ELECTRON SPIN RESONANCE STUDIES OF RADIATION EFFECTS

MASTER

FINAL REPORT 1964-1979

(Including Annual Progress Reports for 1978 and 1979)

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FINAL REPORT 1964-1979

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ELECTRON SPIN RESONANCE STUDIES OF RADIATION EFFECTS

ABSTRACT

The discovery of new free radicals, largely in irradiated single crystals of nonmetallic solids, and the determination of the molecular and electronic structures of these paramagnetic species by electron spin resonance (ESR) spectroscopy, have been carried out using a wide variety of organic and inorganic materials. The mechanisms of production of radicals in solids, their motions, and their reactions have been investigated and some applicable general principles deduced. Emphasis has been on aliphatic free radicals from irradiated carboxylic acids and amides and their halogen-substituted derivatives, organometallic radicals and substituted cyclic hydrocarbon radicals; inorganic radicals studied include V centers, hypervalent radicals and electron adducts. Extensive investigations of paramagnetic transition metal complexes, particularly cyanides and fluorides, have been made. In all cases quantum mechanical calculations have been employed as far as possible in interpreting the data. An improved method for analyzing experimental ESR spectra of single crystals has been developed and a number of crystal structures have been determined to supplement the ESR studies.

Applications of nuclear quadrupole resonance spectroscopy to the study of structure and bonding in inorganic solids have been made and a method for using nuclear magnetic relaxation data for estimating quadrupole coupling constants in liquids has been developed.

ELECTRON SPIN RESONANCE STUDIES OF RADIATION EFFECTS

This project was started to carry out complete single-crystal ESR studies of paramagnetic species and to advance our knowledge of the electronic and molecular structures of free radicals. Also, to build up some knowledge of the mechanisms of radiation damage in crystals, of the motions and reactions of radicals in solids and of the nature of radiation damage in a wide variety of materials - both organic and inorganic. Although solution or powder ESR data are very much easier to collect and interpret they ordinarily do not provide the details of structure that single-crystal spectra do, particularly when the crystal structure of the host is known. We have frequently either determined the necessary crystal structures or have arranged to have them carried out here through a departmental crystal structure service.

In addition to the main part of the research program we have carried out a number of related magnetic resonance studies by NMR and NQR spectroscopy and have examined by ESR some transition metal complexes prepared by doping single crystals as well as by irradiation. These contributions are also discussed in this report (Sections III, VIII and IX).

The first analyses of single-crystal ESR data for organic compounds were made in 1959 [Ghosh and Whiffen; Cole, Heller and McConnell; Miyagawa and Gordy] and only a few amides or carboxylic acids had been studied at the time this project began (1964). Through continued support from AEC, ERDA and DOE we have been able to make significant contributions to this growing area of research. The principal investigator believes that the original aims of the project have been met to a very satisfactory degree.

SUMMARY 1964-79

I. Radiation damage in single crystals of organic compounds studied by ESR

Initial successes were the discovery of the methyl radical in irradiated sodium acetate, the trifluoromethyl radical in irradiated trifluoroacetamide and the trichloromethyl radical in irradiated trichloroacetamide. Although these radicals, among the simplest and most fundamental of all for theoretical study, had been reported in solutions or powders, we were the first to obtain detailed ESR data for them and provide the accompanying details of their molecular and electronic structures. This work is described in reports COO-1385-14, 16, 17, 23 and 47 (seven years were required to analyze the spectra of $\cdot\text{CCl}_3$ and of $\cdot\text{CF}_2\text{COO}^-$ to our satisfaction).

We then made detailed ESR studies of the radiation products of the very important series of organic acetates and amides. A knowledge of the radicals produced from these single acids and amides was required before radiation damage in more complex biological molecules such as proteins could be understood. A broad initial survey of irradiated organic amides was first made (COO-1385-9) followed by single crystal ESR studies of $\cdot\text{CH}_2\text{COO}^-$ in CH_3COONa , $\cdot\text{CF}_2\text{CONH}_2$ in CF_3CONH_2 , $\cdot\text{CF}_2\text{COO}^-$ in $\text{CF}_2\text{ClCOONa}$, $\cdot\text{CCl}_2\text{CONH}_2$ in $\text{CCl}_3\text{CONH}_2$ and $\cdot\text{CHICONH}_2$ radical in $\text{CH}_2\text{I CONH}_2$ [COO-1385-9, 13, 14, 16, 17, 18, 35, 47 and 55]. In addition a detailed investigation of radicals produced by irradiation of the series of ammonium fluoroacetates was carried out. These include $\cdot\text{CHF}\text{COO}^-$, $\cdot\text{CF}_2\text{H}$, $\cdot\text{CF}_2\text{COO}^-$ and $\cdot\text{CF}_3$ and their relative proportions observed show that a C-F bond is broken in preference to a C-H bond (COO-1385-56). In order to locate the directions of the radical axes in the crystal structures, the x-ray analysis of sodium acetate trihydrate, ammonium monofluoroacetate and ammonium difluoroacetate were carried out at

