. F. Brode, B.S., Frostburg State College, 1974. Teaching Assistant in Chemistry, supported in part by USERDA Contract No. E-(11-1)-3435.

Ms. E. B. Edelheit, B.S., University of Illinois, 1972. Teaching Assistant in Chemistry, supported in part by USERDA Contract No. E-(11-1)-3435.

Mr. D. W. Grandy, B. S., University of Pittsburgh, 1973. Teaching Assistant in Chemistry. Received M.S. in April, 1976.

Two additional research assistants will be added to the group before the end of the contract year.

d. Technicians.

Mr. R. J. Baseman, undergraduate in Chemistry. Supported in part by USERDA Contract No. E-(11-1)-3435.

Mr. R. F. Klemens, undergraduate in Chemistry.

Mr. K. A. Kraft, undergraduate in Chemistry at Westminster College. Supported in part by USERDA Contract No. E-(11-1)-3435.

Mr. F. M. Rommel, undergraduate in Chemistry at Bethany College.

Ms. C. Soltau, undergraduate in Chemistry.

2. Bibliography.

a. Previous reports.

COO-3435-1. Progress report for the period February 1, 1971 - January 31, 1972.

COO-3435-2. "EPR Study of Alkylimino Radicals Obtained by Photoinduced Decomposition of Aminoalkyl Radicals in Adamantane", *J. Amer. Chem. Soc.* **92**, 4115 (1970).

COO-3435-3. "EPR Spectra of Pyrrolidino and Pyrrolino Free Radicals. The Structure of Dialkylamino Radicals", *J. Phys. Chem.* **75**, 3468 (1971).

COO-3435-4. "The Absolute Signs of the ZF Parameters from MODR Spectroscopy: 1,2,4,5-Tetrachlorobenzene in Durene", *Chem. Phys. Letters* **15**, 73 (1972).

COO-3435-5. "Conformational Effects in the EPR Spectra of Cyclohexanonyl Radicals in Adamantane", *J. Amer. Chem. Soc.* **94**, 9258 (1972).

COO-3435-6. Progress Report for the Period February 1, 1972 - January 31, 1973.

COO-3435-7. "2-Alkanonyl Radicals. Allylic or Not?, *J. Amer. Chem. Soc.* **95**, 4075 (1973).

COO-3435-8. "Bromine Hyperfine and Quadrupole Fine Structure in the MODR Spectrum of *sym*-Tetrabromobenzene in Its Lowest Triplet State", *Chem. Phys. Letters* **20**, 339 (1973).

COO-3435-9. "Structure of 2-Alkanonyl Radicals. III. EPR Study of Radicals Produced by X-Irradiation of Aliphatic Ketones in Adamantane", *J. Amer. Chem. Soc.* **95**, 7978 (1973).

COO-3435-10. "On the Assignment of the Lowest Triplet State of 1,4-Dihalobenzenes. MODR Spectrum of the $^3B_{1u}$ State of *p*-Dichlorobenzene in a *p*-Dibromobenzene Host Crystal", *J. Chem. Phys.* **60**, 3605 (1974).

COO-3435-11. Progress Report for the period February 1, 1973 - January 31, 1974.

COO-3435-12. "Quadrupole Fine Structure and the Determination of the Absolute Signs of the ZF Parameters of Excited Triplet States. MODR Spectrum of the $^3A'$ State of 1-Bromonaphthalene in Durene", *J. Chem. Phys.* **61**, 2102 (1974).

COO-3435-13. "MODR Spectroscopy of the Lowest Triplet States of Halogenated Benzenes", H. J. Yue, Ph.D. Thesis, 1974.

COO-3435-14. "Direct Observation of the Optical Absorption Spectra of Reactive Free Radicals at Room Temperature", *J. Amer. Chem. Soc.* **96**, 5588 (1974).

COO-3435-15. "An EPR Study of Manganese (II) Binding to 5'-ATP, Hemoglobin, and Hemocyanin", *J. Magn. Res.* **18**, 117 (1975).

COO-3435-16. "Level Anticrossing and Mixing Effects in Excited Molecular Triplet States. Direct Observation by ODMR", *Chem. Phys. Letters* **30**, 181 (1975).

COO-3435-17. "Anomalous ZF Splitting of the Lowest Triplet State of 1-Iodonaphthalene", *Bull. Am. Phys. Soc.* **20**, 47 (1975).

COO-3435-18. Progress Report for the Period February 1, 1974 - January 31, 1976.

COO-3435-19. "ODMR Spectroscopy of the Lowest Triplet States of Benzophenone and Halogenated Benzophenone", J. A. Mucha, Ph.D. Thesis, 1974.

COO-3435-20. "EPR and Optical Studies of Free Radicals in an Adamantane Matrix", J. E. Jordan, Ph.D. Thesis, 1975.

