Title
NUCLEAR MAGNETIC RESONANCE STUDIES. PART I: HIGH TEMPERATURE-DEPENDENT CHEMICAL SHIFTS. PART II: F19 SPIN-SPIN COUPLINGS

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NUCLEAR MAGNETIC RESONANCE STUDIES
PART I: $^1H$ TEMPERATURE-DEPENDENT CHEMICAL Shifts
PART II: $^{19}F$ SPIN-SPIN COUPLINGS

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NUCLEAR MAGNETIC RESONANCE STUDIES

PART I: $^1\text{H}$ TEMPERATURE-DEPENDENT CHEMICAL SHIFTS

PART II: $^{19}\text{F}$ SPIN-SPIN COUPLINGS

Leonidas Petrakis

(Ph.D. Thesis)

June 6, 1961
### NUCLEAR MAGNETIC RESONANCE STUDIES
PART I: \( ^1H \) TEMPERATURE-DEPENDENT CHEMICAL SHIFTS

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</table>
NUCLEAR MAGNETIC RESONANCE STUDIES

PART I: H\textsuperscript{1} TEMPERATURE-DEPENDENT CHEMICAL SHIFTS

Leonidas Petrakis

Lawrence Radiation Laboratory
University of California
Berkeley, California

June 6, 1961

ABSTRACT

The temperature dependence of the proton chemical shifts of various gaseous compounds has been investigated. It is found that the chemical shifts of most of these compounds vary with temperature. This effect is ascribed to excitation of vibrational modes of the molecules, the protons in the excited molecules being differently shielded than the protons in the molecules in the ground vibrational states. The data are interpreted to yield approximate chemical shifts associated with the excitation of various types of vibrational modes. Nuclear magnetic resonance (NMR) isotopic shifts are discussed on the basis of these data.
PART I. TemperatURe-DEPENDENT CHEMICAL SHIFTS

I. INTRODUCTION

Knight first observed for metals that resonance occurs in different parts of the nuclear magnetic resonance (NMR) spectrum for chemically distinct positions of the same nuclear species. Later, similar observations of shifts in different chemical compounds were made by Proctor and Yu for N, by Dickinson for F, and for protons by Lidstrom, Thomas, and Arnold and co-workers.

Because of the diamagnetic shielding of the nucleus due to orbital motion of the electrons, the resonance frequency of a given nuclear species is proportional to the local magnetic field $H_{\text{local}}$. If $\sigma$ is the diamagnetic screening constant, then $H_{\text{local}}$ is written as

$$H_{\text{local}} = H_0 (1 - \sigma).$$

The screening constant is a reflection of the actual electronic (chemical) environment of the nucleus. The difference in resonance $\delta$ (chemical shift) between two chemically nonequivalent environments of the same nuclear species is written as

$$\delta = \sigma_1 - \sigma_2.$$

Recently Gutowsky, Tiers, and Saunders and co-workers have reported several examples of an NMR chemical shift of proton and fluorine resonance, resulting from an isotopic substitution in the vicinity of the nucleus under consideration. In all cases so far reported, the resonance of the observed species moves to higher field, that is to greater shielding, whenever an atom in the immediate vicinity is replaced by a heavier isotope.

Ramsey has shown that the chemical shift results from a difference in the average of the electronic wave function of the isotopic compounds. This difference could come about as a result of the
nucleus-electron interactions that depend upon the nuclear volume and the nuclear electric quadrupole moment. However, these interactions are not only small, but they are also expected to be of short range only. Gutowsky has suggested that the observed isotopic chemical shifts come about, not as a result of perturbations of the electronic wave function caused by the isotopic substitution, but as a result of changes in the dynamic state of the molecule not directly affecting the electronic wave function. The observed isotopic chemical shift could be calculated by averaging $\sigma$ over the molecular motions of the isotopic molecules and taking the difference. The altered effective mass for the vibrations in which the substituted nucleus participates results in altered zero-point vibrational energies for these modes, and thus is a different average $\sigma$. Ramsey and co-workers have found the ratio of the shielding in $D_2$ to that in $H_2$ to be

$$\frac{\sigma_{H_2}}{\sigma_{D_2}} = 1.006 \pm 0.005,$$

with the shielding constant for $H_2$ as

$$\sigma_{H_2} = (2.62 \pm 0.03) \times 10^{-5}.$$

A heavier isotope has smaller vibrational amplitudes than a lighter one, and as a result, it does not get as close to its neighbors, nor does it polarize them as much. This electrostatic polarization is reflected in the shielding, and therefore in the chemical shift. The chemical shifts are altered as a result of changes in the effective mass for vibrations which are completely harmonic; however, the effect should be larger if anharmonic vibrational modes are involved. This is consistent with the interpretation of a series of experiments in which molecular vibrations are taken into account and for which it has been shown that the anharmonicity of the vibrations plays an important role.
Gutowsky has made a calculation of the chemical shift resulting from the change in the zero-point energy of the bending vibration of the CH\(_2\) group, assuming this to be a harmonic oscillator.\(^7\) His calculation gives the proper direction for the shift and an order-of-magnitude agreement. Here an attempt has been made to investigate and verify experimentally the explanation given for this isotope effect, by measuring precisely the chemical shift that accompanies the thermal excitation of the vibrational modes in various molecules. For if, according to this electrostatic deformation model, deuterium substitution produces an upfield shift, then thermal excitation of the higher vibrational modes should result in increased vibrational amplitudes, and, therefore, increased deformation of the electron distribution about the vibrating nuclei. Thus, the NMR signal should shift to lower field (decreased shielding) as the temperature is increased. In addition, we attempt to evaluate here the relative importance of the various types of vibrational modes and to associate with each type, if possible, a characteristic chemical shift. The shifts under consideration here are approximately 0.001 c/sec per °C in magnitude. On the other hand, the temperature-dependent shifts due to solvent effects are usually orders of magnitude greater than this.\(^\text{13}\) Such effects include differences in the bulk diamagnetic susceptibility of the solute, and the solvent and intermolecular interactions between solute molecules, or between solute and solvent molecules. Since knowledge of the behavior of the free unassociated molecules is required here, this investigation was carried out entirely on gaseous samples, to avoid interference from the much larger temperature-and concentration-dependent shifts due to solvent effects.
II. EXPERIMENTAL PROCEDURE

A. Preparation of Samples

Table I shows the compounds used in this study, except H$_2$. Other than cyclobutane, tetramethyl tin, and 2-butyne, the samples were made up from commercially available sources in standard NMR 5-mm thin-walled sample tubes. For each substance, a mixture of the gaseous sample and gaseous methane, and at a partial pressure of approximately 5 atm if possible, was condensed from a vacuum line by using liquid nitrogen. The sample tubes were collapsed at a distance 5 cm from the bottom so that the temperature of the entire gaseous sample could be controlled in the insert (see Fig. 1). The portion of the tube above the collapsed section provided a means for spinning the sample, which increased the resolution even of the gaseous samples.

Considerable difficulty was encountered in preparing the hydrogen sample, for liquid nitrogen proved inadequate to trap hydrogen in the sample tube at a high enough pressure for its NMR spectrum to be seen.

Several attempts were made to prepare hydrogen samples by adsorbing hydrogen onto a platinum gauze at low temperatures, and then heating the sample; or by decomposing solid hydrides previously enclosed in the sample tube. But all these efforts gave too low pressures of hydrogen gas. In another effort, an all-copper-tubing vacuum line was constructed and the sample tubes were equipped with a Housekeeper seal and then attached to the vacuum line. A positive pressure of about 20 atm was placed in the sample tubes, and the copper tubing of the seal was then pinched. Although this procedure allowed the preparation of hydrogen samples at high enough pressures for the NMR signal to be seen, spinning the samples was hindered because of eddy currents set up in the copper. Finally, a satisfactory hydrogen sample was prepared by condensing hydrogen from a vacuum line, using liquid helium and collapsing the sample tube by means a gas-
Fig. 1. Part I. Variable-temperature, high-resolution insert.
oxygen torch 3 cm above the surface of the liquid helium bath. But even this otherwise acceptable sample proved insufficient owing to the inherent nature of the hydrogen NMR signal. This point is examined further below.

B. Variable-Temperature Apparatus

Measurement of the chemical shifts as a function of temperature required the design of apparatus that could be attached to the standard V-4331A probe of a Varian spectrometer, in order to control the temperature of the sample and at the same time allow rapid spinning of the cylindrical sample tubes.