Michigan State University (D. L. Ward). The methyl radical appears to undergo a tunneling rotation about the threefold axis when trapped in the sodium acetate lattice and a theoretical study to explain the ESR and ENDOR spectra was carried out (COO-1385-67).

Radiation damage in more complex carboxylic acids and carboxamides were then carried out to determine the effects of structure on the products and to study the structures of more complex radicals, particularly those containing halogen substituents. An ESR study of a bromine-containing radical believed to be $\cdot\text{CHBrCONH}_2$, in a single crystal of $\text{CHBr}(\text{CONH}_2)_2$ was carried out along with the crystal structure determination of bromomalonamide. This and $\cdot\text{CHICONH}_2$ were the first simple bromine- and iodine-substituted amide radicals to be investigated (COO-1385-51, 53). A detailed investigation of the α -hydroxybenzyl radical ($\text{C}_6\text{H}_5\dot{\text{C}}\text{HOH}$) in irradiated single crystals of mandelic acid provided the first study of a radical of this type in a solid matrix (COO-1385-54). The crystal structure of mandelic acid was also redetermined here for this purpose (D. L. Ward). The radical $\text{CO}_2^-\text{CF}_2\dot{\text{C}}\text{FCO}_2^-$ shows interesting changes in the ESR spectrum as temperature is lowered. A detailed lineshape analysis showed that motion about the central C-C bond occurs above 130°K leading to an averaging of the hyperfine splitting tensors. This is one of the very few cases where the details of the motion of a radical in a single crystal matrix have been worked out (COO-1385-33). The effects of hydrogen bonding in the host lattice leading to preferential breaking of a C-C bond to give $\cdot\text{CH}_3$ in hydrated acetates, versus breaking a C-H bond in anhydrous metal acetates, was noticed and reported in detail (COO-1385-22).

Some other simple organic radicals were investigated by ESR including a single-crystal analysis of the ESR spectra of the $\cdot\text{CH}_2\text{C}(\text{NH}_2)_2^+$ and Cl_2^- radicals in irradiated acetamidine (COO-1385-31) and detailed study of a series of cyclic radicals in adamantane, where both isotropic and anisotropic spectra are observed depending on temperature. It was shown by Fessenden *et al.* (1963, 1964, 1967) that barriers to inversion in cyclic radicals in liquid solutions could be determined from temperature dependence of the ESR lineshapes. Since this provides the only known method for measuring these interesting barriers, we have studied by the same method a series of cyclic radicals produced by irradiation of organic molecules in solid solution in adamantane where the radicals are reasonably long-lived. Hydrocarbon radicals (cyclopentyl, cyclohexyl), heterocyclic radicals (tetrahydrofuranyl, tetrahydropyranyl, tetrahydrothiophenyl, 2-pyrrolidinyl, tetrahydrothiopyranyl), various substituted radicals (1,-cyclopentanecarboxylic acid, 1-cyclohexanecarboxylic acid, 2-cyclopentanonyl, 2-cyclohexanonyl), and others, were studied in this way and the inversion barriers related to the structures of the radicals and the natures of the substituents (COO-1385-70, 72).

II. Radiation Damage in Single Crystals of Inorganic Compounds Studied by ESR

Irradiation of inorganic compounds may lead to the production of new radical species by oxidation, reduction or bond breakage and we have examples of all three. Potassium oxyfluoroiodate gives IO_2F^- by breakage of an I-F bond and the g and hyperfine splitting tensors from the ESR spectra provide details of the structure and orientation in the crystal of the radical (COO-1385-34). On the other hand AsF_3 and AsCl_3 appear to add an electron on irradiation and the reduced species AsF_3^- , AsCl_3^- were identified through their powder ESR spectra (COO-1385-36). Irradiation of hydrazinium

dichloride and dibromide leads to the oxidation products Cl_2^- and Br_2^- (V centers), identified through single crystal ESR spectra (COO-1385-32). A more complex V_t center, F_3^- , is observed on irradiation of KAsF_6 (COO-1385-37).

