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EPR AND OPTICAL ABSORPTION STUDIES OF ELECTRON ATTACHMENT TO FLUORINE COMPOUNDS IN SOLID SOLUTIONS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Robert Irving McNeil

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ABSTRACT

The main contribution of this work is the preparation and spectroscopic characterization of radical anions derived from fluorine-containing compounds which were formed in condensed phases as a result of electron capture. These ions are of interest because they represent novel classes of negative ions.

The ions, produced by gamma irradiation of frozen solutions of various fluorine-containing compounds in 2-methyltetrahydrofuran (MTHF) or tetramethylsilane (TMS), were characterized by EPR and then studied by optical spectroscopy. Photolysis of similar solutions containing N,N,N',N'-tetramethyl-p-phenylenediamine provided confirmation that the anions did result from electron capture. The distinctive feature of this work was the extensive use of TMS to obtain spectra which were nearly isotropic or which were completely anisotropic but showed orientation dependence.

The radical anion of tetrafluoroethylene, observed by EPR in a gamma-irradiated solution of tetrafluoroethylene in TMS-d_{12} at 120°K, exhibited hyperfine coupling to four equivalent fluorine nuclei, the values of the g factor and coupling constant of the isotropic spectrum being 2.0027 and 94.7 G. Analysis of the anisotropic spectrum, obtained from a gamma-irradiated solution of tetrafluoroethylene in MTHF at 87°K, revealed that the radical exhibited an axially symmetric hyperfine tensor, with parallel coupling $A_{//}$ = 135.9 G and perpendicular coupling $A_{\perp}$ = 74.4 G.

Warming to 95°K a gamma-irradiated solution of

tetrafluoroethylene in MTHF or 3-methylhexane resulted in the complete decay of the EPR spectrum of $C_2F_4^-$ and the growth of the anisotropic spectrum of $c\text{-}C_4F_8^-$. The transformation was interpreted as the cycloaddition of C_2F_4 to $C_2F_4^-$. A similar reaction was believed to occur in an irradiated solution of chlorotrifluoroethylene in MTHF.

Evidence for the tetrafluoroethylene cycloaddition reaction was also obtained by optical spectroscopy. The optical spectrum of $C_2F_4^-$, obtained in MTHF or 3-methylhexane at 77°K, exhibited vibrational fine structure with a maximum at 508 nm. Warming the MTHF sample produced a decrease in the intensity of the $C_2F_4^-$ spectrum, a slight increase in absorption at 390 nm, the maximum in the optical spectrum of $c\text{-}C_4F_8^-$, and a color change from red to gold.

Gamma irradiation of frozen solutions of chloro-, bromo-, and iodotrifluoroethylene in TMS-d_{12} yielded EPR spectra that were orientation dependent, so that rotation of the sample in the magnetic field enhanced one or another set of features. Each of the radicals exhibited an axially symmetric hyperfine tensor for the unique halogen. On the basis of the large spin densities in the highest p orbitals of the unique halogens, as calculated from the anisotropic coupling constants, the radicals were tentatively identified as CF_2CFCl^-, CF_2CFBr^-, and CF_2CFI^-.

This work shows the usefulness of the EPR technique for the study of negative ions in the condensed phase.

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CHAPTER I

INTRODUCTION

A. Absorption of Radiation

When high energy radiation interacts with matter, a variety of processes occurs by which the energy of the radiation is transferred to the medium.[1] Two general cases can be distinguished on the basis of the two most common types of radiation, electromagnetic radiation and charged particle beams. As discussed below, the interactions of electromagnetic radiation with matter are by pair production, the Compton effect, and the photoelectric effect, whereas for charged particles, interaction occurs by bremsstrahlung and inelastic or elastic scattering. The relative importance of the interactions is determined by the energy of the incident radiation and the mass of the charged particles.

Electromagnetic radiation of energy greater than about 2 Mev (million electron volts) can create, in a process called pair production, an electron and a positron, the direct transformation of energy into matter requiring 1.02 Mev, according to Einstein's equation $E=mc^2$; the excess energy is taken up as kinetic energy of the particles. The energy of the electron is degraded by the process described below for charged particles, while the positron continues its motion until it encounters an electron, at which time both disappear, with the formation of two quanta, each of energy 0.51 Mev. This pair production process is of importance only for photons of energy greater than 5 to 10 Mev.

For intermediate photon energies, roughly 0.5 to 5 Mev, the dominant mode of energy loss is the Compton effect, in which the

interaction of a photon with a bound electron results in a sharing of the energy and momentum of the incident photon between a scattered photon of lower energy and a recoil electron which, having been ejected from the molecule, loses its energy as described below. On the average, a large fraction of the energy of the incident photon is transferred to the recoil electron. Phenomenalogically, this process resembles a classical elastic collision of a moving particle with a stationary one.

Photons of still lower energy interact primarily by the photoelectric effect, which differs from the Compton effect in that the photon is completely absorbed, all of its energy being transferred to an electron, which is ejected from the molecule with a kinetic energy equal to the photon energy less the binding energy of the electron.

Absorption of high energy electromagnetic radiation can be described mathematically by Equation 1, in which I_o is the intensity

$$I = I_o \exp[-(\rho N_o Z A^{-1}) Q_e x] \qquad (1)$$

of the incident radiation, I is the intensity after passing a distance of x cm through the sample, ρ is the density in g cm^{-3} of the sample (assumed here for simplicity to be an element), N_o is Avogadro's number, Z is the atomic number, A is the mass number, and Q_e is the cross section in cm^2 per electron. The expression $(\rho N_o Z A^{-1})$, the electron density in electrons per cm^3, is analogous to the concentration term c of the familiar Beer-Lambert Law (shown in Equation 2) for the absorption of photons in the visible-uv region of the electromagnetic spectrum.

$$I = I_o \exp(-2.303\ \varepsilon c x) \qquad (2)$$

The counterpart of the decadic molar extinction coefficient ε is Q_e, which can be broken down into components for pair production, the

Compton effect, and the photoelectric effect, which are proportional to Z^1, Z^0, and Z^3, respectively. Thus, for the Compton effect, interaction depends solely on the electron density.

In contrast to high energy photons, beams of charged particles interact with matter by two mechanisms, bremsstrahlung and elastic and inelastic scattering. In the former process, electromagnetic radiation (the continuous x-ray spectrum) is emitted as a result of deceleration of a fast particle as it passes near a molecule. Scattering of a particle as a result of collision with a neutral molecule can be either inelastic or elastic, depending on whether the molecule acquires or does not acquire internal energy. The excess internal energy is manifested as excitation or ionization of the molecule, which can then undergo chemical reactions. Electrons liberated by this process are capable of inducing further ionization and excitation, losing energy with each event until they finally reach thermal energy (until they are thermalized).

For incident beams of fast electrons and a target of high Z, bremsstrahlung is the dominant process of energy loss at particle energies greater than about 10 MeV; inelastic scattering predominates at lower energy for materials of low Z. Interaction of heavier charged particles with matter is primarily by elastic and inelastic collisions.

It can be seen, then, that the modes of interaction with matter of both electromagnetic radiation and charged particle beams all result in the production of primary or recoil electrons with high energy which give rise to a track structure. Since high energy photons (γ and x-rays) are very penetrating, requiring collision with an electron for an interaction to occur, the recoil electrons are spaced uniformly throughout the medium. Incident charged particles, however, begin their

tracks at the point where the beam strikes the surface of the system. It should be emphasized that, for electrons of the same energy, the track structure from recoil electrons produced by electromagnetic radiation is identical to that from high energy electrons produced by an accelerator, except for their point of origin.

The presence of track structure provides a practical basis for the distinction between radiation chemistry, in which ejected electrons have very high energies, and photochemistry in the far ultraviolet region, in which any ejected electrons have such low energies that they are incapable of effecting ionization of neighboring molecules to form tracks.

B. Ionization Processes in Condensed Phases

Irrespective of the type of radiation, most of the radiation's energy is communicated to the absorber by secondary electrons, produced as a result of ionization by incident particles or recoil electrons. Incident fast electrons and recoil electrons (the latter, for example, from the Compton effect, with up to 500 KeV of energy for 1.2 MeV γ rays), because of their high velocity, only infrequently pass near enough to a bound electron to transfer a significant fraction of their energy. Consequently, major interaction events are spaced relatively far apart, of the order of several hundreds or even a few thousands of Angstroms in condensed phases; infrequently, the secondary electrons produced in these events (δ-rays) may have enough energy (5 KeV or so) to initiate short tracks of their own. Much more common, however, is the transfer of a much smaller amount of energy, of the order of 100 eV, enough to produce a few ionization events within a few molecular diameters of the point of deposition. Thus, the track of the primary

electron is marked by shorter tracks from δ-rays and by pockets of relatively high ion concentration called spurs, all widely separated from each other. The overall low ion concentration in the medium allows many of the electrons to escape the spurs and enter into chemical reactions with other species in the system.

Heavier charged particles such as α rays or protons produce very short cylindrical tracks, in which the spurs overlap. The very high concentration of ions allows ready recombination, resulting in very few ions' escaping the track volume and being available for chemical reactions with other species.

The ease of penetration and the track pattern have been the main reasons for the widespread use of γ or x-rays and fast electrons in the study of the intermediates (ions and radicals) produced by irradiation. The use of heavier charged particles requires, because of the short ranges involved, more elaborate arrangements for irradiation, including great restrictions on sample cell size and materials of construction. Moreover, the high concentrations of ions and radicals in the tracks of heavier particles facilitates fast recombination reactions. In contrast, the greater penetration of fast electrons and high energy photons allows much more freedom in sample cell design, and the track structure allows a much larger fraction of the ions to be observed. Because the research described in this dissertation was concerned with the initial events following the absorption of radiation, further discussion will be limited to radiation effects from fast electrons, whether produced directly (from electron beams) or indirectly (from γ or x-rays).

In liquids, where mobility of the electrons is often very high, the ions are classified into two categories, free and geminate. The

important parameter in this distinction is the Onsager escape radius (symbolized r_c), the distance between the electron and positive ion at which the Coulombic attraction between the two ions is equal to the thermal energy, kT, the Boltzmann constant multiplied by the absolute temperature. The probability that an electron will escape from the parent positive ion is equal to $\exp(-r_c/r)$, where r is the distance between the ions at the time the electron's energy has been degraded to thermal energy. Those ions which do not escape are called geminate, and those which do are called free.

This distinction is reflected experimentally in the lifetimes of the ions. Ions which undergo geminate recombination have extremely short lifetimes, during which they may or may not become solvated by the medium. Free ions, which undergo random recombination in the bulk of the solution, have much longer lifetimes (microseconds or longer); they definitely do become solvated. Introduction of electron scavengers, compounds capable of accepting excess electrons and so preventing their combination with positive ions, allows the two classes to be distinguished on the basis of the concentration of scavenger required to intercept them. For scavenging, a concentration of scavengers is needed such that the product of the scavenger concentration and the rate constant for electron attachment must be greater than τ^{-1}, the inverse of the lifetime of the electron in the absence of a scavenger, as shown in Equation 3. It can be seen that the shorter lifetimes of the geminate

$$k_s[s] >> \tau^{-1} \tag{3}$$

ions requires a higher scavenger concentration. For example, for an electron lifetime of 10^{-7} sec and a diffusion controlled reaction with the scavenger (k_s of the order of 1×10^{10} $M^{-1}sec^{-1}$), the scavenger

concentration must be greater than 10^{-3}M; lower concentrations will result in scavenging of only the free ions.

For the direct observation of transient chemical intermediates generated by irradiation in liquid solution, pulse or continuous irradiation techniques may be used, both requiring high dose rates from accelerators. Pulse radiolysis requires fast detection by physical methods; these include optical absorption studies, which have been extended to the picosecond range,[2] and conductivity methods.[3] Although detection by electron paramagnetic resonance (EPR) is now capable of time resolution in the microsecond range,[4] most applications of EPR to liquids have utilized the continuous irradiation technique with conventional detection techniques.[5]

In solids, where the rate of diffusion is much lower, the division into geminate and free ions is no longer meaningful. Instead, in amorphous matrices, the mobile electrons either combine with positive ions or become trapped by suitable arrangements of solvent molecules. Because of the lack of translational motion in the solid, the trapped electrons have much longer lifetimes than do their counterparts in liquid media and so may be studied by conventional optical spectroscopy or EPR. Products resulting from electron capture by solutes are also prevented from reacting and so can be studied thoroughly by conventional techniques.

The classic example of work with irradiated glasses is the study by Hamill and co-workers[6] of 2-methyltetrahydrofuran (MTHF) at 77°K. Introduction of a small amount of biphenyl reduced the intensity of the optical band at 1200 nm compared to that in the pure compound and produced a new band at 409 nm. From experiments with sodium and biphenyl

in solution, it was known that the shorter wavelength absorption was due to the radical anion of biphenyl. The absorption at 1200 nm was therefore assigned to the trapped electron. It is important to note that in MTHF no absorption was found corresponding to that of the biphenyl cation, indicating that positive ion transfer from the solvent does not occur in this system.

In crystalline solids, trapped electrons are only very rarely observed, and then only in very low yields. On the other hand, in the case of molecules having low-lying unoccupied orbitals, an electron may localize on a molecule of the solvent to form a trapped radical ion.[7] Scavengers can also be introduced to intercept electrons ejected from the solvent molecules by irradiation; however, the scavengers must be of such size and shape that they can be incorporated into the matrix.[8] As in amorphous matrices, the products of electron capture frequently have long lifetimes due to the lack of translation.

C. Additional Methods of Producing Electrons

Though all the work described heretofore has utilized high energy radiation, photochemical methods have also been used to generate electrons, usually without the complication of radical production resulting from excitation of solvent molecules to high levels; that is, there is usually a greater specificity for electron production by the lower energy methods. These methods complement the studies by high energy irradiation methods in that production of the same species by both methods is taken as proof that the species is formed as a result of electron addition. Examples of systems which can be used for the photogeneration of low-energy electrons include sodium co-deposited on a cold

surface with the solution of interest,[9] ferrocyanide ion in polar solvents,[10] and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in solution in organic matrices.[11] In practice, each system requires irradiation with UV light at a particular wavelength.

D. Evolution of the Problem

As discussed previously, the fates of electrons in solids can involve combination with positive ions, trapping by the matrix, or capture by molecules having positive electron affinities. In the last case, as shown in Equations 4 and 5 for electron acceptors A and RX,

$$A + e^- \longrightarrow A^- \tag{4}$$

$$RX + e^- \longrightarrow R^\bullet + X^- \tag{5}$$

two pathways are available to a molecule when it accepts an extra electron; it can retain the electron, or it can expel a diamagnetic negative ion and produce a neutral radical. Any of a wide variety of methods could be used to study these products of electron attachment. However, the fact that both A^- and $R^\bullet$ are paramagnetic makes electron paramagnetic resonance (EPR) a suitable general technique. In favorable cases EPR can be used to identify the radical from first principles, without recourse to previously obtained spectra, as would be necessary with optical spectra, for example. Moreover, EPR can be used to provide information about the electronic structure of the radical. But even this method presents difficulties. For radical identification, the ideal case would be a well-resolved isotropic spectrum exhibiting a well-defined hyperfine pattern showing coupling to all nuclei with nonzero spin. Although this is encountered occasionally, a far more common occurrence in the solid state involves a poorly resolved spectrum

resulting from the anisotropic character of the g tensor and the hyperfine interaction. Interpretation in all but the simplest cases is far from routine.

In liquid solution, radicals tumble freely, averaging out the anisotropies of the g factor and of the hyperfine interactions due to spin density in the p orbitals. High resolution isotropic spectra are commonly observed in these systems. Many radicals, however, are extremely reactive and so, because of their own instability or the likelihood of reaction with other species due to diffusion, they are short-lived and cannot be detected in liquid solution.

In the solid state, where diffusion does not occur, the radicals often have much longer lifetimes. The EPR spectra of radicals in the solid state can be of three types, depending on the matrix. Irradiation of single crystals of pure compounds produces well-resolved anisotropic spectra which change upon rotation of the sample in the magnetic field. From detailed studies of the angular dependence, the g and hyperfine coupling tensors can be obtained with their principal components corresponding to the direction of the applied field along the three principal axes of the radical, allowing much more information to be gained about the electronic structure of the radical than would be available from an isotropic spectrum. Such studies are possible because the radicals are oriented in one or, at most, a few directions in the single crystal. That is, the radicals produced by irradiation retain the spatial orientation of the original molecules.

In contrast, spectra in polycrystalline or glassy solutions exhibit broad, asymmetric, anisotropic features. Since the molecules are rigidly held, without the possibility of translation or even

rotation in many cases, the spectra are anisotropically broadened by the presence of random orientations. However, analysis of these powder spectra (so-called because they are observed in powders, randomly oriented microcrystals) is facilitated in cases in which the radical has a high degree of symmetry.

The third type of EPR spectrum which can be obtained in solid state studies is close to isotropic. A very few solids (the "rotator solids" or plastic crystals[12]) have been found that will allow enough internal motion or rotation of solute radicals, without the possibility of translation, to result in isotropic or nearly isotropic spectra. Examples of such systems with radical anions produced in the rotator solids, are SF_6^- in sulfur hexafluoride,[13] SiF_4^- in 2,2-dimethylpropane (neopentane),[14] $\underline{c}$-$C_4F_8^-$ in neopentane[15] and tetramethylsilane,[16] and the fluorinated pyridine anions[17] and $C_6F_6^-$ [18] in adamantane. These studies demonstrated the utility of the matrices. But an extension to other solutes was desirable, as was a search for other matrices of this type that might be of use when these are not satisfactory.

As part of these studies, an investigation of a possible solvent effect on electron capture was undertaken, in which the rate of electron attachment to the scavenger might be influenced by the solvent. Though such an effect is well-known in the liquid state,[19] only a small amount of work had been done in the solid state[20] prior to this investigation. The method of attack was to utilize the competitive approach, in which two scavengers would compete for the electrons in a given solvent, determination of the relative reaction rates being made through comparison of the EPR signal intensities. Initially, a wide variety of solvents was to be used, including polar compounds such as alcohols in addition

to the hydrocarbons. However, the aims of the project had to be modified somewhat when it was discovered that the solvent may exert not only a quantitative effect on electron capture but a qualitative one as well, the products being different in different matrices.

These solvent-related effects constituted one path along which effort was directed toward the goal of this research, the extension of our knowledge of the electron capture process and the products resulting from it. The other path was the preparation and study of new species arising from electron attachment.

Earlier work in this laboratory had shown that octafluorocyclobutane, a fully saturated system, is capable of accepting extra electrons when in solid solution in neopentane.[15] The C_3 and C_5 perfluorinated cycloalkanes were shown to behave similarly,[16] as were the perfluorinated cycloalkenes.[21] The next logical step was the ethylenes.

No reports have appeared on the acceptance of excess electrons by ethylene, in which the electron would presumably enter a π^* orbital. But it was thought, on the basis of work by Yim and Wood[18] on the fluorinated benzenes and by Robin and co-workers[22] on the photoelectron spectra of ethylene and tetrafluoroethylene that perfluorination might cause a lowering of the energies of the σ^* orbitals compared to the π^* orbital. Such an effect, termed the perfluoro effect,[22] might result not only in a reversal of the $\sigma^* > \pi^*$ orbital energies presumed in the unsubstituted compound, but it could also lead to the fluorinated molecule's having a positive electron affinity. Thus, operation of the perfluoro effect might allow electron addition to occur to produce a σ radical which would have enough stability to allow observation of its EPR spectrum. Tetrafluoroethylene seemed the most likely candidate to

accept electrons and so was chosen as the entry point into the ethylene series. The observation of the radical anion of this compound would then allow a systematic study of other fluorinated ethylenes.

Tetrafluoroethylene had been found not to accept electrons in the gas phase[23] and not to react when bombarded with cesium atoms in the gas phase.[24] The only direct evidence for the existence of the anion in the gas phase was the detection of a negative ion with the correct mass following bombardment of tetrafluorosuccinic anhydride with electrons.[24]

No evidence was obtained for the anion in previous work on the irradiation of frozen tetrafluoroethylene; the poorly resolved EPR spectrum showed three broad features which the authors[25] believed were due to fluoroalkyl radicals and an unidentifiable species whose spectrum, obtained by subtraction, was a singlet which disappeared on exposure of the sample to light. Though such bleaching is frequently indicative of a negative ion, the poorly resolved spectrum precluded identification. The tetrafluoroethylene radical anion was not considered.

Some previous work has also been reported on the high-energy irradiation of gaseous tetrafluoroethylene. Barchenkova, Baberkin, and Volkova[26] showed that γ and fast electron irradiation at 20°C of tetrafluoroethylene at pressures up to 60 cm Hg resulted in production of small amounts of octafluorocyclobutane. Even though this compound is not formed by photolysis of tetrafluoroethylene, the mechanism was assumed to be the reaction of an excited ethylene molecule with an unexcited one. Since thermally induced dimerization to produce octafluorocyclobutane is known to occur at high temperatures in the gas phase,[27] it is possible that at least some of the product resulted from a thermal

reaction. However, in view of the results to be presented in this dissertation on the cycloaddition of C_2F_4 to $C_2F_4^-$, it is possible that this ionic reaction may also have been operative.

In view of the absence of information about $C_2F_4^-$, the preparation and spectroscopic characterization of the tetrafluoroethylene radical anion by EPR would give information on the singly occupied molecular orbital (the distribution of spin density among the atomic orbitals) and would probably allow a determination to be made of the σ or π character of the radical. In addition, optical studies could be carried out, if an absorption spectrum were obtained, in order to obtain information on the electronic transition.

CHAPTER II

EXPERIMENTAL

A. Purification of Materials

All the fluorocarbons were from PCR Research Chemicals, Inc. Chlorotrifluoroethylene (boiling point -27°C) and tetrafluoroethylene b.p. -76.3°C) were purified by trap-to-trap distillation from a dry ice-isopropanol bath on the vacuum line immediately prior to use. Iodotrifluoroethylene (b.p. -30°C) was treated the same way except that the bath was acetone cooled to about -20°C. These treatments served to remove the polymerization inhibitors and to remove any dimers that might be present as contaminants. Bromotrifluoroethylene, trifluoroethylene, 1,1-difluoroethylene, 1,1-dibromo-2,2-difluoroethylene, 1,1-dichloro-2,2-difluoroethylene, octafluorocyclobutane, decafluorocyclopentane, dodecafluorocyclohexane, hexafluorobenzene, 1,2-dichlo-1,2,3,3,4,4-hexafluorocyclobutane, 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane, hexafluoroethane, trifluoromethane, and tetrafluoromethane were used as received, as were Sulfur hexafluoride (from Matheson Gas Products), 2,2-dimethylpropane (from Matheson Gas Products), tetramethylsilane (from Norell Chemical Co.), and tetramethylsilane-$\underline{d}_{12}$ (from Crescent Chemical Co.)

Practical grade 3-methylhexane (from Matheson, Coleman, and Bell) was dried over magnesium sulfate (from Baker Chemical Co.) and distilled at atmospheric pressure. It was de-aerated by the freeze-pump-thaw method and stored <u>in vacuo</u> in a bulb equipped with a stopcock and a ground joint for connection to the vacuum line.

2-Methyltetrahydrofuran (from Aldrich Chemical Co.), tetrahydrofuran (from Baker Chemical Co.), and 1,4-dioxane (from Baker Chemical Co.) were distilled from lithium aluminum hydride (from Alfa Products, Ventron Corp.) under nitrogen and stored in similar bulbs. For some of the earlier work, purification of 2-methyltetrahydrofuran was effected by washing with portions of concentrated aqueous sodium hydroxide until the aqueous layer no longer turned brown, washing with water, and drying with magnesium sulfate and then with calcium hydride. Sodium-potassium alloy was occasionally used for the final drying. There was no difference in the results obtained using 2-methyltetrahydrofuran purified by the various methods.

Ethanol (from Baker Chemical Co.) was distilled at atmospheric pressure and then stored in vacuo over magnesium sulfate.

Gold Label adamantane (from Aldrich Chemical Co.) was purified by the method of Yim and Wood.[18] Trimethylamine borane (from PCR Research Chemicals, Inc.) was used as received.

N,N-Dimethylformamide (from Baker Chemical Co.), hexamethylphosphortriamide (from Aldrich Chemical Co.), methylamine, dimethylamine, and trimethylamine (all from Matheson Gas Co.) were used as received.

N,N,N',N'-Tetramethyl-p-phenylenediamine (from Eastman Chemical Co.), received as the dihydrochloride salt, was added to a concentrated aqueous solution of sodium hydroxide. The suspension was filtered and the solid sublimed at 40°C at a pressure of about 15 mm Hg.

B. Sample Preparation

Standard vacuum techniques were used in the preparation of samples. The compounds, after being de-aerated by the freeze-pump-thaw method, were separately metered into the EPR tubes or optical cells.

The EPR tubes were of standard type, Spectrosil (from Thermal American Fused Quartz Co.) or Suprasil quartz (from Amersil Co.), of 3 mm internal diameter.

For some experiments, it was desirable to avoid the hydrogen atom signals resulting from water adsorbed on the quartz. In these cases, use was made of tubes made of FEP Teflon (a fluoroethylene-propylene copolymer obtained from Fluorocarbon Process Systems Division, P.O. Box 3640, Anaheim, California 92803). The tubes, of 1/16 inch internal diameter, were attached to the vacuum line by a Swagelok tubing-to-tubing connector in conjunction with a Kovar metal to glass connection.

The optical cells were of two types, parallelepipeds 1 cm by 2 cm with a 1 cm path length (thick cells) and flat 1 cm by 1 cm with a 1 mm path length (thin cells). All were of Spectrosil or Suprasil quartz.

An attempt to prepare the anion of bromotrifluoroethylene in adamantane made use of the following procedure, which was a modification of that used by Yim and Wood.[18] Into a six-inch piece of 8 mm Pyrex tubing (sealed at one end) was placed about half a gram of adamantane, along with an amount of trimethylamine borane in the amount of one-fifth the volume of the adamantane. The tube was evacuated and sealed off. One end was placed in a paraffin bath at 125°C. When the adamantane had sublimed to the other end, the tube was cooled and opened, and the contents were scraped out and packed into an EPR tube. The EPR tube was attached to the vacuum line and evacuated, and the

bromotrifluoroethylene (2.5×10^{-5} moles) was introduced by standard vacuum techniques. The tube was sealed off and set aside for three days to allow the solute to diffuse into the matrix.

C. Radical Production

Three methods were used for the preparation of radical ions, γ-irradiation, photolysis of a solution containing N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD),[28] and pulse radiolysis (a pulsed electron beam).

The γ source was a Gammacell 200 cobalt-60 source with a dose rate of about 0.25 Mrad/hr, as determined by Fricke dosimetry.[29] Unless otherwise noted, doses were about 0.7 Mrad.

Photolysis of TMPD solutions involved a BH6 high pressure mercury arc lamp with Corning 9863 and Pyrex filters to remove any light with wavelength below 290 nm and above 400 nm. The light passed corresponds to the wavelengths of the absorption envelope of TMPD.[11]

The pulse radiolysis experiments utilized the facilities at the Center for Fast Kinetics Research, Patterson Building 131, University of Texas at Austin, Austin, Texas 78712. The radiation source was a Van de Graaff accelerator delivering electron pulses of duration 200 to 800 nsec.

D. Spectra

EPR spectra were obtained with a Varian V-4502 spectrometer system equipped with a variable-temperature controller. To obtain spectra at temperatures below about 90°K, the lowest temperature accessible with this apparatus, it was necessary to use a modified system installed by Drs. M. Shiotani and A. Hasegawa in this laboratory. A heating coil was

placed inside a 30-ℓ dewar (from Minnesota Valley Engineering, Inc.) and connected to a variable transformer. Liquid nitrogen could then be vaporized at a controlled rate, the cold vapor being led out the vent at the top of the dewar, through insulated connections, and into a 3/8-inch diameter metal coil immersed in liquid nitrogen. The vapor was then led directly into the cavity. By this method, temperatures as low as 80°K could be maintained.

The magnetic field strengths required for spectral analysis were obtained through use of a Walker/Magnemetrics Precision NMR Gaussmeter (Model G-502 from O. S. Walker Co., Inc.), in combination with a Systron-Donner 1037 frequency counter. The klystron frequency was determined with the same frequency counter. The magnetic field H at the center of the spectrum and the klystron frequency ν could then be substituted into the equation $h\nu = g\beta H$ to obtain the g factor; in the equation, h is Planck's Constant and β is the Bohr magneton.

The x-y recorder was a Hewlett-Packard 7001AM.

Optical spectra were obtained with a Cary 17 instrument equipped with a constant temperature insert dewar for observation at 77°K.[30] The solvents of choice were 3-methylhexane and 2-methyltetrahydrofuran, both of which form glasses at 77°K and so could be used with either the thick or thin cells.

The photobleachability of the radicals was investigated by use of a 1000-watt tungsten lamp, with a quartz lens to focus the beam. The EPR samples could be photolyzed in the cavity through a grating in the front. The optical dewar had to be removed from the spectrometer housing for photolysis.

E. Synthesis of trans-1,2-Dibromohexafluorocyclobutane

The procedure was essentially that of Cullen and Singh.[31] For the first two days, irradiation was by light from a 1000-watt tungsten lamp. The next day, the mixture of bromine and hexafluorocyclobutene was exposed only to visible light from the fluorescent lighting of the room. During this day, observation of a change in viscosity of the solution suggested that the tungsten lamp was unnecessary. The solution was then exposed only to visible light for another five days. Distillation gave a clear liquid having peaks in the mass spectrum at m/e 320,322,324 (c-$C_4F_6Br_2$, with bromine isotopes 79-79, 79-81, 81-81); 251,253,255 (loss of CF_3, $C_3F_3Br_2$); 241,243 (C_4F_6Br, loss of Br); 220,222,224 (loss of C_2F_4 by a retro-Diels-Alder reaction, $C_2F_2Br_2$); 190,192 (loss of CF_2Br); and 160,162 (loss of C_2F_3Br by a retro-Diels-Alder reaction, C_2F_3Br). This spectrum is entirely consistent with the molecular formula of the desired product.

