[Contribution from the Department of Chemistry, University of Washington, Seattle 5, Washington, and Varian Associates]

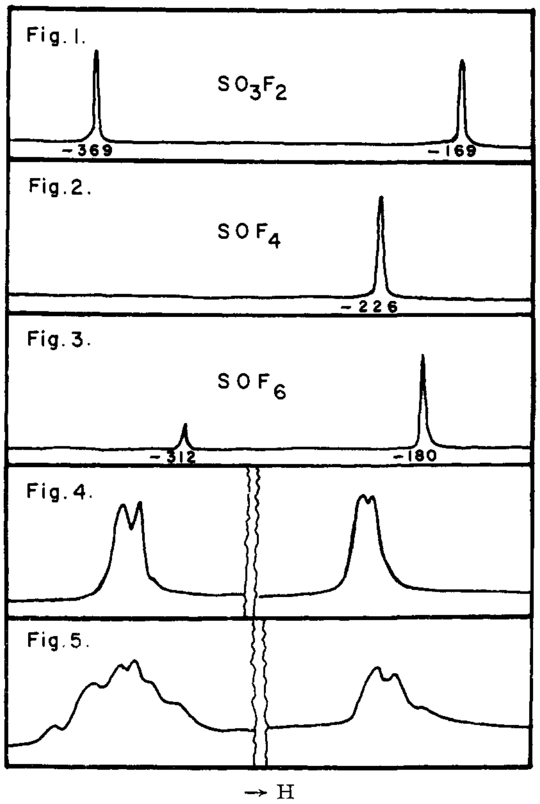
Nuclear Magnetic Resonance Spectra of Fluorine Fluorosulfonate, Thionyl Tetrafluoride and Pentafluorosulfur Hypofluorite

By F. B. Dudley,[1] J. N. Shoolery and G. H. Cady

Received October 31, 1955

The preparation and properties of fluorine fluorosulfonate (SO_3F_2), thionyl tetrafluoride (SOF_4) and pentafluorosulfur hypofluorite (SOF_6) have been described elsewhere.[2,3] From infrared spectra it was concluded that the first and the last of these three each contained an O–F group but that thionyl tetrafluoride did not. Additional evidence regarding structures of these molecules has now been obtained through the help of their nuclear magnetic resonance spectra.

The spectra were studied using Varian Associates Model V-4300 High Resolution n-m-r-Spectrometer. This operated at a highly stable crystal-controlled frequency of 30 mc., corresponding to a resonance field of approximately 7500 gauss for fluorine. The gaseous samples were sealed in glass tubes at atmospheric pressure. These tubes had 2-mm. tubing sealed to one end, and by suitable cooling, the sample was liquefied in these small-diameter tubes just prior to taking the spectrum. The spectra obtained are reproduced in Figs. 1–5.



Shift = $10^6 \times (H - H_{\text{ref}})/H_{\text{ref}}$.

All peaks in the spectra were measured relative to the resonance in perfluorocyclobutane. This compound should have highly ionic C–F bonds. It has been established by Saika and Slichter[4] that shifts to lower fields (negative shifts) represent a decrease in the ionic character and an increase in the covalent character of the fluorine bond. This is reflected in the spectra of these compounds, all three of which show large negative shifts. As is to be expected, the O–F bond appears more covalent than the S–F bond but the latter is more highly covalent than the carbon-fluorine bond in perfluorocyclobutane.

The spectrum of fluorine fluorosulfonate contains two equal peaks (Fig. 1). This means that the structure is $SO_2F.OF$. Under high resolution, each peak is found to be a doublet (Fig. 4), indicating that each is coupled to a nucleus of spin $^1/_2$, *i.e.*, the other fluorine atom.

The thionyl tetrafluoride spectrum consists of a single peak (Fig. 2). This indicates that the fluorine atoms all have the same environment and that the structure is $F_4S{=}O$ rather than $SF_3.OF$. Such a state of affairs would be true for a square pyramidal molecule with the four fluorine atoms at the corners of the base and the oxygen atom at the apex. It could also be true for a molecule in which the four fluorine atoms are not continually equivalent to each other. A rapid changing from one such structure to another in such a way that on the average the four fluorine atoms are equivalent would produce the observed spectrum.

The spectrum of pentafluorosulfur hypofluorite is composed of two peaks (Fig. 3) which have amplitude ratios such that the structure can only be $SF_5.OF$. Spin coupling between the fluorine atoms occurs, which splits the SF_5 resonance under high resolution into a doublet and the O–F resonance into six peaks (Fig. 5). The peculiar lack of symmetry in the multiplet pattern resembles that found in some compounds with restricted rotation. It suggests that the O–F group may be hindered in its rotation against the SF_5 group. The O–F peak is in the same region as that from fluorine fluorosulfonate.

Structures which would result in the presence of five equivalent fluorine atoms are: (1) a pentagonal pyramid, (2) an octahedral structure in which fluorine atoms bonded directly to the sulfur atom can exchange between the planar and out-of-plane positions. The latter case appears to be the more likely even though it would require the breaking of bonds.

Acknowledgment.—This work was supported in part by a contract between the Atomic Energy Commission and the University of Washington.

Palo Alto, California

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[1] University of New England, Armidale, N.S.W., Australia.

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