U. D. C. 538.113 : 547.221

Electron Spin Resonance Spectra of Fluorocarbon Radicals

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A systematic account has been given of the information currently available about the components of the hyperfine coupling tensor of fluorocarbon radicals and also information about the form of the spectra of fluorocarbon radicals containing one and two α-fluorine atoms in polycrystalline specimens. Recent information on the paramagnetic centres in irradiated polytetrafluoroethylene, including fluorocarbon radicals and also radicals formed in their oxidation, is presented. The bibliography includes 24 references.

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I. INTRODUCTION

Fluorocarbon compounds are finding increasing application in a wide variety of branches of the national economy. In this connection it is particularly necessary to obtain information about the processes occurring which involve fluorocarbon radicals.

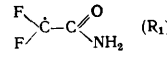
The studies on fluorocarbon radicals by the ESR method have specific features and present certain difficulties. So far the number of unambiguously identified fluorocarbon radicals does not exceed several tens and even as regards the identification of the most thoroughly studied magnetic centres (PC) there exist various mutually exclusive views.

In the present review an attempt is made to give a systematic account of certain radiospectroscopic data on a number of fluorocarbon paramagnetic centres. The first part of the review deals with the available data on the components of the hyperfine coupling tensor of fluorocarbon radicals obtained in the study of irradiated single crystals. The characteristics of the spectra of radicals with one or two α-fluorine atoms in polycrystalline specimens are discussed. The second part of the review considers the results from studies of paramagnetic centres in irradiated polytetrafluoroethylene (PTFE).

II. HYPERFINE COUPLING CONSTANTS OF FLUOROCARBON RADICALS

The broadening of the ESR spectra of fluorocarbon radicals in polycrystalline specimens is caused mainly by hyperfine anisotropic coupling. In order to understand the characteristic features of such spectra, it is extremely important to have information about the constants of the hyperfine coupling tensor for α- and β-fluorine atoms. The values of the constants for α-fluorine atoms in some radicals are presented in the Table

Analysis of the spectra of an irradiated single crystal led Lontz and Gordy[1] to the conclusion that in the radicals



(R₁)

the fragment $\diagdown C-\dot{C}F_2$ is planar and is probably located in the plane of the CON group.

If the magnetic field H_0 is perpendicular to the plane of the crystal, the ESR spectrum consists of three lines with a splitting of 178 Oe between the components. If the field H_0 is in the plane of the radical, a triplet is also observed but the splitting between the components is 24 Oe. In this triplet the splitting is independent of the angle between the direction of the C–C bond in the radical and the direction of the external field.

Constants of the hyperfine coupling tensors

Radical	Constants of HFC tensor for α-F atoms, Oe				Radical	Constants of HFC tensor for α-F atoms, Oe			
	A_1	A_2	A_3	$\bar{A}$		A_1	A_2	A_3	$\bar{A}$
$\dot{C}F_2CONH_2$	178	24	24	75	$CF_3\dot{C}FCONH_2$	201	12	8	74
$\dot{C}HFCONH_2$	189	−4	−16	56	$CO_2^-CF_2\dot{C}FCO_2^-$	150	59	4	71

In the R_1 radical the unpaired electron density is mainly localised at the C–C molecular orbital. At first sight it might appear that, for certain orientations of the magnetic field, the fluorine atoms should be non-equivalent and consequently the spectrum should consist of four lines. However, it is found that, for any orientation, the spectrum consists of three lines the splitting between which depends on the orientation of the radical. The authors believe that the hyperfine coupling constants are due mainly to the unpaired electron density at the fluorine nucleus.

The ESR spectrum of the R_1 radical can be described by the Hamiltonian

$$\mathbf{H} = \beta\,\mathbf{S}\mathbf{g}\mathbf{H}_0 + \sum_{i=1}^{2} \mathbf{S}\mathbf{A}_i\,\mathbf{I}_i - \sum_{i=2}^{2} g_I \beta_I \mathbf{I}_i \mathbf{H}_0 . \qquad (1)$$

The first term of the Hamiltonian represents the coupling between the magnetic moment of the electron and the external field, the second the coupling of the nuclear moments of the fluorine atoms with the magnetic moment of the electron, and the last term is due to the coupling between the nuclear moments of fluorine and the external magnetic field. The tensors g and A characterise the

spin–orbit and hyperfine coupling in the radical. Experiments showed that in the case under discussion the tensors g and A have axial symmetry and their axes of symmetry coincide.

The authors calculated theoretically the energy levels and the ESR spectrum for the paramagnetic centres described by the Hamiltonian (1) in the case where the electron–nucleus interaction is small compared with the interaction with the external magnetic field. The diagram of the resulting energy levels is presented in Fig. 1. The frequencies ν_1, ν_2, and ν_3 correspond to allowed transitions and ν_4, ν_5, ν_6, and ν_7 to forbidden transitions in which the orientations of the electronic and nuclear spins change.

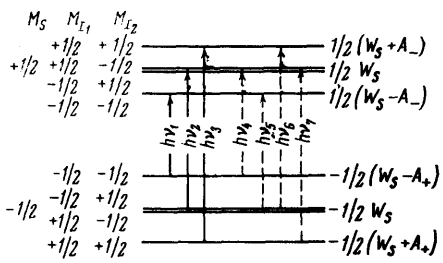


Figure 1. Diagram of energy levels due to the interaction of the unpaired electron with two equivalent fluorine nuclei in the radical $\dot{C}F_2CONH_2$. The continuous and dashed lines indicate the allowed and forbidden transitions respectively.