CHAPTER III

RESULTS

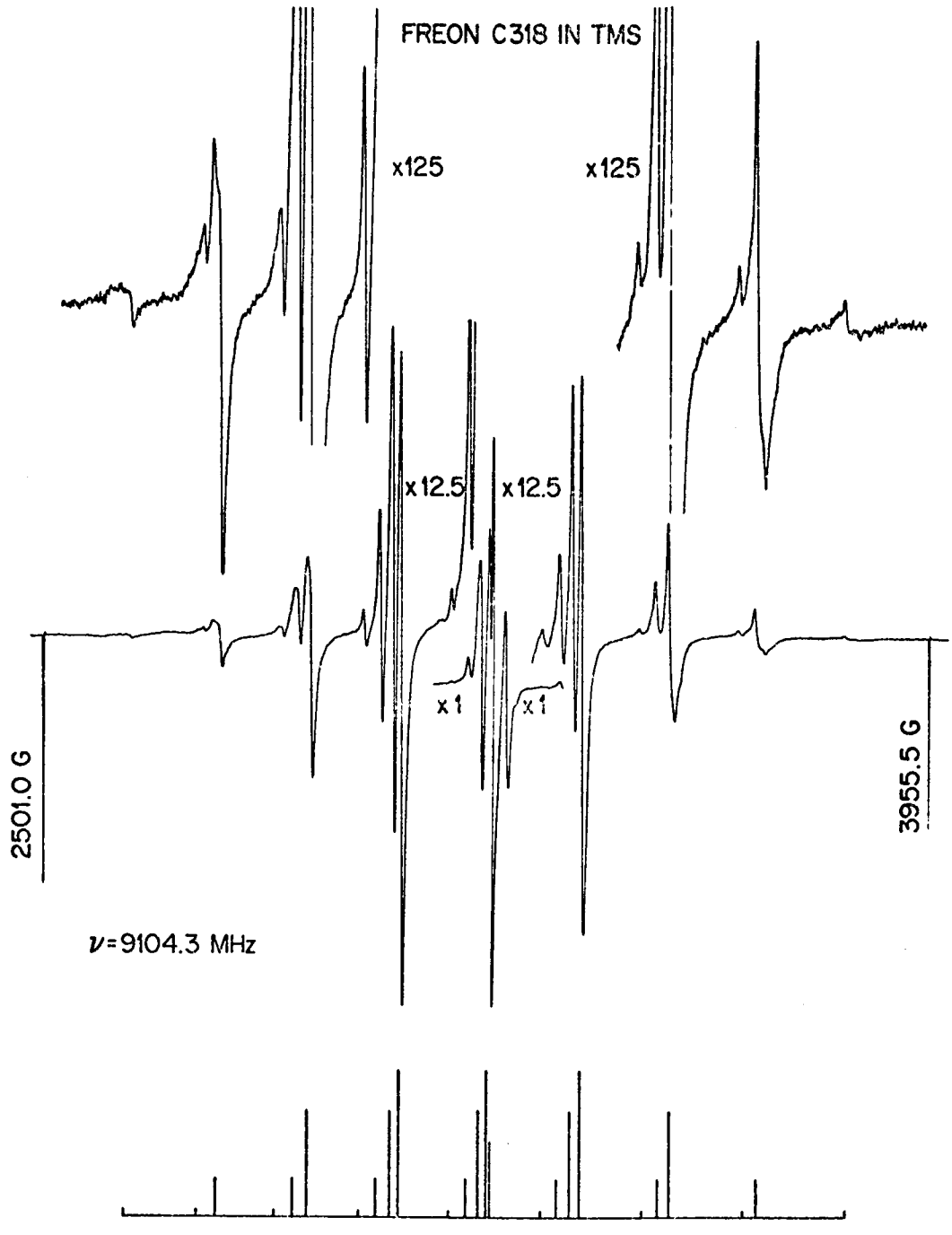
A. Perhalocycloalkanes

Previous work carried out in this laboratory had shown that the EPR spectra obtained after irradiation at 77°K of 5% solutions of hexafluorocyclopropane, octafluorocyclobutane, and decafluorocyclopentane in tetramethylsilane (TMS) became nearly isotropic when the temperature was raised above about 130°K.[15,16] Analyses of these spectra were straightforward, with coupling to six, eight, and ten equivalent fluorine atoms,[16] respectively, as revealed by the total number of lines, their relative intensities, and the anticipated second-order structure.[32] The spectrum of an irradiated solid solution of dodecafluorocyclohexane in TMS was not sufficiently well-resolved to allow a detailed analysis.[16] The values of the ^{19}F hyperfine coupling constants for the perfluorocyclopropane, perfluorocyclobutane, and perfluorocyclopentane radical anions were $\underline{a}_F$ = 197, 147, and 115 G, respectively.[16] The total widths of all the spectra were nearly the same. Generation of identical spectra by photolysis of solutions containing TMPD showed that the radicals were formed by electron addition and confirmed the assignments to the radical anions of the perfluorocycloalkanes. The spectrum of $\underline{c}\text{-}C_4F_8^-$ in TMS is shown in Figure 1.

For comparable solute concentrations, the EPR signal intensity of $\underline{c}\text{-}C_5F_{10}^-$ was less than that of $\underline{c}\text{-}C_4F_8^-$; no comparison was possible with $\underline{c}\text{-}C_6F_{12}^-$ because of the anisotropic character of the spectrum. The $\underline{c}\text{-}C_4F_8^-$ spectrum could be completely removed by photolysis for ten minutes with a 1000 watt tungsten lamp; the other anions were less

Figure 1. The EPR spectrum of a 5% solution of octafluorocyclobutane in TMS, observed at 120°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The center of the spectrum contains the central features of $\underline{c}$-$C_4F_8^-$ and the 1:2:1 pattern of $-CH_2^{\cdot}$ from TMS, identified on the basis of a blank experiment. Second order splittings are shown in the stick diagram.


FREON C318 IN TMS
x125
x125
x12.5
x12.5
x1
x1
2501.0 G
3955.5 G
ν=9104.3 MHz

stable, requiring shorter periods of photolysis.

In frozen 2-methyltetrahydrofuran (MTHF), anisotropic spectra were obtained which were usually too complicated for analysis. Hence, only those spectra are presented which were sufficiently distinctive to be used for identification, it being assumed that the same species are formed in TMS and MTHF. The spectrum of a gamma-irradiated 5% solution of octafluorocyclobutane in MTHF is shown in Figure 2; observation of the spectrum at 50 db showed the absence of the trapped electron signal. The spectrum of a gamma-irradiated 5% solution of dodecafluorocyclohexane in MTHF was so broad as to be unobservable, while that from 5% decafluorocyclopentane in MTHF was poorly resolved; in both cases, the signal of the trapped electron was observed. Gamma irradiation of a 16% solution of dodecafluorocyclohexane produced neither a spectrum from the solute nor a signal from the trapped electron.

Photolysis of a frozen solution of octafluorocyclobutane in MTHF containing a small amount of TMPD generated a spectrum identical to that in the gamma-irradiated system; the spectrum is shown in Figure 3. Because the same procedure was shown to generate $\underline{c}\text{-}C_4F_8^-$ in TMS solution, the anisotropic spectrum in MTHF is believed to be due to $\underline{c}\text{-}C_4F_8^-$. By analogy, the radicals produced by irradiation of solutions of dodecafluorocyclohexane are hereafter referred to as the radical anions of the parent molecules.

A gamma-irradiated solution of <u>trans</u>-1,2-dibromohexafluorocyclobutane in TMS showed an unresolved EPR spectrum which decayed at 110°K without the growth of a new spectrum. No enhancement of resolution was obtained as the temperature was raised.

In MTHF at 95°K, the EPR spectrum from gamma-irradiated

Figure 2. The EPR spectrum of a 5% solution of octafluorocyclobutane in MTHF, observed at 87°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The center of the spectrum is dominated by the seven-line pattern from MTHF, identified on the basis of a blank experiment.

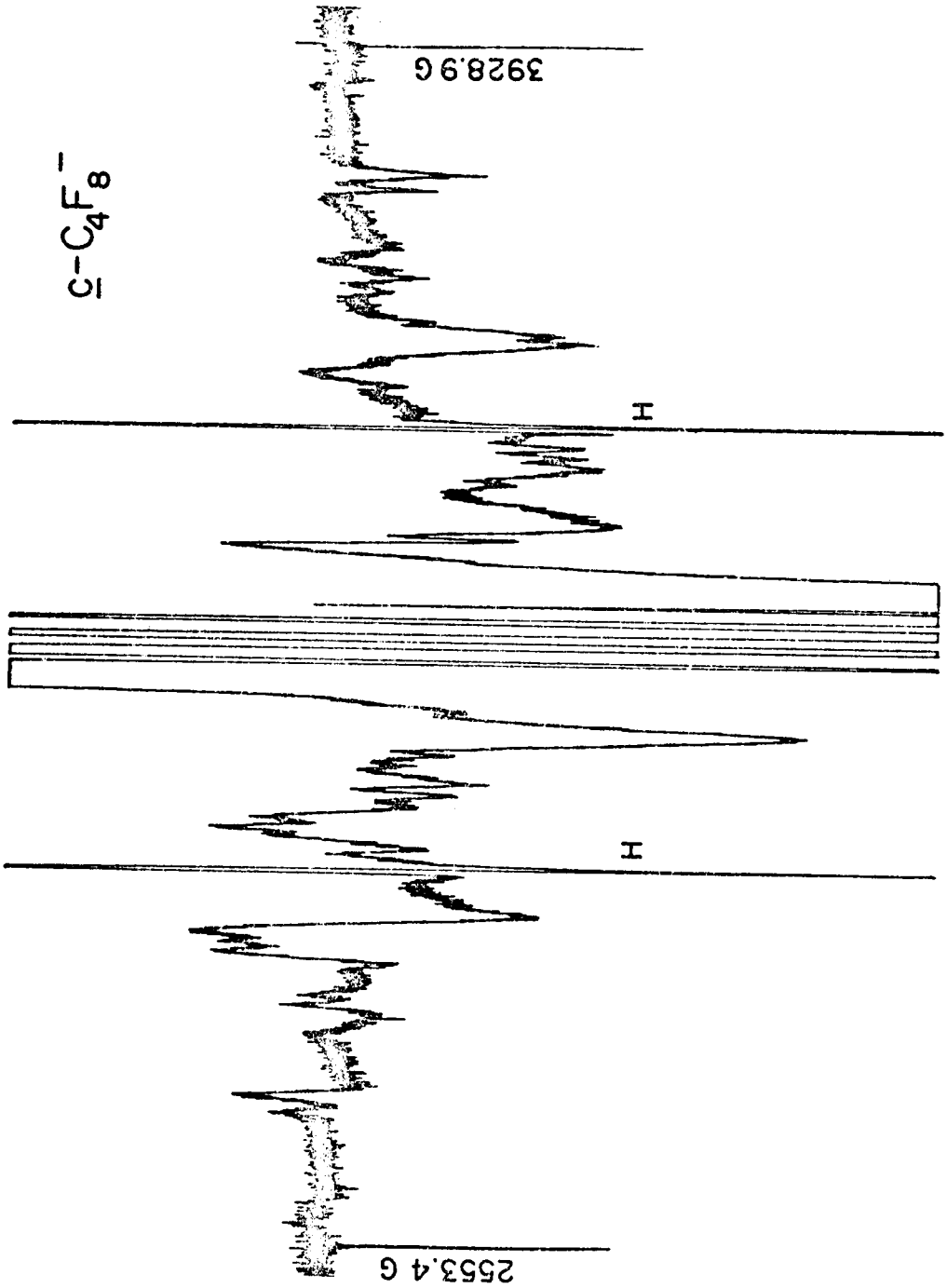
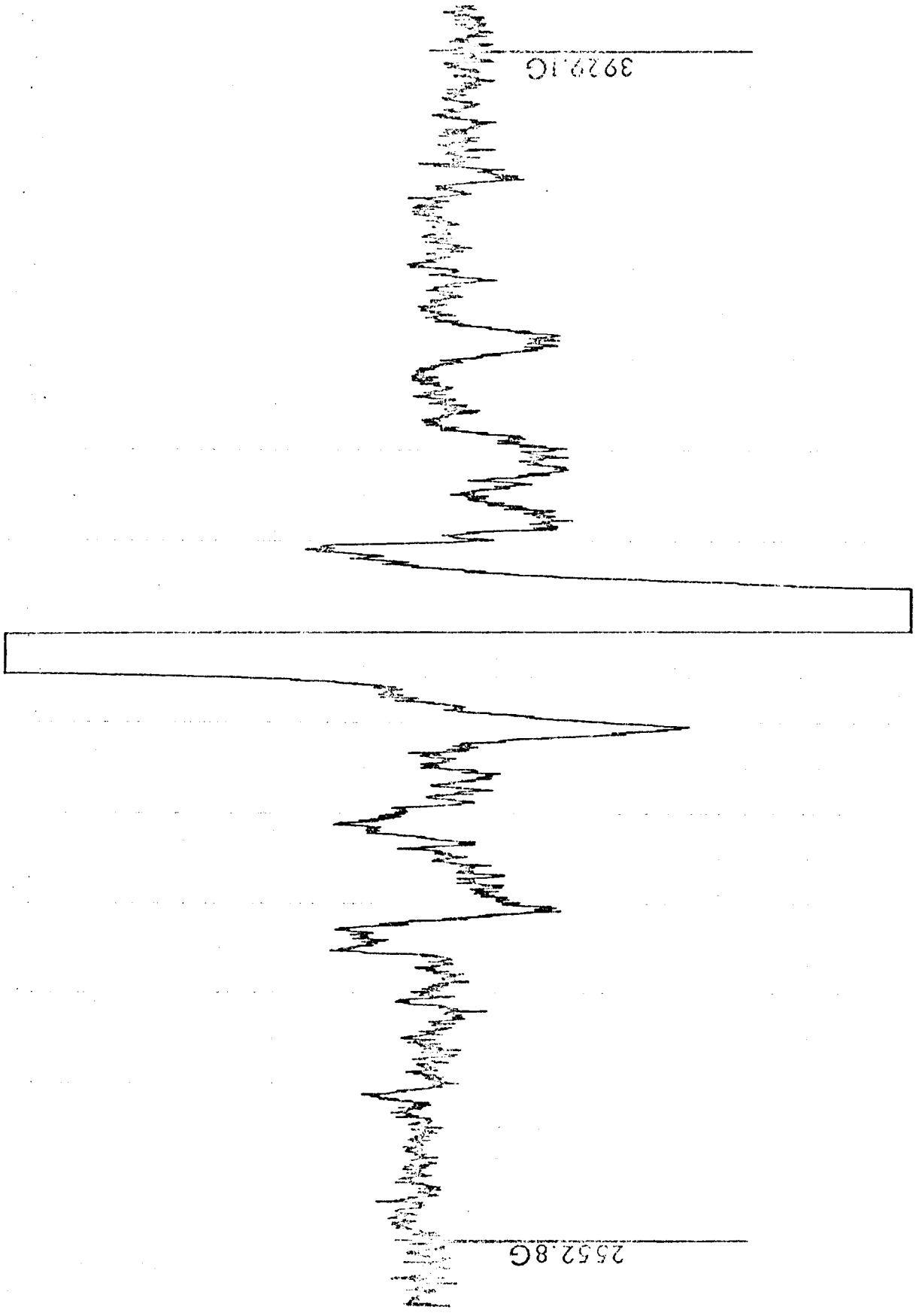

c-C4F8-
3928.9 G
H
H
2553.4 G

Figure 3. The EPR spectrum of a 5% solution of octafluorocyclobutane in MTHF containing TMPD, observed at 87°K after photolysis at that temperature with uv light of wavelength 290-390nm.

The center of the spectrum is dominated by the spectrum of $TMPD^{+}$, which was observed in a blank experiment.


3929.1G
2552.8G

1,2-dichlorohexafluorocyclobutane consisted of broad features in the wings (Figure 4). The spectrum from the corresponding dibromo compound was much broader and less well-resolved. No trapped electron signal was observed in 5% solutions of these compounds.

The optical spectra from all the perhalocycloalkanes, obtained by difference between spectra taken before and after irradiation in MTHF or 3-methylhexane solution at 77°K, consisted of structureless bands, the maxima of which are listed in Table I. The wavelengths of the maxima of the decafluorocyclopentane and dodecafluorocyclohexane solutions are perhaps a little low since the signals were low-intensity shoulders on the high wavelength tail of the MTHF spectrum; subtraction of the MTHF spectrum may have resulted in some error.

Compared with perfluorocyclobutane, both the perfluorocyclopentane and the perfluorocyclohexane seem to have lower electron capture efficiencies, as shown by the presence in the optical spectra from 5 mole % solutions of both compounds in MTHF of an intense signal at 1200 nm, characteristic of the trapped electron.[33] This absorption, however, was not as intense as that from pure MTHF. No trapped electron absorption was present in 5 mole % gamma-irradiated solutions of perfluorocyclobutane in MTHF. Photolysis of the decafluorocyclopentane solution with unfiltered light from a tungsten lamp resulted in loss of the absorption of the trapped electron, accompanied by growth of the absorption of $\underline{c}\text{-}C_5F_{10}^-$. The corresponding photolysis of the dodecafluorocyclohexane solution led to the loss of the signal of $\underline{c}\text{-}C_6F_{12}^-$. However, use of a Corning 2030 filter to cut out all light with wavelengths below 650 nm allowed the photolysis to remove the trapped electron signal, while the $\underline{c}\text{-}C_6F_{12}^-$ absorption was enhanced by a factor of two.

Figure 4. The EPR spectrum of a 5% solution of 1,2-dichlorohexafluorocyclobutane in MTHF, observed at 87°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The center of the spectrum from the solute is dominated by the seven-line spectrum from MTHF.

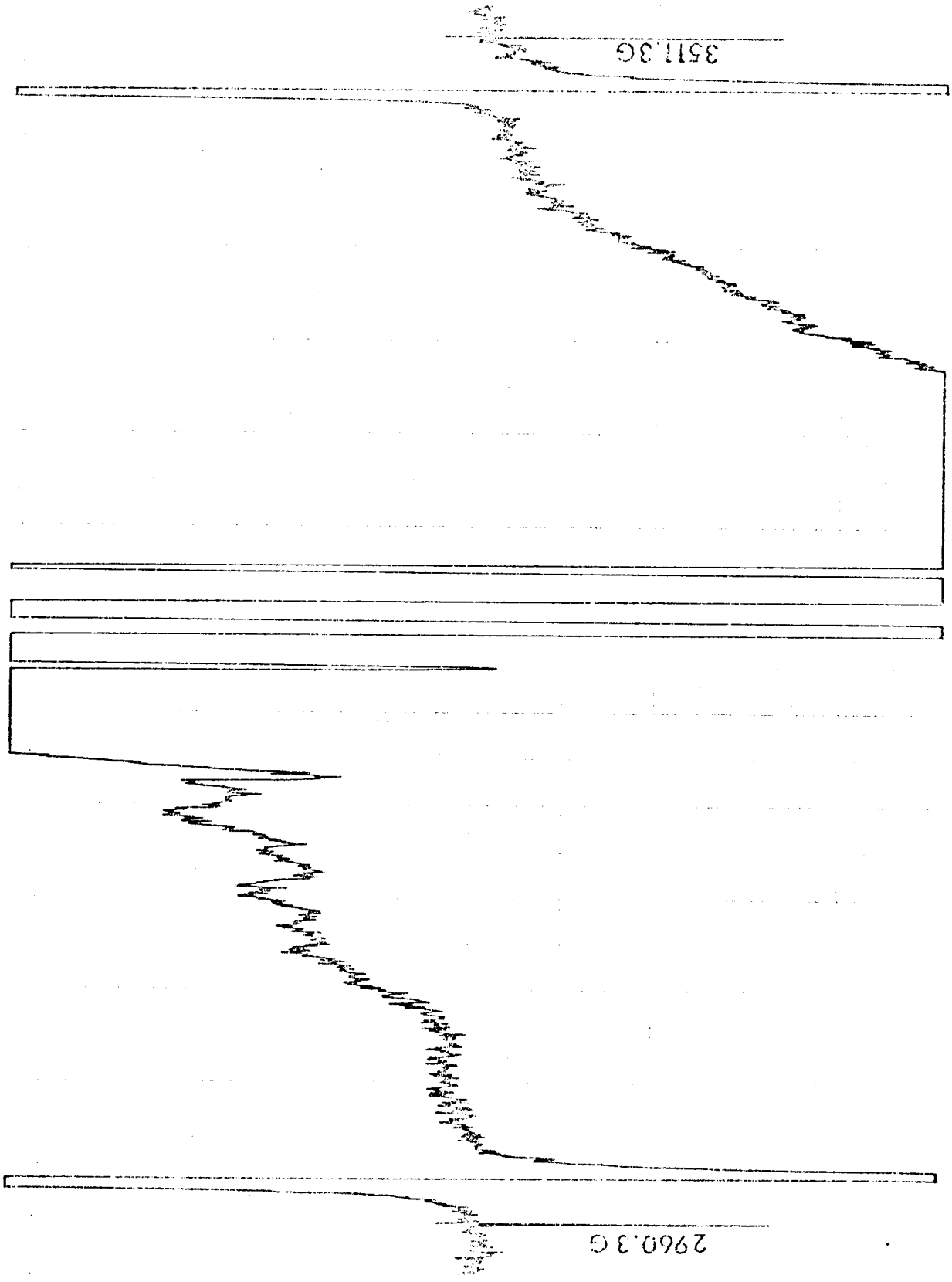

3511.3G
2960.3G

TABLE I

OPTICAL CHARACTERISTICS OF GAMMA-IRRADIATED SOLUTIONS OF PERHALOCYCLOALKANES[a]

Solute	Solvent	λ_{MAX} (nm)	OD (λ_{MAX})
Octafluorocyclobutane	2-Methyltetrahydrofuran (MTHF)	390	0.22
Decafluorocyclopentane	MTHF	420	0.25[b]
			2.5[c]
Dodecafluorocyclohexane	MTHF	460	0.08[b]
			>3.0[c]
1,2-Dichlorohexafluorocyclobutane	MTHF	342	1.2
1,2-Dibromohexafluorocyclobutane	MTHF	367	1.1
	3-Methylhexane	376	1.0

a. For solute concentration of 6%, dose 0.75 Mrad, path length 1 mm, 77°K.

b. After photolysis. See text.

c. Optical density of trapped electron absorption at 1200 nm before photolysis.

It was found that intense optical absorption bands were obtained from solutions of any of the perhalocycloalkanes if the samples were exposed to light at room temperature for more than a few hours before being frozen for the spectrum taken before gamma irradiation. Since these bands overlapped the bands of the perhalocycloalkane anions, it was impossible to obtain reliable results using such solutions.

B. Fluorinated Ethylenes--EPR Studies

1. 1,1-Difluoroethylene

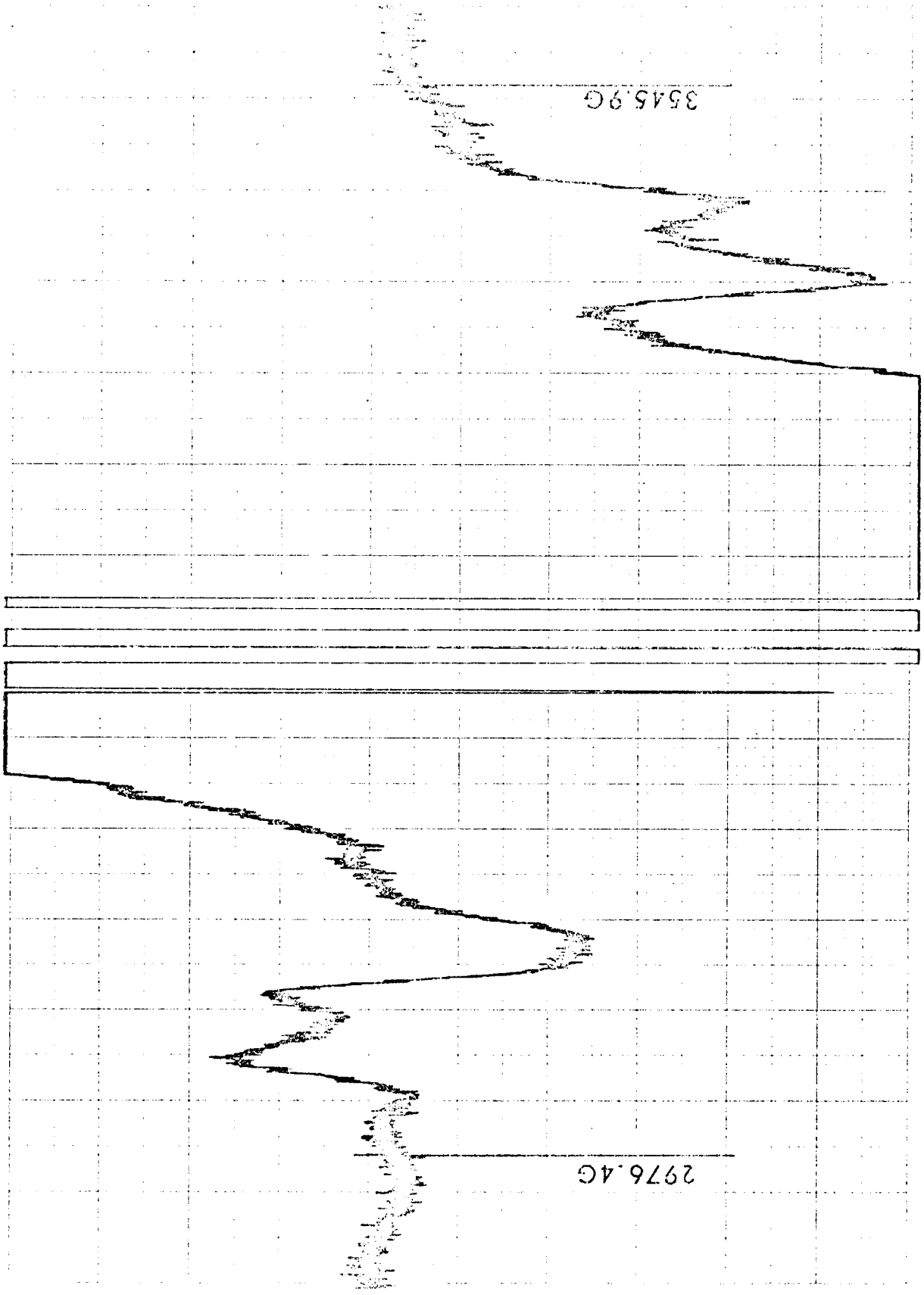
Gamma irradiation at 77°K of a 5% solution of 1,1-difluoroethylene in TMS produced at 83°K a low-intensity, anisotropic EPR spectrum which, except for the narrower features, looked very much like the spectrum described below for irradiated 1,1-difluoroethylene in MTHF. The spectrum was not affected by rotation of the sample in the magnetic field. Raising the temperature to 110°K resulted in the complete decay of the spectrum, which never became isotropic. A solution in neopentane had essentially the same spectrum and behaved similarly.

Gamma irradiation of a 5% solution in MTHF yielded an EPR spectrum consisting of two well-defined sets of anisotropic features, as shown in Figure 5. An FEP tube was used for this spectrum because it was found that the outer feature on the high-field side overlapped the hydrogen atom line. The extreme breadth of the solvent spectrum totally obscured the center, making it impossible to determine how many additional sets of features were present there.

If it is assumed that the two fluorine atoms are anisotropically equivalent and that the total hyperfine coupling of the hydrogen atoms is less than the linewidths of the features, an analysis of the spectrum

Figure 5. The EPR spectrum of a 5% solution of 1,1-difluoroethylene in MTHF, observed at 87°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The intense seven-line spectrum from the solvent obscures all but the wings of the spectrum from the solute.


3545.9G
2976.4G

can be carried out. The ^{19}F hyperfine tensors are assumed to be axially symmetric. The two outer features, which have the shape expected for parallel features,[34] are separated by 459.5 G, while the two inner ones, with the shape expected for perpendicular features,[34] are separated by 343.9 G. These spacings are approximately twice the ^{19}F coupling since these observed features are taken to be the outer components of a 1:2:1 pattern.

For anisotropic spectra with axially symmetric hyperfine tensors and large hyperfine couplings, second-order corrections[35] must be applied separately to the parallel and perpendicular features, as shown in Equation 6, where I is the total nuclear spin of all the equivalent

$$(I^2 + I - m_I^2)\frac{A^2}{2H} = \text{shift} \qquad (6)$$

atoms, m_I is the component of this spin along the direction of the applied field, H is the magnetic field at which the feature is detected, and A is the magnitude of the hyperfine coupling constant. For the correction to the parallel set of features, $A^2 = A_\perp^2$, and for the perpendicular set, $A^2 = \frac{1}{2}(A_\perp^2 + A_{//}^2)$, where $A_\perp$ is the coupling in the perpendicular spectrum and $A_{//}$ is the coupling in the parallel spectrum.