The apparatus as designed and constructed is shown in Figs. 1 and 2. The standard insert of the V-4331A probe has been replaced by a special pyrex insert (Fig. 1) with an evacuated Dewar jacket to prevent heat losses to the probe. The receiver coil was wound around the insert proper and the connecting wires led to the coaxial connector through a specially constructed bakelite ring, the latter to provide a firm basis for the Dewar and insert and to reduce heat losses to the coaxial connector. The bottom of the insert was provided with a Teflon cushion on which the sample tube spins. Holes just above the Teflon cushion let heated air flow in the space between sample tube and insert, thus controlling the temperature of the sample. Figure 2 shows the aluminum housing unit built to replace the standard part. Heated air enters the unit through the lower inlet and proceeds downward only (in the space between insert and Dewar). It proceeds through the holes at the bottom of the insert, around the sample tube, and through the air outlet. This unit also supports the plastic rotor and allows for rapid spinning of the tube-carrying plastic rotor.

The dry air used for the temperature regulation is brought to the desired temperature by means of a nichrome-coil heater wound on a pyrex tube. The air flow is regulated by a means of a flow gauge, and the temperature is varied by adjusting the current in the heater.
Fig. 2. Part I. Variable-temperature apparatus.
with a Varian® transformer. Thermocouples are placed at the air inlet and outlet. A third thermocouple is inserted in a dummy sample tube and its temperature determined in relation to the inlet and outlet over a period of time. When this temperature has become stabilized at the required value, the actual sample tube is placed in the insert, and the inlet and outlet temperatures are monitored while the sample is reaching thermal equilibrium (about 5 min.). Thus, monitoring the inlet and outlet temperatures readily provided an accurate indication of the actual sample temperature to within ± 1°C.

C. Measurement of Chemical Shifts

All the $^1H$ spectra were obtained on an HR-60 NMR Varian spectrometer. All chemical shifts are reported in cycles per second, measured at 60 Mc/sec.

The separation between signals had to be measured to an accuracy of a few hundredths of a cycle per second. Such accuracy can be obtained by using the wiggle-beat method, but this method is not applicable to widely separated signals. Therefore, the following method was used, which yields a precision of approximately 0.02 cps to 0.10 cps depending upon the condition of the field and the instrument. Basically, the method is the side-band technique with certain modifications. A Hewlett-Packard model 200J audio oscillator was modified by placing three 5-to-25 μF condensers in parallel with the three variable condensers in the tuning section. The oscillator, so modified, was stable to ± 1 part in $10^5$, and the frequency could be changed by increments of 1 part in $10^5$. The period of the modulating signal, rather than its frequency, was measured with a Hewlett-Packard counter. This indirect technique allowed rapid measurement of the frequency to within less than one-thousandth of a cycle per second.

The frequency of the signal generator was adjusted so that one sideband of the methane signal was close to, but resolvable from, the signal due to the protons whose shift was to be measured; and the
amplitude of the sideband was adjusted so that the two peak heights were equal. Then the sideband frequency was adjusted so that one peak was nearly superimposed on the other. The resulting signal was recorded in both directions of sweep, along with the period of the audio signal. The frequency of the audio signal was changed by approx 1 or 2 parts per $10^5$, and the entire process was repeated. In this manner, a record was made of a pair of peaks as a function of the audio frequency. Looking at this record, it was quite easy to distinguish an envelope of these peaks. The amplitude of the signal increased from the starting point, went through a maximum, and then decreased. Consequently, the random fluctuations in the magnitude of the signal owing to changes in field homogeneity, scan rate, or noise could be disregarded. The audio signal corresponding to the maximum of the envelope was selected as representing the separation between the methane and sample resonances (see Fig. 3).

This method was used unless the signals were very close together, approx 5 cps, in which case it was assumed that the scan rate was linear with time over this time interval, and the separations were measured graphically by use of a sideband near the peak to be measured. In every case, five or six independent measurements were made. Typically, the root-mean-square deviation of these individual measurements was 0.06 cps and the most probable error was 0.02 cps. (see Table I and figures 4-14).
Fig. 3. Part I. Precise determination of chemical shift: typical pattern of the reference sideband superimposed on the signal and recorded in both directions of sweep.
Table I. Observed temperature-dependent chemical shifts from methane

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<th>Compound</th>
<th>Temp (°C)</th>
<th>δ (c/sec)</th>
<th>Compound</th>
<th>Temp (°C)</th>
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<td>C₂H₃</td>
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<td>-44.68 ± 0.01</td>
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Fig. 4. Part I. Temperature dependence of the chemical shift of acetylene from methane.
Fig. 5. Part I. Temperature dependence of the chemical shift of 2-butyne from methane.
Fig. 6. Part I. Temperature dependence of the chemical shift of ethane from methane.
Fig. 7. Part I. Temperature dependence of the chemical shift of ethylene from methane.
Fig. 8. Part I. Temperature dependence of the chemical shift of neopentane from methane.
Fig. 9. Part I. Temperature dependence of the chemical shift of tetramethylsilane from methane.
Fig. 10. Part I. Temperature dependence of the chemical shift of tetramethyl tin from methane.
Fig. 11. Part I. Temperature dependence of the chemical shift of cyclopentane from methane.
Fig. 12. Part I. Temperature dependence of the chemical shift of cyclobutane from methane.
Fig. 13. Part I. Temperature dependence of the chemical shift of cyclopropane from methane.
Fig. 14. Part I. Temperature dependence of the chemical shift of hydrogen bromide from methane.
III. DISCUSSION

A. Temperature Dependence and Choice of Standards

In order to determine precisely the temperature dependence of chemical shifts, a readily available and simple reference is required, whose NMR signal is temperature-independent, at least in the narrow temperature range considered here. It would be desirable to use gaseous hydrogen for such a standard, since its only vibrational mode is 4159 cm\(^{-1}\), and for all practical purposes it remains unpopulated even at the highest temperatures considered here. However, beside experimental difficulties encountered in preparing hydrogen samples, there is another more fundamental reason that prohibited its use as a standard.

Purcell and co-workers have measured the spin-lattice relaxation time \(T_1\) of hydrogen.\(^{19}\) At room temperature and 10 atm pressure, \(T_1\) was found to be approx. 0.015 sec, and to increase with temperature. The line width, due to spin-lattice relaxation measured on a frequency scale and in the absence of magnetic dipole broadening, is on the order of \(1/T_1\). Therefore, this inherently broad \(H_2\) NMR signal (approx. 70 cps) cannot be used conveniently as a standard, for the superimposition of sidebands from such a wide signal cannot be made with the precision required here.

In place of \(H_2\), hydrogen bromide was adopted as a temperature-independent standard. \(HBr\) is readily available, and also its single high-lying vibrational\(^{18}\) mode (2560 cm\(^{-1}\)) should ensure the temperature independence of its signal.

Observed chemical shifts are an average of the chemical shifts associated with the possible molecular configurations, averaged over the molecular motions. However, the extent to which a given vibration affects the chemical shift of a species under consideration may be expected to depend not only on the relative population of the vibrational level at given temperature, but also on the type of the mode, and on whether the species considered participates directly in the vibrational mode. Thus, the observed chemical shift \(\nu_0\delta\) (in cps) is the sum
of the shifts associated with the various vibrational levels:

\[
\nu_0 \delta = \sum_{i=0}^{v_0} \nu_0 \delta_i N_i,
\]

where \( \nu_0 \) is the spectrometer frequency; \( \delta \) is the dimensionless observed chemical shift; \( \delta_i \) is the shift from the reference signal of the \( i \)th vibrational mode; and \( N_i \) is the fractional population of the same \( i \)th vibrational state.