The splitting between the energy levels of the allowed transitions is given by the expressions

$$\begin{aligned} h\nu_1 &= W_s - \tfrac{1}{2}(A_+ + A_-)\,, \\ h\nu_2 &= W_s\,, \\ h\nu_3 &= W_s + \tfrac{1}{2}(A_+ + A_-)\,, \end{aligned} \tag{2}$$

where

$$A_+ = [(A_\parallel + W_I)^2\cos^2\theta + (A_\perp + W_I)^2\sin^2\theta]^{1/2},$$

$$A_- = [(A_\parallel - W_I)^2\cos^2\theta + (A_\perp - W_I)^2\sin^2\theta]^{1/2},$$

$$W_s = g_s\beta_s H_0;\quad W_I = 2g_I\beta_I H_0\,.$$

In the case considered the hyperfine coupling tensors for both fluorine nuclei have axial symmetry and, moreover, their principal values coincide. The constant $A_\parallel = A_\perp$ corresponds to the direction of the principal axis of the tensor, which is perpendicular to the plane of the radical; θ is the angle between the direction of the external magnetic field H_0 and the normal to the plane of the radical. The splitting in the ESR spectrum between adjacent components of the triplet is given by the expression

$$t = \frac{1}{2}(A_+ + A_-)\,. \tag{3}$$

When the magnetic field is perpendicular to the plane of the radical ($\theta = 0$), then $t = A_\parallel$. For $\theta = 90°$, $t = A_\perp = A_2 = A_3$. In the case considered the g-factor is determined by the relation familiar for the case with axial symmetry:

$$g(\theta) = (g_\parallel^2\cos^2\theta + g_\perp^2\sin^2\theta)^{1/2}\,, \tag{4}$$

where $g_\parallel$ and $g_\perp$ correspond to the parallel and perpendicular orientations of the permanent magnetic field relative to the plane of the radical.

For the R_1 radical, the parameters of the g-tensor are

$$g_\parallel = 2.0025 \pm 0.0010\,,$$

$$g_\perp = 2.0045 \pm 0.0010\,.$$

We may note that in the 3 cm band, for the splitting of the adjacent components of the triplet, W_I may be neglected to a first approximation, particularly for directions of H_0 close to those of the principal axes of the tensor, and Eqn. (3) becomes

$$t = A = [A_\parallel^2\cos^2\theta + A_\perp^2\sin^2\theta]^{1/2}\,.$$

The average value of the principal components of the hyperfine coupling tensor corresponding to isotropic hyperfine coupling is

$$\bar{A} = \pm\frac{1}{3}(A_\parallel + 2A_\perp)\,.$$

For splittings between adjacent components, one can obtain approximately

$$A = \bar{A} + A_\mu(3\cos^2\theta - 1)\,,$$

where

$$A_\mu = \pm\frac{1}{3}(A_\parallel - A_\perp)\,.$$

The frequencies of the forbidden transitions, indicated in Fig. 1 by dashed lines, are given by the expressions

$$\begin{aligned} h\nu_4 &= W_s - \tfrac{1}{2}A_+\,, \\ h\nu_5 &= W_s - \tfrac{1}{2}A_-\,, \\ h\nu_6 &= W_s + \tfrac{1}{2}A_-\,, \\ h\nu_7 &= W_s + \tfrac{1}{2}A_+\,. \end{aligned} \tag{5}$$

The ratio of the probability of forbidden transitions to the probability of allowed transitions is

$$r = \frac{C^2(A_+ - A_- + 2W_I)^2}{(A_{ZZ} + A_- - W_I)(A_{ZZ} + A_+ + W_I) + C^2}\,, \tag{6}$$

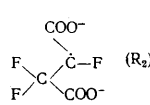
where

$$A_{ZZ} = A_\parallel\cos^2\theta + A_\perp\sin^2\theta\,,$$

$$C^2 = (A_\parallel - A_\perp)^2\sin^2\theta\cos^2\theta\,.$$

It is easily seen from Eqn. (6) that the probability of the forbidden transitions depends significantly on the difference $A_\parallel - A_\perp$ and on the value of W_I. For fluorocarbon radicals, the anisotropy characterised by the value of $A_\parallel - A_\perp$ is very high and the forbidden transitions make a significant contribution to the observed spectrum,

In the 8 mm band for certain orientations of the radical, the intensity of the spectra due to the forbidden transitions is comparable to that of the spectra corresponding to the allowed transitions. As an example, Fig. 2 presents the ESR spectra of the radicals



obtained in an irradiated single crystal[2]. For the chosen orientation of the single crystal, two groups of lines consisting of four components are seen on the second derivative absorption spectrum obtained in the 3 cm band (Fig. 2*a*). The splitting between the centres of these groups is due to the interaction with the one α-fluorine atom and the splitting into four components within the

groups is due to interactions with the two non-equivalent β-fluorine atoms.

In the spectrum obtained for the same orientation using the 8 mm band, the components corresponding to the forbidden transitions are very intense (Fig. 2*b*).

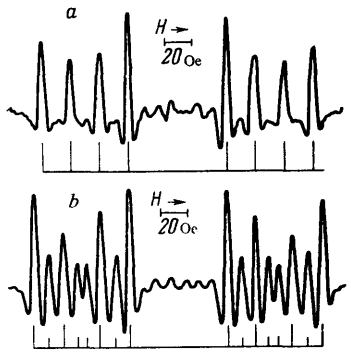
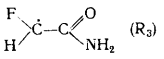


Figure 2. Second derivative absorption spectra for a certain orientation of the radical $CO_2-CF_2\dot{C}FCO_2-$ in a magnetic field H_0 in the 3 cm (curve *a*) and 8 mm (curve *b*) wavelength ranges.

