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INVESTIGATION OF RELAXATION PROCESSES IN A SERIES OF FLUORINE COMPOUNDS OF CARBON

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A study is made of the influence of anisotropy of the chemical shift tensor on the relaxation time of fluorine nuclei. It is found that the difference in relaxation times of fluorine nuclei and of protons in one and the same molecule depends on the presence of nuclei of another halogen.

FLUORINE is one of the most electronegative elements. The methods of nuclear magnetic resonance are currently applied successfully to the investigation of fluorine compounds. These investigations are devoted chiefly to the fine structure of the fluorine resonances, and also to the study of relaxation processes. Gutowsky and Hoffman[1,2] examined nuclear magnetic screening of hydrogen fluoride and of a large number of other inorganic fluorides. A considerable number of aromatic fluoride compounds have been studied by Borodin and Skripov.[3,4] Gutowsky and Woessner[5] measured relaxation times in a series of fluorocarbons. They found that protons have considerably longer relaxation times than do fluorine nuclei in the same molecule. The maximum value of the ratio $R = T_1(H^1)/T_1(F^{19})$ came to 9.2, in connection with which the authors emphasized the dependence of the given ratio on the strength of the magnetic field. They also express the hypothesis that fluctuations in the screening field, stipulated by the anisotropy of the chemical shift tensor, add a contribution to the relaxation time of the fluorine. On superimposing a constant magnetic field H_0 on the specimen, the molecular electrons undergo a precession, by virtue of which an additional field $-\sigma H_0$ arises, proportional but opposite to the applied field, σ (σ is a constant that characterizes the degree of screening of the nucleus by the electrons). In the general case, σ is represented by some second rank-tensor, since the screening is a function of direction in the molecule. Assuming axial symmetry of the chemical shift tensor (this name is due to the circumstance that a difference in screening leads to a shift of the resonances of nuclei of a given type in various chemical compounds), Gutowsky and Woessner obtained the approximate formula:

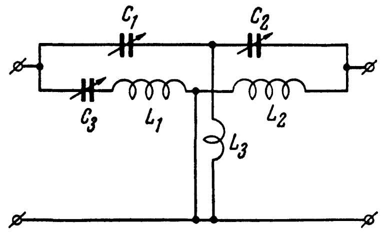
$$R = \frac{T_1(H^1)}{T_1(F^{19})} = 1 + \frac{2\gamma_F^2 H_0^2 (\sigma_{z'z'} - \sigma_{x'x'})^2 \tau_c T_1(H^1)}{15(1 + 4\pi^2\nu_0^2\tau_c^2)}, \quad (1)$$

where γ_F is the gyromagnetic ratio of the fluorine nuclei, H_0 is the intensity of the external magnetic field, τ_c is the Debye correlation time, $T_1(H^1)$ the longitudinal relaxation time of the protons, $T_1(F^{19})$ the longitudinal relaxation time of the fluorine nuclei, $(\sigma_{z'z'} - \sigma_{x'x'})$ is the anisotropy of the chemical shift tensor, and ν_0 is the resonance frequency. The authors point out the poor agreement with the experimental data for the compounds which they studied.

The present work was done with the aim of studying the question further. It is necessary to observe that the relaxation mechanism proposed by Gutowsky and Woessner, even in the absence of axial symmetry of the screening field, is not able to explain the great difference in relaxation times of protons and fluorine nuclei in certain compounds.

EXPERIMENTAL PROCEDURE

We measured the relaxation times by Bloch's method of nuclear induction, since in this method the generator and receiver are separated, so that large radio-frequency fields can be used and saturation can be observed in a broad class of substances. The high-frequency generator contained a Hartley oscillator for the 20 to 40 Mcs range. Through a buffer cascade provided with an attenuator, the r-f oscillations were fed to the exciting coil. The Bloch coils were of high mechanical stability; they were encased in polystrene jackets. The exciting coil had 12 turns and the receiving coil 10. Adjustment of the coupling between the coils was accomplished by the use of a little copper flag and the bridge circuit shown in the figure. For the circuit given, it is easy to obtain the approximate conditions for complete balance:



Balanced bridge circuit for observation of nuclear induction signals.

$$L_3 = M; \; C_2L_2 + C_2M = MC_1; \quad \omega^2 = 1/C_2(L_2 + M), \quad (2)$$

where L_1 is the inductance of the exciting coil, L_2 the inductance of the receiving coil, and M the coefficient of mutual inductance of the coils. Capacitors C_3 and C_2 had a maximum rating of 50 μμf, while that of C_1 was 30 μμf. Capacitor C_3 was tuned to precise resonance with L_1. Inductor L_3 consisted of two turns, the distance between which could be varied in the process of tuning the circuit.