Assuming a Boltzmann distribution of the population among the various vibrational states, one can write the observed chemical shift as

\[
\nu_0 \delta = \sum_{i=0}^{v_0} \frac{\nu_0 \delta_i g_i \exp[-\hbar \omega_i /kT]}{\sum_{i=0}^{v_0} g_i \exp[-\hbar \omega_i /kT]} - \nu_0 \delta_0
\]

\[
= \frac{\nu_0 \delta_0 + \sum_{i=1}^{v_0} g_i \exp[-\hbar \omega_i /kT]}{1 + \sum_{i=1}^{v_0} g_i \exp[-\hbar \omega_i /kT]}
\]

where \( \omega_i \) and \( g_i \) are the vibrational frequency and degeneracy, respectively, of the \( i \)th vibrational state. Furthermore, if \( \Delta_i \) defines the chemical shift of the \( i \)th vibrational state from the ground vibrational state, i.e., if \( \Delta_i = \nu_0 \delta_i - \nu_0 \delta_0 \), then Eq. (2) is written
When all the vibrations with sizeable $\Delta$'s have vibrational frequencies greater than 200 cm$^{-1}$, and when the temperature range considered is close to 50 °C, Eq. (3) can be simplified to

$$\nu_0 \delta = \nu_0 \delta_0 + \frac{\sum_{i \geq 1} g_i \Delta_i \exp \left[ -\frac{\hbar \omega_i}{kT} \right]}{1 + \sum_{i \geq 1} g_i \exp \left[ -\frac{\hbar \omega_i}{kT} \right]}$$

When this formula is differentiated with respect to the temperature, the dependence of the observed chemical shift on temperature can be written as

$$\frac{d(\nu_0 \delta)}{dT} \approx \sum_{i \geq 1} g_i \Delta_i \frac{\hbar \omega_i}{kT^2} \exp \left[ -\frac{\hbar \omega_i}{kT} \right].$$
For HBr, then, one could readily obtain the dependence of the observed shift on temperature, if one only knew the chemical shift $\Delta$ associated with the single vibrational mode of HBr.

The great majority of inorganic and organic compounds shows proton resonance spectra in a radio-frequency region that is only a few hundred cps wide at customarily used magnetic fields. There is no simple correlation between the $s$ character of the electronic environment of a given nucleus and the chemical shift, but it is expected that changes in the $s$ character due to excited vibrational states in the same electronic potential are not as great as when the given nucleus finds itself in a totally different potential. On this basis, it is expected that the chemical shifts of excited vibrational states from the ground state should be only a fraction of the range of proton chemical shifts in the various chemical environments. There is no easy way to assign an expected value of chemical shifts of excited vibrational modes. However, an assignment of 100 cps has been made to the single excited mode of HBr to establish its temperature independence in the temperature range considered here. This choice (which is probably too high) can be made plausible not only on the basis of the range of proton chemical shifts, but also because a consistent picture can be obtained for the isotope effect and for the results of this temperature-dependent study. Assuming, then, that $|\Delta(HBr)| \sim 100$ cps, and remembering that the vibrational frequency of HBr is $2560 \text{ cm}^{-1}$, one can calculate, by using Eq. (5), that

$$\left| \frac{d\nu_0}{dT} \right| < 0.0002 \text{ cps per } ^\circ \text{C}.$$ 

The choice of 100 cps may be entirely arbitrary, but the exact number is not important, since only the temperature independence of HBr is of interest here. Even if the chemical shift associated with this vibrational mode were 1000 cps, $d\nu_0/dT$ would still be $\approx 0.002$ c/sec; and for the temperature range considered here, HBr would still be almost temperature-independent! But, as already pointed out above, if proton resonance spectra appear in a radio-frequency region that is only about 600 cps
wide at 60 Mc/sec, then there is no reason to expect the chemical shift of the excited vibrational state to be more than a fraction of 600 cps. Thus, we can expect that HBr should be temperature-independent well within the range of our experimental error.

Table II shows the chemical shifts, and their dependence on temperature, for eleven gaseous compounds, all having a single group of magnetically equivalent nuclei. It is assumed that in the gaseous phase, and under the present experimental conditions, there are only free unassociated molecules, and therefore no other effect (e.g., density corrections, association, etc.) will cause a \( \frac{dv_0}{dT} \) of comparable magnitude. Also, the chemical shifts listed are from methane rather than from HBr. Methane was used as a secondary standard because of the sharpness of its resonance, the large number of equivalent hydrogen per molecules compared with HBr, ease of sample preparation, and finally its temperature independence as measured against the primary standard HBr. Usually, five measurements were made in the temperature range of 15 °C to 100 °C. Within limits of experimental accuracy, these points fell nearly on a straight line for each compound (see Figs. 4-14).

The slopes of these lines at 50 °C are tabulated in Table II, and Figs. 15, 16, and 17 summarize the results for the various series of compounds.

B. Assignment of Effective Chemical Shifts to Excited Modes

It is apparent from Table I that the NMR shift of most of the compounds under consideration is indeed temperature-dependent, and in general, the resonance shifts to low field as the temperature is increased. Also, from Eq. (5) it is apparent that there is an additive contribution to \( \frac{dv_0}{dT} \) from each of the various vibrational modes. However, the question of degeneracy is somewhat complicated by the following consideration.
Table II. Temperature dependence of chemical shifts from methane

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \frac{d(\nu_0\delta_{\text{methane}})}{dT} ) c/sec per °C</th>
<th>( \nu_0\delta_{\text{methane}} ) at 25°C c/sec per °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0 ± 0.</td>
<td>0</td>
</tr>
<tr>
<td>HBr</td>
<td>0.0000 ± 0.0005</td>
<td>-260.5</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0000 ± 0.0005</td>
<td>-44.7</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>-0.0080 ± 0.0027</td>
<td>-3.9</td>
</tr>
<tr>
<td>C₄H₈</td>
<td>-0.0071 ± 0.0009</td>
<td>-113.9</td>
</tr>
<tr>
<td>C₅H₁₀</td>
<td>-0.0035 ± 0.0009</td>
<td>-86.9</td>
</tr>
<tr>
<td>C(CH₃)₄</td>
<td>-0.0061 ± 0.0014</td>
<td>-49.2</td>
</tr>
<tr>
<td>Si(CH₃)₄</td>
<td>-0.0125 ± 0.0015</td>
<td>-8.4</td>
</tr>
<tr>
<td>Sn(CH₃)₄</td>
<td>-0.0102 ± 0.0025</td>
<td>-5.9</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>-0.0087 ± 0.0014</td>
<td>-80.1</td>
</tr>
<tr>
<td>CH₃CCCH₃</td>
<td>-0.0047 ± 0.0008</td>
<td>-87.7</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>+0.0038 ± 0.0015</td>
<td>-310.6</td>
</tr>
</tbody>
</table>
Fig. 15. Part I. Relative temperature dependence of the chemical shifts of acyclic compounds from methane.
Fig. 16. Part I. Relative temperature dependence of the chemical shifts of cyclic compounds from methane.
Fig. 17. Part I. Relative temperature dependence of the chemical shifts of tetrahedral compounds from methane.
Consider a single hydrogen atom vibrating against a carbon skeleton. There is a \( \Delta \) associated with exciting this mode of vibration. Now consider two identical hydrogen atoms attached to the same carbon atom. In order to achieve the same observed chemical shift of the two hydrogen nuclei, one would have to excite both the symmetric and antisymmetric stretching modes. The \( \Delta \) associated with either of these two modes would be approximately half the \( \Delta \) associated with the stretching mode of a single hydrogen atom. Therefore, if one hopes to assign a given \( \Delta \) to a given kind of vibrational mode, one must collect terms in the sum of Eq. (3) dealing with a given kind of vibration—e.g., \( \text{CH}_3 \) parallel deformations or \( \text{CH}_2 \) deformations—and consider this set of terms as a single contribution. One should then use an average of the individual vibrational frequencies, assign a degeneracy of one, and a \( \Delta_{\text{eff}} \) to this average mode. In the case of a single group, \( \Delta_{\text{eff}} \) is equal to the chemical shift brought about by exciting all the modes of one kind in that group. These \( \Delta_{\text{eff}} \)'s should not depend upon the symmetry of the molecule, but only upon the type of motion involved.

Over the temperature range studied, it is impossible to gain much information about \( \Delta_{\text{eff}} \) for any mode whose frequency is above 2000 cm\(^{-1}\), since these modes are always so lightly populated that the term in the sum for \( (dv_0 \delta/dT) \) associated with them is less than our experimental error, even if \( |\Delta_{\text{eff}}/| < 130 \) cps. Therefore, although exciting such modes as the \( \text{CH} \) stretching mode is probably very effective in causing a chemical shift, the effect is too small to be measurable in the temperature range under consideration.

\[ \text{C. Paraffins} \]

1. \textbf{Methane}

The stretching modes in methane\(^{18}\) are 2914 cm\(^{-1}\) and 3020 cm\(^{-1}\) and so would contribute nothing to the temperature dependence even if
the $\Delta_{\text{eff}}$ associated with these modes were several hundred cps. On the other hand, the bending modes are 1526 cm$^{-1}$ and 1306 cm$^{-1}$, and could be expected to contribute more readily to any temperature dependence. Since both of these modes involve only changing H-C-H bond angles, one would expect the $\Delta_{\text{eff}}$ for these two modes to be of the same sign. One then readily calculates that $\Delta_{\text{eff}}$ for each of the bending modes in methane must be less than approximately 10 cps.