Application of this correction yielded $\underline{A}_{//}^F(2) = 229.6$ G and $\underline{A}_\perp^F(2) = 171.6$ G. An estimation of the g factor was made from a spectrum in a quartz tube, where the spectrum of the hydrogen atom was used to calculate the frequency, this procedure being necessary because the frequency counter was not operational during the time these spectra were obtained. The corrected centers of the parallel and perpendicular sets of features were then used in the calculation of the g factors. The values obtained, $g_\perp = 2.002$ and $g_{//} = 2.003$, are accurate to only perhaps ±0.001 because of the uncertainties in the positions of the

features.

Gradually raising the temperature resulted in decay of the spectrum, starting at 89±1°K. By 96°K, the spectrum had completely disappeared, without the appearance of any new features. Exposure of a sample to room light at 89°K resulted in decay of the spectrum at a rate much faster than that observed for thermally-induced decay alone.

An attempt to generate the spectrum by photolysis of a solution of 1,1-difluoroethylene in MTHF containing a small amount of TMPD failed.

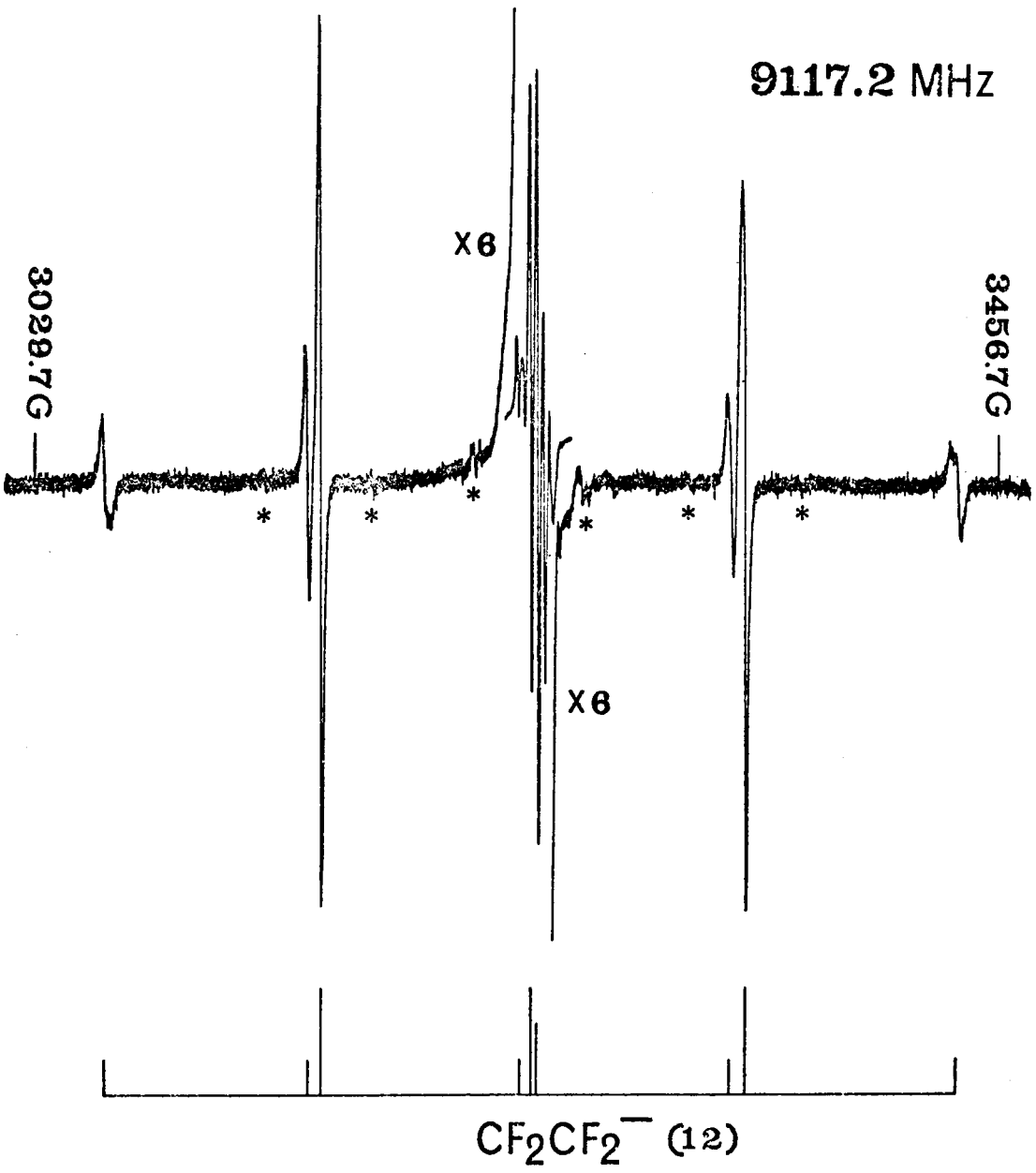
2. Tetrafluoroethylene

The EPR spectrum of a 5% solution of tetrafluoroethylene in TMS-$\underline{d}_{12}$,[36] observed at 120°K after gamma irradiation at 77°K, consisted of lines from two distinct spectral patterns. Both spectra were isotropic or nearly so, one being of much higher intensity than the other. Raising the temperature briefly to 140°K resulted in loss of the low-intensity spectrum. The remaining spectrum, shown in Figure 6, consisted of six components, corresponding to the (m_I,I) values (±2,2), (±1,2), and (±1,1) of a species possessing four equivalent fluorine nuclei, which have spin 1/2. The placement of all the components agreed with the second-order structure calculated[32] for such a radical with a fluorine hyperfine coupling ($\underline{a}_F$) of 94.3 G and a g value of 2.0027 ± 0.0004. The central line of the 1:4:6:4:1 pattern consisted of the (0,0), (0,1), and (0,2) components, the first two of which were buried under the spectrum of radicals from the solvent. Other studies carried out in these laboratories yielded a value of 48.7 G for the coupling to carbon-13.[36]

The low-intensity spectrum was identified as belonging to $\underline{c}$-$C_4F_8^-$, which had been previously observed by Shiotani and Williams[15] after gamma

Figure 6. The EPR spectrum of a 5% solution of tetrafluoroethylene in TMS-$\underline{d}_{12}$, observed at 120°K after gamma irradiation to a dose of 0.75 Mrad and annealing at 140°K.

Second-order splittings are shown in the stick diagrams. The central features from the solute are clearly visible in the center but are partially overlapped by the 1:2:3:2:1 pattern from the solvent. Stars are placed at the positions of C-13 satellites.


9117.2 MHz
3028.7G
3456.7G
X6
X6
$CF_2CF_2^-$ (12)

irradiation of a frozen solution of octafluorocyclobutane in neopentane.

It has also been shown[36] that a spectrum identical to the high-intensity spectrum can be generated by photolysis of a frozen solution of tetrafluoroethylene in TMS containing TMPD; this showed that the radical resulted from electron capture. The wavelength of the photolyzing light was carefully controlled with Corning 9863 and Pyrex filters (passing light of wavelength 290 to 390 nm) since separate experiments had shown that photolysis with unfiltered light from a tungsten lamp effected removal of the EPR spectrum from an irradiated sample.

Irradiation at 77°K of a 5% solution of tetrafluoroethylene in TMS-$\underline{d}_{12}$ produced a species having some orientation dependence below 110°K. That is, the EPR spectrum changed in appearance upon rotation of the sample within the magnetic field. The parallel spectrum could be strongly enhanced at certain orientations; the changes were much smaller in the less intense, less well-resolved perpendicular spectrum. In addition to these features, a more intense set of apparently isotropic features was present having the same coupling constant and g factor as the isotropic spectrum described above. A spectrum containing both isotropic and anisotropic features is shown in Figure 7.

The temperature of the oriented sample was lowered in an attempt to produce the same degree of anisotropy in the spectrum of $C_2F_4^-$ in TMS-$\underline{d}_{12}$ as was found in the spectrum in MTHF (see below). However, though line positions did change slightly, the spectrum at 77°K still did not have quite the same total width (spectral extent) as the spectrum in MTHF. Raising the temperature to 120°K resulted in a change in the spectrum from partially anisotropic to totally isotropic; the spectrum remained isotropic when the temperature was lowered to 90°K.

Figure 7. The EPR spectrum of a 5% solution of tetrafluoroethylene in TMS-$\underline{d}_{12}$, observed at 95°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

Stick diagrams are used to distinguish isotropic and anisotropic features. The center of the spectrum contains also the features of the 1:2:3:2:1 quintet from the solvent.

3523.2G
iso
⊥
//
2968.2G

The second-order shifts of the parallel and perpendicular features were analyzed as previously described. In this case, as in all others studied in the course of this work, the parallel features had the larger coupling constants, causing the shifts in the positions of the perpendicular features to be larger than the shifts of the corresponding parallel features.

Analysis by this method of the spectrum of the oriented sample observed at 95°K yielded $\underline{A}^{F}_{\perp}(4)$ = 78.0 G, $\underline{A}^{F}_{//}(4)$ = 126.2G, $g_{\perp}$ = 2.0044, and $g_{//}$ = 2.000, which led to the isotropic values $\underline{a}_{F}$ (4) = 94.7 G and g = 2.0029, in good agreement with the values 94.3 G and 2.0027 determined from the isotropic spectrum.

The EPR spectrum observed at 87°K after gamma irradiation of a 2% solution of tetrafluoroethylene in MTHF, shown in Figure 8, was anisotropic and had a slightly greater spectral extent (width) than did the anisotropic spectrum of $C_2F_4^-$ in the oriented TMS sample. The (+2,2) feature of the parallel set, almost obscured by the low-field hydrogen line in this spectrum, was clearly revealed in a spectrum obtained in FEP tubing (see inset). Analysis by the method outlined above yielded $\underline{A}_{\perp}$ = 74.4G and $\underline{A}_{//}$ = 135.9G, from which an isotropic coupling constant $\underline{a}_{F}$ = 94.9 G was derived.

A spectrum matching that obtained by gamma irradiation was produced by photolysis of a solution of tetrafluoroethylene in MTHF containing TMPD; the spectrum is shown in Figure 9. This experiment demonstrated that the spectrum arose as a result of electron addition to $C_2F_4^-$.

When a gamma-irradiated 2% solution of tetrafluoroethylene in MTHF was warmed above 83°K, major spectral changes were observed starting at

Figure 8. The EPR spectrum of a 2% solution of tetrafluoroethylene in MTHF, observed at 87°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

Inset: the low-field part of a spectrum obtained under the same conditions in FEP tubing, showing the (+2,2) feature previously hidden under the hydrogen line.
The second-order splitting is shown in the stick diagram of the perpendicular spectrum but is omitted from that of the parallel spectrum because the linewidths and magnitude of the shifts are such that the splitting cannot be observed. The center of the spectrum is complicated by the presence of the seven-line spectrum from MTHF. The inset spectrum was obtained on a slightly wider scale than the other spectrum.

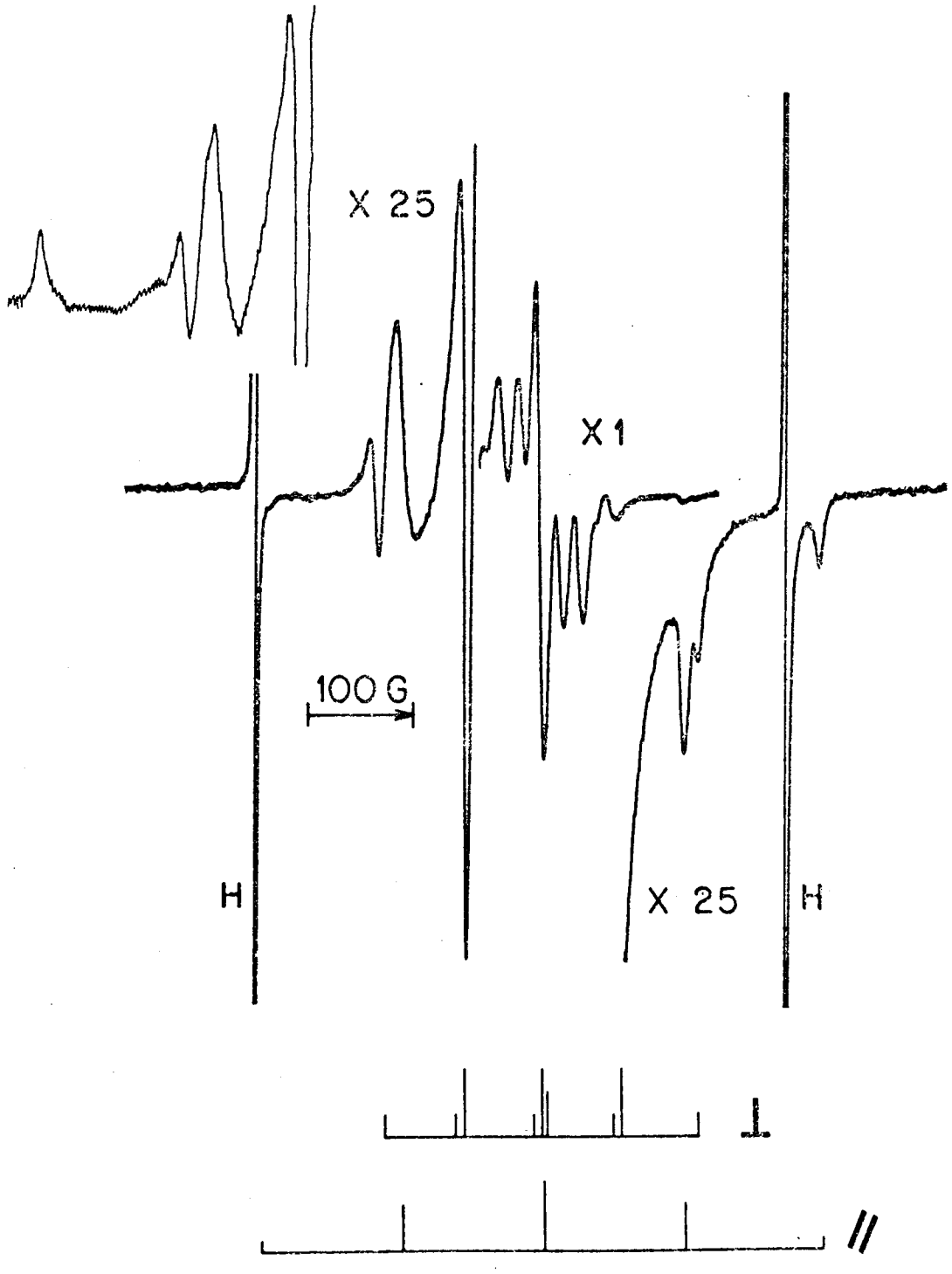
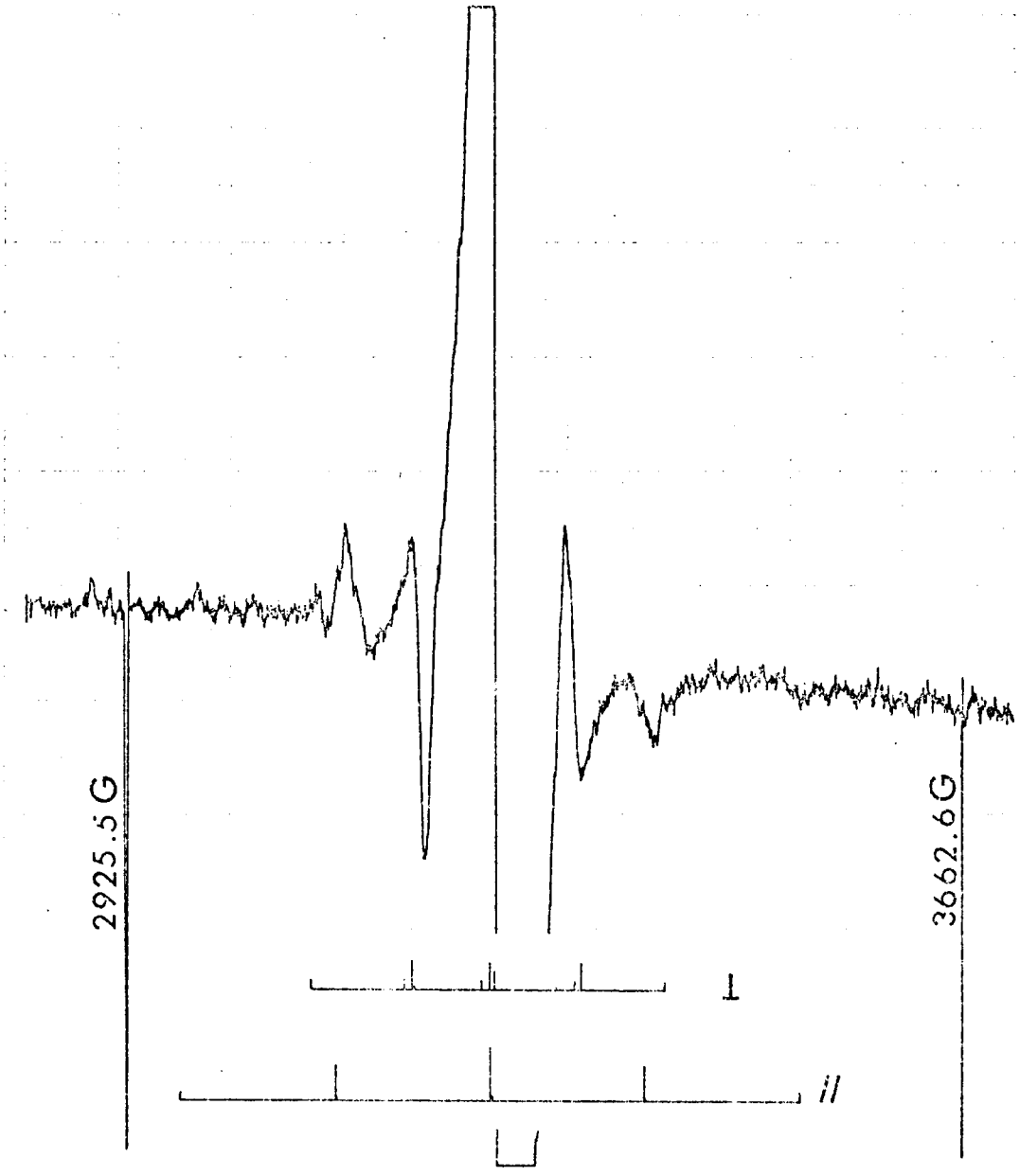

X 25
X 1
100 G
H
X 25
H
⊥
//

Figure 9. The EPR spectrum of a 2% solution of tetrafluoroethylene in MTHF containing TMPD, observed at 87°K after photolysis at 77°K with light of wavelength 290-390 nm.

The stick diagram identifies the parallel and perpenpicular components. The center of the spectrum is dominated by the spectrum of $TMPD^{+}$.


2925.5G
3662.6G
⊥
//

93°K. The decay of the features ascribed to $C_2F_4^-$ was accompanied by the growth of a set of features matching those observed in gamma-irradiated octafluorocyclobutane in MTHF and therefore attributable to $\underline{c}$-$C_4F_8^-$. The transformation is shown in Figure 10, spectrum $\underline{a}$ having been recorded at 84°K before the annealing process and spectrum $\underline{b}$ at 84°K after the temperature had been raised to 95°K and held there for several minutes. Raising the temperature to 97°K resulted in loss of the spectrum of $\underline{c}$-$C_4F_8^-$, while the seven-line spectrum of the MTHF radical was found not to change until the temperature reached 102°K.

An estimation of the efficiency of this secondary reaction was obtained by comparison of the signal intensities of $\underline{c}$-$C_4F_8^-$ obtained indirectly, in this way, and directly, by gamma irradiation of a frozen solution of octafluorocyclobutane in MTHF. Frozen solutions of tetrafluoroethylene and octafluorocyclobutane, present at the same concentration, yielded after gamma irradiation and annealing spectra of $\underline{c}$-$C_4F_8^-$ whose signal intensities were in the ratio of 0.4:1. If the yields of $C_2F_4^-$ and $\underline{c}$-$C_4F_8^-$ were the same, the conversion was 40%.

Gamma-irradiated solid solutions of MTHF with higher concentrations of tetrafluoroethylene (5%, for example) produced mostly the $C_2F_4^-$ spectrum but also the spectrum of $\underline{c}$-$C_4F_8^-$, even at 83°K before any annealing.

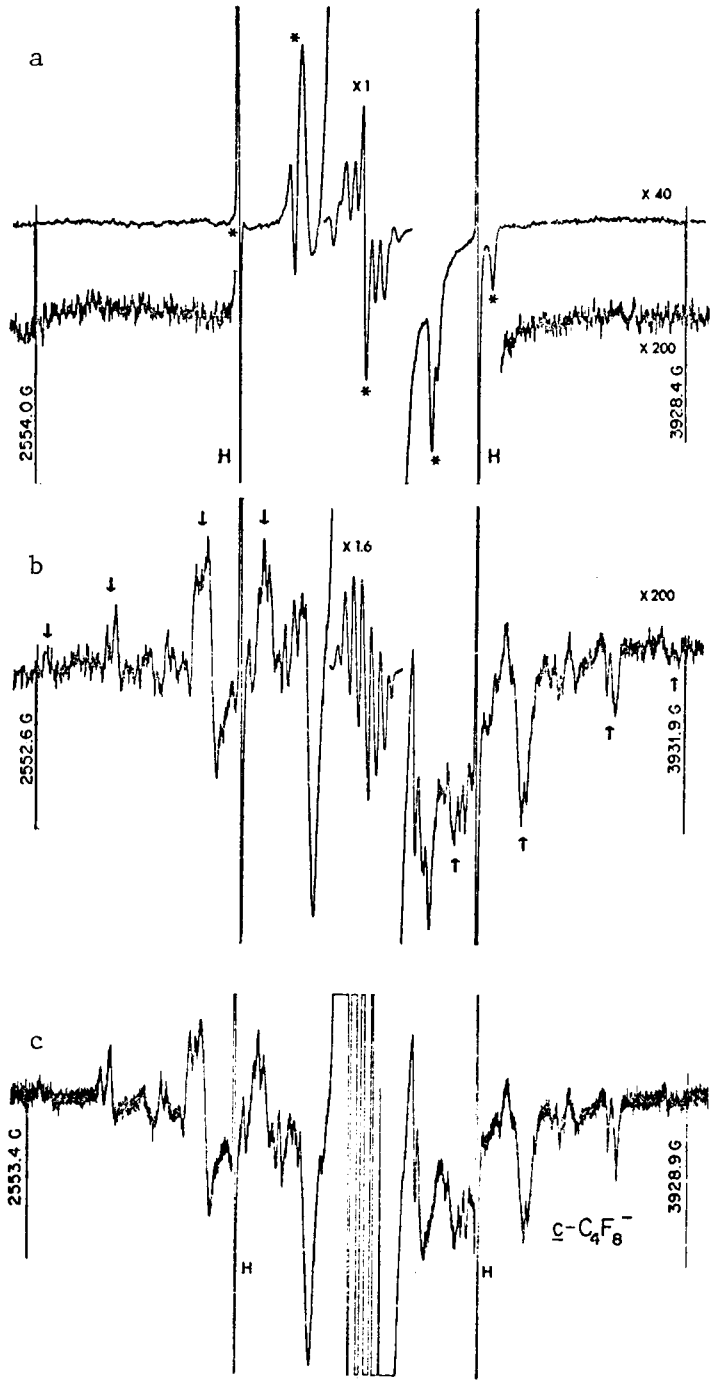
A similar transformation was carried out in 3-methylhexane. As in MTHF, a temperature of 95°K was required.

3. 1,1-Dichloro-2,2-difluoroethylene

A 5% solution of 1,1-dichloro-2,2-difluoroethylene in TMS-$\underline{d}_{12}$ exhibited, after gamma irradiation at 77°K, an EPR spectrum which changed on rotation of the sample in the magnetic field. The features

Figure 10. The EPR spectrum of a 2% solution of tetrafluoroethylene in MTHF, observed at 87°K before (a) and after (b) annealing at 95°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The arrows of b refer to features of the anisotropic spectrum of c-C_4F_8. Spectrum c resulted from gamma irradiation at 77°K to a dose of 0.75 Mrad of a 5% solution of octafluorocyclobutane in MTHF. The seven-line spectrum from MTHF dominates the centers of all three spectra.


a
X 1
X 40
X 200
2554.0 G
3928.4 G
H
H
b
X 1.6
X 200
2552.6 G
3931.9 G
c
2553.4 G
3928.9 G
H
H
c-C4F8-

of Figure 11 were replaced by those of Figure 12 by a 90° rotation of the sample in the cavity. The spectra, which were obtained at 98°K, could not be analyzed. The total width of the "parallel" spectrum was 384 G.

Gamma irradiation at 77°K of a 5% solution of 1,1-dichloro-2,2-difluoroethylene in MTHF produced the spectrum shown in Figure 13, observed at 87°K. Warming the sample resulted in loss of the signal, without the appearance of any new features.

Since the spectrum in TMS was more distinctive than the one in MTHF, generation of the former by photolysis of a frozen solution containing TMPD was considered a more definitive demonstration that electron capture had occurred. Part of the spectrum resulting from photolysis of a frozen solution of 1,1-dichloro-2,2-difluoroethylene in TMS containing TMPD is shown as an inset in Figure 11.

4. 1,1-Dibromo-2,2-difluoroethylene

The EPR spectra obtained after gamma irradiation were essentially unchanged between 77°K and the temperature at which the species disappeared and consisted of a few broad, unresolved features in either MTHF or TMS, with no apparent orientation dependence. The spectra could not be analyzed.

5. Trifluoroethylene

A gamma-irradiated solution of trifluoroethylene in TMS-d_{12} resulted in a low-intensity EPR spectrum which exhibited at 98°K no observable orientation dependence and which defied analysis. Raising the temperature did not produce an improvement in resolution.

Gamma irradiation at 77°K of a 5% solution of trifluoroethylene in MTHF produced spectrum a of Figure 14, observed at 87°K. Warming the sample to 100°K for a minute and re-cooling to 87°K produced spectrum b,

Figure 11. The perpendicular EPR spectrum of a 5% solution of 1,1-dichloro-2,2-difluoroethylene in TMS-$\underline{d}_{12}$, observed at 98°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

Inset: a portion of the spectrum obtained at 98°K by uv photolysis at 77°K of a similar solution containing TMPD.
The complete spectrum is dominated by the 1:2:3:2:1 quintet from the solvent. The inset spectrum was of lower intensity and so was observed at higher modulation; because of this, the resolution is poorer.

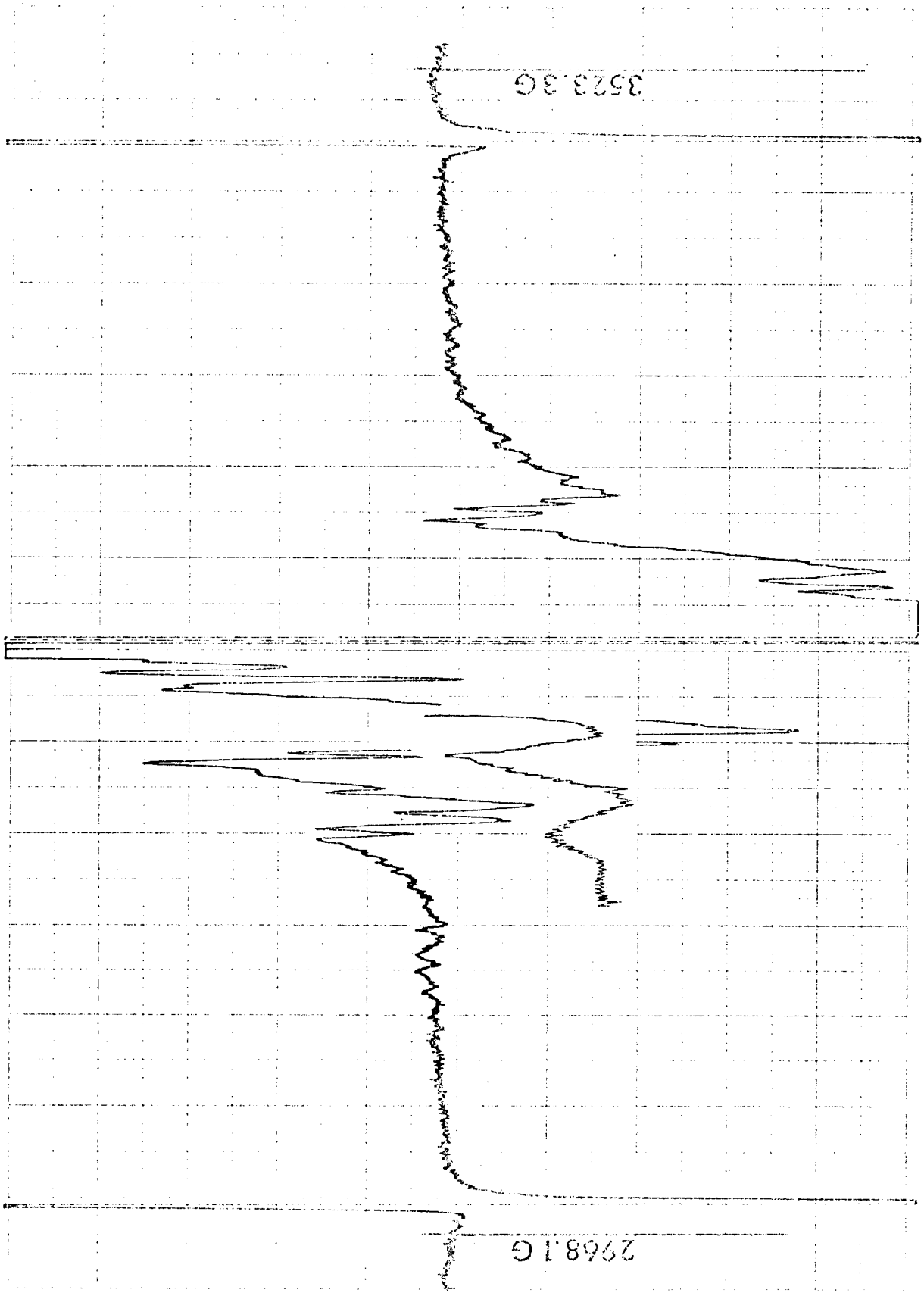

3523.3G
2968.1G

Figure 12. The parallel EPR spectrum of a 5% solution of 1,1-dichloro-2,2-difluoroethylene in TMS-d_{12}, observed at 98°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The center of the spectrum is dominated by the 1:2:3:2:1 quintet from the solvent.