III. Paramagnetic transition metal complexes studied by ESR

A substantial part of the effort of this project over the last 15 years has been devoted to single-crystal ESR studies of transition metal complexes, combined with quantum theory. In most cases the species studied result from radiation damage of either a host crystal or a complex in solid solution in a host; a few have been produced directly by doping the desired host. We have emphasized ligand hyperfine splittings in the more ionic fluorides and more covalent cyanides since these provide maximum structural information.

[a] Complex Cyanides and Fluorides of Chromium and Cobalt

The greater σ covalent bonding to chromium in $[\text{Cr}(\text{CN})_6]^{3-}$ compared to that in $[\text{CrF}_6]^{3-}$ was demonstrated in an early ESR study from this laboratory of $[\text{Cr}(^{13}\text{CN})_6]^{3-}$ doped into diamagnetic $\text{K}_3\text{Co}(\text{CN})_6$ (COO-1385-4) and it was later shown that the same was true for the Cr-C bonds in $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ (COO-1385-3). ESR studies of single crystals of alkali halides doped with $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ were used in the latter study which appears to be the first use in ESR of substitution of an MX_6^{5-} unit from an alkali halide by an approximately octahedral paramagnetic species (COO-1385-6). This technique has since been widely employed.

When a hexacyanide is doped into an alkali halide lattice and irradiated, paramagnetic species are observed showing hyperfine interaction with one or two nitrogen atoms. To settle a controversy concerning whether the distortion

so observed results from turning around one or two nitrogens to give M-N-C bonds, or whether it results from bending and moving out of one or two cyanide ligands ($M-C_{\sim N}$), we carried out a single-crystal ESR study of $[Co(^{13}CN)_6]^{4-}$ in irradiated NaCl and KCl crystals. The data indicate that carbon remains bonded to metal but that the Co-C bond is weakened; a similar conclusion presumably applies in the many other cases where this behavior is observed (COO-1385-62).

Irradiated Complex Cyanides of Iron and Ruthenium (1977-1979)

Single crystals of several alkali halides, including RbCl, RbBr, KCl and KBr, have been grown from aqueous solution doped with $[Fe(CN)_6]^{4-}$. Irradiation with both x rays and γ rays at room temperature leads to the production of a number of paramagnetic species. We have obtained ESR spectra for all these crystals at a series of orientations when the crystals are rotated about a cubic axis. From the resulting plots of magnetic field versus orientation the principal components of the g tensors have been determined. In nearly all cases hyperfine interactions with ligand nuclei are observed and the ligand hyperfine tensors are also obtained.

All the paramagnetic complexes appear to result from addition of an electron on irradiation to $[Fe(CN)_6]^{4-}$ to give $[Fe(CN)_6]^{5-}$ which suffers weak tetragonal distortion to give $[Fe(CN)_5(CN)']^{5-}$ or $[Fe(CN)_4(CN)_2']^{5-}$ radicals in which one or both of the axial cyanide ligands move out slightly and the FeCN bonds bend. Annealing leads to exchange of these weakly bonded axial cyanides with halide ions of the lattice to give $[Fe(CN)_5X]^{5-}$ and $[Fe(CN)_4X_2]^{5-}$, where X = Cl or Br. The ESR parameters have been used to obtain spin densities on the ligands and to discuss the structures of the complexes. In some cases the same radical is observed in more than one matrix and the effect of matrix on structure can be evaluated.

Prolonged irradiation also leads to the formation of a protonated radical $[\text{Fe}(\text{CN})_5\text{CNH}]^{5-}$ in which both proton and nitrogen hyperfine splittings are observed.

This work has been prepared for publication and a preprint is enclosed (COO-1385-75).

A detailed single crystal ESR study of ruthenium cyanide complexes in alkali halide matrices has also been completed. The ESR parameters lead to detailed information concerning the electronic structures of these complexes and permit direct comparison with the first-row analogues, the iron cyanide complexes.