It proved possible to obtain information about the components of the hyperfine coupling tensors for both α- and β-fluorine atoms of the radicals R_2. The anisotropy for the β-fluorine atom is significantly lower than for the α-atoms. The principal values of the hyperfine coupling tensor components for one of the β-fluorine atoms are 63, 23, and 19 Oe and those for the other β-fluorine atom are 71, 27, and 23 Oe.

It is noteworthy that, for reasons which are insufficiently clear, in R_2 the symmetry of the hyperfine coupling tensor for the α-fluorine atom differs from the axial symmetry.

The hyperfine coupling constants of the radicals

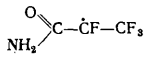


(R₃)

in irradiated single crystals have been investigated. It was found that the symmetry of the hyperfine coupling tensor for the fluorine atom differs somewhat from axial symmetry. By analysing the spectra in the 3 cm and 8 mm bands, the authors succeeded in demonstrating that the isotropic hyperfine coupling constant is positive and equal to 56 Oe. The principal values of the hyperfine coupling tensor for the fluorine atom proved to be 189, −4, and −16 Oe. The highest value of the component corresponds to the principal axis of the tensor being oriented perpendicular to the plane of the radical. The tensor component equal to −16 Oe corresponds to the direction of the principal axis along the C–F bond of the radical.

The authors estimated the contribution to the tensor components due to the unpaired electron density in the $2p_\pi$ carbon orbitals, the $2p_\delta$ fluorine orbital (the orbital responsible for the C–F δ-bond), and the $2p_\pi$ orbital of the fluorine atom. It was found that, although the unpaired electron density in the $2p_\pi$ carbon orbital is very high, the contribution of this orbital to the largest tensor component is insignificant.

Fluorocarbon radicals containing β-fluorine atoms have also been investigated[4]:



(R₄).

It was found that in the R_4 radical the CF_3 group is rotating at room temperature and each β-fluorine atom has the same values of the principal components of the hyperfine coupling tensor, equal to 36, 17, and 14 Oe. The principal values of the hyperfine coupling tensor components for the α-fluorine atom are 201, 12, and 8 Oe.

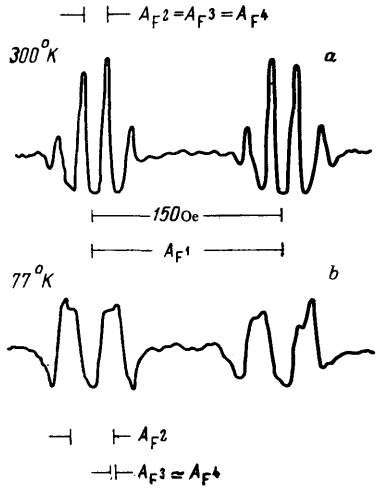


Figure 3. Second derivative absorption spectra for a certain orientation of the radical $CF_3\dot{C}FCONH_2$ in a magnetic field H_0: *a*) 300°K; *b*) 77°K.

Fig. 3 presents the spectra at 300° and 77°K corresponding to a certain orientation of the R_4 radical.

We may note that a decrease of temperature has hardly any effect on the splitting due to the α-fluorine atom. However, the structure due to the interaction with β-fluorine atoms changes significantly.

It follows from the analysis of the spectrum in Fig. 3*b* that at 77°K the rotation of CF_3 is frozen and one of the β-fluorine atoms has higher hyperfine coupling constants than the other two, which may be regarded as equivalent.

III. ESR SPECTRA OF FLUOROCARBON RADICALS IN POLYCRYSTALLINE SPECIMENS

The data for the hyperfine coupling constants of fluorocarbon radicals discussed in the preceding section make it possible to account for the specific features and the form of their ESR spectra in polycrystalline specimens.

The hyperfine coupling constants of fluorocarbon radicals due to α-fluorine atoms are significantly higher than the constants due to β-fluorine atoms. The anisotropic hyperfine interactions of α-fluorine atoms are very large compared with the isotropic interactions. In this connection the broadening of the ESR spectra of fluorocarbon radicals in polycrystalline specimens is due mainly to anisotropic hyperfine interactions.

For hydrocarbon radicals, the overall contour of the spectrum is determined by the broadening of the isotropic hyperfine structure caused both by the anisotropy of the hyperfine coupling and the anisotropy of the g-factor.

The anisotropy of the g-factor for fluorocarbon radicals makes a significantly lower contribution to the overall contour of the spectra in polycrystalline specimens compared with the anisotropy of the hyperfine coupling.

The anisotropy of the hyperfine coupling of β-fluorine atoms is relatively low and therefore hyperfine coupling to them gives rise in the spectra to partially resolved components.

The overall spread of the spectra of fluorocarbon radicals with one α-fluorine atom is approximately equal to the maximum component of the hyperfine coupling tensor for α-fluorine atoms, which usually amounts to about 190 Oe. With two α-fluorine atoms, the spectra extend over about 400 Oe.

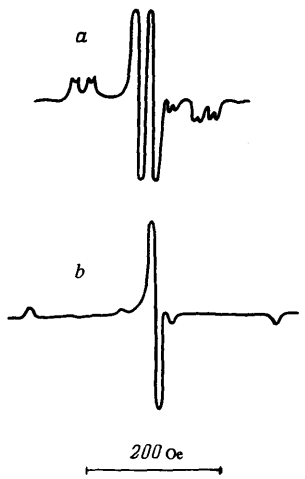
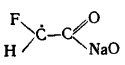


Figure 4. First derivative absorption spectra of the radicals $\dot{C}FHCOONa$ (curve *a*) and $\dot{C}F_2COONa$ (curve *b*).