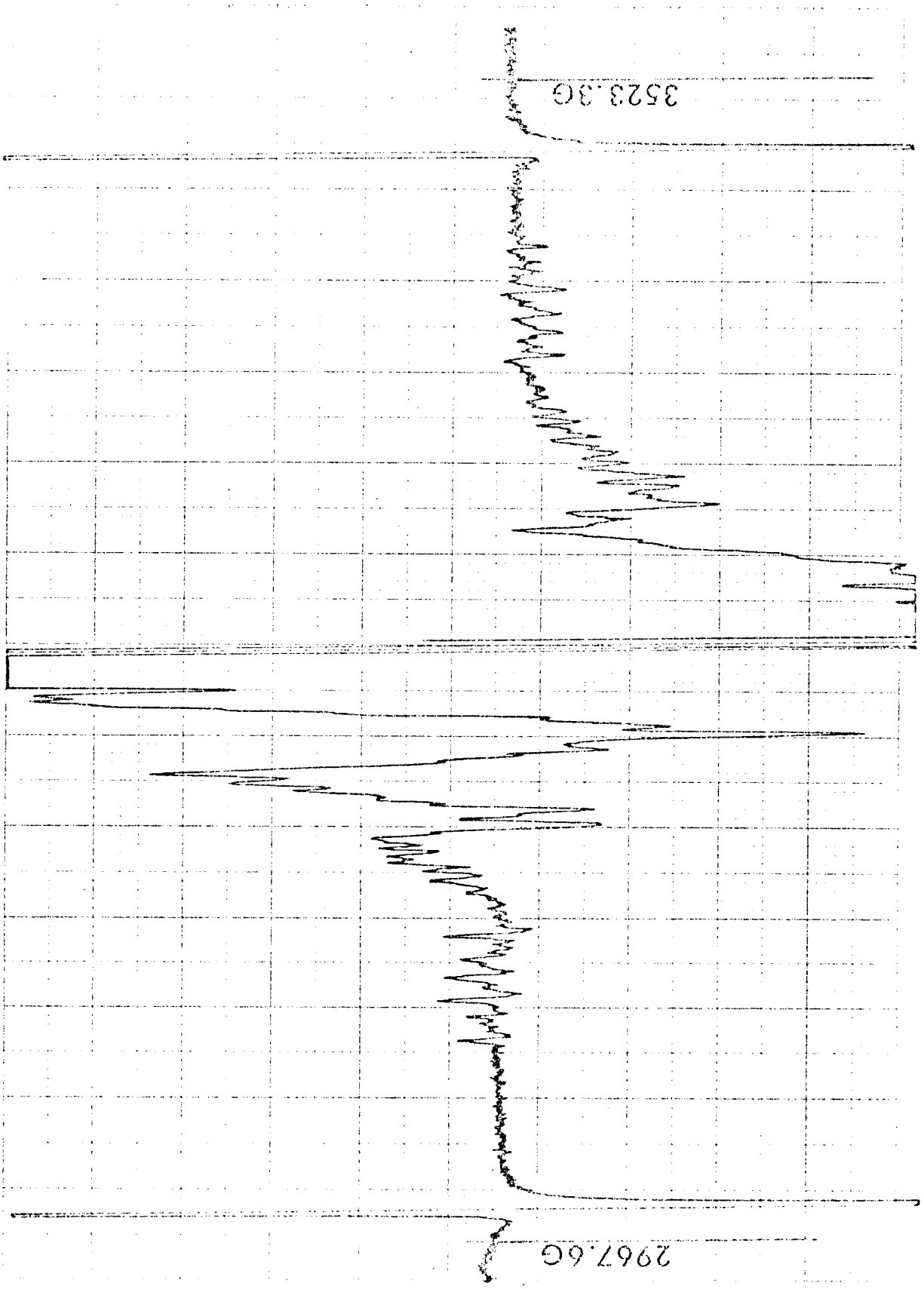

3523.3G
2967.6G

Figure 13. The EPR spectrum of a 5% solution of 1,1-dichloro-2,2-difluoroethylene in MTHF, observed at 87°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

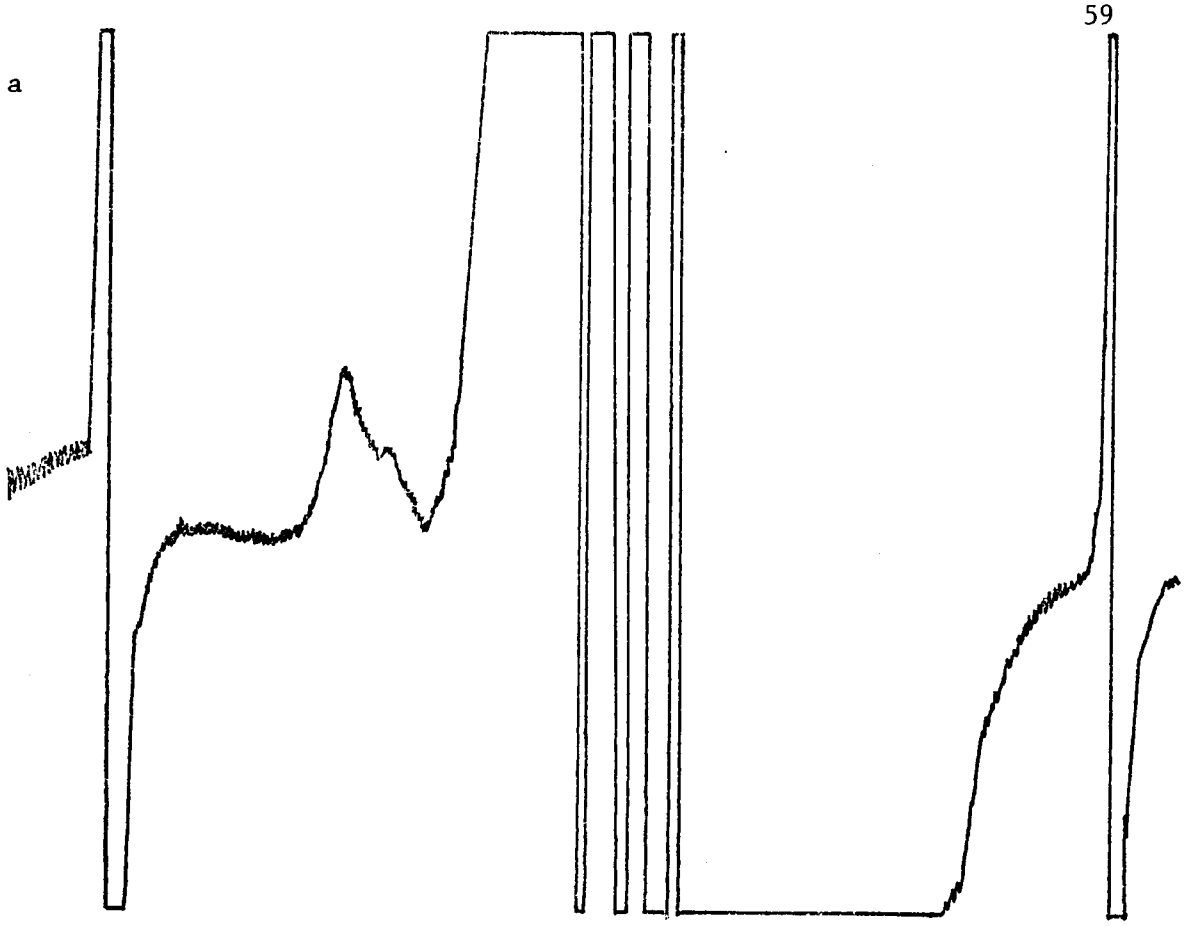
The center of the spectrum is dominated by the seven-line pattern from MTHF.

3929.2G
2553.2G

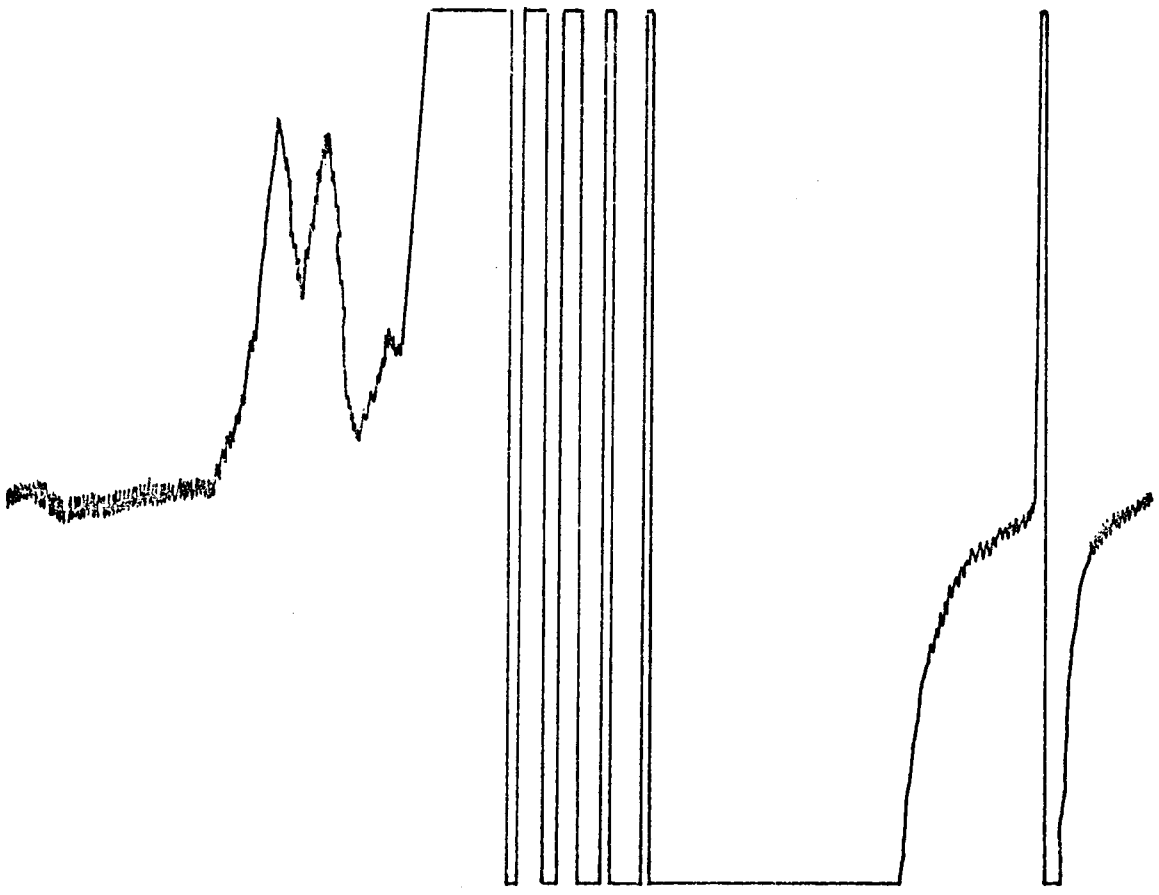
Figure 14. The EPR spectra of a 5% solution of trifluoroethylene in MTHF, observed at 87°K before (a) and after (b) annealing at 100°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The centers of the spectra are dominated by the seven-line pattern from MTHF.

a



b



which was obtained at the same instrumental conditions. In both cases, the solvent spectrum obscures all the features but the pairs in the wings.

Photolysis of a solution of trifluoroethylene in MTHF containing TMPD produced a low-intensity spectrum matching that obtained by gamma irradiation.

6. Chlorotrifluoroethylene

Gamma irradiation at 77°K of a 5% solution of chlorotrifluoroethylene in TMS-$\underline{d}_{12}$ produced an EPR spectrum having an orientation dependence, as shown in Figure 15 and 16, which were obtained by rotation of the sample by 90° in the magnetic field. The features of Figure 15, consisting of predominantly positive excursions on the low-field side and negative excursions on the high-field side, have lineshapes characteristic of parallel features from radicals with axially symmetric hyperfine tensors.[34] This set of features is referred to as the "parallel" set, whereas the set of features in Figure 16 is referred to as the "perpendicular" set. These features also have characteristic lineshapes[34] and, in contrast to the "parallel" features, have predominantly negative excursions on the low-field side and the opposite on the high-field side.

The pattern of the "parallel" spectrum was analyzed as involving coupling from one chlorine nucleus and only two fluorine nuclei rather than three. An unambiguous analysis was possible because of the presence of two isotopes of chlorine, ^{35}Cl (I = 3/2) and ^{37}Cl (I = 3/2), which have magnetic moments[37] and therefore hyperfine couplings in the ratio 1.201 to 1 and isotopic abundances[37] in the ratio 76.4 to 24.6. The couplings are $\underline{A}_{//}$ (^{35}Cl) = 83.8 G, $\underline{A}_{//}$ (^{37}Cl) = 69.6 G, $\underline{A}_{//}$ (F_1) = 134.3 G,

Figure 15. The parallel EPR spectrum of a 5% solution of chlorotrifluoroethylene in TMS-$\underline{d}_{12}$, observed at 98°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The intense 1:2:3:2:1 quintet from the solvent masks the central features of the spectrum from the solute.

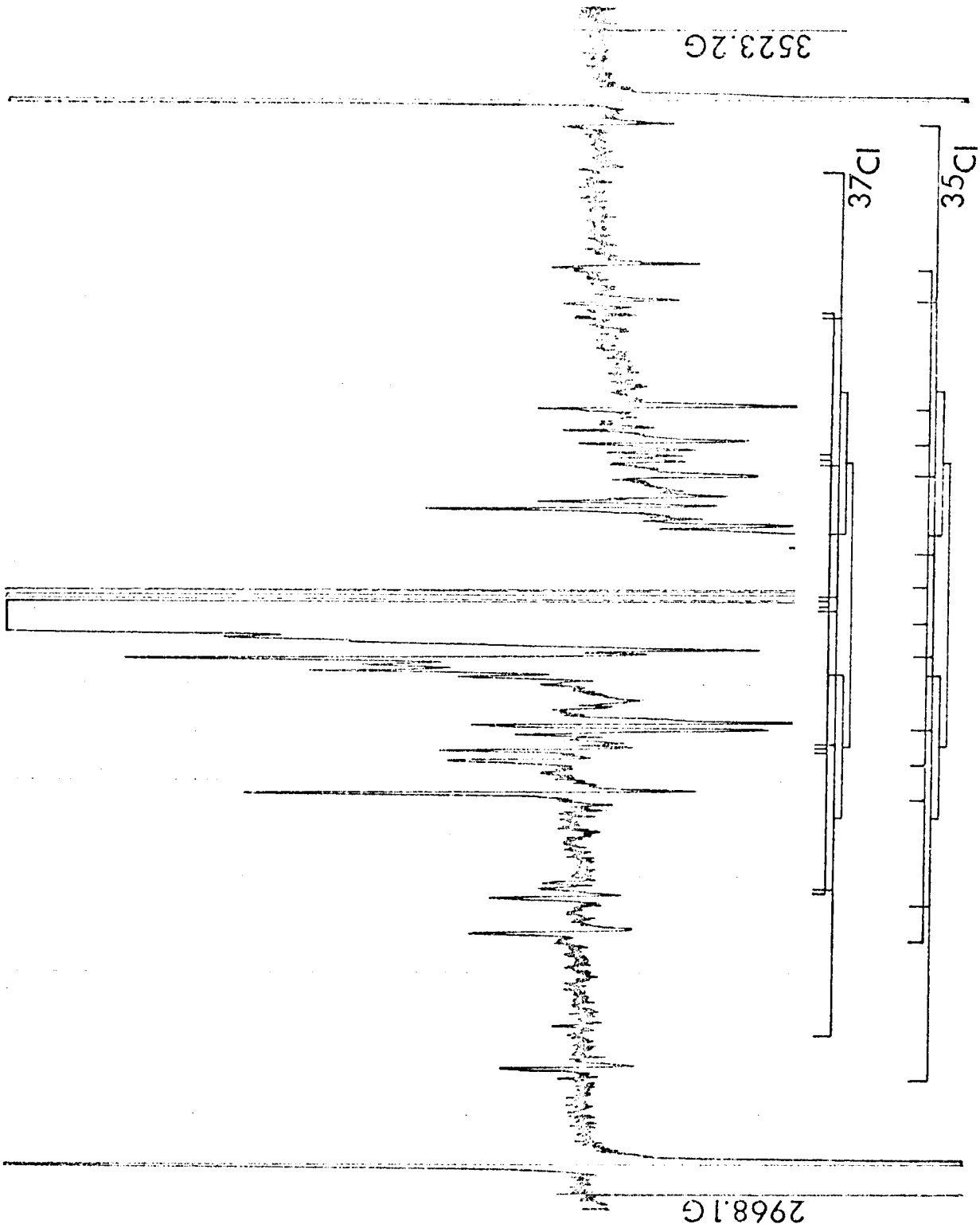
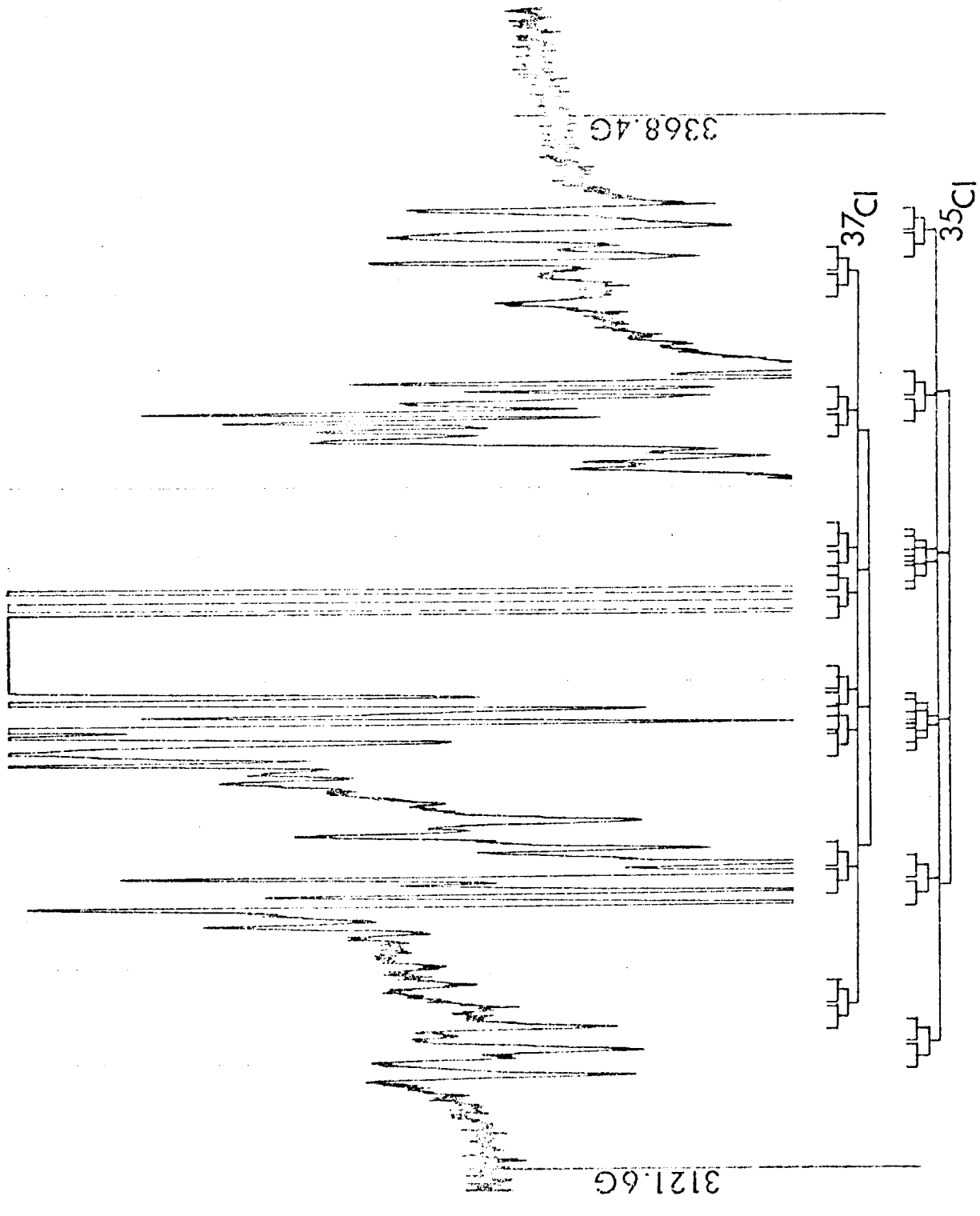

3523.2G
37Cl
35Cl
2968.1G

Figure 16. The perpendicular EPR spectrum of a 5% solution of chlorotrifluoroethylene in TMS-d_{12}, observed at 98°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.

The central features of the spectrum from the solute are masked by the intense 1:2:3:2:1 quintet from the solvent.


3368.4G
3121.6G
37Cl
35Cl

and $\underline{A}_{//}$ (F_2) = 67.7 G.

The "perpendicular" spectrum was analyzed in terms of coupling to one chlorine nucleus and three fluorine nuclei, the coupling constants being $\underline{A}_{\perp}(^{35}Cl)$ = 38.8 G, $\underline{A}_{\perp}$ (^{37}Cl) = 32.3 G, $\underline{A}_{\perp}$ (F_1) = 74.9 G, $\underline{A}_{\perp}$ (F_2) = 6.6 G, and $\underline{A}_{\perp}$ (F_3) = 5.5 G. The F_1, F_2, and F_3 indicate only the presence of non-equivalent nuclei; F_1 of the "parallel" spectrum, for example, does not necessarily correspond to F_1 of the "perpendicular" spectrum.

From the values obtained for the ^{35}Cl couplings in the "parallel" and "perpendicular" spectra, a value of 53.8 G was calculated for the isotropic coupling. Subtraction of this value from the value from the "parallel" spectrum and division by 100, the value calculated[37] for the parallel component ($2B_o$) of the dipolar contribution to the ^{35}Cl hyperfine tensor for unit spin density in the 3p atomic orbital, yielded a spin density of 0.30 in the chlorine 3p orbital.

Gamma irradiation at 77°K of a 5% solution of chlorotrifluoroethylene in MTHF produced spectrum a of Figure 17, which appears to be a "parallel" spectrum with broadened features, the "perpendicular" features being buried under the seven-line spectrum of MTHF. Photolysis with a uv lamp of a similar solution containing added TMPD generated an anisotropic spectrum that matched the spectrum obtained by gamma irradiation. The anisotropic spectrum obtained from an MTHF solution and the "parallel" and "perpendicular" spectra obtained from TMS solution were not affected by photolysis with visible light.

Raising the temperature of a gamma-irradiated 5% solution of chlorotrifluoroethylene in MTHF to 102°K for a few seconds resulted in the loss of the original spectrum and the appearance of spectrum b of

Figure 17. The EPR spectra of a 5% solution of chlorotrifluoroethylene in MTHF, observed before (a) and after (b) annealing at 102°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The centers of the spectra are dominated by the seven-line spectrum from MTHF.

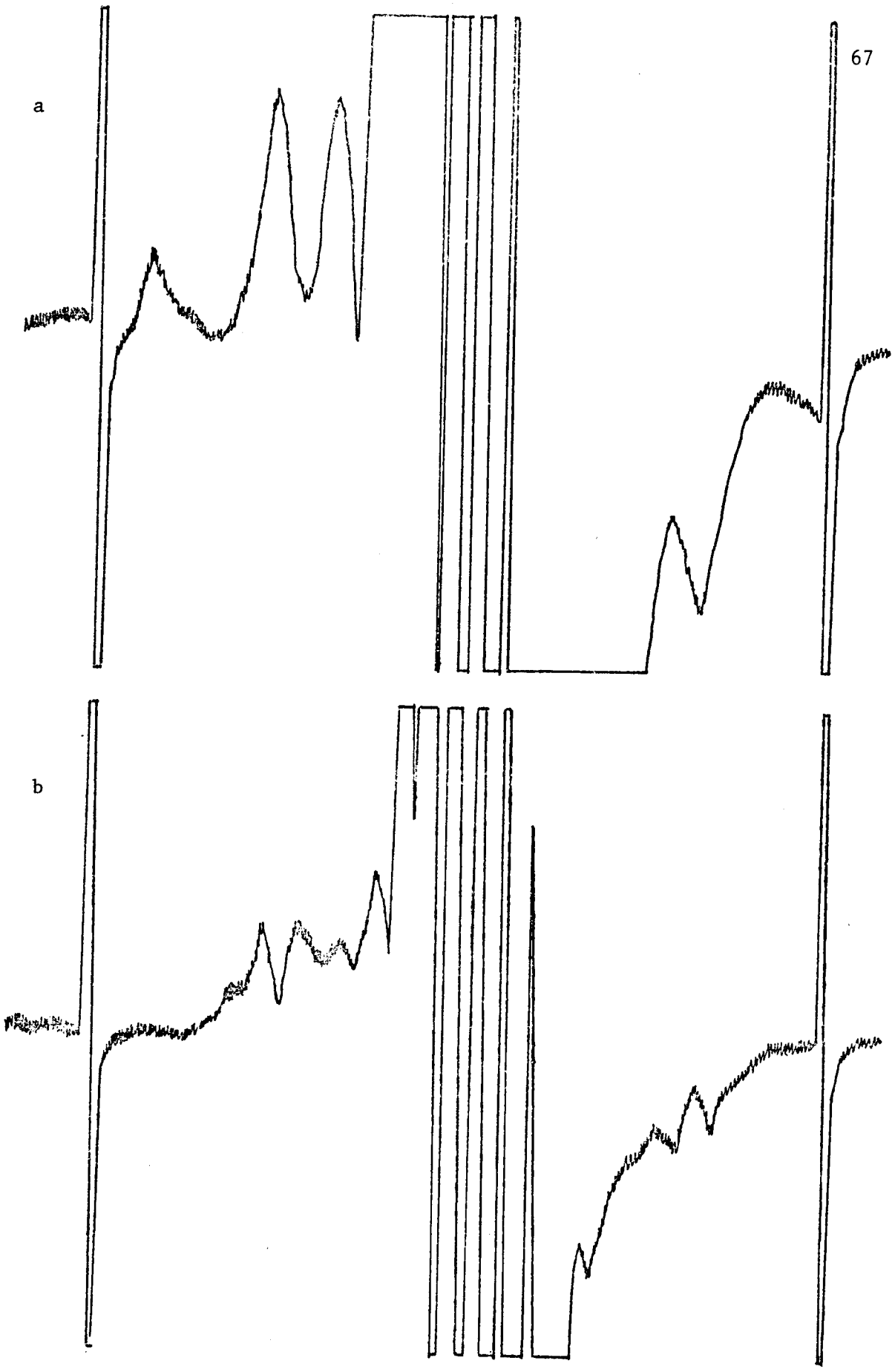

a
b

Figure 17. The spectrum of the matrix radical was unaffected by this annealing process. The new spectrum matched that obtained from gamma irradiation of a frozen solution of 1,2-dichlorohexafluorocyclobutane in MTHF (Figure 4, p. 31).

7. Bromotrifluoroethylene

A 5% solution of bromotrifluoroethylene in TMS produced, upon irradiation at 77°K, the orientation-dependent spectra shown in Figures 18 and 19, the features of which are designated "parallel" and "perpendicular," respectively, on the basis of their shapes.[34] Rotation of the sample tube by 90° in the magnetic field replaced one set of features with the other.

The "parallel" set conformed to the expected pattern for hyperfine coupling to one bromine atom and two fluorine atoms. The analysis was unambiguous because of the presence of two bromine isotopes, ^{81}Br (I = 3/2) and ^{79}Br (I = 3/2), which have natural abundances of 49.43 and 50.57, respectively, and a ratio of magnetic moments (and therefore coupling constants) of 1.076.[37] Because of the magnitude of the coupling to bromine, it was necessary to make second-order corrections according to the procedures described previously. The couplings were found to be $\underline{A}_{//}$ (^{81}Br) = 463.4 G, $\underline{A}_{//}$ (^{79}Br) = 430.8 G, $\underline{A}_{//}$ (F_1) = 134 G, $\underline{A}_{//}$ (F_2) = 66 G. The $g_{//}$ value, obtained using the hydrogen lines as a calibration, was 2.000.

In contrast, the "perpendicular" set of features, detailed expansions of the outermost groups of which are shown in Figures 20 and 21, were interpreted as arising from coupling to <u>three</u> fluorine atoms, the values of the hyperfine coupling constants being $\underline{A}_{\perp}$ (F_1) = 36.6 G, $\underline{A}_{\perp}$ (F_2) = 27.7 G, and $\underline{A}_{\perp}$ (F_3) = 9.9 G. As with chlorotrifluoroethylene,

Figure 18. The parallel EPR spectrum of a 5% solution of bromotrifluoroethylene in TMS, observed at 98°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The center of the spectrum is due to the 1:2:1 pattern from the solvent.