2. Ethane

Here the experimental temperature dependence of the chemical shift in ethane is $0.0000 \pm 0.0005$ c/sec per °C. This, of course, could be the result of an accidental, exact cancellation of two or more temperature-dependent terms of opposite sign; however, this is not only aesthetically unpleasing, but it also seems rather unlikely, particularly since a consistent picture can be presented by assuming all $\Delta_{\text{eff}}$ are negative, except for modes involving delocalization of multiple bonds. To date, all the isotope shifts reported are in the same directions, and the resonance of all saturated compounds in these temperature-dependent experiments invariably moves to low field as the temperature is increased. It is assumed then that for ethane the individual terms in the sum of Eq. (5) do not cancel each other; rather the apparent temperature independence is due to the small $\Delta_{\text{eff}}$ values involved and to the high-lying vibrational modes that cannot be occupied significantly at these temperatures in order to cause any observable temperature-dependent shifts.

One can then easily calculate the following limits on the absolute value of $\Delta_{\text{eff}}$ for the various vibrations in ethane: $\Delta_{\text{eff}}$ for CH$_3$ perpendicular deformation is less than 17 cps; for the CH$_3$ parallel deformation it is less than 13 cps; for the CH$_3$ wag it is less than 3 cps; for the C-C stretch it is less than 3 cps. The assumption made above, namely that the apparent temperature independence of the ethane is not the result of an accidental cancellation of terms, is somewhat further supported by the fact in Gutowsky's calculation of the contribution of the H-C-H bonds a $\Delta_{\text{eff}}$ is predicted for these modes
of approximately 2 cps. If we use this calculated order of magnitude, it need only be assumed, that the contribution to the chemical shift due to the CH₃ wagging (bending) modes does not exactly cancel out the contribution from the C-C stretching mode.

D. Cyclic compounds

Figure 16 summarizes the results for the cyclic compounds. In this series of compounds, the temperature dependence of the chemical shift becomes smaller as the size of the ring is increased. This immediately implies that the low-lying ring deformation modes have very small Δ eff's, since the larger the ring, the lower the ring-mode frequencies become. By comparison with the bending modes in methane and ethane, and considering the predictions of Gutowsky's calculations, it seems unreasonable that the absolute value of Δ eff for the CH₂ deformation should be greater than 10 cps. This would result in a negligible contribution to dν₀δ /dT. In comparison with ethane again, Δ eff for the C-C stretching modes is probably less than 3 cps which also gives a negligible contribution to dν₀δ /dT. One must therefore look to the CH₂ bending modes for the cause of the temperature-dependent chemical shift. In Table III the averages of these modes for the three compounds are tabulated.

Table III. Average infrared vibrational frequencies for CH₂ bending modes in cyclic hydrocarbons

<table>
<thead>
<tr>
<th>Mode</th>
<th>Cyclopropane (cm⁻¹)</th>
<th>Cyclobutane (cm⁻¹)</th>
<th>Cyclopentane (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂ rock</td>
<td>1000</td>
<td>1050</td>
<td>1055</td>
</tr>
<tr>
<td>CH₂ wag</td>
<td>1050</td>
<td>1250</td>
<td>1250</td>
</tr>
<tr>
<td>CH₂ twist</td>
<td>870</td>
<td>1080</td>
<td>1100</td>
</tr>
</tbody>
</table>

*See Ref. 20.*
It can be seen that the CH₂ bending modes are lowest in frequency in cyclopropane and highest in cyclopentane. If these modes all had the same magnitude of \( \Delta_{\text{eff}} \) associated with them, this would result in the proper trend of temperature dependence of chemical shifts with ring size. If one assumes that the \( \Delta_{\text{eff}} \)'s for the three modes in a given compound are equal, one calculates \( \Delta_{\text{eff}} = -14, -16, \) and \(-9\) cps for cyclopropane, cyclobutane, and cyclopentane respectively. Although the experimental agreement is not good, it at least causes one to believe that these are the modes mainly responsible for the temperature dependence, and that \( \Delta_{\text{eff}} = -13 \) cps is of the proper order of magnitude for these modes.

E. Tetrahedral Compounds

The results for the tetrahedral compounds are summarized in Fig. 17. Again, by comparison with ethane one would expect the CH₃ perpendicular and parallel deformations, the CH₃ wags, and the skeletal stretching modes to contribute a negligible amount to \( dv_0 \delta/dT \). The torsional modes are so low in frequency that they must involve very small changes in the electronic structure. Therefore, their contribution to \( dv_0 \delta/dT \) is expected to be very small. This is in agreement with the observation for the low-lying ring modes in the cyclic compounds, where the ring with the lowest deformation modes shows the least temperature dependence.

The temperature-dependent shift must therefore come about as a result of the skeletal bending modes. Making this assignment, one calculates, for the skeletal bending modes, \( \Delta_{\text{eff}} = -6, -11, -11 \) cps for tetramethylmethane, tetramethylsilane, and tetramethyltin respectively. The near equality of these three values is reassuring, considering the differences between the three molecules.

F. Multiple-Bonded Compounds

In acetylene, both the CH stretch and the C≡C stretch are so high in frequency that even if \( \Delta_{\text{eff}} \) were \( \pm 100 \) cps for these modes,
the observed temperature-dependence would be negligible. The only
modes left are the CH bending modes, and these must account for
-0.0083 cps per °C. This implies that Δ_eff for these bending modes
is -17 cps which is quite high compared with the bending modes in the
CH_3 group (3 cps from C_2H_6), and is high even compared with the
bending modes in the CH_2 group (13 cps from the cyclic compounds).

However, this is not very surprising if one takes into account
the effect (on the proton) of the anisotropy of the local atomic sus-
ceptibility on the neighboring carbon atom. Pople has used precisely
this effect to account for the "anomalous" chemical shift of C_2H_2 in
relation to ethane and ethylene. The anisotropy of the local sus-
cceptibility can be thought of as arising from a purely diamagnetic
part (due to the orbital motion of the electrons) and from a purely
paramagnetic part (due to the mixing of the ground state with excited
electronic states by the magnetic field).

It is generally expected that the paramagnetic contribution to
the anisotropy will be the dominant one, and the effects of magnetic
anisotropy on neighboring atoms will be most pronounced in linear
molecules in Σ states. In molecules like C_2H_2, then, since the
electron distribution is axially symmetric about the molecular axis,
there can be no local paramagnetic contribution to the susceptibility
if the figure axis is parallel to the external field. However, if the
figure axis is perpendicular to the external field, the locally induced
paramagnetic contribution to the susceptibility (due to a mixing of the
ground state with one σ → π excited state) is manifested as a
diamagnetic contribution to the field experienced by the proton.

This explains why C_2H_2 appears on the high-field side of
ethylene, although from purely chemical criteria acetylene is ex-
pected to be less shielded than ethylene. In these temperature-
dependent experiments, exciting the CH bending modes causes the
protons to spend a greater fraction of their time off the figure axis,
thus moving their resonance signal downfield in excess of the shift
observed in the other CH bending modes cited above.
In 2-butyne, again assuming that the CH₃ deformation modes, the CH₃ rocking modes, and the C-C stretching modes contribute only a very small amount, as in ethane, one must assign $\Delta_{\text{eff}}$ (skeletal modes) = 4.2 cps. This seems rather large in value compared with other shifts calculated for skeletal modes, such as the C-C stretch.

However, when one considers that bending the molecule again interferes with the $\pi$ electrons, one can believe that 4.2 cps is not too large a $\Delta_{\text{eff}}$ for the skeletal bonds.