The form of the spectra of fluorocarbon radicals in polycrystalline specimens in the 3 cm band may be calculated without taking into account the forbidden transitions. In the 8 mm band forbidden transitions make an appreciable contribution to the spectrum.

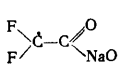
The derivative absorption spectra of radicals containing one or two α-fluorine atoms in polycrystalline specimens are presented in Fig. 4.

For the radicals



(R_5),

the spectrum shows wing components separated from one another by approximately 180 Oe (Fig. 4*a*). For the radicals



(R_6),

containing two α-fluorine atoms, the wing components are separated by a distance of 380 Oe (Fig. 4*b*).

It is noteworthy that the intensity of the wing lines is almost ten times less than the intensity of the central components. The intensity of the wings of the lines is so low that, to a first approximation, one may assume that the spectrum of paramagnetic centres with one or two α-fluorine atoms consists of a relatively narrow singlet.

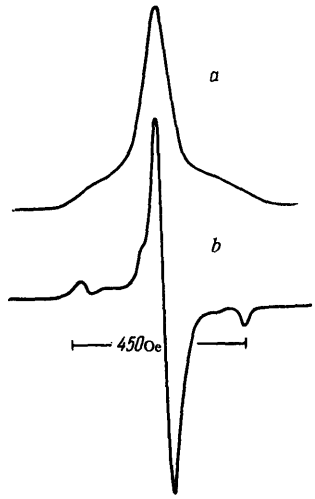
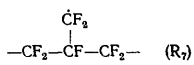


Figure 5. Absorption spectrum and its first derivative for the radicals $-CF_2-CF(\dot{C}F)_2-CF_2-$ at 77°K.

This impression, which arises from an analysis of the derivative of the absorption signals, is due to the characteristic line shape for each fluorocarbon radical. In the spectra of the radicals the overall spread of the absorption is very large but the derivative of the signal decreases fairly rapidly and significantly on passing outside the point corresponding to the maximum slope of the absorption signal. To illustrate these features of the spectra, Fig. 5 presents simultaneously the form of the absorption signal and its derivative for the radicals



(R_7)

in polycrystalline specimens.

IV. PARAMAGNETIC CENTRES IN IRRADIATED POLYTETRAFLUOROETHYLENE

The ESR spectra of irradiated polytetrafluoroethylene (PTFE) have been investigated in a number of studies[5-15]. As a result of radiation-chemical processes, as a rule several types of paramagnetic centres are formed in the irradiated polymers. The fluoroalkyl radicals

$$-CF_2-CF_2-\dot{C}F-CF_2-CF_2- \quad (R_8),$$

are formed in PTFE with a relatively large radiation yield. The ESR spectra of R_8 radicals at two temperatures obtained in two investigations[7,15] are presented in Fig. 6. At 523°K Lebedev et al.[7] observed hyperfine splitting in the spectrum of the R_8 radical due to interaction with four

γ-fluorine atoms (Fig. 6*a*). The γ-splitting is 3.5 Oe. At room temperatures the γ-components are not resolved.

It has been found in studies at room temperature[6] that the isotropic constant for the α-fluorine atom is 92 Oe and that for the β-fluorine atom is 33 Oe. Fig. 6*b* presents the spectrum of the R_8 radical at 77°K.[15] It is noteworthy that at this temperature components due to interaction with the β- and γ-fluorine atoms appear.

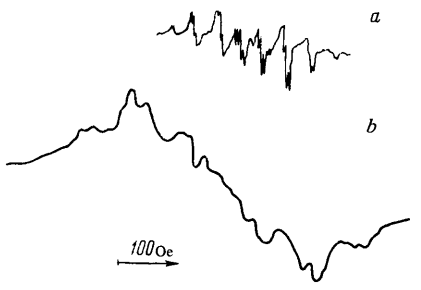
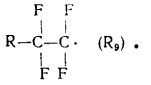


Figure 6. First derivative absorption spectra of the radical $-CF_2-CF_2-\dot{C}F-CF_2-\dot{C}F_2-$ at 523°K (curve *a*) and 77°K (curve *b*).

A relatively detailed study of R_8 radicals in PTFE was made for polymers partially oriented by extrusion[11]. It was observed that the width of the individual spectrum components is 9 Oe in cases where the H_0 field is perpendicular to the extrusion axis. When the H_0 field is parallel to the extrusion axis, the width of the component increases by a factor of two. The splitting by the α-fluorine atom is a minimum, amounting to 25 Oe, when the H_0 field is directed along the extrusion axis. It is noteworthy that the form of the spectrum for R_8 radicals at room temperature is determined to a considerable degree by isotropic interactions. The maximum splitting by the α-fluorine atom is only 92 Oe, although for the other fluorocarbon radicals with one or two α-fluorine atoms discussed previously the splitting at the same temperature is greater by a factor of two. This feature of the hyperfine interactions involving the α-fluorine atom at room temperature is somewhat obscure.

Ovenall[11] succeeded for the first time in detecting the terminal radicals



It was found that in the ESR spectra of PTFE specimens with the extrusion axis oriented parallel to the direction of the external field, wing components are observed, the centres of which are separated from each other by 390 Oe, the components having an additional triplet splitting of 25 Oe (Fig. 7). The paramagnetic centres responsible for these lateral components contribute to the central part of the overall spectrum. The observed spectrum may be attributed to the terminal R_9 radicals, since a splitting of 390 Oe can be produced only by two α-fluorine atoms. The triplet splitting of the wing components is due to the two β-fluorine atoms.