COO-3435-21. "An EPR Study of Conformational Effects in Alkyl-Substituted Cyclohexanonyl Radicals in an Adamantane Matrix", H. F. Walter, Ph.D. Thesis, 1975.

COO-3435-22. "ODMR Spectra of the Lowest Triplet State of 1-Iodonaphthalene in Zero and High Magnetic Fields", J. Chem. Phys. 63, 3337 (1975).

COO-3435-23. "Spin Delocalization in the Lowest Triplet State of Benzophenone", Chem. Phys. Letters 37, 40 (1976). (Reprints enclosed). Removed

COO-3435-24. "Conformational Analysis of the EPR Spectra of Cyclohexenyl Radical and Some of Its Alkyl Derivatives", N. M. de Tannoux, M.S. Thesis, 1975.

COO-3435-25. Progress Report for the Period February 1, 1975 - January 31, 1976.

b. Reports submitted in the present contract year. (In accord with the "Guide for Reporting of Scientific and Technical Information...", March, 1976; preprints and reprints of manuscripts submitted after this date are not assigned report numbers).

COO-3435-26. "A Magnetic Resonance Study of the Lowest Triplet State of 2-Chloronaphthalene", D. W. Grandy, M.S. Thesis, 1976.

"Trimethylenemethane. Experimental Demonstration that the Triplet State is the Ground State", J. Amer. Chem. Soc. 98, 5726 (1976). (Reprints enclosed).

"Optically-Detected Magnetic Resonance Spectra of the Lowest Triplet States of Benzophenone, ^{13}C-Benzophenone, and Three 4,4'-Dihalobenzophenones", submitted to J. Chem. Phys. (Preprints enclosed).

"Level-Anticrossing and Cross-Relaxation Effects in Oriented Molecular Triplet States. $^3(n,\pi^*)$ Benzophenones in 4,4'-Dibromodiphenylether", submitted to J. Chem. Phys. (Preprints enclosed).

"On the Lowest Triplet States of Substituted Naphthalenes. III. Optical and Magnetic Properties of the Lowest Triplet States of 1-Halonaphthalenes in Durene", to be submitted to J. Chem Phys.

"Hyperfine and Quadrupole Effects in the ODMR Spectra of Oriented Triplet States Containing Halogen Atoms", to be submitted to J. Chem. Phys.

"Barrier to Ring Interconversion in Cyclohexenyl Radical", to be submitted to J. Amer. Chem. Soc.

"Optical Detection of Radiofrequency Transitions near Avoided Crossings in the Zeeman Energy Level Diagrams of Oriented Molecular Triplet States", to be submitted to Chem. Phys. Letters.

"Triplet Excitons in 4,4'-Dichlorobenzophenone", to be submitted to Chem. Phys. Letters.

COO-3435-27. Progress Report for the Period February 1, 1976 - January 31, 1977.

c. Reports in progress.

"EPR and Molecular Orbital Study of Allyl Radical and Some of its Simple Derivatives", to be submitted to J. Amer. Chem. Soc.

"EPR and Optical Studies of Free Radicals in an Adamantane Matrix", to be submitted to Accounts Chem. Res.

"Structure of 2-Alkanonyl Radicals. IV. Conformational Effects in the EPR Spectra of Cyclopentanonyl Radicals", to be submitted to J. Amer. Chem. Soc.

"Structure of 2-Alkanonyl Radicals. V. Conformational Analysis of the EPR Spectra of Radicals Derived from Cyclopentanone", to be submitted to J. Amer. Chem. Soc.

"Structure of 2-Alkanonyl Radicals. VI. Conformational Analysis of the EPR Spectra of Radicals Derived from Cyclohexanone", to be submitted to J. Amer. Chem. Soc.

"Structure of Allyl Radicals. II. Conformational Analysis of the EPE Spectra of Radicals Derived from Cyclopentene", to be submtted to J. Amer. Chem. Soc.

"Structure of Allyl Radicals. III. Conformational Analysis of the EPR Spectra of Radicals Derived from Cyclohexene", to be submitted to J. Amer. Chem. Soc.

"On the Lowest Triplet States of Substituted Benzenes. IV. ODMR Spectra of the $^3B_{1u}$ States of 1,2,4,5-Tetrahalobenzenes in Durene", to be submitted to J. Chem. Phys.

"On the Lowest Triplet States of Substituted Naphthalenes. IV. EPR Spectrum and Structure of the Lowest Triplet State of 2-Chloronaphthalene", to be submitted to J. Chem. Phys.

"Conformational Analysis of the EPR Spectra of a Selectively-Deuterated Cyclohexyl Radical", to be submitted to J. Amer. Chem. Soc..

"Carbonyl-^{13}C Hyperfine Tensor of the Lowest Triplet State of Benzophenone", to be submitted to J. Amer. Chem. Soc.