In ethylene, a positive shift is observed with increasing temperature. Using results from the previous calculation, one can make a good estimate of the $\Delta_{\text{eff}}$'s for the CH₂ modes from the cyclic compounds. Again, the frequency of the CH stretches and the C-C stretch are too high to show up as a temperature variation of the chemical shift. The CH₂ rocks and wags should have $\Delta_{\text{eff}}$'s of about 20 cps, taking into account the $\pi$ electrons. All these contributions combine to give a $\Delta v_0 \delta /dT$ of approximately -0.0070 cps °C. The experimentally observed $\Delta v_0 \delta /dT$ of +0.0038 cps per °C varies from this by 0.0108 cps per °C. This large upfield shift must result from the twisting mode about the double bond. As this mode is activated, the double-bond character of the bond should be decreased and the electron density in the vicinity of the protons should be increased, causing an upfield shift as observed. This interpretation is, of course, founded on the naive assumption that greater electron density provides greater shielding, which is not precisely true. On the basis of the above calculation, $\Delta_{\text{eff}}$ for this twisting mode in ethylene is +36 cps. The results for the various modes investigated are summarized in Table IV.
<table>
<thead>
<tr>
<th>Mode</th>
<th>$\Delta_{\text{eff}}$ (c/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ and CH$_2$ deformations</td>
<td>-13</td>
</tr>
<tr>
<td>CH$_2$ rocks, wags, and twists</td>
<td>-13</td>
</tr>
<tr>
<td>Skeletal bending modes in tetrahedral compounds</td>
<td>-10</td>
</tr>
<tr>
<td>C-H bends in C $\equiv$ C-H</td>
<td>-17</td>
</tr>
<tr>
<td>CH$_2$ twists in C $=$ CH$_2$</td>
<td>+36</td>
</tr>
</tbody>
</table>
G. Isotope Shifts

The observed shifts due to isotopic substitution can be explained on the basis of the magnitude of the shifts reported here. For example, assuming shift to be linearly connected with position in the potential well, if excitation of a $\text{CH}_2$ deformation mode from the ground state to the first excited state ($E = (1/2) \ h \nu$ to $(3/2) \ h \nu$) produces a shift less than 13 cps, substitution then of $\text{D}$ for $\text{H}$ [$E = (1/2) \ h \nu$ to $(\sqrt{3}/4) \ h \nu$] should produce a shift of less than 0.2 cps at the deuterium and hydrogen atoms. This is less than, but of the order of magnitude of, the observed shifts. $\text{CH}_2$ rock, wag, and twist should each make a contribution of approximately the same magnitude as the one calculated above.

Gutowsky, in his explanation of the observed isotope shifts, has attributed the entire effect to the $\text{CH}_2$ deformation modes. However, the results of this work lead us to believe that one cannot hope to explain the observed isotopic shifts unless one also considers vibrational modes other than the $\text{CG}_2$ deformation. Although no quantitative information can be gained from this work on the shift associated with excitation of the CH stretching mode, excitation of modes other than the $\text{CH}_2$ deformation produces large chemical shifts and this suggests that the CH stretching modes may be very important in the isotope shifts.
IV. SUMMARY

The dependence of the chemical shift on temperature for several gaseous compounds with a single group of magnetically equivalent nuclei has been measured. It is found that the chemical shifts of most of these compounds are indeed temperature-dependent, and may move to either higher field (increased shielding) or lower field (decreased shielding) as the temperature is increased. It is assumed that only free unassociated molecules exist under the experimental conditions, and therefore that no association effects can be responsible for these temperature-dependent shifts. Rather, the latter are ascribed to excitation of the various vibrational modes of the molecules, the protons in the excited molecules being differently shielded than the protons in the molecules in the ground vibrational states. According to an electrostatic deformation model, thermal excitation of the higher vibrational modes (which results in increased vibrational amplitudes) brings about increased deformation of the electron distributions about the vibrating nuclei. This decreased shielding is reflected in the downfield shift of resonance that accompanies the excitation of all modes except those involving delocalization of double bonds. The data are interpreted to yield approximate chemical shifts associated with the excitation of various types of modes. Finally, the reported "isotope shifts" due to the substitution of a heavier isotope in the vicinity of the observed nucleus are discussed in terms of the chemical shifts associated with the various modes, and it is shown that modes other than the \( CH_2 \) deformations must be considered also in any explanation of the "isotope shifts."
REFERENCES

14. The sample of cyclobutane was kindly provided by Professor W. Gwinn of this department.
15. The samples of tetramethyl tin and 2-butyne were kindly provided by California Research Corporation, Richmond, California.
NUCLEAR MAGNETIC RESONANCE STUDIES
PART II. F$^{19}$ SPIN-SPIN COUPLINGS

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NUCLEAR MAGNETIC RESONANCE STUDIES
PART II: F\textsuperscript{19} SPIN-SPIN COUPLINGS

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June 6, 1961

ABSTRACT

The F\textsuperscript{19} NMR spectra of certain saturated organic compounds have been investigated. It is found that generally the spin coupling constant between 1,2 fluorine atoms $J_{1,2}$ approximates 0 cps, and that $J_{1,3}$ approximates 7 to 10 cps, if all intermediate skeletal atoms are carbon atoms; $J_{1,3}$ approximates 10 to 17 cps if one of the intermediate skeletal atoms is a nitrogen atom; and $J_{1,4}$ approximates 2 to 7 cps.

A critical examination of the "long range" spin-spin interaction between fluorine atoms is given. It is shown that, in contradistinction to coupling between protons, magnetic dipolar and electron orbital terms must play an important part in the coupling mechanism between fluorines; and that "long range" coupling takes place through space by the formation of a long bond between the interacting atoms, rather than the interaction being "telegraphed" via the intervening chemical bonds.
1. INTRODUCTION

Soon after the discovery of the chemical shift (see Refs. 1 to 6, Part I) a second kind of fine structure was observed in the nuclear magnetic resonance (NMR) spectra of various nuclear species. It was found that a number of liquids showed more lines than were required by the number of magnetically nonequivalent nuclei, and that the multiplet splittings were independent of the externally applied field $H_0$.\textsuperscript{1-4} Direct magnetic dipole-dipole interactions average to zero because of the high-frequency molecular motions characteristic of the liquid state, and so cannot account for this kind of fine structure. However, on the basis of the above observations it was proposed that these multiplets were due to the indirect magnetic interaction between nuclear spins,\textsuperscript{5,3} the interaction being proportional to the scalar product of the nuclear spin vectors

$$ I(i) \cdot I(j). \quad (1) $$

A successful interpretation of this spin-spin coupling was given by Purcell and Ramsey,\textsuperscript{6} and later developed in detail by Ramsey.\textsuperscript{7,8} Essentially, the mechanism is the magnetic interaction of each nucleus with the spin of a "local" electron, together with the coupling of electron spins with each other. Ramsey has shown that the interaction energy can be calculated by second-order perturbation theory,\textsuperscript{7} with the perturbing interaction being the magnetic interactions of the nuclear moments with the electron spin.

The Hamiltonian for the motion of the electrons in the field of nuclei possessing nonvanishing nuclear moments may be written\textsuperscript{7,9-12} as

$$ \mathcal{H} = \mathcal{H}(1) + \mathcal{H}(2) + \mathcal{H}(3). \quad (2) $$

The first part involves the total electronic kinetic energy, the magnetic interactions between electronic orbital motions and nuclear moments, and the various interactions between the electrons,
\[ \mathcal{H}(1) = \sum_{K} \left( \frac{1}{2m} \right) \left[ \frac{\mathbf{p}_K}{c} + \frac{e}{c} \mathbf{A}_K \right]^2 + \text{other terms not involving nuclear spin vectors} \]

where \( m \) is the electron mass, \( \mathbf{p}_K \) the linear momentum of the \( K \)th electron, and \( \mathbf{A}_K \) the vector potential for the same electron due to the nuclear moments. \( \mathcal{H}(1) \) can be put in the appropriate quantum mechanical form by allowing for the substitution \( \mathbf{p}_K \rightarrow \frac{\hbar}{i} \nabla \). Also, a specific choice of vector potential \( \mathbf{A}_K \) is made in terms of the nuclear magnetic moment \( \mathbf{\mu}_N = \gamma_N \hbar \mathbf{I}_N \) and the distance \( r_{KN} = r_K - r_N \) between the \( K \)th electron and the \( N \)th nucleus, by writing \( \mathbf{A}_K = \mathbf{\mu}_N \times \frac{\mathbf{r}_{KN}}{r_{KN}^3} \). Thus, this first part of the Hamiltonian is written

\[ \mathcal{H}(1) = \sum_{K} \left( \frac{1}{2m} \right) \left[ \frac{\hbar}{i} \nabla + \frac{e}{c} \sum_{N} \gamma_N \mathbf{I}_N \times \frac{\mathbf{r}_{KN}}{r_{KN}^3} \right]^2 + \text{other terms}, \]

where \( \gamma_N \) is the magnetogyric ratio of nucleus \( N \) and \( \mathbf{I}_N \) its spin vector operator.