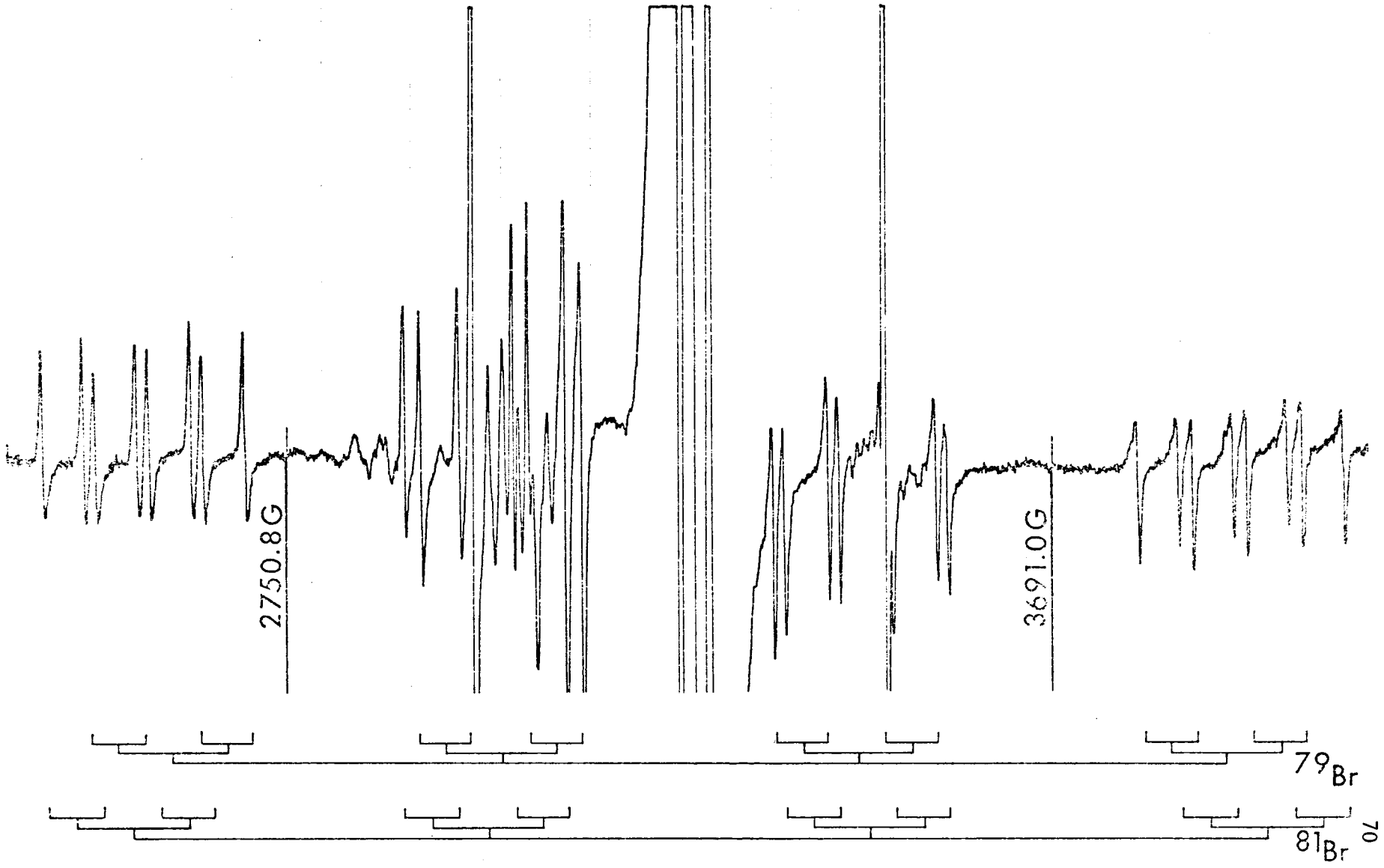

2750.8G
3691.0G
79Br
81Br

Figure 19. The perpendicular EPR spectrum of a 5% solution of bromotrifluoroethylene in TMS, observed at 98°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The (-1/2,3/2) set of features is obscured by the 1:2:1 pattern from the solvent.

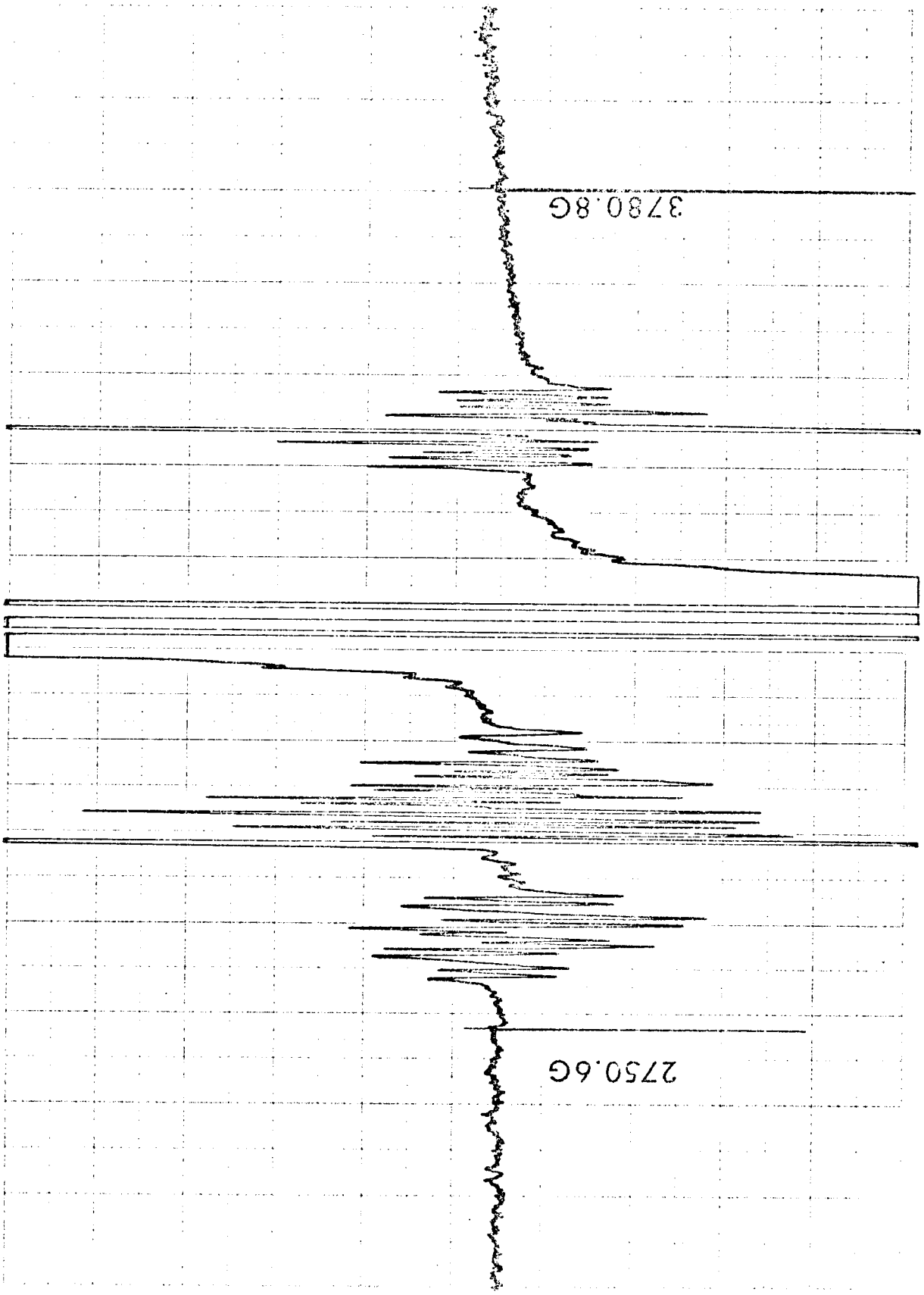

3780.8G
2750.6G

Figure 20. The (+3/2,3/2) set of features of the perpendicular EPR spectrum of a 5% solution of bromotrifluoroethylene in TMS, observed at 98°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

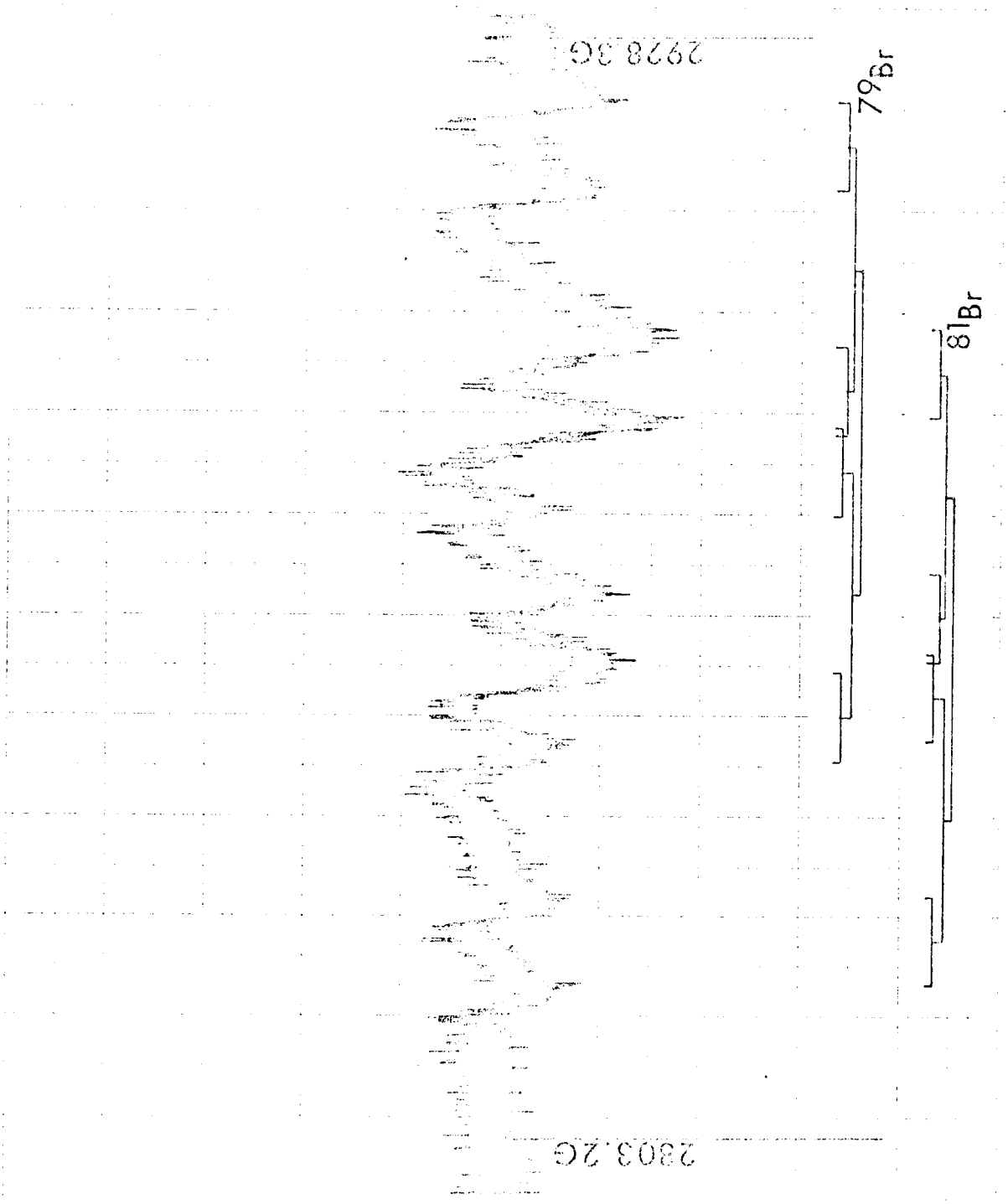
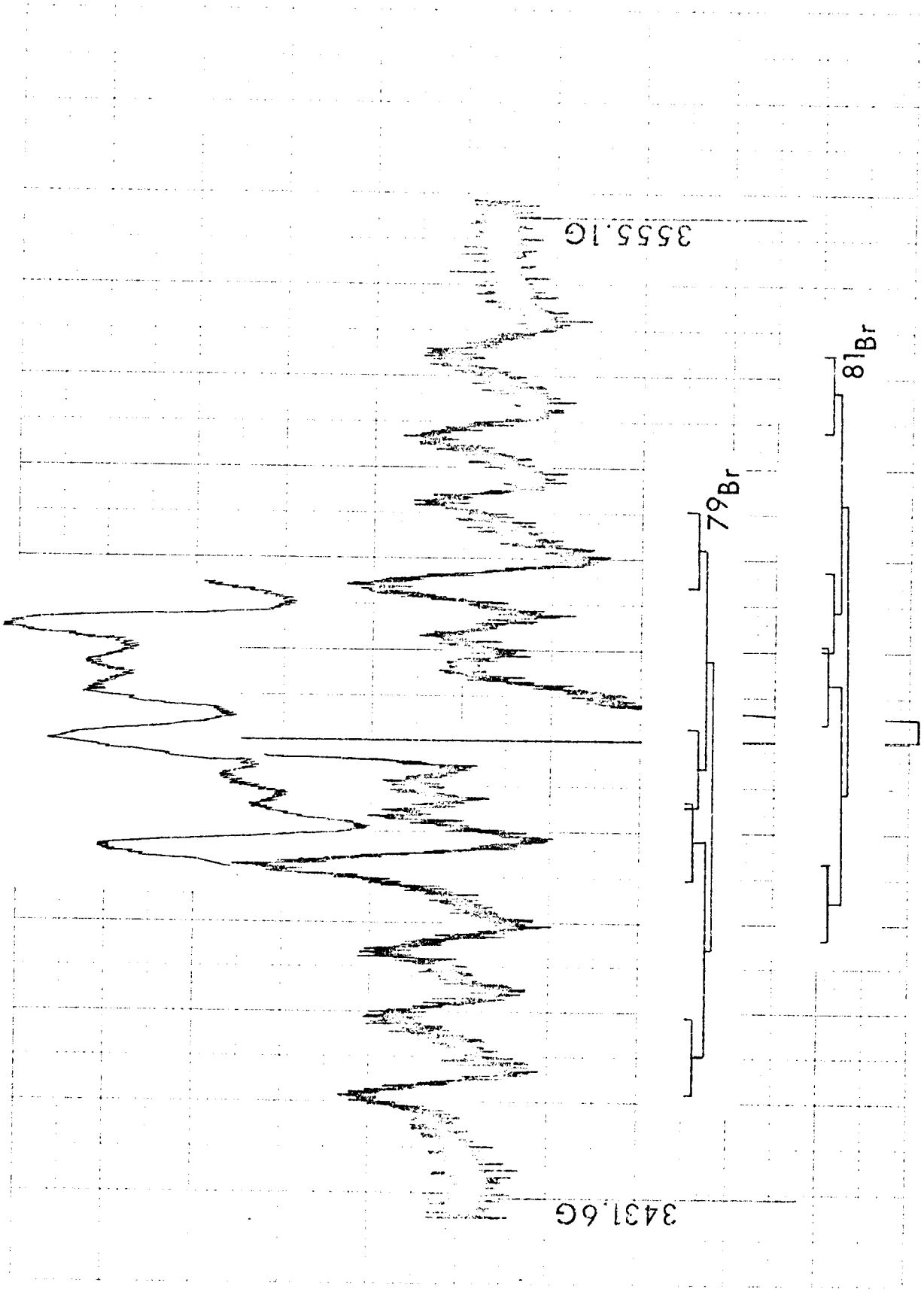

2928.3G
2803.2G
79Br
81Br

Figure 21. The (-3/2,3/2) set of features of the perpendicular EPR spectrum of a 5% solution of bromotrifluoroethylene in TMS, observed at 98°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

Inset: a portion of a spectrum obtained at 98°K after gamma irradiation of a similar solution in FEP tubing to a dose of 1.5 Mrad at 77°K.
The inset spectrum was observed on a slightly smaller scale than the other spectrum.


3555.1G
3431.6G
79Br
81Br

F_1 and F_2 of the "parallel" spectrum do not necessarily correspond to F_1 and F_2 of the "perpendicular" spectrum. As shown by the stick diagrams under the spectra, this analysis accounts for the intensity of the features which are apparently of double strength and for the slightly different structures of the m_I (Br) = +3/2 and -3/2 patterns. A spectrum in FEP tubing (part of which is shown as an inset of Figure 21) revealed that one feature of the "perpendicular" spectrum was hidden under the high-field hydrogen line; the analysis accounts for this feature, too. The bromine hyperfine tensor was axially symmetric, with couplings $A_\perp$ (^{81}Br) = 213.8 G and $A_\perp$ (^{79}Br) = 198.7 G. The $g_\perp$ was found to be 2.036.

Another interpretation of the "perpendicular" spectrum was considered, in terms of a slight departure from axial symmetry, in which the high-intensity features on the high-field side originated from one set of tensor components, while the low-intensity features arose from another set. However, this interpretation did not produce a satisfactory match for the low-field pattern.

Use of the values of the parallel and perpendicular ^{81}Br coupling constants and the procedure described for the radical derived from chlorotrifluoroethylene yielded a spin density in the 4p orbital of bromine of 0.33.

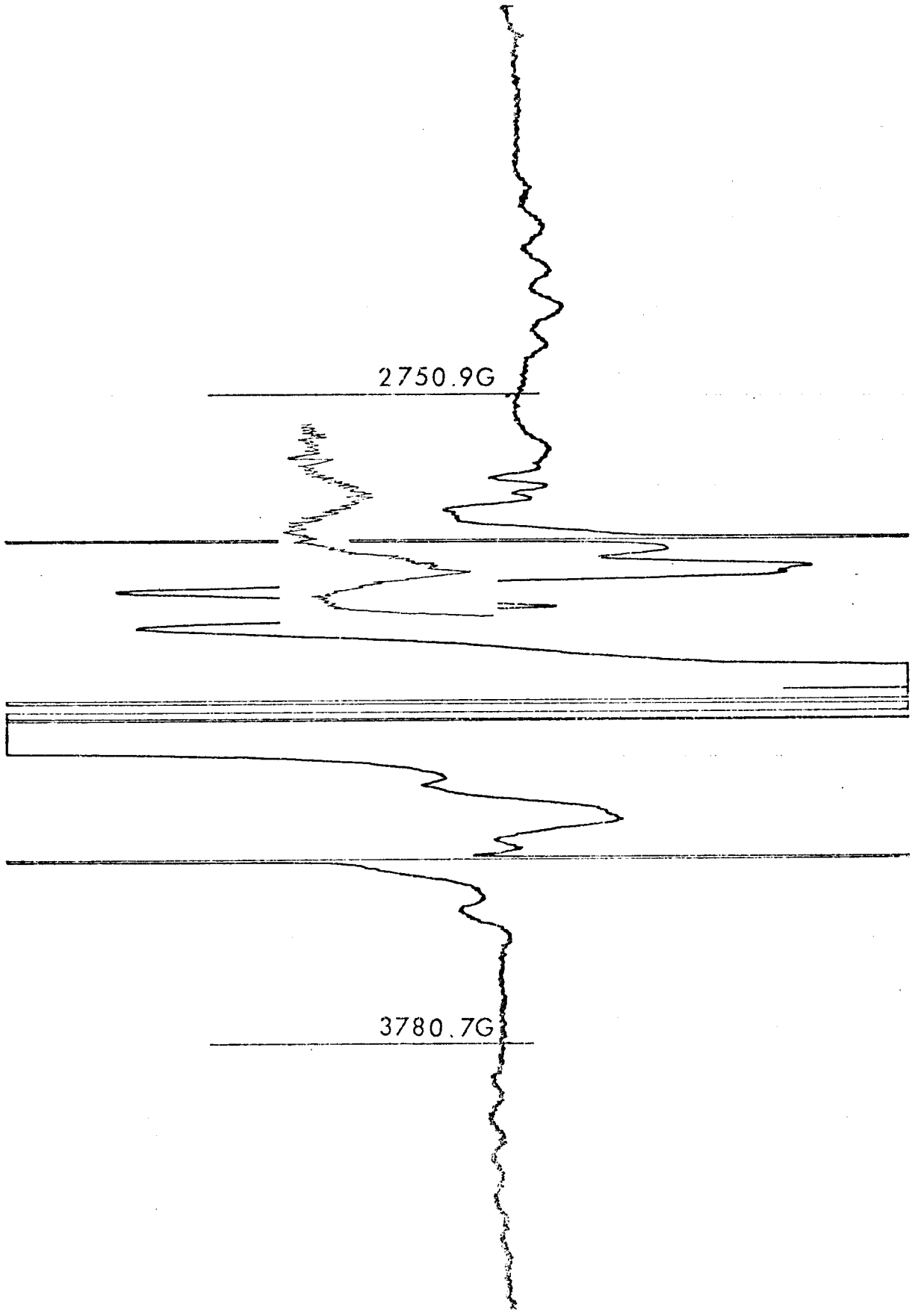
Warming the sample to 109°K resulted only in the disappearance of the spectrum.

Attempts to generate the spectrum of the radical by irradiation of bromotrifluoroethylene in adamantane failed.

The EPR spectrum of a gamma-irradiated 5% solution of bromotrifluoroethylene in MTHF, observed at 87°K, is shown in Figure 22. As can

Figure 22. The EPR spectrum of a 5% solution of bromotrifluoroethylene in MTHF, observed at 87°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

Inset: a portion of an EPR spectrum obtained after uv photolysis at 77°K of a similar solution containing TMPD.
The center of the spectrum is dominated by the seven-line pattern from MTHF.


2750.9G
3780.7G

readily be seen, this spectrum is a composite of the spectral features in TMS solution. Warming the sample to 103°K resulted in the disappearance of the spectrum without the appearance of any new features. This spectrum and those obtained from solutions in TMS were unaffected by photolysis with visible light.

Photolysis of a solution of bromotrifluoroethylene in MTHF containing a small amount of TMPD produced a spectrum matching that obtained by gamma irradiation of bromotrifluoroethylene in MTHF, thereby demonstrating that the radical is formed as a result of electron capture. Part of this spectrum is shown as an inset in Figure 22.

8. Iodotrifluoroethylene

Gamma irradiation at 77°K of a 5% solution of iodotrifluoroethylene in TMS produced an EPR spectrum observed at 98°K which was orientation dependent, as shown in Figures 23 and 24. In Figure 23, it was possible to identify two separate patterns of six features, resulting from coupling to one ^{127} I nucleus, which has spin 5/2. Both patterns, designated as the X and Y sets, exhibited substructure in the form of coupling to only two fluorine nuclei. As shown in Figure 24, there were three features of another pattern of six features, designated as the Z set. These features also exhibited substructure in the form of coupling to only two fluorine nuclei.

Because of the large hyperfine coupling constant of the iodine nucleus, it was necessary to take into account second-order effects using the procedure described previously. The values of the coupling constants were found to be $\underline{A}_X$ (^{127} I) = 258 G, $\underline{A}_X$ (F_1) = 12.8 G, $\underline{A}_X$ (F_2) = 31.0 G, $\underline{A}_Y$ (^{127} I) = 258 G, $\underline{A}_Y$ (F_1) = 17.8 G, $\underline{A}_Y$ (F_2) = 37.9 G, $\underline{A}_Z$ (^{127} I) = 572 G, $\underline{A}_Z$ (F_1) = 54.3 G, and $\underline{A}_Z$ (F_2) = 114 G. As with the radicals from

Figure 23. The perpendicular EPR spectrum of a 5% solution of iodotrifluoroethylene in TMS, observed at 98°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The center of the spectrum is dominated by the 1:2:1 pattern from the solvent.

3591.7 G
2664.0 G

Figure 24. The parallel EPR spectrum of a 5% solution of iodotrifluoroethylene in TMS, observed at 98°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The center of the spectrum is dominated by the 1:2:1 pattern from the solvent. The stick diagram gives the positions of the observed (full lines) and unobserved (dotted lines) features.

3592.1G
2663.6G

chlorotrifluoroethylene and bromotrifluoroethylene, the couplings designated by F_1, for example, are not necessarily due to the same nucleus. The g values were calculated to be $g_X = 2.066$, $g_Y = 2.041$, and $g_Z = 1.996$. A spin density of 0.47 was calculated for the iodine 5p orbital on the basis of the coupling calculated for an isolated atom.[38]

A 5% solution of iodotrifluoroethylene in MTHF produced after gamma irradiation an EPR spectrum at 87°K that was simply a lower-resolution superposition of the spectra obtained in TMS. All of these spectra were unaffected by visible light.

C. Fluorinated Ethylenes--Optical Studies

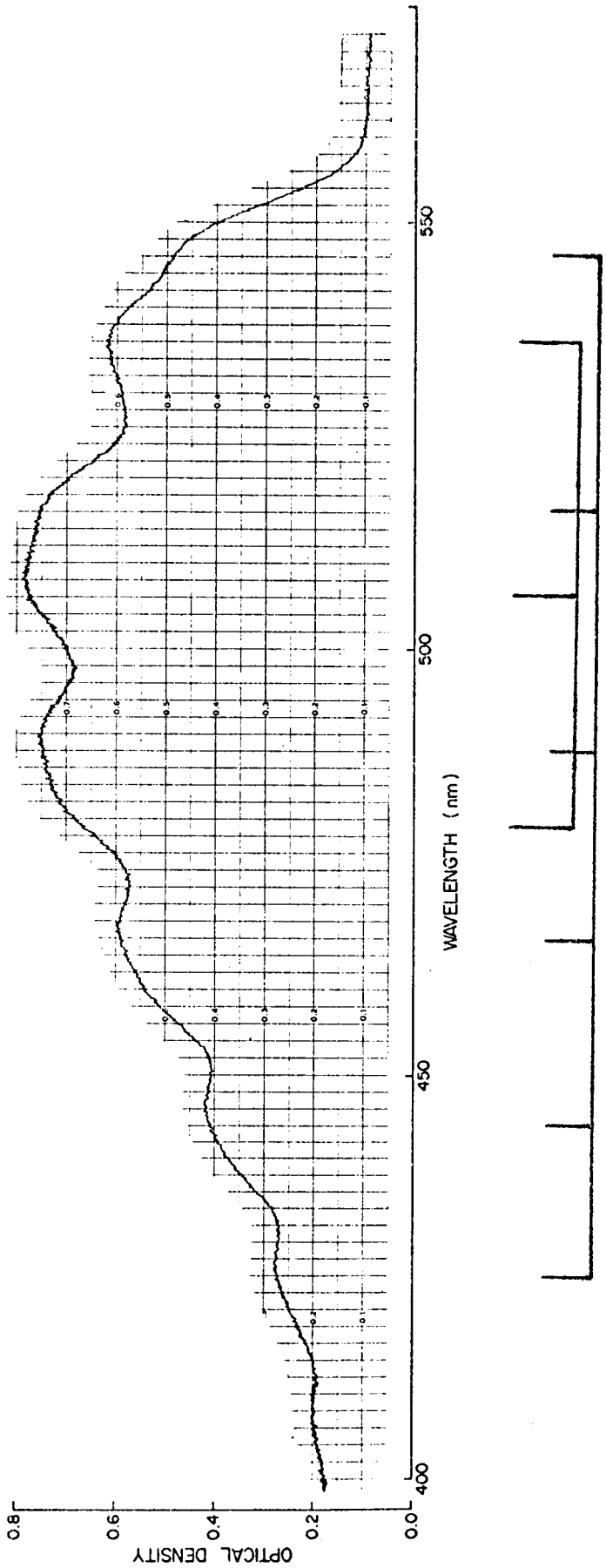
Solid solutions in MTHF and/or 3-methylhexane of all of the ethylenes studied in the course of this work were subjected to gamma irradiation; the only ethylene which produced a species absorbing in the visible or ultraviolet was tetrafluoroethylene, the spectrum of which in MTHF is shown in Figure 25. The maximum absorption in the spectrum, for tetrafluoroethylene in either MTHF or 3-methylhexane, was at 508 nm. Two progressions could be seen in the vibrational structure, both of spacing 1020 ± 20 cm^{-1}, with one displaced 320 cm^{-1} to longer wavelength from the other. These progressions are illustrated in Figure 25.

That the absorption was due to electron attachment to tetrafluoroethylene was shown by the absence of an absorption in MTHF at 1200 nm, the maximum in the trapped electron absorption. Also, the samples were red, while the color of irradiated MTHF is blue when no electron acceptors are present. Thus, the optical absorption is believed to be due to $C_2F_4^-$.

For calculation of the extinction coefficient, a solution of

Figure 25. The optical absorption spectrum of a 5% solution of tetrafluoroethylene in MTHF, observed at 77°K in a 1-mm cell after gamma irradiation to a dose of 1.0 Mrad at 77°K.

The progressions in the vibrational fine structure are indicated by the stick diagram.


OPTICAL DENSITY
0.0
0.2
0.4
0.6
0.8
400
450
500
550
WAVELENGTH (nm)

tetrafluoroethylene in 3-methylhexane was chosen in preference to a solution in MTHF because the glass in the former was clearer, with fewer cracks to scatter the incident light. The optical density (OD) after a dose of 1 Mrad was 0.40 for a 1-mm cell. Assuming a yield of 0.9 electrons produced for each 100 eV of incident energy, obtained from electron scavenging by methyl halides in frozen MTHF,[20] it was determined that the concentration C of $C_2F_4^-$ was 3.6×10^{-3} M. The extinction coefficient ε, calculated from $OD = \varepsilon C \ell$ (where ℓ is the path length), was 4400 at 508 nm. Because of potential errors in the yield of electrons and in the path length, which was nominally 1 mm, the uncertainty is probably ± 100%.