The ESR spectrum of the terminal R_9 radicals in polycrystalline specimens was observed for the first time by Bruk et al.[16] It has been shown[17] that the R_9 radicals are formed in irradiated PTFE and the reasons found why they could not be detected for a long time although their concentration is comparable to that of the R_8 fluoroalkyl radicals. The experimental results and spectroscopic considerations on the basis of which the R_9 spectra were identified are considered briefly below.

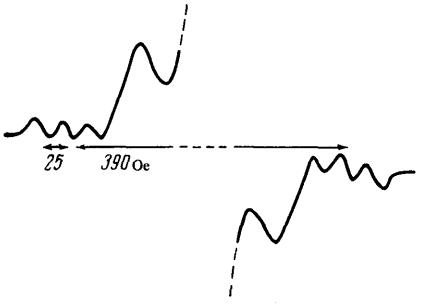


Figure 7. Lateral components of the first derivatives of the absorption signals of the radicals $R-CF_2-\dot{C}F_2$ on irradiation of oriented PTFE (extrusion axis parallel to H_0).

Irradiation of a frozen tetrafluoroethylene (TFE) monomer and secondary processes result in the formation of polymeric PTFE. After an irradiated tetrafluoroethylene specimen is heated to room temperature and the monomer is vaporised, the resulting polymer shows ESR spectra. The intensity of these spectra as well as the yield of the polymer depend on the irradiation temperature. A correlation between the intensity of the spectra and the yield of the polymer is observed also as a function of the radiation dose. As an illustration, Fig. 8 presents the spectra of tetrafluoroethylene specimens irradiated by an identical dose of 125 mrad at 98° and 128°K. It is seen that in the specimen irradiated at 98°K the overall concentration of radicals is higher than in the specimen irradiated at 128°K. After heating, the relative concentrations of paramagnetic centres change. Since the monomer was evaporated at room temperature, evidently the spectra in Figs. 8*b* and 8*d* are due to polymeric radicals.

The form of the spectra of these paramagnetic centres depends relatively little on temperature (Fig. 9). The average g-factor is 2.008.

We believe that the validity of the assignment of the spectrum in Fig. 9 to terminal polymeric radicals follows from the analysis of its form. The triplet spectrum may be accounted for by the presence of hyperfine interactions with the two β-fluorine atoms which in fact determine the splitting between the components, equal to 43 ± 1 Oe at room temperature. The splitting is consistent with the data obtained for single crystals in studies on the R_2 radicals; it was found that the isotropic constants for their β-fluorine atoms differ somewhat and are 34.5 and 40 Oe.

The absorption in the central part of the spectrum, where the triplet is in fact observed, is due to the R_9 radicals where the net nuclear spin of the two α-fluorine atoms is zero.

The R_9 spectrum does not show lateral components at a distance of 400 Oe characteristic of radicals with two

α-fluorine atoms. However, the presence in these paramagnetic centres of two α-fluorine atoms follows from the overall width of the spectrum. It is seen in Fig. 9*a* that the width of the absorption signal measured at a level of 0.1 of the maximum value is 300 Oe, while at a level of 0.02 it exceeds 450 Oe. We believe that such a large width of the spectrum can only be caused by the presence of two α-fluorine atoms.

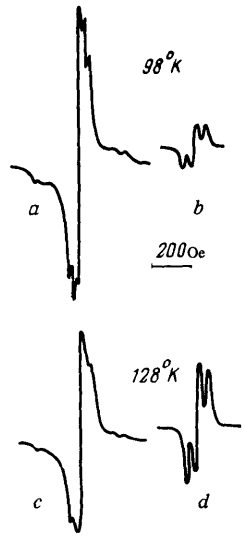


Figure 8. ESR spectra of tetrafluoroethylene irradiated at 98°K (curves *a* and *b*) and at 128°K (curves *c* and *d*). The spectra *a* and *c* were recorded at 77°K; the spectra *b* and *d* were obtained at 300°K after warming the specimens to room temperature.

We may note that recently a spectrum was obtained[19], which was attributed to R_9 radicals stabilised in a hydrocarbon matrix. In its central part it coincides with the spectrum in Fig. 9 and, moreover, it has wing components characteristic of two α-fluorine atoms.

In studies of irradiated copolymers of tetrafluoroethylene and hexafluoropropene (HFP) Iwasaki et al.[20,21], observed that, as a result of irradiation, the radicals

$$-CF_2-\dot{C}(CF_3)-CF_2- \quad (R_{10})$$

$$-CF_2-\dot{C}F-CF_2- \quad (R_{11})$$

are formed in the copolymer together with the R_8 radicals. The form of the spectra of the R_{10} radicals at 77°K and room temperature is presented in Fig. 10. The form of the absorption spectra and of the derivatives of the absorption spectra of the R_{11} radicals at 77°K is shown in Fig. 5.

As in the majority of other cases, the observed spectrum of the irradiated copolymer is due to the superposition of the spectra of paramagnetic centres of several types. Therefore the determination of the true form of the spectra of the R_{10} and R_{11} radicals and their identification presents certain difficulties.

It has been found[20] that the overall spectrum observed for the irradiated copolymer depends on the hexafluoropropene content. With increase of the concentration of hexafluoropropene, the form of the spectrum differs increasingly from the spectrum in TPFE. The authors attributed these spectral changes to the formation in the copolymer of new types of paramagnetic centres containing CF_3 groups.

By studying the dependence of the form of the spectra on the percentage content of hexafluoropropene and also the changes in the form of the overall spectrum as a result of heating the specimens, the authors[20] succeeded in obtaining the spectra of the individual types of paramagnetic centres by the method of graphical subtraction.