\( \mathcal{H}(2) \) represents the dipole-dipole interaction between the nuclear magnetic moments and the spins of electrons in non-\( s \) orbitals:

\[ \mathcal{H}(2) = -\frac{\mathbf{\mu}_N}{\hbar} \cdot \mathbf{e} \ell, \]

where
Here we have $\mu_e = -2\beta S$ as the magnetic moment due to the electron spin; $\beta$ as the Bohr magneton and $S$ as the electron spin. Thus, for a system of $K$ electrons and $N$ nuclei, (2) may be written

$$\Psi (2) = 2\beta \hbar \sum_{K, N} \gamma_N \left[ \frac{3(S_K \cdot r_{KN}^3)(I_N \cdot r_{KN})}{r_{KN}^5} - \frac{S_K \cdot I_N}{r_{KN}^3} \right]$$

(6)

$$\Psi (3) = \frac{16\pi \beta \hbar}{3} \sum_{K, N} \gamma_N \delta (r_{KN}) S_K \cdot I_N$$

(7)

is the Fermi interaction between electron spins in $s$ orbits and nuclear spins. Such a contact term was introduced by Fermi to explain the hyperfine structure in atomic spectra, and it is also used in the discussion of electron resonance experiments. It depends on the electrons being inside the nucleus, as implied by the Dirac delta function $\delta (r_{KN})$.

To find the energies of the indirect nuclear moment couplings that take place via the electronic system, one may treat the parts of the above Hamiltonian depending on $I_N$ as a perturbation on the remainder, and carry the calculation to second order. Such a calculation of the coupling energy requires a knowledge of the energies and wave functions of the triplet states.
It has been shown that for protons only the Fermi contact term makes an important contribution to the coupling, and that magnetic dipolar and electron-orbital interactions may be neglected.\textsuperscript{7,16-30}

The perturbational calculation involves the summation of an infinite number of terms, but most theoretical interpretations have been based on an approximation of the original general equations, using an average excitation energy. In this approximation, only the ground-state wave function is required, and for this purpose both\textsuperscript{18} LCAO-MO and valence bond\textsuperscript{19,21} wave functions have been utilized.

Unlike the case of the proton spin couplings, not much real progress has been made in the prediction of F-F coupling constants, although a considerable number of such coupling constants have been determined experimentally. The most complete treatment of the problem is that by McConnell, who applied MO theory to the evaluation of the couplings in C\textsubscript{2}F\textsubscript{4}, and demonstrated that reasonable order-of-magnitude values could be obtained by considering the contribution from magnetic dipolar and electron-orbital terms.\textsuperscript{18} McConnell concluded that "nuclear spin coupling between pairs of nuclei other than protons present a much more complex problem from a theoretical point of view, because, in general, both one-electron orbital and two-electron orbital spin and orbital interactions make significant and sometimes comparable contributions to nuclear spin coupling."

Karplus attempted to interpret observed coupling constants in fluoroethylenes by considering only the contact term,\textsuperscript{25} although he suggested that F-F couplings are more complicated than the H-H coupling because terms other than the contact-electron spin interaction may make significant contributions. In this work, the long-range coupling constants (more than one chemical bond intervening) between fluorines in several saturated organic compounds are presented with a critical examination of the long-range coupling mechanism between nuclei processing non-s orbital electrons. Up to the present, it has been generally assumed that long-range couplings proceed through the bonds in a manner analogous to the proton couplings. However, it is shown
here that such long-range couplings take place primarily through space rather than through the bonds, as hitherto assumed. Previously "anomalous" experimental results are discussed and are shown to be consistent with through-space coupling. Although no detailed calculations have been carried out to establish the relative importance of the various pertinent terms in the Hamiltonian, it is shown that the orbital parts play an increasingly important role in the determination of the F-F couplings. These results can be easily generalized to molecules in which non-s electrons contribute appreciably to the bonding.
II. EXPERIMENTAL PROCEDURE AND INTERPRETATION OF SPECTRA

All spectra were run on a Varian HR-60 spectrometer at 56.4 Mc/sec. The samples were kindly provided by Dr. Klapper and Dr. Zeffert of the Army Chemical Center, Dr. Young of the University of Florida, and Dr. J.F. Harris of the duPont company; they were in the liquid phase and sufficiently pure so that no extraneous lines appeared. Although the temperature of the samples was not controlled in the insert, the magnet was insulated and the temperature of the room housing the whole apparatus was controlled at about $24^\circ\text{C} \pm 2$ or 3 degrees.

The coupling constants obtained, accurate to 0.5 cps, are tabulated in Table I, Part II. All the compounds listed gave first-order spectra, with the exception of small second-order perturbations of some of the intensities. The chemical shifts are as reported by Muller and co-workers, except for perfluoropropylamine for which compound they have erroneously interchanged the resonances of the two perfluoromethylene groups.

Figures 1, 2, and 3 show the spectra of perfluorodiethylamine, Compound 1. The observed spectra are compared with the calculated spectra based on the values of the coupling constants listed in Table I, Part II.

Figures 4 and 5 show the spectra of perfluorotriethylamine. The integrated signals were in the ratio of 6:9, corresponding to the methylene and methyl groups. The methylene signal has ten equally spaced components showing equal coupling for the adjacent methyl groups, and to the methyl groups across the central nitrogen through five chemical bonds. The methyl groups show seven equally spaced components, confirming the equal coupling to the methylene fluorines, through three and five chemical bonds. No observable splitting is expected from the interaction of the equivalent methylene atoms with each other. The same is true for the methyl groups. Figures 6 and 7 show the spectra of Compound 3. The integrated signals were in the ratio of 4:6, corresponding to perfluoromethylene and perfluoromethyl groups. The analyses of these spectra were unambiguous and yielded the values of $J$ listed in Table I, with equal coupling between the
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<th>Coupling constants (c/sec)</th>
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<td>1</td>
<td>(\text{CF}_3\text{-CF}_2) (\text{N-CF}_3) (\text{CF}_3\text{-CF}_2) (\text{CF}_3\text{-CF}_2)</td>
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<td>(\text{CF}_3\text{-CF}_2) (\text{N-CF}_2\text{-CF}_3) (\text{CF}_3\text{-CF}_2) (\text{CF}_3\text{-CF}_2)</td>
<td>(J_{ab} = 6.8) (J_{ab'} = 6.8)</td>
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<td>(\text{CF}_3\text{-CF}_2) (-\text{O-CF}_2\text{-CF}_3) (\text{CF}_3\text{-CF}_2) (\text{CF}_3\text{-CF}_2)</td>
<td>(J_{ab} = 1.7) (J_{ab'} = 1.7)</td>
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<td>(\text{CF}_3\text{-CF}_2) (-\text{COOH}) (\text{CF}_3\text{-CF}_2) (\text{CF}_3\text{-CF}_2)</td>
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<td>(\text{CF}_3\text{-CF}_2) (-\text{N}) (\text{CF}_3\text{-CF}_2) (\text{CF}_3\text{-CF}_2)</td>
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<td>J_{gauche} = 9.6</td>
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⁺See Ref. 33.
⁺⁺See Ref. 34.
⁺⁺⁺See Ref. 35.
⁺⁺⁺⁺See Ref. 36.
⁺⁺⁺⁺⁺See Ref. 37.
⁺⁺⁺⁺⁺⁺See Ref. 50.
Fig. 1. Part II. Experimental and theoretical fluorine resonance of \((\text{CF}_3-\text{CF}_2)_2-\text{N}-\text{CF}_3: (\text{CF}_3)_2\) group.
Fig. 2. Part II. Experimental and theoretical fluorine resonance spectrum of $(\text{CF}_3 - \text{CF}_2)_2 - \text{N} - \text{CF}_3 : (\text{CF}_2)_2$ group.
Fig. 3. Part II. Experimental and theoretical fluorine resonance spectrum of $(\text{CF}_3 - \text{CF}_2)_2 - \text{N} - \text{CF}_3$ : \text{CF}_3 groups.
Fig. 4. Part II. Fluorine resonance spectrum of 
\((CF_3 - CF_2)_3 N\): \((CF_3)_3\) group.
Fig. 5. Part II. Fluorine resonance spectrum of $(\text{CF}_3 - \text{CF}_2)_3\text{-N: (CF}_2\text{)}_3\text{ group.}$
Fig. 6. Part II. Fluorine resonance spectrum of \((\text{CF}_3 - \text{CF}_2)_2 - \text{O: (CF}_3)_2\) group.
Fig. 7. Part II. Fluorine resonance spectrum of 
$(\text{CF}_3 \cdot \text{CF}_2)_2 \cdot \text{O}: (\text{CF}_2)_2$ group.
perfluoro-methylene and the adjacent perfluoromethyl, and the perfluoromethyl across the central oxygen atom. Surprisingly, the coupling again through three chemical bonds is the same as through five chemical bonds.