The oscillator strength f was calculated using Equation 7,[39] where m and e are the mass and charge of an electron, respectively, c is the velocity of light, N is Avogadro's number, $\varepsilon(\tilde{\nu})$ is the extinction

$$f = \frac{me}{\pi Nc^2} \int \varepsilon(\tilde{\nu})\, d\tilde{\nu} \qquad (7)$$

coefficient as a function of $\tilde{\nu}$, the energy of the absorption expressed in cm^{-1}, and the integral is over the absorption. The integration was done graphically by division of the spectrum into two right triangles starting at 400 and 560nm and ending at 508nm. Multiplication by the constants, the value of which was 4.32×10^{-9}, yielded an oscillator strength of 0.07.

Warming a gamma-irradiated frozen solution of tetrafluoroethylene in MTHF by holding it a short distance above the surface of liquid nitrogen in a wide-mouth dewar resulted in a change in color of the sample, from red to gold, and disappearance of the original absorption accompanied by a small increase in the absorption at 390 nm, the maximum in the spectrum of $\underline{c}\text{-}C_4F_8^-$. Thus, this experiment supports the EPR

results showing the transformation from $C_2F_4^-$ to $c\text{-}C_4F_8^-$.

A cautionary note must be injected concerning the possibility of spurious results in the observation of the optical spectra of the ethylenes, all of which were found to react when allowed to remain in MTHF solution at room temperature exposed to room light for more than a few hours before being frozen and irradiated. This is the same type of phenomenon observed in the perhalocycloalkane series. As was the case with those compounds, the intensity of the optical spectrum of the product depended on the starting compound and on the duration of the exposure to light. In all cases, the absorptions were in the region 400 to 700 nm.

D. Hexafluorobenzene

Gamma irradiation to a dose of 0.3 Mrad at 77°K of a 5% solution of hexafluorobenzene (C_6F_6) in MTHF produced an anisotropic EPR spectrum recorded at 88°K and shown in Figure 26. Photolysis by light from a tungsten lamp had no effect on the spectrum.

A similar spectrum was found after gamma irradiation of C_6F_6 in 3-methylhexane. In this case, though, photolysis for ten minutes reduced the signal intensity by half.

A 6% solution of C_6F_6 in MTHF, gamma-irradiated to 0.80 Mrad at 77°K, had a deep golden color. The optical spectrum, with peaks at 326, 373, and 468 nm, was recorded at 77°K and is shown in Figure 27.

Optical spectra obtained through pulse radiolysis of C_6F_6 in dioxane and tetrahydrofuran exhibited low-intensity bands at about 380 and 470 nm, on the high-wavelength tail of the solvent spectrum.

Figure 26. The EPR spectrum of a 5% solution of hexafluorobenzene in MTHF, observed at 87°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The center of the spectrum is dominated by the seven-line pattern from MTHF.

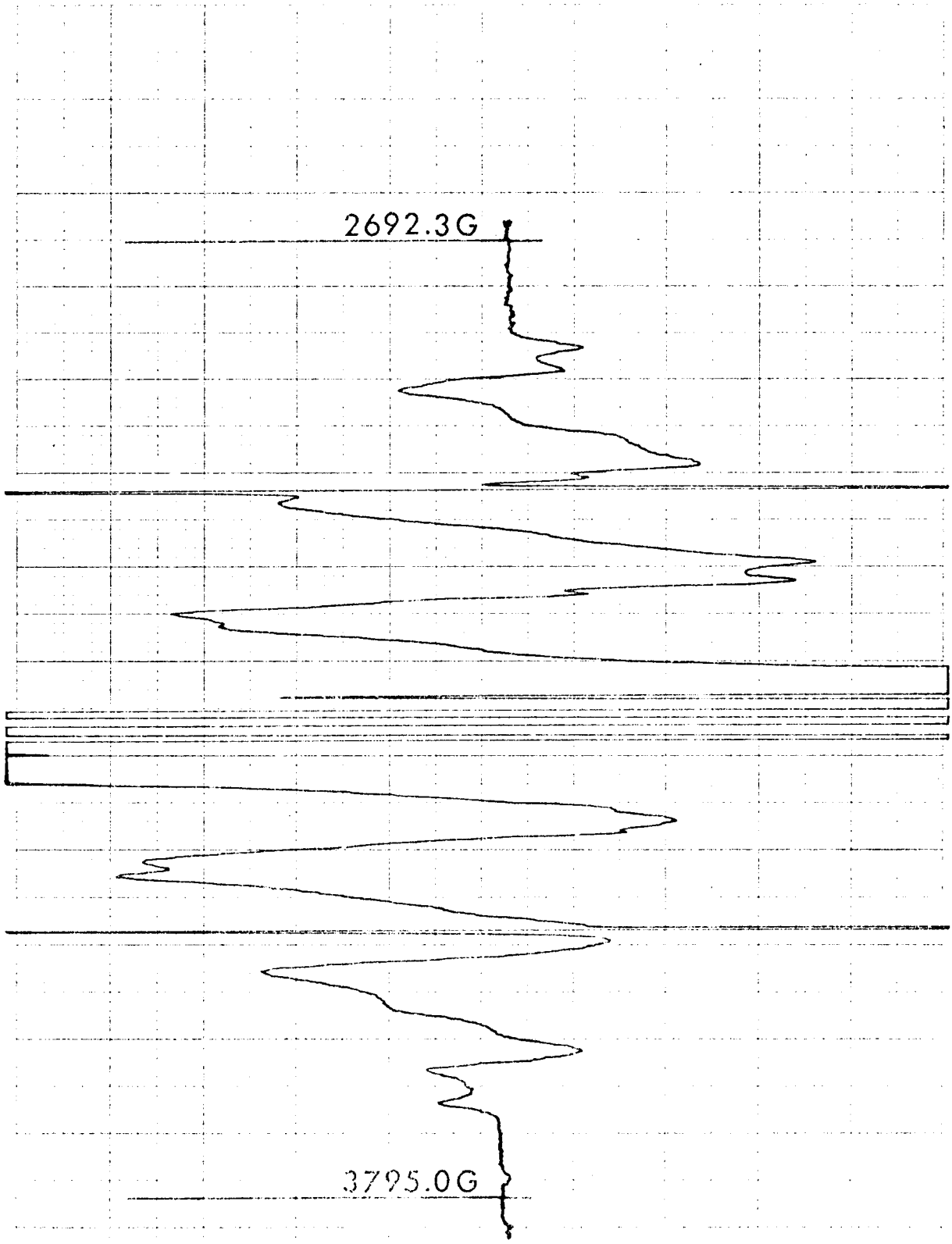
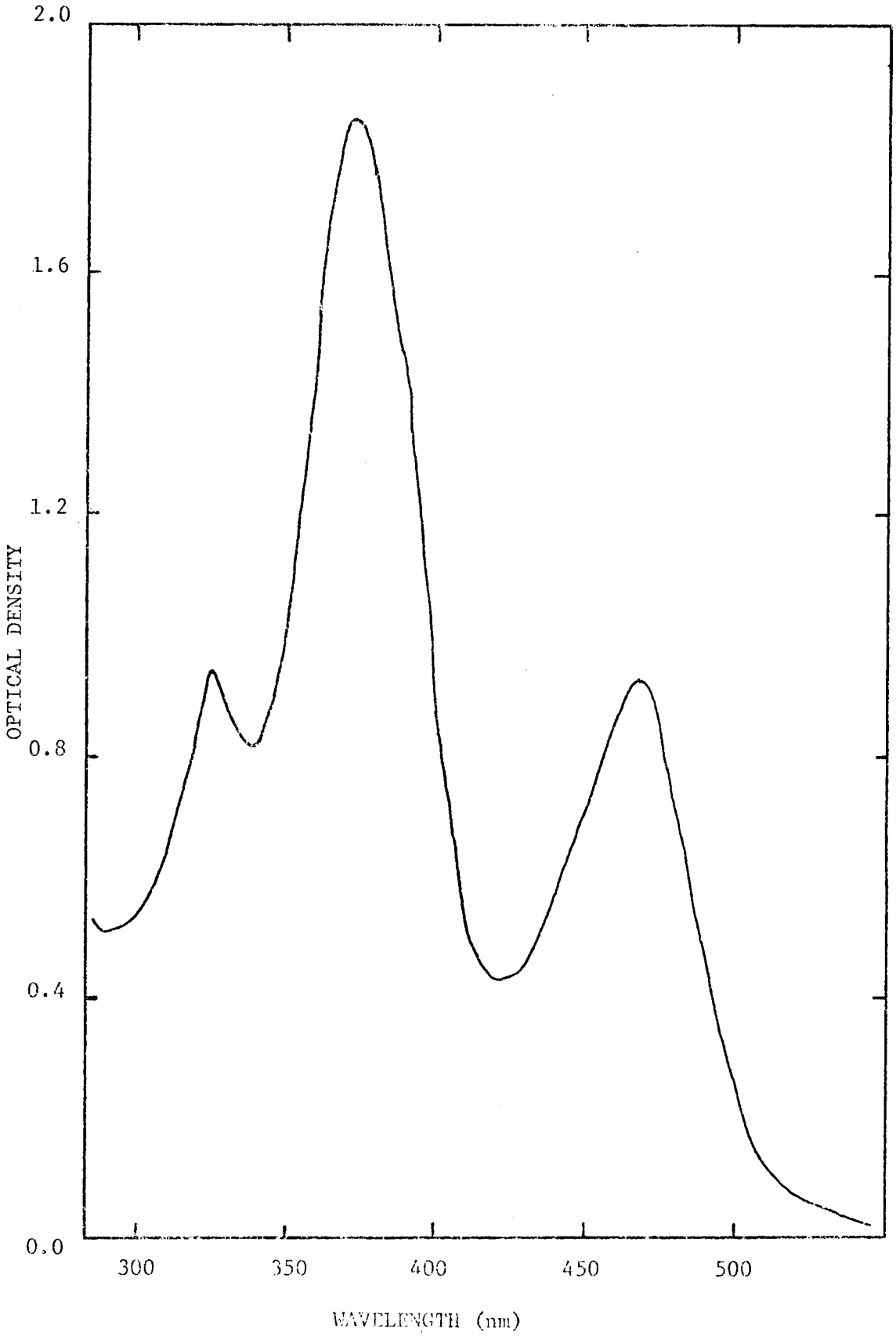

2692.3G
3795.0G

Figure 27. The optical absorption spectrum of a 5% solution of hexafluorobenzene in MTHF, observed in a 1-mm cell at 77°K after gamma irradiation to a dose of 0.75 Mrad at 77°K.


2.0
1.6
1.2
0.8
0.4
0.0
OPTICAL DENSITY
300
350
400
450
500
WAVELENGTH (nm)

C. Sulfur Hexafluoride

Gamma irradiation to doses of 0.75 Mrad at 77°K of 5% solutions of sulfur hexafluoride (SF_6) in neopentane, TMS, dimethyl formamide, silicon tetrafluoride, and hexamethylphosphortriamide produced isotropic or nearly isotropic EPR spectra when observed in the range 120-130°K, which could be fitted using the parameters given for SF_6^-.[13,40]

Gamma irradiation at 77°K of 5% solutions of SF_6 in MTHF, trifluoromethane, and 3-methylhexane produced anisotropic spectra at 90°K which were significantly wider than that of isotropic SF_6^-[13,40] and much wider than that of anisotropic SF_5 in SF_6^-.[41] In addition, the spectrum could be generated by photolysis of a solution of SF_6 in MTHF containing TMPD. On these bases, the radical is believed to be SF_6^-. The spectrum is shown in Figure 28.

A 0.5% solution of SF_6 in hexafluoroethane, observed at 97°K after gamma irradiation at 77°K, had an anisotropic spectrum very similar to that from SF_6 in MTHF. When the sample was warmed above about 100°K, the anisotropic spectrum of SF_6^- gradually decayed, disappearing at about 108°K, without the growth of any other recognizable pattern. Although a low-intensity isotropic spectrum appeared between 108 and 109°K that had the same hyperfine coupling constant as did SF_5,[42] it is unlikely that this SF_5 signal originated from the decay of the initial SF_6^-.

Gamma irradiation to a dose of 2.2 Mrad at 77°K of a 0.5% solution of SF_6 in ethanol produced an EPR spectrum at 80°K that was similar to the anisotropic spectrum of SF_5 obtained by Hasegawa and Williams[41] from gamma-irradiated SF_6. This spectrum is shown in Figure 29. Also present was an anisotropic spectrum of very low intensity that resembled

Figure 28. (a) The EPR spectrum of a 5% solution of sulfur hexafluoride in MTHF containing TMPD, observed at 77°K following uv photolysis at 77°K. (b) The EPR spectrum of a similar solution without TMPD, observed at 92°K after gamma irradiation at 77°K to a dose of 0.75 Mrad.

The center of spectrum a contains the spectrum of $TMPD^{+}$, while that of b is dominated by the seven-line pattern from MTHF.

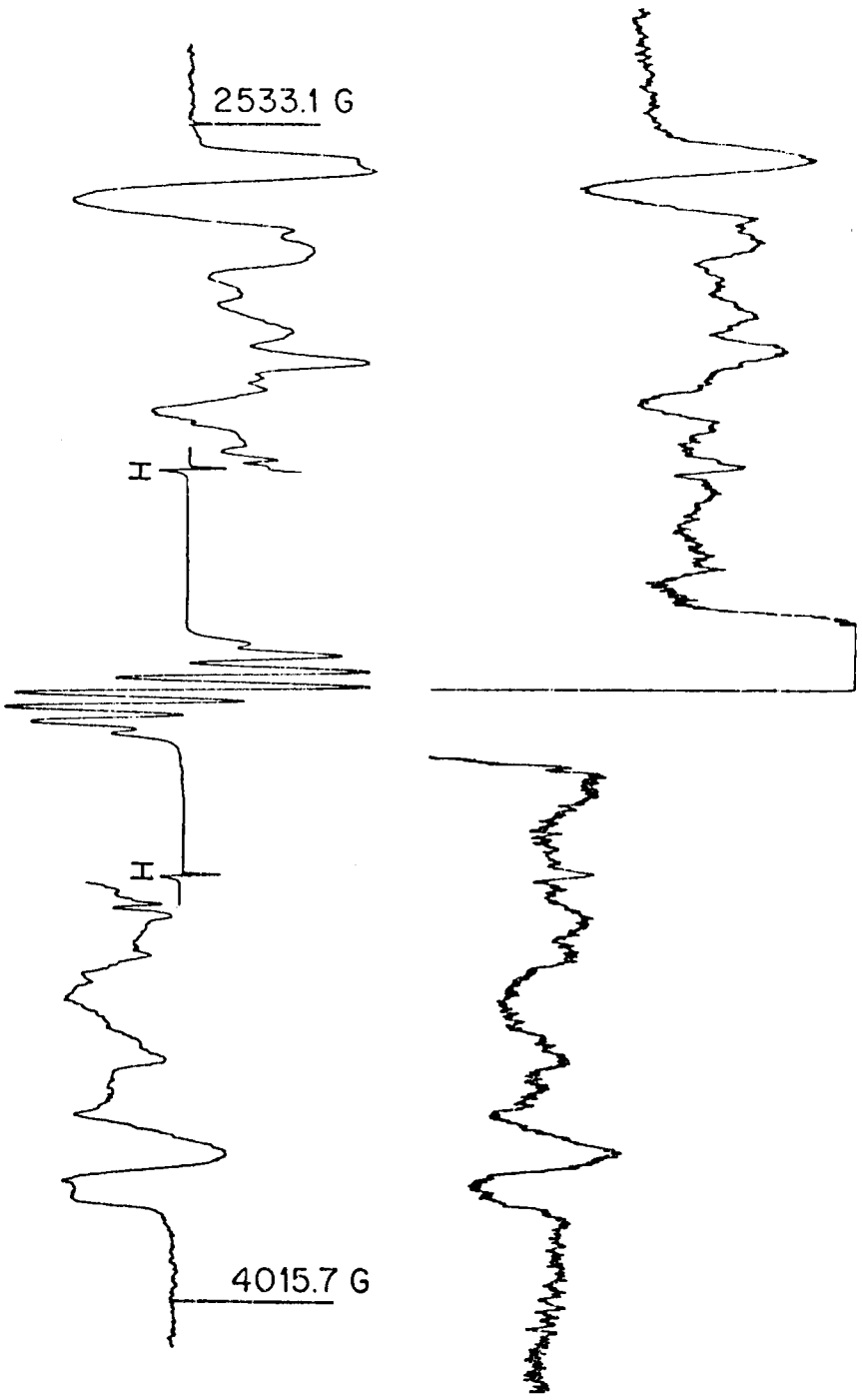
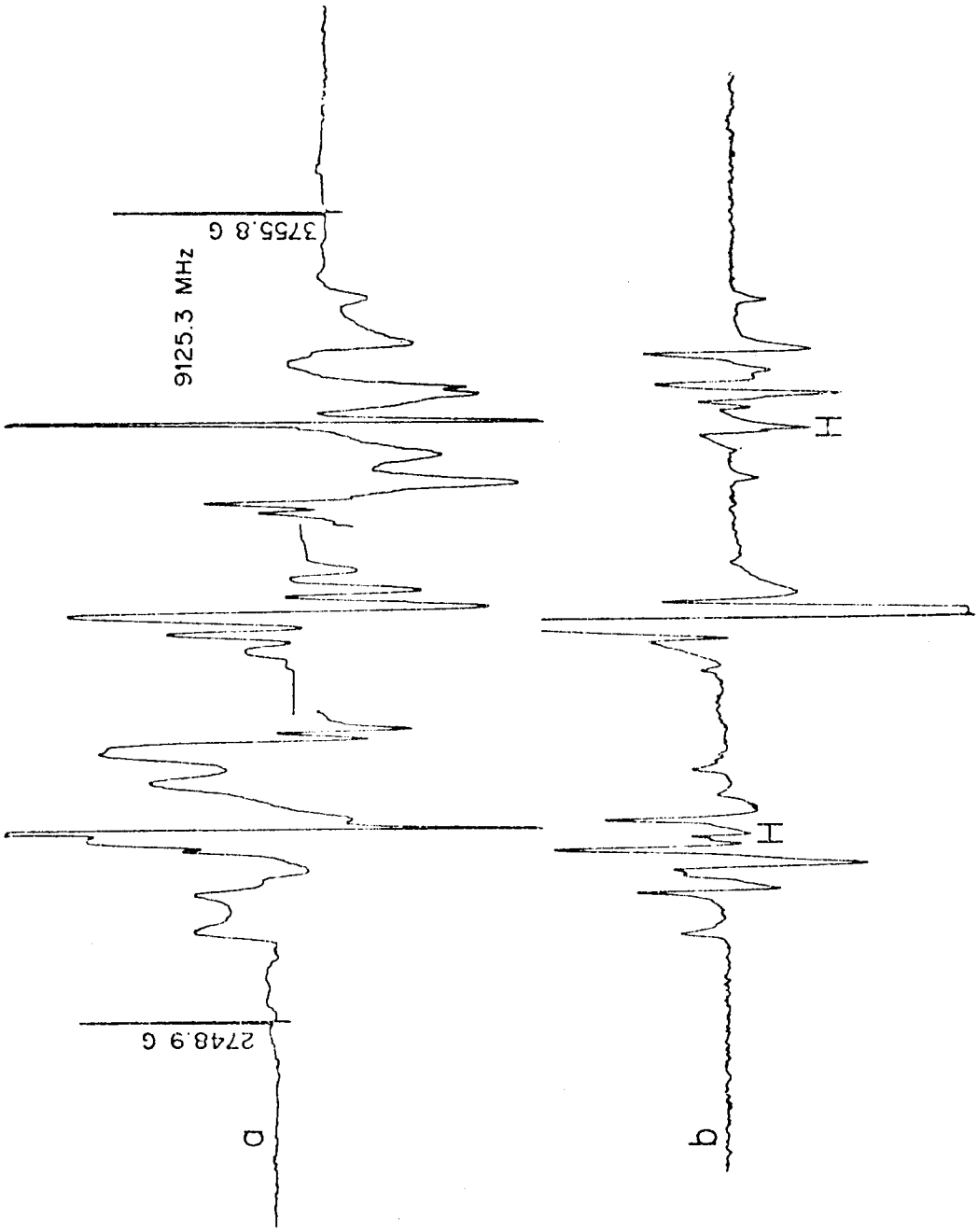

2533.1 G
H
H
4015.7 G

Figure 29. (a) The EPR spectrum of a 3% solution of sulfur hexafluoride in ethanol, observed at 92°K after gamma irradiation to a dose of 0.75 Mrad at 77°K. (b) The EPR spectrum of SF_5 in sulfur hexafluoride, observed at 77°K after gamma irradiation to a dose of 0.75 Mrad at 77°K and annealing for twenty minutes at 136°K.

The center of spectrum a is dominated by the 1:2:1 and 1:1 patterns of the solvent.


3755.8 G
9125.3 MHz
2748.9 G
a
H
H
b

the general shape of the anisotropic spectrum described above for an MTHF solution and ascribed to SF_6^-. However, the spectral extent here was only about 900 G compared to about 1380 G for the spectrum of SF_6^- in MTHF. This spectrum disappeared when the temperature was raised to 96°K.

Solutions (1%) of SF_6 in methyl, dimethyl, and trimethyl amine were gamma-irradiated at 77°K. The spectra did not appear to be those of SF_6^- or SF_5 but could not be analyzed.

A 10% solution of SF_6 in 11 M NaOH in water was gamma-irradiated at 77°K to a dose of 1 Mrad. The EPR spectrum at 92°K had the features observed in an irradiated solution of SF_6 in MTHF and therefore can be ascribed to SF_6^-. No SF_5 was observed.

F. Effect of the Matrix on Competitive Electron Capture by Solutes

Direct competition between two electron scavengers was chosen as the best procedure for the determination of whether the rate of electron attachment to solutes is affected by the solvent in the solid state. The ratio of cross sections for electron capture by the two solutes was determined through observation of the EPR spectra of the products, where signal intensities were measured by double integration of certain lines from the first-derivative spectrum.

In a typical experiment, a series of seven samples in matched EPR tubes was prepared, with a constant low concentration of the standard (ranging from 0.02 to 2 mole % for different experiments) and different concentrations of the other solute, ranging from none to several times the concentration of the standard. The samples were allowed to warm to room temperature. Then they were shaken to effect mixing, plunged into

liquid nitrogen, and gamma-irradiated, all at the same time. The conditions of observation were the same for all. All samples were kept in total darkness at all times during and after irradiation.

Analysis was by application of Equation 8, which could be transformed into Equation 9. In these equations, I_o and I are the integrated intensities of the signal of the standard s in the absence and presence,

$$\frac{I_o - I}{I} = \frac{\sigma_x[x]}{\sigma_s[s]} \tag{8}$$

$$\frac{I_o}{I} = 1 + \frac{\sigma_x[x]}{\sigma_s[s]} \tag{9}$$

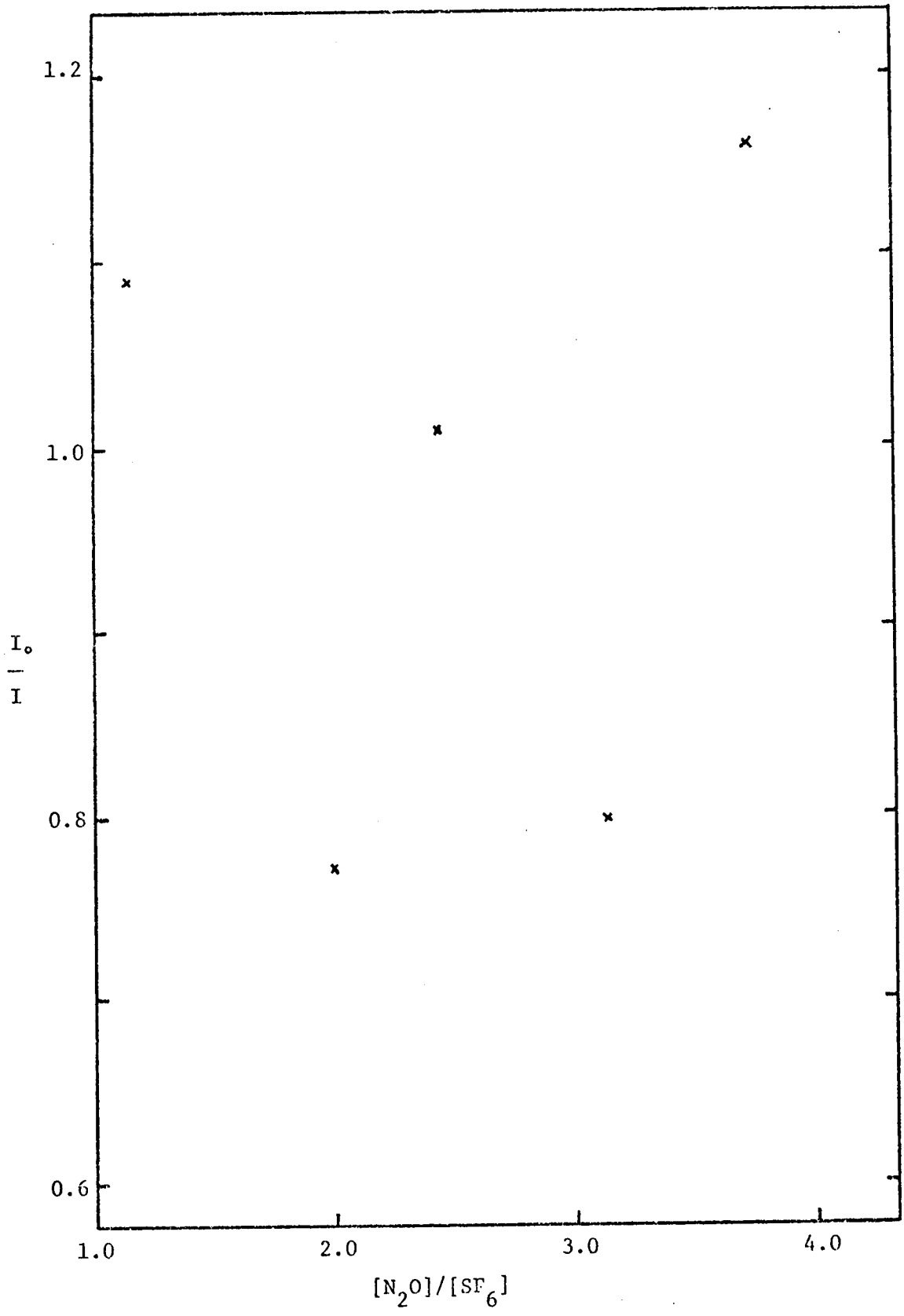
respectively, of a competitive electron acceptor x, the σ's are cross sections for electron capture, and the brackets denote molar concentrations of the solutes. Plots made of I_o/I against the ratio of concentrations were expected to show straight lines, the slopes of which would be the ratio of the cross sections.

The system chosen for initial testing, sulfur hexafluoride (SF_6) as a standard in neopentane, had been found to produce a nearly isotropic EPR spectrum of SF_6^-. An additional advantage of SF_6^- was that the spectrum was very wide, thus increasing the likelihood that at least one set of lines would not be overlapped by components of the spectrum of the radical from the other scavenger.

Competition experiments using octafluorocyclobutane, nitrous oxide and methyl bromide as co-solutes gave complete scatter in the plots; samples with higher concentrations of the second scavenger often produced more intense SF_6^- signals than were observed in samples with lower concentrations. The results of an experiment using SF_6 and nitrous oxide are shown in Figure 30.

Figure 30. A plot of the results of a competitive-scavenger experiment in frozen neopentane at 100°K using sulfur hexafluoride as the standard and nitrous oxide as the co-solute.

The ordinate is the ratio of the integrated intensities of the (+1,3), (+1,2), (+1,1) set of features of SF_6^- in the absence and presence of nitrous oxide. The abscissa is the ratio of concentrations of the two electron acceptors. See text for a discussion.


1.2
1.0
0.8
0.6
$\frac{I_o}{I}$
1.0
2.0
3.0
4.0
$[N_2O]/[SF_6]$

The irreproducible results obtained in neopentane may have been due to the violent bumping that was observed to occur when the samples were being cooled. Tetramethylsilane also exhibited this behavior but to a lesser degree. However, even solutions of SF_6 alone in this solvent yielded irreproducible results; plots of signal intensity against concentration of SF_6 exhibited a great deal of scatter. Attempts to use octafluorocyclobutane as a standard were unsuccessful because, as with the SF_6 solutions, the signal intensities from solutions of nominally higher solute concentration were sometimes even lower than those from solutions of much lower concentration.

Hamill[6] and Kuri and co-workers[20] were able to obtain reproducible results using various electron acceptors in MTHF and 3-methylhexane, both glassy matrices. So it is believed that the failure in the present case to obtain reproducible results is due to the crystallinity of the matrices used. The concentration of the solute in the crystal was not necessarily related to the concentration introduced into the sample tube but may have depended on the conditions of cooling.

Gamma irradiation of frozen solutions of neopentane containing both SF_6 and octafluorocyclobutane produced EPR spectra at 120°K which contained the components of SF_6^- and $c\text{-}C_4F_8^-$, both isotropic, and SF_5, anisotropic. No definite conclusions can be reached concerning the origin of the SF_5 or the reason it is anisotropic. The unexpected behavior may be due to a solid state phase effect.