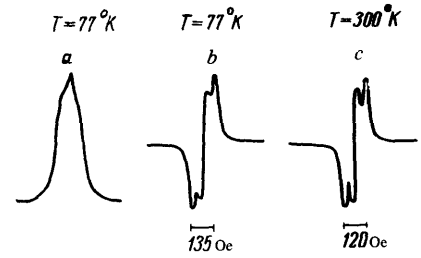


Figure 9. The absorption spectrum (*a*) and its derivatives for the $R-CF_2-CF_2$ radicals at 77° and 300°K (curves *b* and *c* respectively).

Oriented copolymers were prepared to identify the R_{10} radicals. It was found that the form of the spectrum in the copolymer at 77°K is almost independent of the orientation of the specimen in the magnetic field, while at room temperature relatively small spectral changes are observed. At the same time the form of the spectrum in oriented PTFE depends very significantly on orientation. Certain changes in the form of the spectrum as a function of the orientation of the specimen, which may be observed for the irradiated copolymer, can be accounted for by the superposition of the spectra of the R_8 radicals.

The anisotropy of the hyperfine coupling of β-fluorine atoms is known to be significantly less than the anisotropy for α-fluorine atoms[2,4]. The absence of an orientation dependence for the paramagnetic centres which disappear on heating shows that these cannot be α-fluorine atoms.

Using the isotropic hyperfine coupling constants for β-fluorine atoms, Iwasaki et al. constructed model spectra for the R_{10} radicals assuming that the form of the spectrum is due to the superposition of an unresolved isotropic hyperfine structure and obtained satisfactory agreement with the spectra of the paramagnetic centres which disappear on heating the copolymers.

The ESR spectrum of the R_{10} radicals at room temperature consists of weakly resolved components corresponding to the interaction with seven β-fluorine atoms, the splitting between adjacent components being 29 Oe.

At 77°K the R_{10} spectrum consists of a singlet line where the distance between the points of maximum slope is 80 Oe (Fig. 10*b*). It is noteworthy that, since R_{10} contains only β-fluorine atoms, the overall width of the spectrum changes only slightly as temperature is reduced. As a result of the different broadening of the R_8 and R_{10} spectra

over a range of temperatures due to the difference between the anisotropic hyperfine coupling constants, at 77°K the radicals R_{10} make the main contribution to the overall spectrum of the irradiated copolymer, while at room temperature the contribution by R_8 radicals is very significant.

It has been shown[21] that at 77°K and R_{10} radicals are converted into R_{11} radicals under the influence of ultraviolet radiation:

$$-CF_2-\dot{C}(CF_3)-CF_2- \xrightarrow[77^\circ K]{h\nu} -CF_2-CF(\dot{C}F_2)-CF_2- .$$

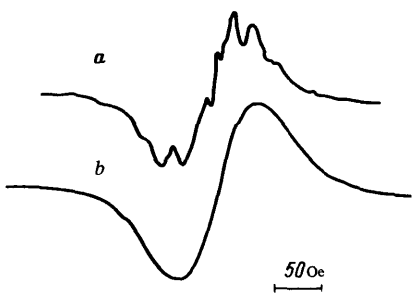


Figure 10. First derivative absorption spectra of the radicals $-CF_2-\dot{C}(CF_3)-CF_2-$ at 300°K (curve *a*) and 77°K (curve *b*).

The R_{11} radicals are stable only at low temperatures. At room temperature R_{11} is reconverted into R_{10}. The changes in the concentrations of R_{10} and R_{11} on ultraviolet irradiation at 77°K and on heating are reversible. The ESR spectrum of the R_{11} radicals has wing components, with a splitting of 450 Oe, characteristic of fluorocarbon radicals with two α-fluorine atoms. The R_{11} spectra were identified both by a comparison with the spectra of known radicals with two α-fluorine atoms, and by chemical considerations following from the reversible changes in the spectra as a result of heating or illumination.

When the copolymer is irradiated at 77°K the spectrum may be represented by the sum of the spectra of the R_8 and R_{11} radicals. On this basis, it was concluded[20] that at 77°K the most probable processes involve the following mechanisms:

a) copolymer $+\gamma \rightarrow \sim CF_2-CF(\dot{C}F_2)-CF_2\sim$;

b) copolymer $+\gamma \rightarrow \sim CF_2-\dot{C}F-CF_2\sim$.

V. PEROXY-RADICALS IN IRRADIATED POLYTETRAFLUOROETHYLENE

The radicals

$$-CF_2-\underset{\displaystyle O-\dot{O}}{CF}-CF_2- \quad (R_{12})$$
$$-CF_2-CF_2-O-\dot{O} \quad (R_{13})$$
$$-CF_2-CF_2-\dot{O} \quad (R_{14})$$

have been detected[12] in irradiated PTFE. Until recently only the R_8 fluoroalkyl radicals could be detected in vacuum-irradiated PTFE. For this reason some investigators regarded the presence of R_{13} and R_{14} radicals in PTFE and the interpretation of the corresponding spectra as controversial[22,23].

The ESR spectra of the radicals R_{12}, R_{13}, and R_{14} at room temperature, obtained by Matsugashita and Shinohara[12], are presented in Fig. 11. Subsequent investigations[24] showed that the interpretation of these spectra is correct. However, bearing in mind that even in review articles[22,23] contradictory views are expressed, below we shall consider in detail the results, which confirm the validity of the suggested interpretation.