Figure 8 shows the $^1H$ spectra of Compound 18, and illustrates the simplification achieved in the spectral analysis when the NMR spectra of two different nuclear species are available. One readily distinguishes the pattern of a symmetric triplet (due to the hydrogen $\beta$ to sulfur being split by a pair of geminal fluorines), and a pair of triplets (because the hydrogen $\alpha$ to the sulfur is split first into a doublet by the fluorine on the same carbon, and then each component is split into a triplet by the pair of $\beta$ fluorines). The components of the $\beta$ hydrogen are further split by the $\alpha$ fluorine (5.0 cps) and by the $\alpha$ hydrogen (2.5 cps). The components of the $\alpha$ hydrogen are of course also split by this last-mentioned interaction with the $\beta$ proton (2.5 cps). There are eight nonvanishing coupling constants in this molecule, and the proton spectra have yielded five of them.
Fig. 8. Part II. Proton resonance spectrum of CF₃-S-CF₂-CFH Cl.
III. F-F COUPLINGS

A. General Considerations

The problem of F-F coupling, as already pointed out, is certainly more complicated than the corresponding coupling between protons, because of the expected contribution to the coupling constant by the magnetic dipolar and electron-orbital terms in addition to the Fermi contact term. The Fermi interaction, proportional to \( |\psi (r = 0) |^2 \), makes the principal contribution to the coupling constant between protons, because electrons on a hydrogen atom are well represented by 1-s atomic orbitals. However, for non-s electrons, the Fermi term vanishes, and as a result, the other spin-coupling terms which depend on the presence of angle-dependent atomic orbitals become more important. Of course, it is hard to determine the relative importance of the different parts of the Hamiltonian discussed in the introduction, because the s and p characters of the bonding are not known. However, atomic p orbitals centered on F atoms contribute greatly to the bonding, while the p character of atomic orbitals centered on protons is generally considered small. Hence the expected increased importance of the angle-dependent terms in the fluorine couplings.

If the spins of the electrons around two nuclei A and B are entirely uncorrelated (as in the perfect-pairing approximation) then the nuclear spin coupling should vanish. \(^19, 38\) Effectively, then, long-range coupling may be considered as the formation of a long bond A-B. Indeed, Karplus and co-workers have stated that the numerical value of the coupling constant between nonbonded protons is directly related to the deviations from perfect pairing; and Hiroike\(^23\) has shown for protons that \( J_{AB} \) is linearly related to the weight of structures involving a long bond A-B. In saturated molecules, the coupling constants between protons \( J_{AB} \) diminish rapidly with the number of intervening chemical bonds between the interacting nuclei. McConnell has suggested an attenuation factor of 10 for each additional intervening bond. \(^18\)
Qualitatively, one can readily account for all F-F coupling constants in saturated compounds so far investigated if one assumes that the major contribution to the coupling constants comes about as a result of a direct through-space coupling rather than coupling through the bonds. The existence of nonvanishing coupling constants between fluorines separated by several chemical bonds is not only consistent with direct through-space coupling, but it also favors such a mechanism (nonvanishing coupling constants through 5 and 6 chemical bonds have been observed repeatedly). The large excursion of the $p$ electrons centered on fluorine atoms make it reasonable to assume that direct through-space coupling could be significant in F-F coupling constants, and not significant in H-H coupling constants. Similar arguments would apply to couplings between other atoms which have non-$s$ electrons. Direct through-space coupling of two nuclei A and B, separated by two or more bonds, may take place either through one-electron or two-electron interaction. Physically, the one-electron part arises because nucleus A interacts magnetically with an electron, which in turn interacts with nucleus B (nuclear moment A: electron: nuclear moment B); the two-electron part arises because nucleus A induces a perturbation on a local electron, which in turn interacts directly with an electron on nucleus B, which then interacts magnetically with nucleus B (nuclear moment A: electron1: electron 2: nuclear moment B).

B. Near-Zero Coupling Constants

In 1956, Saika and Gutowsky reported a near-zero coupling constant between the fluorine atoms on adjacent carbon atoms in the F$^{19}$ NMR spectrum of CF$_3$-CF$_2$-N-(CF$_3$)$_2$. This appeared anomalous to them, since fluorine-fluorine coupling constants were known to be large, and particularly since the coupling constant between the fluorine atoms in the two nonequivalent perfluoromethyl groups was found to be 6 cps. Since that time, several other similar cases
have been reported in the literature. Furthermore, it has been generally assumed that the restrictions upon rotation are responsible for these near-zero coupling constants. This idea was originally presented in the literature by Crapo and Sederholm.39

These near-zero coupling constants appear in many cases between fluorine atoms on adjacent saturated carbon atoms. These cases fall into two classes, one in which relatively free rotation is allowed about the carbon-carbon bond, and another in which rings limit the free rotation about the carbon-carbon bond. However, there seems to be no set type of molecule that always yields a near-zero coupling constant. For instance, in Compounds 1, 2, 3, and 4 the coupling constants between the CF3 group and the adjacent CF2 group are nonvanishing, whereas the coupling constants between the CF3 group and the adjacent CF2 group are nearly zero in a whole host of compounds. It has been assumed that the near-zero coupling constants come about as a result of averaging nonzero coupling constants over the three stable configurations with respect to rotation about the connecting carbon-carbon bond. Owing to the common occurrence of this phenomenon, if this explanation is valid, one must assume that the coupling constant does not vary much from compound to compound, but is only a function of the dihedral angle, as in the case of hydrogen. However, this would lead one to predict that the coupling constants in all compounds having the CF3-CF2-group would be nearly zero, which is not the case. Hence, it appears that the near-zero coupling is not explained by any accidental mutual cancellation of the coupling constants averaged over three staggered configurations.

In terms of the various contributions to the coupling constant, one might assume that these vanishing coupling constants are the result of mutually canceling interactions (one- and two-electron integrals of the same order of magnitude but of opposite sign). This, however, seems unreasonable, because: (a) the appearance of the near-zero couplings is rather widespread, and an accidental mutual cancellation.
to better than 1 cps of contributing interactions, each of which is probably several cps, seems highly unlikely; and (b) this explanation does not account for the appearance of similar anomalous couplings in several other systems structurally unrelated to the perfluoroethyl groups. For example we have

\[ J_{\text{C}^{13}}^{\text{CH}} = 4.1 \text{ cps} , \]

as compared with

\[ J_{\text{C}^{13}}^{\text{C}^{13}-\text{C}^{13}} = 5.1 \text{ cps} \]

in diisopropylketone. Similar anomalous results have been recorded for lead tetraethyl, where

\[ J_{\text{CH}_2}^{\text{Pb}} = 42 \text{ cps} \]

compared with

\[ J_{\text{CH}_3}^{\text{Pb}} = 142 \text{ cps} \]

there are like examples for several mercury compounds. Such results have usually been dismissed as anomalous, since they are inconsistent with through-the-bonds coupling and do not show the expected monotonic decrease with the number of intervening bonds. A more likely explanation of the anomalous coupling constants can be given in terms of through-space coupling.

The near-zero coupling constants always occur between fluorine atoms on adjacent carbon atoms. Such fluorine atoms are held apart in space by the bonding. If all bonding is tetrahedral, the carbon-carbon bond distance is 1.54 angstrom units, and the carbon-fluorine bond distance is 1.33 angels, and assuming that the staggered configurations are the favored ones, the closest fluorine-fluorine approach between the two sets of fluorine atoms in the CF\(_3\)-CF\(_2\) or
R-CF₂-CF₂-R' group is 2.73 Å. It is proposed that the coupling through the bonds is small, in contradistinction to the case in the hydrogen analogs; that such through-the-bonds coupling diminishes rapidly with increasing number of intervening bonds; that in coupling between fluorines the main contribution is directly through space; that 2.73 Å is too great a distance to result in an observable through-space contribution; and that 2.73 Å is just outside the distance at which through-space coupling becomes important (it is reassuring to note that the distance at which the coupling approaches zero is equal to the sum of the Van der Waal radii of the two interacting fluorine atoms). One can then readily see that a small change in the C-C-R bond angle would result in closer stable distances between the adjacent fluorine atoms, and thus also in an observable coupling constant. This opening of the C-C-R angle can be brought about by steric hindrance, if R is sufficiently bulky.