Single crystals of KCl doped with $[\text{Ru}(\text{CN})_6]^{4-}$ were irradiated at room temperature and the species $[\text{Ru}(\text{CN})_6]^{5-}$, $[\text{Ru}(\text{CN})_5(\text{CN})']^{5-}$, $[\text{Ru}(\text{CN})_5\text{Cl}]^{5-}$, $[\text{Ru}(\text{CN})_4(\text{CN})'\text{Cl}]^{5-}$, $[\text{Ru}(\text{CN})_4\text{Cl}_2]^{5-}$ and $[\text{Ru}(\text{CN})_5\text{CNH}]^{5-}$ were detected by ESR. The g tensors and some ligand hyperfine splitting tensors were obtained from spectra taken on rotation about a cubic axis. Spin density distributions on the ligands were derived and the results compared with those for the analogous Fe(I) cyanide complexes.

This work was published in abstract form for the American Chemical Society/Chemical Society of Japan Congress, Honolulu, April, 1979 (COO-1385-74).

ESR Studies of Oxyfluoro Complexes of Vanadium and Molybdenum

We have completed an extensive ESR study of oxyfluorovanadium and oxyfluoromolybdenum complexes in single crystals of $(\text{NH}_4)_2\text{SbF}_5$. The host was chosen since it appears to favor, on suitable doping, the formation of square pyramidal paramagnetic complexes with five ligands, rather than octahedral complexes, since the impurity ion replaces a square pyramidal SbF_5^{2-} ion in the lattice. Crystals of $(\text{NH}_4)_2\text{SbF}_5$ doped with VO^{2+} show

the presence of VOF_4^{2-} ions which have the d^1 configuration and give good ESR spectra showing both vanadium and fluorine hyperfine splittings. ESR spectra recorded as a function of orientation about three mutually perpendicular axes were used to obtain the g and A tensors; $g_{||} = 1.9330$, $g_{\perp} = 1.9810$, $A_{||}({}^{51}\text{V}) = -200$ G, $A_{\perp}({}^{51}\text{V}) = -73.5$ G. Similarly crystals of $(\text{NH}_4)_2\text{SbF}_5$ doped with MoO^{3+} show the presence of MoOF_4^{1-} , also a d^1 species. ESR spectra were again recorded as a function of single crystal orientation and the g and hyperfine interaction tensors extracted; $g_{||} = 1.8948$, $g_{\perp} = 1.9250$, $A_{||}({}^{95}\text{Mo}) = 95.5$ G. When crystals of $(\text{NH}_4)_2\text{SbCl}_5$ are doped with MoO^{3+} the ion MoOCl_4^- is obtained and the ESR spectra lead to the parameters $g_{||} = 1.9650$, $g_{\perp} = 1.9461$, $A_{||} = 81.5$ and $A_{\perp} = 40.75$ G.

Interpretation of the g and hyperfine tensors in terms of structure is underway and will be combined with some quantum mechanical calculations for these complexes (also in progress). A complete analysis of the single-crystal ESR spectra of γ -irradiated $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ was carried out and it was shown that the hole species $[\text{NbOF}_5]^-$ and NbOF_4 are present. These have the odd electron in a degenerate orbital of e symmetry with mostly oxygen $2p_{\pi}$ character (COO-1385-64).

Quantum Theory of Transition Metal Complexes (1977-79)

Theoretical studies of the electronic structures and ESR parameters of transition metal complexes have been carried out using the extended Hückel method. A series of iron cyanides and of oxyfluorovanadium complexes, including those studied in this work by ESR, have been compared.

In order to obtain more reliable quantum mechanical results with these rather large systems we are now using Slater's $X\alpha$ -SCF method. A program has been adapted for our computer from one provided by Dr. W. Case (UC Davis)

and we have begun a systematic study of the series MOX_5^{n-} ($M = \text{V, Nb, Mo, Cr}$ and $X = \text{F, Cl, Br, I}$). Other complexes will be treated by this technique as experience with the method is obtained. It has the great advantage that it can give ESR parameters for complexes of the second and third row transition series where many other sophisticated methods, such as the pseudo-potential method, cannot.

IV. ESR Studies of Organic Radicals in Irradiated Solutions

We have contributed to knowledge of the structures and conformations of organic radicals, particularly halogen-substituted species and organo-metallic species, by a series of ESR studies of irradiated solutions.