We believe that there are at least two reasons why the results of Matsugashita and Shinohara[12], which were obtained in 1961, are still controversial. Firstly the R_{12}, R_{13}, and R_{14} spectra of the individual types of paramagnetic centres were obtained by graphical subtraction and their interpretation was in many ways based on chemical considerations associated with the study of the reactions of the paramagnetic centres with various gases. The spectroscopic considerations based on the analysis of the line shape and g-factors were insufficient, although we believe that they were in fact correct.

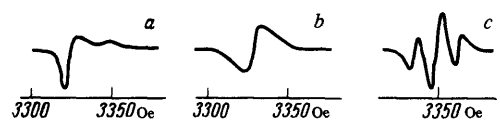


Figure 11. First derivative absorption spectra at 300° of the radicals $-CF_2-\underset{\displaystyle O-\dot{O}}{CF}-CF_2$ (*a*), $-CF_2-CF_2-O-\dot{O}$ (*b*), and $-CF_2-CF_2-\dot{O}$ (*c*).

Secondly Matsugashita and Shinohara[12] failed to resolve the following important problem. According to their data the concentration of R_{13} radicals is comparable to the concentration of R_{12} and therefore it was necessary to postulate the presence of the radical $R-CF_2-\dot{C}F_2$ and the oxidation reaction

$$R-CF_2-\dot{C}F_2+O_2 \rightarrow R-CF_2-CF_2-O-\dot{O} . \quad (7)$$

However, neither Matsugashita and Shinohara nor other investigators were able to detect R_9 radicals in PTFE.

In the R_{12} and R_{13} radicals the unpaired electron is localised mainly in a molecular orbital involving the two oxygen atoms. In this connection it was not clear why at room temperature the R_{12} spectrum is significantly asymmetric, while the R_{13} spectrum is virtually symmetrical. It was also obscure why on irradiation of evacuated specimens containing only small traces of oxygen R_{14} radicals are observed and not R_{12} or R_{13}.

One of the important results associated with the study of the reactions with carbon monoxide was the observation of changes in the spectrum which were attributed[12] to the occurrence of the reaction

$$R-CF_2-O-\dot{O}+CO \rightarrow R-C\dot{F}_2-\dot{O}+CO_2 . \quad (8)$$

However, since there were doubts concerning the validity of the identification of both R_{13} and R_{14} radicals, the interpretation of the changes in the spectra after the introduction of carbon monoxide into the tube remained unconvincing.

According to Matsugashita and Shinohara[12], after oxygen has been admitted at a pressure of 100 mmHg into evacuated tubes containing PTFE irradiated at room temperature, the ESR spectrum of the peroxy-radicals formed is due to the superposition of the spectra of R_{12} and R_{13}.

When the same specimen is heated and re-evacuated at 423°K, it is possible to show by graphical subtraction that the radicals R_{12} disappear from the overall spectrum. On further heating and evacuation at 523°K, the spectrum due to R_{13} vanishes. As a result of heating, the R_{12} and R_{13} radicals disappear and the R_8 fluoroalkyl radicals reappear.

The average value of the g-factor of the R_{13} radicals is $g = 2.016$ and the width of the spectrum measured between the points of maximum slope is about 10 Oe.

Analysis of the width and intensity of the R_8 and R_{14} spectra shows that in evacuated PTFE specimens the concentration of R_{14} is almost one hundred times small than that of R_8. The possibility of detecting R_{14} radicals in a mixture with such values of the relative radical concentrations arises from the fact that the R_{14} radicals have a significantly narrower spectrum.

It is not altogether clear why, despite careful degassing of the polymer, R_{14} radicals are still detected in the specimens.

Iwasaki et al.[20] suggested that the principal chain of the polymer has units containing oxygen bridges:

$$\sim CF_2-CF_2-O-CF_2-CF_2\sim ,$$

the concentration of which is relatively high.

The dissociation of the C–O bond in these units in fact leads to the formation of R_{14}. We believe that this hypothesis is confirmed by the data of Barnaba et al.[24]

The ESR spectrum of R_{14} radicals is a triplet with a splitting of about 14 Oe between the components. The R_{14} radicals were identified on the basis that such triplet splitting is due to fluorine atoms. Since the splitting is small, the implication is that the unpaired electron density at the carbon atom linked to the fluorine atoms is low.

Indirect evidence supporting this interpretation comes from the spectral changes observed with specimen containing peroxy-radicals after the introduction of carbon monoxide. It was noted that the spectrum due to R_{13} disappeared and the intensity of the spectrum of the R_{14} radicals increased; this was explained by the occurrence of reaction (8).

The validity of the interpretation of the R_{13} and R_{14} spectra was confirmed in special experiments carried out by Barnaba et al.[24] in studies on paramagnetic centres in irradiated polytetrafluoroethylene oxide (PTFEO) polymers:

$$\sim O-CF_2-CF_2-O-CF_2-CF_2-O\sim .$$

Barnaba et al.[24] chose experimental conditions where predominantly either R_{13} or R_{14} radicals are detected in irradiated PTFEO. They succeeded in obtaining the spectra of R_{13} and R_{14} radicals using the different stabilities of these paramagnetic centres and in obviating the necessity of using graphical subtraction.

Additional evidence for the validity of the interpretation of the R_{13} and R_{14} spectra was based on the following experimental results. In the overall ESR spectrum recorded at 300°K directly after irradiation in a vacuum (at 273°K) of PTFEO specimens (Fig. 12) it proved possible to isolate the spectra of three types of paramagnetic centres. It was noted that, after treatment at 300°K for 24 h, the wing components of the spectrum of the specimen with a splitting of about 320 Oe disappeared.

Kinetic studies showed that the rate of disappearance of the outer components is the same as the rate of disappearance of one of the components contributing to the central part of the spectrum.