G. Electron Transfer Between Solutes in the Solid State

When octafluorocyclobutane alone in solid TMS solution was exposed to gamma radiation, the spectrum shown in Figure 1 (p. 23) was obtained;

exposure of the sample for ten minutes to unfiltered light from a tungsten lamp resulted in complete loss of the $\underline{c}$-$C_4F_8^-$ spectrum. The spectrum of SF_6^-, obtained after gamma irradiation of SF_6 in solid TMS solution, was stable to visible light.

A solution in TMS of 0.03 mole % SF_6 and 1.2 mole % octafluorocyclobutane, irradiated to a dose of 0.50 Mrad at 77°K and observed at 105°K, exhibited spectrum $\underline{a}$ of Figure 31. which is dominated by the features of $\underline{c}$-$C_4F_8^-$. Exposure of the sample for five minutes to light of the same intensity resulted in the disappearance of the $\underline{c}$-$C_4F_8^-$ spectrum and the growth of the SF_6^- spectrum, as shown by spectrum $\underline{b}$. Warming a similar sample to 115°K in the dark produced the same result, though much more slowly.

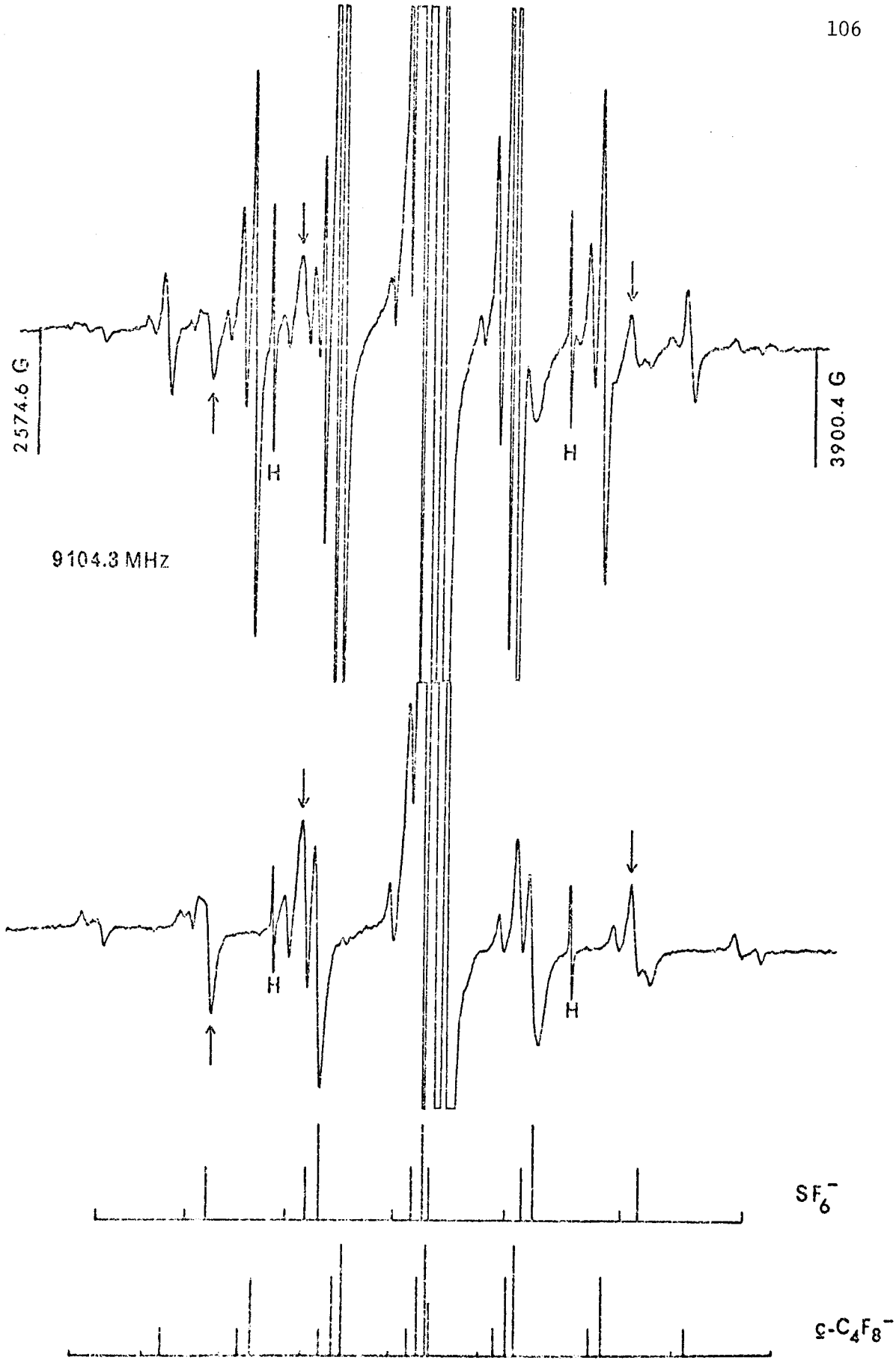
A mixture of octafluorocyclobutane and methyl bromide (0.4 mole % each) in TMS was irradiated to a dose of 0.5 Mrad at 77°K and observed at that temperature. Apart from the spectrum of the matrix radical, the spectrum was a composite of two, that of $\underline{c}$-$C_4F_8^-$ and a quartet having the 1:3:3:1 pattern of the methyl radical, resulting from electron addition to methyl bromide followed by loss of bromide ion. Photolysis for four minutes with light of the intensity used above resulted in complete loss of the spectrum of $\underline{c}$-$C_4F_8^-$ and a 300% increase in the intensity of the lines of the methyl radical.

H. Matrices

It was already known that in certain temperature ranges solid adamantane, sulfur hexafluoride, 2,2-dimethylpropane (neopentane), and tetramethylsilane (TMS) allow sufficient motion of small solute radicals to average out most of the anisotropy, so that EPR spectra of the

Figure 31. The EPR spectra of a gamma-irradiated solution of 0.03% sulfur hexafluoride and 1.2% octafluorocyclobutane in TMS, observed at 105°K before (a) and after (b) visible photolysis.

The dose was 0.50 Mrad. The temperature of gamma irradiation was 77°K.


2574.6 G
3900.4 G
H
H
9104.3 MHz
H
H
SF_6^-
c-$C_4F_8^-$

radicals are nearly isotropic. Attempts were made to determine whether tetrafluoromethane, hexafluoroethane, perfluoroisobutane, silicon tetrafluoride, and hexamethyldisilane exhibit similar behavior.

Tetrafluoromethane is roughly the same size as neopentane and so might be expected to have similar properties. Irradiation of the pure solvent at 77°K produced only a very low intensity spectrum, indicative of a low concentration of radicals stable at that temperature; thus, the solvent spectrum would not obscure the spectrum of a solute-derived radical. However, no new features appeared on gamma irradiation of solutions containing 5% SF_6 or octafluorocyclobutane. It is believed that the solvent melting point (89°K) is so close to 77°K, the lowest routinely available temperature for observation of the spectrum, that enough diffusive motion occurred to permit intermolecular reaction of any radicals that were produced.

After irradiation at 77°K, hexafluoroethane exhibited an anisotropic EPR spectrum extending over 700 G at 85°K. (In comparison, the spectrum of gamma-irradiated TMS or neopentane extended over no more than about 125 G under the high-gain conditions commonly employed for observation of solute radicals.) The poor resolution of the features was not improved at higher temperatures; the signal only decayed slowly, disappearing completely at about 110°K.

At 87°K, gamma-irradiated solutions of hexafluoroethane containing SF_6 exhibited a spectrum matching that of Figure 28 (p. 96), obtained after gamma irradiation of a solid solution of SF_6 in MTHF and ascribed to SF_6^-. When the samples were warmed, the SF_6^- spectrum gradually decayed, finally disappearing at about 108°K. During this annealing

process, at about 107°K, an isotropic spectrum grew in very rapidly; the coupling to four equivalent fluorine nuclei and the second-order structure matched the parameters reported for SF_5.[13,40] Raising the temperature to 110°K resulted in loss of the solvent spectrum, while the SF_5 spectrum was stable to 112°K. No anisotropic features could be detected corresponding to those of SF_6 in ethanol and ascribed to SF_5.

Two interpretations can be set forth to account for these results. It may be that the SF_6^- simply gives up its extra electron and that the SF_5 arises from polycrystalline SF_6, which may be rotating slowly at lower temperatures so that the anisotropic features are so broad as to be unobservable. It is known, however, that the transition from anisotropic to isotropic SF_5 occurs at 94°K[41] instead of 108°K.

An alternative view is that the SF_6^- decays by expelling a fluoride ion to form SF_5, which tumbles slowly, so that the broadened anisotropic spectrum is unobservable. The onset of rotation about the carbon-carbon bond in the pentafluoroethyl radical has been reported at about 103°K.[5] A change of this type in hexafluoroethane could permit rapid rotation of SF_5, resulting in an isotropic spectrum.

(Trifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane (perfluoroisobutane) exhibited after gamma irradiation an EPR spectrum that extended farther and had broader features than that from hexafluoroethane. A solution of SF_6 in this matrix exhibited at 120°K a spectrum containing a set of features resulting from coupling to six equivalent fluorine nuclei and second-order structure and a ^{19}F hyperfine coupling constant that matched those from the isotropic spectrum of SF_6^-.[13,42] At 120°K, a solution of octafluorocyclobutane in this matrix exhibited after

gamma irradiation a spectrum which did not match either the isotropic or anisotropic spectrum of $\underline{c}\text{-}C_4F_8^-$.

Silicon tetrafluoride is known to accept an extra electron during gamma irradiation in frozen neopentane to produce SiF_4^-, the EPR spectrum of which is known.[14] In spite of the fact that the spectrum of the anion in neopentane is wide, it was thought that the linewidths of the spectrum of SiF_4^- in silicon tetrafluoride might be sufficiently narrow to allow observation of the spectra of radicals derived from solutes. A gamma-irradiated 5% solution of SF_6 in this matrix exhibited a spectrum matching that described above for SF_6 in perfluoroisobutane. However, the spectrum of a 5% solution of methyl bromide in silicon tetrafluoride contained no features corresponding to those of the methyl radical.

Pure hexamethyldisilane produced on gamma irradiation at 77°K a species exhibiting in its EPR spectrum at 80°K a very broad 1:2:1 set of features, extending over about 80 G. Warming the sample did not result in increased resolution. Gamma irradiation of frozen solutions containing SF_6, tetrafluoroethylene, sulfuryl fluoride, or octafluorocyclobutane, all up to 5% concentration, yielded only the solvent radicals.

CHAPTER IV

DISCUSSION

A. Matrices and Their Properties

The matrices used in this investigation were of two types, glassy and polycrystalline, in the former of which the solute radicals are distributed in random orientations, so that features in the EPR spectra are broadened and poorly resolved, making analysis difficult except in the case of radicals for which axial symmetry of the hyperfine and g tensors results in a relatively simple spectrum. Though most of the powder spectra in the glasses could not be analyzed, some proved to be useful for radical identification by comparison with the "parallel" and "perpendicular" spectra obtained in oriented polycrystalline matrices, which could be analyzed (vide infra). A further use of glassy matrices like MTHF and 3-methylhexane was facilitated by their low melting points and lack of crystallinity; warming solutions to temperatures slightly below those at which solvent radicals decayed permitted some motion of solute molecules, allowing an investigation of some of the reactions of the radicals.

The rotator solids, which form polycrystalline matrices, do not allow translational motion of solute radicals and so cannot be used for studies of radical reactions. They are, however, extremely useful for the identification of primary radicals. The EPR spectra were quite well resolved in some cases because of sufficient motion of the radical to average out most of the anisotropy from the hyperfine interactions and the g factor to produce isotropic or nearly isotropic spectra. In other cases, the radicals were preferentially oriented in the matrix, so that rotation of the sample by 90° within the magnetic field effected

replacement of one set of anisotropic features by another. Better line resolution was obtained for these anisotropic spectra in TMS than was obtained in glassy matrices, perhaps as a result of motional effects which, however, did not average out the main anisotropic interactions. Axial symmetry of the hyperfine tensors of many of these oriented radicals facilitated analysis of the spectra. However, in some cases, the spectral resolution was still not sufficient to allow assignment of a complete set of coupling constants or unambiguous identification of the radicals.

Among the rotator solids, TMS was found to be the most useful for studies of electron capture. Sulfur hexafluoride had been used as a matrix in the production of fluoro-alkyl radicals by gamma irradiation of ethylenes[5] and so was unsuitable for the production of radical anions. Neopentane was found to be less suitable than TMS, as shown, for example, by the degrees of isotropic character in the EPR spectra of $\underline{c}\text{-}C_4F_8^-$ in neopentane[15] and TMS,[16] which may be due to larger cavities in the latter matrix. Very little was known at the time this work was begun about the use[18] and limitations of the adamantane matrix (for example, the necessity of using trimethylamine borane) in stabilizing radical anions formed by electron capture. Later, it was learned[43] (and experimentally confirmed) that materials which are gases at room temperature apparently cannot be easily incorporated in the matrix. Since most of the compounds of interest have boiling points below about 30°C, this matrix was not employed as frequently as TMS.

B. Electron Attachment to Perhalocycloalkanes

It has long been known that fully fluorinated cyclic alkanes (perfluorocycloalkanes) have larger cross sections for electron

attachment than their acyclic counterparts. Gas phase studies have also shown the existence of long-lived negative ions of the cyclic compounds resulting from electron attachment to the neutral molecules, while radiation chemical studies involving competition with known electron scavengers such as nitrous oxide in condensed phases[45] and involving reduction of the trapped electron yield[46] are all consistent with the thesis that perfluorocycloalkanes are efficient electron scavengers.

The detection by EPR[15] of the radical anion of octafluorocyclobutane was the first direct evidence for electron capture by perfluorocycloalkanes in the condensed phase. Hexafluorocyclopropane[16] and decafluorocyclopentane[16] were also found to accept extra electrons. In these radical anions, all the fluorine atoms are equivalent, indicating either planarity of the carbon skeleton (D_{3h}, D_{4h}, or D_{5h} symmetry) or time-averaged D_{4h} or D_{5h} symmetry brought about by rapid ring inversion of the cyclobutane or cyclopentane rings on the EPR time scale.[15,16] There appears to be complete delocalization of the unpaired electron in the anions of the perfluorocycloalkanes.

The reason why a fully saturated molecule can capture an extra electron has been the subject of occasional interest. Mittal and Libby[46] postulated intramolecular electrostatic traps arising from C-F bond dipoles, while Liebman[47] suggested a conventional molecular orbital approach involving electron addition to a combination of localized $>CF_2$ sigma antibonding orbitals. As mentioned previously, Hasegawa, Shiotani, and Williams[16] obtained experimental evidence which is consistent with a molecular orbital description.

The species resulting from electron attachment to 1,2-dichlorohexafluorocyclobutane and 1,2-dibromohexafluorocyclobutane probably have

a non-uniform spin distribution similar to the radical anions of chloro- and bromotrifluoromethane, in which the unpaired electron is localized mainly in the bond between the carbon and the unique halogen.[16]

The observation by optical spectroscopy that solutions of comparable concentrations of octafluorocyclobutane, decafluorocyclopentane, and dodecafluorocyclohexane in MTHF decrease the trapped-electron signal in the order $\underline{c}\text{-}C_4F_8 > \underline{c}\text{-}C_5F_{10} > \underline{c}\text{-}C_6F_{12}$ suggests that these solutes have electron capture cross-sections decreasing in that order. That the radical anion of perfluorocyclohexane is more easily photobleachable in MTHF than are the other anions suggests perhaps that the cyclohexane has a lower electron affinity than the other cycloalkanes.

It is not known at present whether the transitions observed in the optical spectra of solutions in MTHF are bound-free or bound-bound. For $\underline{c}\text{-}C_6F_{12}^-$, the loss of signal upon photolysis with visible light strongly suggests that the excess electron is ejected into the solvent. But for the other two anions, it is not known whether a charge transfer-to-solvent state reverts to the anion or whether the anion is produced in an electronically excited state. Attempts to effect photo-induced electron transfer from $\underline{c}\text{-}C_4F_8^-$ to SF_6 in MTHF were unsuccessful.

C. Electron Attachment to Fluorinated Ethylenes --EPR Studies

1. 1,1-Difluoroethylene

Before discussing the EPR results, it may be pertinent to mention that in mass spectrometric studies of 1,1-difluoroethylene, Thynne and MacNeil[48] found that an unstable "compound-ion" $CF_2CH_2^-$ apparently is formed upon electron impact but fragments to produce F^- and H^-, in addition to other ions, the corresponding radicals presumably being

$C_2FH_2^{\cdot}$ and $C_2F_2H^{\cdot}$. These authors noted that the hydride ion signal was of very low intensity regardless of the energy of the incident electron, while the fluoride ion signal was of low intensity for energies up to about 5 eV. Thus, dissociative attachment was found not to be an important process in the gas phase.

The results of EPR studies of gamma-irradiated frozen solutions of 1,1-difluoroethylene in MTHF suggest that associative electron attachment predominates in the solid state, too. That electron capture does, indeed, take place is shown by the absence of a trapped-electron signal in the EPR spectrum and of the blue color characteristic of the trapped electron in MTHF. The shapes of the features in the EPR spectrum (Figure 5, p. 35) are strongly suggestive of axially symmetric hyperfine interactions in the radical; the outer features have the shape generally ascribed to parallel,[34] while the inner features have the shape of perpendicular features.[34] Also, the observation of unequal spacings between the two features on each side of the spectrum supports the breakdown of the spectrum into parallel and perpendicular components and rules out the possibility that the splitting could be caused by coupling to one nucleus of spin 1/2 (for example, either H or F in $CFCH_2$ or CF_2CH).

The width of the spectrum obtained after gamma irradiation of a frozen solution of 1,1-difluoroethylene in MTHF (457 G for the parallel, 340 G for the perpendicular) suggests that the coupling is due to two fluorine nuclei since couplings to hydrogen are generally much smaller. For example, the largest coupling in the vinyl radical is 65 G,[49] while fluorine couplings can be much larger, of the order of 150 to 200 G.[15,16] The coupling to the hydrogen nuclei appears to be lost in the linewidth.

The radical, then, is identified as $CF_2CH_2^{-}$ on these bases, that

the large hyperfine interaction is indicative of coupling to two fluorine nuclei, and that the ^{19}F hyperfine tensors appear axially symmetric. There seems no experimental basis for a distinction between the two fluorine nuclei; they appear to be equivalent.

2. Tetrafluoroethylene

The identity of the radical produced by gamma irradiation of solid solutions of tetrafluoroethylene has been established unequivocally as $C_2F_4^-$ through the observation in the EPR spectrum of hyperfine coupling to four equivalent fluorine nuclei and the generation of an identical EPR spectrum by photolysis of a solution of tetrafluoroethylene containing TMPD. As discussed below, it is believed that the order of the unoccupied orbitals in neutral tetrafluoroethylene is different from that in ethylene, with the result that $C_2F_4^-$ is a σ rather than π radical.

It might be expected that tetrafluoroethylene might be similar to unsubstituted ethylene in having as its lowest unoccupied orbital a π^* orbital, with a σ^* orbital at higher energy. According to the *ab initio* molecular orbital calculations of Snyder and Basch,[50] this is the case, the unoccupied orbitals of tetrafluoroethylene being, in order of increasing energy, $2b_{1g}$ (π^*) < $5b_{1u}$ (σ^*) < $6b_{3u}$ (σ^*) < $7a_g$ (σ^*), etc. The highest occupied molecular orbital was found to be a π type.

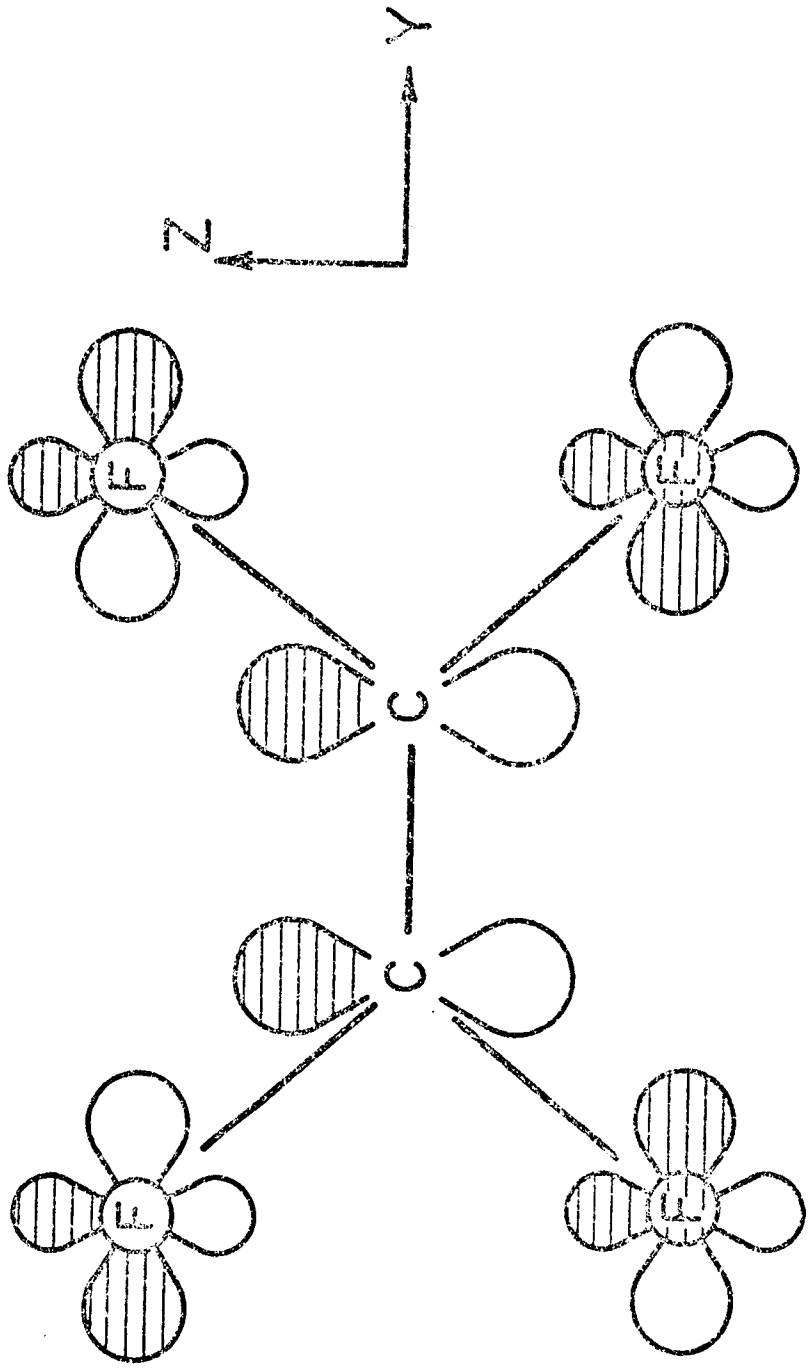
Experimental work, however, appeared to indicate that the π^* and σ^* orbitals might be reversed. Belanger and Sandorfy,[51] observing the vacuum ultraviolet spectrum of tetrafluoroethylene in the vapor phase, found the maximum in the $\pi^* \leftarrow \pi$ absorption to be at 71,680 cm^{-1} but were unable to assign the $\sigma^* \leftarrow \pi$ transition. Robin[52] stated that the $\pi^* \leftarrow \pi$ transition is at 71,600 cm^{-1} and that a weak absorption at 62,000 cm^{-1} could tentatively be assigned to the $b_{1u} \leftarrow b_{2u}$ transition, which is a

parity forbidden $\pi^* \leftarrow \pi$ transition. This suggestion implies that in tetrafluoroethylene a σ^* orbital is of lower energy than the lowest π^* orbital, the opposite of the order usually accepted for the unsubstituted molecule.

Studies using photoelectron spectroscopy have shown a shift in the order of the occupied molecular orbitals of tetrafluoroethylene and ethylene[22] and of hexafluorobenzene and benzene.[53] This has been attributed to the preferential stabilization of σ orbitals upon complete substitution of fluorine for hydrogen. Thus, if a σ and a π orbital happen to have similar energies in the unsubstituted molecule, the σ orbital is expected to have a lower energy in the perfluoro compound. That this perfluoro effect can affect the unoccupied orbitals also has been shown by EPR studies of the radical anions of fluorinated benzenes.[18]

Thus, it seems not unreasonable to believe that the lowest unoccupied orbital of tetrafluoroethylene, the singly occupied orbital of $C_2F_4^-$, could be of the σ^* type. The large hyperfine coupling constant obtained from the isotropic spectrum confirms that $C_2F_4^-$ is a σ radical, the value (94 G) being too large for a π radical with planar geometry[18,36] and more consistent with a σ^* radical. But, as mentioned above, there are several σ^* orbitals. The low value of the ^{13}C hyperfine coupling constant (49 G) seems to rule out σ^* orbitals having large contributions from the carbon 2s orbitals since this value corresponds to a spin density in those orbitals of only about 0.09.[36] Among the σ^* orbitals listed by Snyder and Basch,[50] the $5b_{1u}$ seems to fit the data better than do the others since it is a σ^* orbital with no direct contribution from the 2s orbitals of carbon. The composition of this orbital is shown in Figure 32.

Figure 32. The $5b_{1u}$ orbital of tetrafluoroethylene.



$5b_{1u}$

The above orbital analysis is based on retention by the anion of the $\underline{D}_{2h}$ symmetry of the neutral molecule. But another geometry could be envisioned for the anion,[36] in which the fluorine atoms might be bent out of the original plane of the molecule to form a structure reminiscent of the chair conformation of cyclohexane. Although this $\underline{C}_{2h}$ structure cannot be entirely ruled out, the fact that the sum of the carbon-13 couplings (2x49 = 98 G) is much closer to that of the planar perfluoro-$\underline{t}$-butyl radical (44.3 G[54]) than to the value found for the tetrahedral trifluoromethyl radical (271.6 G[55]) suggests that the deviation from planarity must not be very large.[36]

3. The Trifluoroethylene Series

The radicals resulting from gamma irradiation of frozen solutions of the trifluoroethylenes in TMS or TMS-$\underline{d}_{12}$ could not be identified with absolute certainty, analyses of the EPR spectra being consistent either with the loss of a fluoride ion by dissociative attachment or with electron attachment to produce a negative ion having a very small hyperfine coupling constant to one fluorine nucleus. The latter process, however, is favored by the author for the reasons presented below.

The spectra from gamma-irradiated chloro-, bromo-, and iodotrifluoroethylene in TMS were generally well-resolved, a factor which, combined with preferential orientation of the solutes in the matrix, led to determination of the coupling constants for the unique halogen and the fluorines. These values are listed in Table II. All of the radicals exhibited axially symmetric hyperfine coupling tensors to the unique halogen, the breakdown into parallel and perpendicular being suggested by the shapes of the features and supported by the magnitudes of the second-order shifts, which involve the squares of the coupling constants

TABLE II

EPR DATA OF THE RADICAL ANIONS OF SUBSTITUTED TRIFLUOROETHYLENES IN TMS[a]

	$A_{//}$ (G)	$A_{\perp}$ (G)	$g_{//}$	$g_{\perp}$	Spin density[b]
CF_2CFCl^-			1.997	2.011	0.30
Cl-35	83.3	38.8			
Cl-37	69.6	32.3			
F_1	134.3	74.9			
F_2	67.7	6.6			
F_3		5.5			
CF_2CFBr^-			2.000	2.036	0.33
Br-79	463.4	213.8			
Br-81	430.8	198.7			
F_1	134	36.6			
F_2	66	27.7			
F_3		9.9			
CF_2CFI^-			1.996	2.041, 2.066	0.47
I-127	572	258, 258			
F_1	114	31.0, 37.9			
F_2	54.3	12.8, 17.8			

a. Obtained at 98°K after gamma irradiation of 5% solutions to a dose of 0.75 Mrad.

b. Spin density in the 3p, 4p, and 5p orbitals of chlorine, bromine, and iodine, respectively.

of the parallel and perpendicular components. The unambiguous determination of coupling to only two fluorine nuclei in the parallel spectra from all three compounds could be taken as evidence in favor of preferential loss of a fluoride ion upon electron attachment, resulting in the formation of a tri-substituted vinyl radical C_2F_2X (X=Cl,Br,I), a previously unknown species. However, at least one case is known[42] in which coupling to one fluorine nucleus is undetectably small while couplings to the other fluorine nuclei are over 100 G. So it is possible that the radicals are the radical anions of the trifluoroethylenes. Support for this assignment comes from the interpretations of the perpendicular spectra from chloro- and bromotrifluoroethylene in terms of coupling to three fluorine nuclei.

The spin densities on the unique halogen provide strong evidence in favor of identification of the radicals as the radical anions. Values of 0.30, 0.33, and 0.47 for the spin densities in the chlorine 3p, bromine 4p, and iodine 5p orbitals, respectively, seem much too large for a vinyl radical.

Further support for the assignment to the radical anions is provided by the chemistry of perhalo compounds. EPR studies of frozen solutions have shown that trifluoromethyl chloride, bromide, and iodide undergo electron attachment at low temperatures but dissociate on warming, releasing chloride, bromide, and iodide ions.[16] Rothe and coworkers[56] studied these compounds and other perhalomethanes in the gas phase by the molecular beam technique, bombarding them with cesium atoms. Their results showed that the higher the atomic number of the halogen atom, the more readily is the halide ion lost. If the same behavior is found in the trifluoroethylene series, the ease of loss of the halide ion upon

electron attachment should follow the order $I^- > Br^- Cl^- > F^-$.