The perfluoro radicals $\cdot\text{CF}_2\text{CF}_3$, $\cdot\text{CF}(\text{CF}_3)_2$ and $\cdot\text{C}(\text{CF}_3)_3$ were prepared by irradiation of the iodides and the observed fluorine hyperfine splittings used to show that the radicals bend from planarity increasingly as the number of α fluorines increases (COO-1385-44). A similar investigation of the isotropic hyperfine interactions for the series $\cdot\text{Sn}(\text{CH}_3)_n\text{Cl}_{3-n}$ ($n=0,1,2,3$) showed that these, along with $\cdot\text{GeCl}_3$ and $\cdot\text{SiCl}_3$, are nearly tetrahedral in solution (COO-1385-46); other radicals of the type $\cdot\text{M}(\text{CH}_3)_2(\text{CH}_2\text{X})$ with $M = \text{C, Si}$ and $X = \text{H, Br, Cl}$ were also shown to be nonplanar (COO-1385-41). The interesting β -chloro- and β -bromo-tert-butyl radicals in adamantane were prepared in this laboratory by irradiation of the isobutyl halides, the latter being the first well-characterized β -bromo aliphatic radical; the bromine hyperfine splittings shows that the bromine is nearly in the nodal plane of the odd electron orbital (COO-1385-60). A study of the ENDOR spectrum of 2-adamantyl radical in irradiated adamantane provided a value for the proton-hyperfine splitting of a β proton in an alkyl radical with dihedral angle 90° by symmetry (COO-1385-45).

The only aromatic free radicals studied on this project were the radical cations from octamethylnaphthalene and from two hexamethylnaphthalenes which are of interest because crowding forces the methyl groups to be nonplanar (COO-1385-25).

Quantum mechanical calculations, usually at the CNDO/INDO level, were employed in interpreting the ESR parameters and discussing radical geometries in all the above cases (COO-1385-25, 41, 44, 45, 46 and 60).

V. Analysis of Single-Crystal ESR Spectra

In the course of work on this project, we noted that no systematic investigation of the methods for determining g and hyperfine interaction tensors from experimental spectra had been reported which made use of the inherent overdetermination of tensor elements in the usual method of rotating a crystal about three mutually perpendicular axes. A series of three theoretical articles resulted in which we showed that rotations could be about nonorthogonal sets of axes and that overspecification of tensor elements could be used to estimate experimental crystal misalignments. An accompanying set of computer programs was written and provided free to a large number of laboratories (COO-1385-43, 52 and 59).

VI. Reviews of ESR Studies of Radicals

A review of our investigations of radicals in irradiated single crystals of amides and carboxylic acids was prepared for an international conference (COO-1385-20). A long book chapter covering the structure of inorganic radicals as deduced from ESR data was prepared for the monograph "Spectroscopy in Inorganic Chemistry, Vol. II" (COO-1385-29).

VII. X-ray Crystallographic Investigations

Complete interpretation of the ESR data for several irradiated single crystals required details of the crystal structures not available in the literature. We, therefore, determined the crystal structure of bromomalonamide (COO-1385-63). Dr. D. L. Ward and K.-T. Wei, of the crystallographic service group in the Department of Chemistry, determined the structures of mandelic acid, ammonium fluoroacetate, ammonium difluoroacetate and sodium acetate trihydrate. The complex hydrogen bonding networks in the acetates and the amide were discussed in detail in these articles (Acta Cryst. B32, 797, 2768; B33, 522).

VIII. Nuclear Quadrupole Resonance Spectroscopy

One of the most useful methods for the study of structure and bonding in solids utilizes the directly observed nuclear quadrupolar transitions which give, in turn, the electric field gradient at the quadrupolar nucleus. We opened up a new area for research in NQR spectroscopy with the discovery that a series of perrhenates and periodates with the Scheelite structure ($M\text{ReO}_4$, MIO_4 with $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Ag}, \text{NH}_4$), and so containing ions with nearly tetrahedral configurations, showed rhenium (or iodine) nuclear quadrupole resonances (COO-1385-24, 27). Detailed investigation of the temperature dependences of these revealed an unusual anomaly in that of NH_4ReO_4 which is still the subject of intense investigation in a number of other laboratories to provide a definitive explanation (COO-1385-49, 50).