The splitting between the outer components (320 Oe) and the presence of lines associated with these paramagnetic centres in the central part of the spectrum show unambiguously that the mixture of paramagnetic centres includes radicals with two α-fluorine atoms. These centres are either

$$\sim O-\dot{C}F_2 \quad (R_{15})$$

or

$$\sim O-CF-\dot{C}F_2 \quad (R_{16}) .$$

Possibly both R_{15} and R_{16} are present in the specimens.

It is seen in Fig. 12*a* that the concentration of the terminal radicals (i.e. either R_{15} or R_{16}) exceeds the concentration of paramagnetic centres of other types. This follows from the fact that the spectra of the terminal radicals have the largest overall width and their intensities are comparable with those of the spectra of other types of paramagnetic centres.

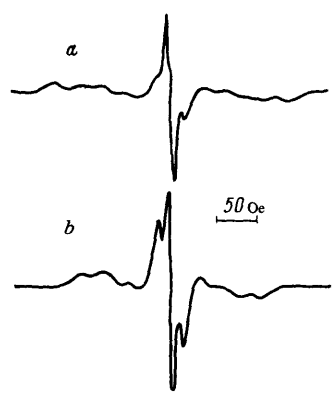


Figure 12. First derivative absorption spectra at 300°K of PTFEO irradiated in a vacuum at 273°K: *a*) immediately after irradiation; *b*) 24 h after irradiation.

After the destruction of the terminal radicals, two further types of paramagnetic centres remain in the specimen. The overall spectrum, corresponding to a particular ratio of the concentrations of these two paramagnetic centres, is presented in Fig. 12*b*.

The triplet spectrum, with a splitting between the components is 12.5 ± 1 Oe and contributing to the central part of the [overall] spectrum, was attributed to the R_{14} radicals.

The fact that the spectrum in Fig. 12*b* is due to the superposition of the spectra of two types of paramagnetic centres was proved by the authors using the different stabilities of these centres. During the storage of irradiated PTFEO in a vacuum at room temperature for several days, the intensity of the outer components (Fig. 12*b*) hardly changed, while the intensity of the central part was appreciably reduced. It was found that

after the admission of ethane to the specimen tube, these paramagnetic centres are destroyed at different rates; according to the authors, this also confirms the presence in the specimen of two types of paramagnetic centre.

In the spectrum in Fig. 12*b* the splitting between the centres of the outer wings is 180 Oe and the splitting within the wing components is 30 Oe. This shows that in the mixture there are paramagnetic centres with one α-fluorine atom and two β-fluorine atoms and therefore the authors reasonably suggested the presence of the radicals

$$\sim O-\dot{C}F-CF_2-O\sim \quad (R_{17}).$$

The relatively high stability of the radicals R_{17} in a vacuum confirms the validity of the suggested identification. The g-factor of the R_{14} radicals is virtually the same as the g-factor of diphenylpicrylhydrazyl (DPPH), which is 2.0036.

Directly after irradiation of PTFEO at 273°K, the concentration of terminal radicals is a maximum. This enabled Barnana et al.[24] to obtain the spectrum of the R_{13} radicals in a virtually pure form, which was found to coincide with the spectrum in Fig. 11 obtained by Matsugashita and Shinohara[12].

Barnaba et al. observed that after the admission of air to the PTFEO specimen irradiated in a vacuum, the reactions

$$R-\dot{C}F_2+O_2 \rightarrow R-CF_2-O-\dot{O}, \qquad (9)$$

$$\sim O-\dot{C}F-CF_2-O\sim + O_2 \rightarrow \sim O-\underset{\displaystyle O-\dot{O}}{\overset{|}{C}}F-CF_2-O\sim \qquad (10)$$

take place. After the admission of air, the PTFEO spectrum is due to the superposition of the R_{12} and R_{13} spectra. When the PTFEO specimen irradiated in a vacuum is allowed to stand so that the concentration of terminal radicals in it is appreciably reduced, the R_{12} radicals make the principal contribution to the overall spectrum after the admission of air. On the other hand, when air is introduced directly after irradiation when the terminal radicals have the maximum concentration, the overall spectrum is due largely to the R_{13} radicals.

The ESR spectra of PTFE specimens irradiated in air are due to the R_{13} radicals. It was found that the R_{13} radicals are less stable at room temperature than R_{12}.

When the specimens are stored, the form of the overall spectrum is seen to change in accordance with the change in the concentration of the radicals R_{12} and R_{13}.

At room temperature the R_{13} concentration diminishes by a factor of two in the course of 100 h, while a similar change in the concentration of R_{12} requires 500 h.

Important evidence confirming the validity of the identification of the R_{13} spectrum is provided by the fact that Barnaba et al. detected the terminal R_9 radicals, showed that their concentration is greatest, and saw directly how the intensity of the ESR signal due to the R_{13} radicals increases by a factor of almost five as a result of reaction (7). The increase of signal intensity as a result of reaction (7) is associated with the fact that the R_{13} radicals have a significantly narrower ESR spectrum compared with that of R_9 and consequently at the same concentrations of paramagnetic centres the amplitude of the R_{13} signal is greater.

We believe that the work of Matsugashita and Shinohara[12] and Barnaba et al.[24] has shown that irradiated PTFE usually contains three types of peroxy-radicals. The present authors' results explained the reasons for the failure to detect the terminal radicals in PTFE.

It was found that the concentration of R_9 is comparable to the concentration of the R_8 fluoroalkyl radicals and that the R_9 radicals in PTFE at room temperature are relatively stable[17]. Therefore there is reason to believe that the R_{12}, R_{13}, and R_{14} spectra have been correctly identified.

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