Adjustment of the balancing circuit permitted isolation of the dispersion signal or of the absorption signal for observation. After high-frequency amplification, the nuclear-resonance signal was detected and amplified by a broadband low-noise low-frequency amplifier which had two stages with 6Zh4 tubes. The magnet employed gave an effective inhomogeneity of magnetic field on the order of 0.005 Oe/cm³.

All the measurements were made at 25 Mcs, and the absorption signal was separated out for measurement. The dependence of the amplitude of the nuclear magnetic resonance signals on the intensity of the radiofrequency field was photographed and saturation curves were constructed. The transverse relaxation time was estimated from the half-width of the absorption lines. A multiplet structure of fluorine resonances was observed. Within the limits of error, the components of the multiplets did not show different relaxation times. Distilled water used as a standard, gave a signal of optimum amplitude with a radiofrequency field of the order of 0.01 Oe.

TABLE I*

Substance	T_1 (H^1) sec	T_1 (F^{19}) sec	R
$X\cdot(CF_2-CFCl)_nY$	—	1.21	—
$C_3F_5OH_2COOH$	0.8	0.62	1.29
$C_3F_4OH_3COOH$	0.65	0.47	1.35
$X\cdot(CF_2-CFCl)_nCOOH$	0.21	0.14	1.5
H_2O	2.6	—	—

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* ν_0 = 25 Mcs

TABLE II

Substance	R (20 Mcs)
CH_2FCl	3.8
$CHFCl_2$	9.2
CHF_2Cl	3.56
$C_6H_3F_3$	1.56

EXPERIMENTAL RESULTS

Our results are plotted in Table I and those of Gutowsky and Woessner[5] in Table II. Numerical comparison of theory with experiment for $C_3F_5OH_2COOH$ gives

$$(R-1)_{\text{theor}} = 0.147; \quad (R-1)_{\text{exptl}} = 0.29.$$

The theoretical calculation made here is very approximate. It is assumed that the value of the anisotropy of the chemical shift tensor of fluorine is of the order of the shift itself, i.e., 7×10^{-4}. The correlation time was estimated from the Debye formula and taken equal to 10^{-10} sec. The difference in results by a factor of two can be regarded as a good approximation of theory to experiment for the estimate given. From Tables I and II it is seen that the value of R decreases with increasing number of fluorine nuclei in a molecule in which the number of nuclei of another halide remains the same. This, apparently, is a consequence of the reduced screening of fluorine. An increase in the number of chlorine nuclei in a molecule leads to an increase in R. The relaxation mechanism in question, connected in all probability with the properties of chlorine atoms, is for the time being still not clear.

Thus, the theory of Gutowsky and Woessner can explain only the not-too-large values of R. Very large values of R are observed, as a rule, in the presence of chlorine atoms in a molecule. Therefore, further development of the theory is required for the detailed explanation of the observed effects. The problem at hand is made difficult at the present time, however, by the fact that no complete theory of screening exists.

In conclusion, I express my thanks to F. I. Skripov and P. M. Borodin for their interest in the work and its evaluation.

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ON THE DISTRIBUTION OF NUCLEON DENSITY IN NUCLEI

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The distribution of the orbital moments in nuclei is considered on the basis of the statistical nuclear model using various distribution functions of the nucleon density. It is shown that reasonable nucleon density distribution functions can be found, satisfying the experiments on scattering of fast electrons on nuclei, the saturation properties of nuclear forces, and the fundamental requirements of the shell model.

THE problem of nuclear structure, namely the distribution of nucleons in the nucleus, is being studied at present from different angles of approach.

Experimental and theoretical investigations of the scattering of fast electrons on nuclei[1-4] have shown that the proton density is approximately constant over the main part of the nuclear volume and falls off smoothly at its boundary. The most characteristic feature of the distribution function, found as the result of the above investigations, is the fact that the thickness of the surface layer is constant — independent of the mass number A in a wide range of A — and that the mean (proton) radius of the nucleus varies as $A^{1/3}$,[4] i.e. that there is no