An investigation of structure and bonding in some molecular adducts of POCl_3 was made (COO-1385-19) and analysis of the results showed that Sternheimer antishielding factors for chlorine in these molecular crystals are smaller than for chloride ion in alkali chlorides (COO-1385-66). NQR

investigations of $\text{BiCl}_3 \cdot \text{H}_2\text{O}$ (COO-1385-40), substituted ureas (COO-1385-39) and organic hydrochlorides (COO-1385-28) have also been published.

IX. Nuclear Magnetic Resonance Spectroscopy

Keto-enol tautomerism in substituted acetylacetonates is unusually important in chemistry since these are widely employed for metal chelation. We made an extensive investigation of the effects of structure, solvents and temperature on the keto-enol equilibrium using NMR spectroscopy (COO-1385-2, 7, and 10). A method for analysis of complex NMR spectra by computer was devised (COO-1385-11) and a review of this complex subject prepared (COO-1385-12).

Nuclear relaxation measurements in deuteriochloroform and bromoform were employed to estimate the nuclear quadrupole coupling constants for deuterium in these liquids; the rotational correlation times were obtained independently from Raman lineshape analysis (COO-1385-61), providing a new method for obtaining these parameters.

Principal Investigator's Time Contribution 5/1/78 - 7/31/79

5/1/78 - 6/18/78	40% of full time
6/19/78 - 9/1/78	100% of full time, 10 weeks, Summer
9/2/78 - 6/17/78	40% of full time, 1 week Summer
6/18/79 - 6/24/79	100% of full time
6/25/79 - 7/31/79	40% of full time

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CONSISTING OF 46 SCIENTIFIC ARTICLES, 2 REVIEWS and 6 PREPRINTS

PLUS 22 REPORTS

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M. T. Rogers

Annual Progress Report, U.S. Atomic Energy Commission Contract

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5. "Chlorine Nuclear Quadrupole Resonance Study of Some Molecular Adducts of Phosphorus Oxychloride"
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Atlantic City, September (1968)
8. "Solid-State Effects in Pure Quadrupole Resonance Spectroscopy"
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9. "ESR Studies of Irradiated Crystalline KIO_2F_2 , AsF_3 and AsCl_3 "
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11. "NMR of Nitrogen Compounds"
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Electron Spin Resonance of Transition Metal Complexes
- 1966 Yuh-Kung Pan
Quantum Mechanical Analysis of High-Resolution Nuclear
Magnetic Resonance Spectra
- 1966 Lowell Donald Kispert
Electron Spin Resonance of Irradiated Organic Single Crystals
- 1967 James Austin Ryan
Nuclear Quadrupole Resonance Study of Charge-Transfer Complexes
- 1970 James Clyde Watson
An ESR Study of Radicals in Some Irradiated Single Crystals
- 1971 Richard Allen Johnson
Temperature Dependence of the NQR Frequencies of Periodates
and Perrhenates and Calculation of Electric Field Gradients
from X-ray Diffraction Data
- 1973 John Robert Shock
ESR Studies of Transition Metal Ions in Unstable Oxidation
States
- 1973 William George Waller
Part I. An Electron Spin Resonance Study of Radicals in
Irradiated Single Crystals of Mandelic Acid.
Part II. A Generalization of Methods for Determining g Tensors.
- 1973 Richard Clark Schoening
Electron Spin Resonance Studies of Radicals in Irradiated
Acetates
- 1973 Robert Francis Picone
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of Bromomalonamide.
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 γ -Irradiated Bromomalonamide and Iodoacetamide.
- 1974 David Allen Wright
Molecular Motion in Condensed Phases. Nuclear Magnetic
Relaxation and Raman Lineshape Studies of Several Small
Species.
- 1977 John Choo Wang Song
ESR Studies of Alicyclic Radicals in Adamantane
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ESR and Theoretical Studies of Transition Metal Fluorides
and Oxyfluorides (thesis in preparation)

Postdoctoral Research Associates 1964-1979

Supported, in part, through Contracts AT(11-1)-1385, E(11-1)-1385
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F. Greenaway	1973-74	Syracuse University
W. G. Waller	1973-76	Louisiana State University
Joon Y. Lee	1974-75	Illinois Institute of Technology
A. Kasi Viswanath	1976-79	University of Maine