Rothe and co-workers,[56] studying chlorotrifluoroethylene by the same technique, found that the ratio of fluoride to chloride ion loss varied with the energy of the incident cesium atoms, being very low for lower energy projectiles but reaching a plateau value of 0.8 for cesium energies above about 100 ev. The chloride ion is thus lost preferentially.

Hickam and Berg,[57] studying electron attachment to chlortrifluoroethylene using mass spectrometry, found the appearance potential of chloride to be 0.9 ev. No mention was made of fluoride ions. Christoulides, Schumacher, and Schindler[58] observed thermal electron attachment to chlorotrifluoroethylene by ion cyclotron resonance. No evidence was presented for loss of either fluoride or chloride ion.

It therefore is believed that if dissociation were to occur following electron capture, the higher halide ions would be preferentially lost. The product should be the trifluorovinyl radical. However, the EPR data show that the higher halogens are retained, as evidenced by the very large coupling constants observed for these nuclei. Hence, it is believed that dissociation does not take place under the conditions of these experiments, that the EPR spectra from gamma-irradiated solutions of chloro-, bromo-, and iodotrifluoroethylene in TMS are those of the radical anions.

In contrast, the EPR spectrum of a gamma-irradiated solution of the other member of the trifluoroethylene series, trifluoroethylene, in TMS was weak and poorly resolved and so could not be analyzed. The spectrum of a gamma-irradiated solution in MTHF was not subject to unambiguous analysis. That electron capture occurred was shown by the absence of the

signal of the trapped electron. But it is not clear whether the outer features are parallel features which are unobservable in the spectrum obtained in TMS or whether they arose from the dimer, dihydrohexafluorocyclobutane, present as an impurity or formed during the irradiation by an ion-molecule reaction similar to that observed in solutions of tetrafluoroethylene in MTHF.

D. Fluorinated Ethylenes --Optical Spectra

In order for an electronic transition to be allowed[59] (to have a high probability of occurrence), the transition moment, the square of the integral in Equation 10, must be non-zero. The ψ's represent wavefunctions of the vibrational (v) and electronic (e) states, the stars

$$\int \psi_{vf}^{*} \psi_{ef}^{*} \vec{r} \psi_{ei} \psi_{ei} \, d\tau = M_{f \leftarrow i} \tag{10}$$

indicating the complex conjugates, and i and f being the initial and final states. The $d\tau$ indicates integration over all space. The vector $\vec{r}$ is the electric dipole operator. In many cases, there is negligible vibronic coupling, coupling of vibrational and electronic terms, so that the terms can be treated independently, as shown in Equation 11. The

$$\int \psi_{vf}^{*} \psi_{vi} \, d\tau \int \psi_{e}^{*} \vec{r} \psi_{e} \, d\tau = M_{f \leftarrow i} \tag{11}$$

integrals must then be separately non-vanishing.

A simple means of determining whether the integrals are non-zero is by group theory, according to which the product of the irreproducible representations of the ground and electronic excited states must contain the representation of one of the three components (x,y, or z) of the dipole operator in order for the transition to be allowed, to have a non-zero oscillator strength. For this procedure to be used, geometries of ground and excited states must have been previously assumed and at

least the symmetries of the molecular orbitals determined. It is helpful to know which orbitals are occupied and which unoccupied. The order of the unoccupied orbitals and the energy separations between the orbitals as provided by theory may or may not be significant, depending on the reliability of the calculation.

The product of the irreproducible representations of the vibrational states must contain the totally symmetric representation. That is, only vibrational states of the same symmetry can interact. According to Herzberg,[60] if the representation is totally symmetric, all of the vibrations of this symmetry can mix, so that the observed transitions involve sums and differences of all the totally symmetric vibrations which are excited.

Once it has been determined by the above procedure which transitions are allowed, the following procedure may be followed in a determination of the degree of allowedness.

For an allowed transition without a significant amount of vibronic coupling, the integrals of Equation 10 can be treated separately. The electronic wavefunctions ψ_v can be expressed as a linear combination of atomic orbitals and substituted into the integral for the purely electronic transition. Use of the approximations of the CNDO/2 method[61,62] allows reduction of Equation 11 to the form shown in Equation 12, where the value of the integral of the vibrational transition is assumed to be

$$M^{z}_{f \leftarrow i} = e \sum_{\mu}^{AO} z_{\mu} c_{f\mu} c_{i\mu} \qquad (12)$$

one. The summation is over all the atomic orbitals, whose coefficients in the expansion of the ψ_v's are $c_{f\mu}$ and $c_{i\mu}$ for the final and initial states, respectively. The dipole operator $\vec{r}$ is represented in this

equation as the product of the electronic charge e and the z component of the dipole. Similar equations must be set up with the x and y components.

Relative values of the transition moment for various transitions can be obtained by substitution of the appropriate co-ordinates of the atomic centers and the values of the atomic orbital coefficients provided by a CNDO/2 calculation. The program used in this work, supplied by Dr. J. E. Bloor of this department, was similar to one used by Pople and Beveridge.[63]

The observed spectrum of $C_2F_4^-$ had an extinction coefficient at 508 nm, the position of the maximum, of 4400 $M^{-1}cm^{-1}$. In view of the observation[52] that the extinction coefficient of the allowed $\pi^* \leftarrow \pi$ transition of the neutral molecule is 11,400 $M^{-1}cm^{-1}$, the above value is fairly large, suggesting that the transition might be allowed. The oscillator strength was calculated to be about 0.07, a small but still reasonable value for an allowed transition.[64]

If $C_2F_4^-$ retains the $\underline{D}_{\underline{2h}}$ symmetry of the parent molecule, the excess electron is expected to enter the orbital designated $5\underline{b}_{\underline{1u}}$ by Snyder and Basch[50] but $\underline{b}_{\underline{2u}}$ in the notation of Herzberg,[65] according to which the x and y axes are in the plane of the molecule, the x being along the carbon-carbon bond, and the z axis is perpendicular to the molecular plane. In Herzberg's notation, the unoccupied orbitals accessible from the $\underline{b}_{\underline{2u}}$ level, according to group-theory, are $\underline{b}_{\underline{2g}}$, $\underline{b}_{\underline{1g}}$, $\underline{a}_{\underline{g}}$, and $\underline{b}_{\underline{3g}}$. Use of the procedure described above for determination of the relative allowedness of the transitions reveals that only one transition $\underline{a}_{\underline{g}} \leftarrow \underline{b}_{\underline{2u}}$ (or $\underline{A}_{\underline{g}} \leftarrow \underline{B}_{\underline{2u}}$, if molecular states are used) is expected to have any intensity at all. The contribution to M from the carbon atoms is

zero, meaning that the only vibrations which should be excited are those involving C-F bonds.

Tetrafluoroethylene has three vibrations of a_g symmetry (totally symmetric vibrations), which could mix, according to Herzberg,[60] if they were to be excited in the electronic transition. In the gas phase,[66] the frequencies are 1872 cm^{-1} for the C=C stretch, 778 cm^{-1} for the symmetric C-F stretch, and 394 cm^{-1} for the F-C-F scissors. The last two of these are fairly close to the values of 1020 and 320 cm^{-1} observed for the anion, offering experimental evidence in support of the theoretical prediction that the observed absorption band is due to an excitation in which the C-F bonds are changed rather than the C-C bond.

E. Reactions of Radical Anions of Ethylenes

Though some examples are known of ion-molecule reactions involving positive ions of olefinic and aromatic hydrocarbons to form dimer cations M_2^+,[67] attempts to carry out similar reactions with negative ions have been unsuccessful.[68] As for as the author is aware, only two reactions involving negative ions have been well-characterized, reactions resulting in the production of the dimer radical anions of acetonitrile[7,69] and trimethyl borate.[70] The present work provides at least one more example of this type of reaction in the production of $\underline{c}\text{-}C_4F_8^-$ from $C_2F_4^-$ and C_2F_4. This reaction, however, differs from those of acetonitrile and trimethyl borate in that the product is a radical anion derived from a <u>stable</u> compound.

If acetonitrile in its upper crystalline phase is gamma-irradiated, the alignment of molecules is such that two molecules are capable of sharing an electron between them. The electron is not simply trapped, as it is, for example, in gamma-irradiated MTHF, but is found to reside

within the orbitals of both molecules, forming a species $(CH_3CN)_2^-$.[7,69]

Gamma irradiation of crystalline trimethylborate results in the production of $[(MeO)_3B\cdot\ B(OMe)_3]^-$, in which a one-electron bond is formed between the two boron atoms.[70]

The present work is believed to provide at least one more example of an ion-molecule reaction involving a negative ion in the solid state, a reaction which differs from those described above in that it could be directly observed after gamma-irradiation and that it results in the formation of the negative ion of a stable compound. The observation of the decay of the spectrum in either MTHF or 3-methylhexane of the spectrum of $C_2F_4^-$ and the growth of the spectrum of $\underline{c}$-$C_4F_8^-$ is interpreted as the cyclization reaction of $C_2F_4^-$ with C_2F_4.

An alternative interpretation, that electron transfer occurs between $C_2F_4^-$ and $\underline{c}$-C_4F_8 present in the matrix, is rejected on the grounds that $C_2F_4^-$, which is solvated by the medium, probably would be unable to migrate at the temperature at which the reaction takes place and that, of the neutral molecules, the flat tetrafluoroethylene would be expected to migrate more readily than the more bulky octafluorocyclobutane, which is puckered. These migration arguments are believed to be reasonable because the radicals of the solvent do not begin to decay until a higher temperature is reached.

That the cyclization reaction has a very low activation energy is suggested by the fact that it takes place readily at 95°K. Further evidence comes from the very high efficiency of the conversion, as shown by the observation that the yield of $\underline{c}$-$C_4F_8^-$ from the irradiation of tetrafluoroethylene is about half that obtained from a parallel experiment with octafluorocyclobutane, a compound roughly equivalent to SF_6 in

its ability to capture electrons.

This cyclization was explained theoretically[71] using the frontier orbital scheme,[72] according to which interactions can take place between the singly occupied molecular orbital of the radical (SOMO) and either the lowest unoccupied or highest occupied orbital of the diamagnetic molecule (LUMO or HOMO). As discussed previously, the extra electron in the tetrafluoroethylene radical anion is believed to be in a $5\underline{b}_{1u}$ orbital (in the notation of Snyder and Basch[50]), if the anion retains the D_{2h} symmetry of the neutral molecule. This then is the SOMO of the radical and the LUMO of the neutral molecule. The HOMO of the neutral molecule is the $2\underline{b}_{2u}$ orbital.[50] As shown in Figure 33, in which only the in-plane p orbitals on carbon are represented, interaction can occur by a supra-facial process for either SOMO-LUMO or SOMO-HOMO.[71]

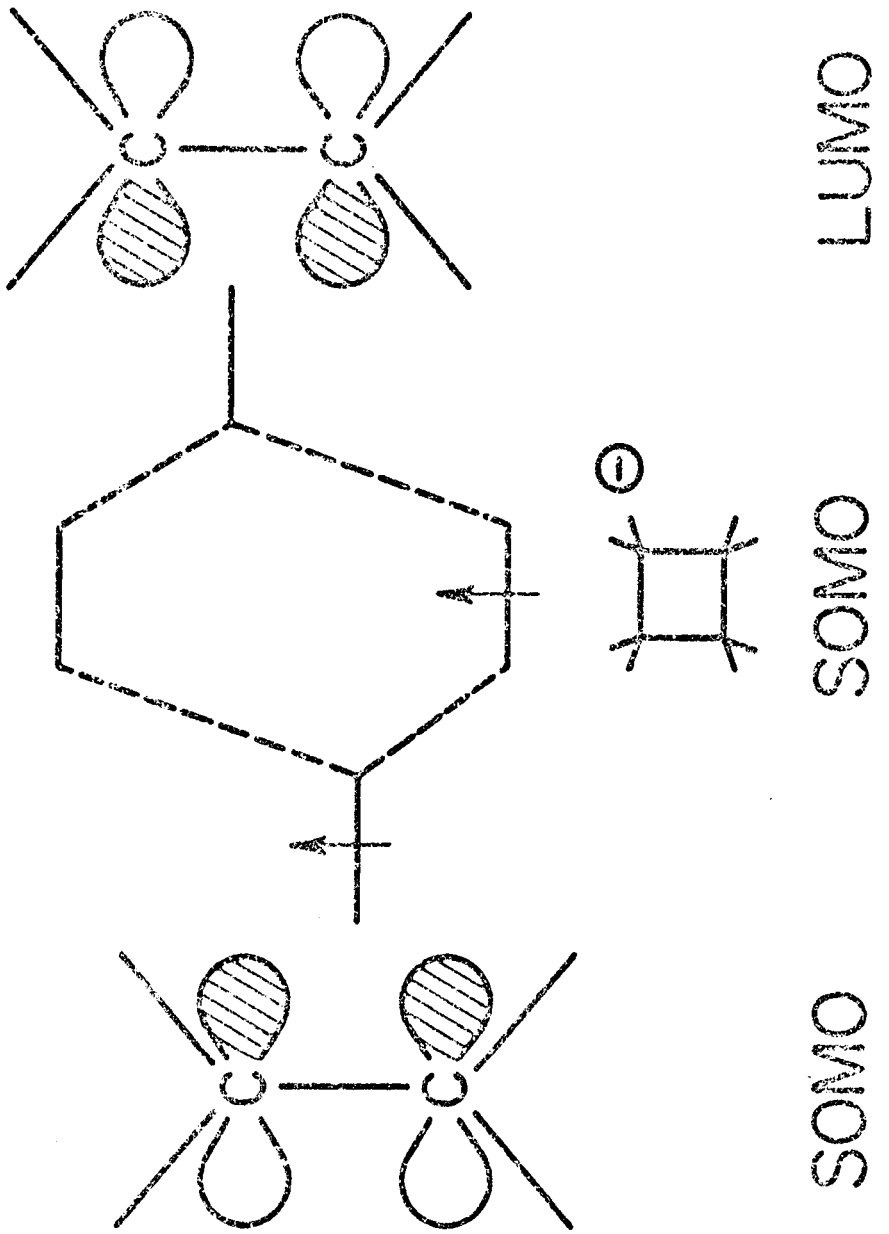
The determination above that the cyclization process is allowed for a σ radical should not be taken as support for the assignment of the tetrafluoroethylene radical anion as such a radical; the reaction is allowed even if the extra electron resides in a π^* orbital.[71]

A similar cyclization reaction may occur with chlorotrifluoro-ethylene. In this case, though, the spectrum of the chlorotrifluoro-ethylene radical anion (Figure 17a, p. 66) strongly overlaps the spectrum of the radical anion of 1,2-dichlorohexafluorocyclobutane (Figure 4, p. 31), making it difficult to observe the precise changes. However, there is some indication that the observed changes are due to a cycloaddition reaction.

F. Sulfur Hexafluoride

Sulfur hexafluoride (SF_6) has long been used in radiation chemistry

Figure 33. The frontier orbital representation of the cycloaddition reaction of $C_2F_4^-$ and C_2F_4 using the $5b_{1u}$ orbital as the SOMO of the anion and the LUMO of the neutral molecule.


LUMO
SOMO
SOMO

as an electron scavenger[73] because of its chemical inertness and high efficiency in capturing electrons. Most of the studies involved observation of the effects of the introduction of SF_6 on the yields of other species. Only a small amount of effort was directed toward understanding the consequences of electron acceptance by SF_6.

Liquid-phase studies focused on the end products of electron attachment to SF_6. The metal sulfides and fluorides were formed in the reactions with SF_6 of sodium in diphenylethylene glycol dimethyl ether[74] and cesium in liquid ammonia.[75] The suggested pathway for both reactions involved electron transfer to SF_6 and the loss of fluoride ion from SF_6^- to form SF_5. Loss of fluoride ion was believed to occur following the reaction of SF_6 with hydrated electrons.[76]

Mass spectrometric studies of pure SF_6 showed that the principal products of electron attachment are SF_6^- and SF_5^-, with F^- being a minor product.[77,78] In the presence of silicon tetrafluoride and some other inorganic fluorides, SF_6^- was seen to undergo an ion-molecule reaction to transfer a fluoride ion.[79] Ion cyclotron resonance experiments[80] demonstrated that SF_6^- is capable of donating a fluoride ion to hydrogen chloride, hydrogen bromide, acetic acid, and formic acid but apparently does not react with ethanol, methanol, and water.

Fluoride ion loss was found to occur in the solid state, too, as shown by the observation of the EPR spectrum of SF_5 after gamma irradiation of SF_6 in ethanol and methanol at 77°K. It may be that fluorine atom loss from SF_6^- also occurs; the products cannot be detected by EPR, SF_5^- because it is diamagnetic and fluorine atoms because they probably react very quickly with the matrix or radicals in the solution.

In contrast, SF_6^- is observed after gamma irradiation of frozen

solutions of SF_6 in TMS, neopentane, silicon tetrafluoride, hexafluoroethane, hexamethylphosphortriamide, N,N-dimethylformamide, MTHF, 3-methylhexane, and 11 M NaOH in water. It may be that these solvents are not as efficient in solvating small anions such as F^- as are the alcohols because of the lack of small, polar groups like the hydroxyl group. The behavior of the frozen alkaline aqueous solution can be understood when one considers that most, if not all, of the water molecules are involved in the solvation of the ions from NaOH; very few water molecules are available for the solvation of SF_6^- or F^-.

G. Electron Transfer Reactions

Electron transfer has long been known to occur in organic solvents in the solid state, an early example being of the solute-to-solvent type, photo-induced ejection of an electron from a radical anion in frozen MTHF to produce a trapped electron.[6] In the radiolysis of solid solutions in the dark, Miller[81] invoked solute-to-solute electron transfer (by tunneling) to explain his observation of an increased yield of the anion of an electron acceptor of high electron affinity in the presence of an acceptor of lower electron affinity.

The present investigation provides what is believed to be the first direct evidence for photo-induced solute-to-solute electron transfer in the solid state. The observation of the photo-induced decay of the EPR spectrum of $\underline{c}\text{-}C_4F_8^-$ and the growth of the spectrum of SF_6^- in a gamma-irradiated solution of octafluorocyclobutane and sulfur hexafluoride in TMS is interpreted as the ejection of an electron from $\underline{c}\text{-}C_4F_8^-$ and its acceptance by sulfur hexafluoride after having traveled through the matrix. Another example of this electron transfer involves the

photo-induced decay of the spectrum of $\underline{c}\text{-}C_4F_8^-$ and the growth of the spectrum of $CH_3^\bullet$ in a gamma-irradiated solution of octafluorocyclobutane and methyl bromide in TMS in the solid state.

These photolysis reactions also demonstrate that an electron is being transferred from $\underline{c}\text{-}C_4F_8^-$, thereby providing confirmation of the identification of the radical.

LIST OF REFERENCES

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1. A. Henglein, W. Schnabel, and J. Wendenburg, "Einfuehrung in die Strahlenchemie," Verlag Chemie, Weinheim, Bundesrepublik Deutschland, 1969, Chapters 5 and 6; J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1976, Chapter 2; L. G. Christophorou, "Atomic and Molecular Radiation Physics," John Wiley and Sons, Inc., New York, N. Y., 1971, Chapter 2.

2. M. J. Bronskill, W. B. Taylor, R. K. Wolff, and J. W. Hunt, Rev. Sci. Inst., 41, 333 (1970).

3. B. S. Yakovlev, I. A. Boriev, L. I. Novikova, and E. L. Frankevich, Int. J. Rad. Phys. Chem., 4, 393 (1972); K.-D. Asmus, Int. J. Rad. Phys. Chem., 4, 417 (1972); K. H. Schmidt, Int. J. Rad. Phys. Chem., 4, 439 (1972); A. M. Hutton, Int. J. Rad. Phys. Chem., 4, 479 (1972).

4. E. C. Avery, J. R. Remko, and B. Smaller, J. Chem. Phys., 49, 951 (1968); R. W. Fessenden and N. C. Verma, J. Am. Chem. Soc., 98, 243 (1975).

5. R. W. Fessenden and R. H. Schuler in "Advances in Radiation Chemistry," Vol. 2, M. Burton and J. L. Magee, Eds., John Wiley and Sons, Inc., New York, N. Y., 1970, p. 1.

6. W. H. Hamill in "Radical Ions," E. T. Kaiser and L. Kevan, Eds., John Wiley and Sons, Inc., New York, N. Y., 1968, p. 321.

7. E. D. Sprague, K. Takeda, and F. Williams, Chem. Phys. Lett., 10, 299 (1971).

8. E. D. Sprague, Ph.D. Dissertation, The University of Tennessee, Knoxville, Tennessee, 1971, p. 93.

9. P. H. Kasai, Acc. Chem. Res., 4, 329 (1971).

10. M. Shirom and G. Stein, J. Chem. Phys., 55, 3372 (1971).

11. G. E. Johnson and A. C. Albrecht, J. Chem. Phys., 44, 3162 (1966).

12. J. Timmermans, Bull. Soc. Chim. Belg., 44, 17 (1935).

13. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 45, 1845 (1966).

14. J. R. Morton and K. F. Preston, Mol. Phys., 30, 1213 (1975).

15. M. Shiotani and F. Williams, J. Am. Chem. Soc., 98, 4006 (1976).

16. A. Hasegawa, M. Shiotani, and F. Williams, Faraday Discussions, No. 63, 157 (1977).

17. M. B. Yim, S. DiGregorio, and D. E. Wood, J. Am. Chem. Soc., 99, 4260 (1977).

18. M. B. Yim and D. E. Wood, J. Am. Chem. Soc., 98, 2053 (1976).

19. A. O. Allen and R. A. Holroyd, J. Phys. Chem., 78, 790 (1974); A. O. Allen, T. E. Gangwer, and R. A. Holroyd, J. Phys. Chem., 79, 25, (1975); K. Mori, K. Ito, and Y. Hatano, J. Phys. Chem., 79, 2093 (1975).

20. T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z.-I. Kuri, Bull. Chem. Soc. Japan, 42, 266 (1969); T. Ito, K. Fueki, and Z.-I. Kuri, J. Phys. Chem., 79, 1513 (1975).

21. M. Shiotani, M. B. Yim, and F. Williams, University of Tennessee, Knoxville, Tennessee, personal communication, 1977.

22. C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, J. Am. Chem. Soc., 94, 1451 (1972).

23. C. Lifshitz and R. Grajower, Intern. J. Mass Spectrom. Ion Phys., 4, 92 (1970).

24. C. D. Cooper and R. N. Compton, J. Chem. Phys., 60, 2424 (1974).

25. V. I. Muromtsev, M. A. Bruk, I. G. Akhvlediani, R. A. Asaturyan, G. M. Zhidomirov, and A. D. Abkin, Theor. Exp. Chem., 2, 498 (1966); [Teor. Eks. Khim., 2, 679 (1966)].

26. A. I. Barchenkova, A. S. Baberkin, and E. V. Volkova, High Energy Chem., 3, 390 (1969); [Khim. Vys. Energ., 3, 433 (1969)].

27. J. R. Lacher, G. W. Tompkin, and J. D. Park, J. Am. Chem. Soc., 74, 1693 (1952).

28. J. Lin, K. Tsuji, and F. Williams, J. Chem. Phys., 46, 4982 (1967).

29. A. M. Adur, University of Tennessee, Knoxville, Tennessee, personal communication, 1976.

30. J. Lin, Ph.D. Dissertation, University of Tennessee, Knoxville, Tennessee, 1968, p. 32.

31. W. R. Cullen and P. Singh, Can. J. Chem., 41, 2397 (1963).

32. R. W. Fessenden, J. Chem. Phys., 37, 747 (1962).

33. M. R. Ronayne, J. P. Guarino, and W. H. Hamill, J. Am. Chem. Soc., 84, 4230 (1962).

34. P. Ayscough, "Electron Spin Resonance in Chemistry," Methuen and Co., Ltd., London, 1967, p. 327.

35. C. M. L. Kerr. K. Webster, and F. Williams, J. Phys. Chem., 79, 2650 (1975) and references cited in this paper.

36. R. McNeil, M. Shiotani, F. Williams, and M. B. Yim, Chem. Phys. Lett., 51, 433 (1977).

37. P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., Inc., Amsterdam, 1967, p. 21.

38. B. A. Goodman and J. B. Raynor in "Advances in Inorganic Chemistry and Radiochemistry," Vol. 13, H. J. Emeleus and A. G. Sharpe, Eds., Academic Press, New York, N. Y., 1970, p. 135.

39. J. P. Simons, "Photochemistry and Spectroscopy," John Wiley and Sons, Inc., London, 1971, p. 77.

40. J. R. Morton, K. F. Preston, and J. C. Tait, J. Chem. Phys., 62, 2029 (1975).

41. A. Hasegawa and F. Williams, Chem. Phys. Lett., 45, 275 (1977).

42. J. R. Morton and K. F. Preston, Chem. Phys. Lett., 18, 98 (1973).

43. M. B. Yim, University of Tennessee, Knoxville, Tennessee, personal communication, 1977.

44. A. A. Altschuler and C. A. Clemms, Anal. Chem., 38, 133 (1966); R. K. Assundi and J. D. Craggs, Proc. Phys. Soc. (London), 83, 611 (1964); B. H. Mahan and C. E. Young, J. Chem. Phys., 44, 2192 (1966).

45. L. A. Rajbenbach and U. Kaldor, J. Chem. Phys., 47, 242 (1967); L. A. Rajbenbach, J. Phys. Chem., 73, 356 (1969); N. H. Sagert, Can. J. Chem., 46, 89, 95 (1968).

46. J. P. Mittal and W. F. Libby, Nature, 220, 1077 (1968).

47. J. F. Liebman, J. Fluorine Chem., 3, 27 (1973/74).

48. J. K. J. Thynne and K. A. G. MacNeil, J. Phys. Chem., 75, 2584 (1971).

49. E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys., 40, 213 (1964).

50. L. C. Snyder and H. Basch, "Molecular Wave Functions and Properties," John Wiley and Sons, Inc., New York, N. Y., 1972, p. T-378.

51. G. Belanger and C. Sandorfy, J. Chem. Phys., 55, 2055 (1971).

52. M. B. Robin, "Higher Excited States of Polyatomic Molecules," Vol. II, Academic Press, New York, N. Y., 1975, p. 50.

53. C. R. Brundle, M. B. Robin, and N. A. Kuebler, J. Am. Chem. Soc., 94, 1466 (1972).

54. P. J. Krusic and R. C. Bingham, J. Am. Chem. Soc., 98, 230 (1976).

55. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 43, 2704 (1965).

56. S. U. Tang, B. P. Mathur, and E. W. Rothe, J. Chem. Phys., 64, 1270 (1970).

57. W. H. Hickam and D. Berg, J. Chem. Phys., 29, 517 (1958).

58. A. A. Christoulides, R. Schumacher, and R. N. Schindler, Ber. Bunsenges. Phys. Chem., 80, 965 (1976).

59. I. N. Levine, "Quantum Chemistry," Vol. II, Allyn and Bacon, Inc., Boston, Mass., 1970, p. 125.

60. G. Herzberg, "The Spectra and Structures of Simple Free Radicals," Cornell University Press, Ithaca, N. Y., 1971, p. 108.

61. J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1970, p. 75.

62. J. E. Bloor, University of Tennessee, Knoxville, Tennessee, personal communication, 1977.

63. J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1970, p. 163.

64. D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry," Plenum Press, New York, N. Y., 1976, p. 15.

65. G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 2, Van Nostrand Publishing Co., Princeton, N. J., 1945, p. 106.

66. L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, "Vibrational Spectra of Polyatomic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1974, p. 437.

67. T. Ichikawa and N. Ohta, J. Am. Chem. Soc., 95, 8175 (1973); B. Badger, B. Brocklehurst, and R. D. Russell, Chem. Phys. Lett., 1, 122 (1967); H. van Willigen, E. de Boer, J. T. Cooper, and W. F. Forbes, J. Chem. Phys., 49, 1190 (1968); I. C. Lewis and L. S. Singer, J. Chem. Phys., 43, 2712 (1965); O. Edland, P.-O. Kinell, A. Lund, and S. Shimizu, J. Chem. Phys., 46, 3679 (1967); B. Badger and B. Brocklehurst, Trans. Far. Soc., 65, 2576 (1969).

68. B. Brocklehurst, J. Phys. Chem., 75, 1177 (1971); O. W. Howarth and G. K. Fraenkel, J. Chem. Phys., 52, 6258 (1970).

69. T. Gillbro, K. Takeda, and F. Williams, J. Chem. Soc., Far. I, 70, 465 (1974).

70. R. L. Hudson and F. Williams, J. Am. Chem. Soc., 99, 7714 (1977).

71. R. McNeil, M. Shiotani, F. Williams, and M. B. Yim, Chem. Phys. Lett., 51, 438 (1977).

72. I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," John Wiley and Sons, Inc., New York, N. Y., 1976, p. 82.

73. G. R. A. Johnson and J. M. Warman, Trans. Far. Soc., 61, 1709 (1965).

74. G. C. Demitras and A. G. MacDiarmid, Inorg. Chem., 3, 1198 (1964).

75. L. Brewer, C. Chang, and B. King, Inorg. Chem., 9, 814 (1970).

76. K.-D. Asmus and J. H. Fendler, J. Phys. Chem., 72, 4285 (1968).

77. F. C. Fehsenfeld, J. Chem. Phys., 53, 2000 (1970).

78. R. K. Curran, J. Chem. Phys., 34, 1069 (1961).

79. T. C. Rhyne and J. G. Dillard, Inorg. Chem., 10, 730 (1971).

80. M. S. Foster and J. L. Beauchamp, Chem. Phys. Lett., 31, 479 (1975).

81. J. R. Miller, J. Chem. Phys., 56, 5173 (1972).

VITA

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