C. Dependence of F-F Couplings on Internuclear Distance

Figure 9 is a plot of the coupling constants between fluorines in various structural groups vs the internuclear distance between the magnetically interacting fluorines. For structures involving free rotation, the constants plotted are "derived" from the observed coupling constants by considering all the staggered configurations that the two interacting groups may assume relative to each other. The internuclear distance between gem-fluorines in perfluoro-cyclohexane, assuming tetrahedral angles and normal bond distances, is 2.17 Å. The coupling \(^{67}\) is 284 cps. For perfluorocyclobutane the gem-fluorine distance is again 2.17 Å and the average coupling constant of several substituted cyclobutanes \(^{47}\) is 211 cps. The near-zero coupling between 1, 2 fluorine atoms separated by approx 2.73 Å in two of the three possible staggered configurations leads one to assign a value of zero to \(J\) for fluorine atoms separated by this distance. Next we consider the coupling constant between 1, 3 fluorines (fluorines
Fig. 9. Part II. Plot of $^{19}$F spin coupling constants as a function of internuclear distance between interacting nuclei.
on skeletal atoms which are β to each other). In two of the nine possible staggered configurations of the -CF₂-ÇF₂-ÇF₂- groups the 1,3 fluorines are closer to each other than the closest stable distance between 1,2 fluorines. Calculated on the basis of the staggered configurations and the above bond distances and angles, the 1,3 fluorine-fluorine distance in these two configurations is 2.51 Å.

The other seven configurations yield F-F distances 2.73 Å, and correspond to zero coupling. We weight all nine of these possible configurations equally, although there may be some small barrier against configurations not corresponding to a zigzag skeleton. On this basis, the coupling constant between 1,3 fluorine atoms should be 9/2 × 12 = 54 if all nine configurations were contributing equally to the coupling constant.

One may extend this calculation with less precision to the 1,4 fluorine coupling constants. These fluorine atoms are separated by five bonds and probably are essentially not coupled through the bonds. In as crude a calculation as this, one cannot hope to tell the difference between a nitrogen atom in the chain with 90-deg bond angles, and a carbon atom in the chain with 109.5-deg bond angles. The calculation is again made for an all-carbon chain with tetrahedral angles, but it should be about the same if a nitrogen takes the place of one of the chain carbon atoms. Again, taking the staggered configurations as the stable ones, there are 27 different relative positions for a pair of fluorines on the 1 and 4 carbon atoms. All the distances between the fluorines are greater than 2.73 Å, except for four configurations in which the distances are 1.76 Å (two cases), and 2.46 Å (two cases). Certainly, the two configurations corresponding to the 1.76 Å cannot exist as preferred configurations, because of the close fluorine-fluorine approach. In order to increase this distance, one must rotate about some of the carbon-carbon bonds. This should be relatively easy to do. It seems reasonable that rotation will occur about the carbon-carbon bonds until the fluorine atoms come to a distance of approx 2.5 Å, or 0.2 Å less than the van der Waals radii. This rotation
lengthens the 2.46-A fluorine-fluorine distance to a distance greater than 2.73 Å and therefore these configurations can be neglected in the calculation. The two contributing configurations have a weight of $2/27$, and therefore the coupling constant for 1,4 fluorines should be $(27/2) (5.2 \approx 70$ cps.

Thus, it appears that the coupling between two magnetic nuclei is a very sensitive function of the internuclear distance. Of course, it would be naive to assume a complete, simple correlation between $J_{FF}$ and internuclear distance $D_{FF}$, for one would be neglecting the obviously important dependence of $J$ on other structural factors. For instance, the gem-fluorine-fluorine distances in the series $C_3F_6$, $C_4F_8$, and $C_6F_{12}$ are nearly equal, and yet the geminal coupling constants vary by a factor of two in this series. On the other hand, through-space coupling is both useful and reasonable, particularly where non-$s$ electrons are available. In this case, one can certainly expect direct through-space interaction to be more effective than the through-the-bonds "telegraphed" interaction, which would require cooperative coupling of many bonding electrons.

D. F-F Couplings in $CF_2X-CFYZ$ Molecules

Direct through-space coupling can also offer an explanation as to why, in compounds with the general formula $CF_2X-CFYZ$, the two coupling constants between the gem-fluorines and the third fluorine atom are almost the same. $36, 37$ Nair and Roberts $49$ have suggested that in all such cases there is a rapid interconversion among the three non-equivalent rotamers, but such rapid interconversion would not average the chemical shift between the gem-fluorines "unless the residence times of the molecule in each of the various rotational conformations are equal." Moreover, the observed chemical shifts and coupling constants would be the time-weighted averages over the three rotamers. In such a case, because of the relative magnitudes involved, we see the
chemical shift as a much more sensitive function of the relative population of the rotamers. A change of a few percent in the population would result in a change in the chemical shift of several hundred cps, but only about 1 cps change in the coupling constant.

At room temperature, the difference in depths of the three potential minima is probably small enough so that approximately equal population of the three rotational isomers is a good approximation. Direct through-space coupling predicts a zero coupling constant between the trans-fluorine atoms, but a small constant \( J_g \) between gauche fluorine atoms. An almost equal population of the three rotational forms, while preserving the nonequivalence of the gem-fluorines, would result in almost equal coupling constants, as observed—approximately \( 2/3 J_g \).

E. Discussion of Individual Molecules

In Compound 5, the coupling constants are what would be expected on the basis of the model presented, the 1, 2 fluorine atoms being coupled by \(< 1\) cps, the 1, 3 fluorine atoms being coupled by 16 cps, and the 1, 4 fluorines being coupled by 6 cps. In Compound 1, the coupling constants are also similar to Compound 5 except for the coupling between the 1, 2 fluorine atoms. That coupling here has gone up to 5.1 cps. This might be anticipated from a model of the compound, since there is a large number of atoms crowded around the central nitrogen atom. This tends to increase the C-C-N bond angle, throwing the 1, 2 fluorine atoms closer to each other and increasing the coupling constant. One might expect this effect to be even more pronounced in Compound 2, where another perfluoroethyl group is taking the place of a perfluoromethyl, and indeed this is the case. Here, the 1, 2 fluorine coupling constant has gone up to 6.8 cps, which would imply an expected further increase in the C-C-N angle.

In Compound 3, the 1, 2 coupling constant is again nonvanishing, because of opening of the C-C-O bond angle owing to steric hindrance between the two ends of the molecule. Note that here the 1, 2 coupling
constant is less than in Compound 1, since the extra perfluoromethyl group is absent, and so does not yield as great an amount of steric hindrance. Also, the 1, 4 coupling constant is about what it is in Compound 6, and less than in Compounds 1 and 2. A tertiary nitrogen in the chain certainly throws the 1, 4 carbon atoms closer together than a secondary oxygen in the chain.

In Compound 4 the coupling constant is small, but nonzero. This may come about through the bonds, although there may also be a small opening of the C-C-C bond angle due to the steric repulsion between the methyl group and the carboxyl group. Compound 7 gives results very similar to this, with the 1, 3 fluorine coupling constant slightly less than the 1, 3 fluorine coupling constants in Compounds 1 and 5. This is expected, since in Compounds 1 and 5 an intermediate chain atom is a nitrogen atom with approximately 90-deg bond angles, whereas in this compound all intermediate chain atoms are carbon atoms with 109.5-deg bond angles, thus throwing the 1, 3 fluorine atoms further apart. It is not readily apparent why the 1, 2 coupling constant in this compound is smaller than in Compound 4; however, the difference is minor and the electronic structure has undoubtedly changed substantially in this area of the molecule. In Compound 8 the coupling constants are very similar to Compound 7. The decrease in the 1, 3 fluorine atom interaction is reasonable, since the added methyl group interferes with the perfluoromethyl group, partially opening up the bond angle between the α, β, and γ carbon atoms, and so taking the 1, 3 fluorine atoms further apart. Compound 6 gives very similar results to this. Again, it should be noted that the 1, 3 fluorine atom coupling constant is smaller when all the intermediate atoms are carbon atoms than when one of them is a nitrogen atom.

Compound 9 again shows two different kinds of 1, 2 coupling constants, a near-zero one that results from normal bond angles; and one equal to 14.6 cps probably resulting from the steric repulsion between the Cl and I atoms and the adjacent CF₂ group, thus throwing the two sets of fluorine atoms closer together. The 1, 3 coupling constant is quite normal. Compound 10 shows a large 1, 2 coupling,
again due to the steric repulsion of the three CF₃ groups, bringing each of them closer to the lone fluorine atom.

The spectra of Compound 11 were reported by G. V. D. Tiers in connection with an isotopic substitution investigation. The two near-zero coupling constants were inferred from his paper. The near-zero coupling assigned to the 1, 2 coupling is quite reasonable; however, on the basis of the other compounds we have investigated, the near-zero coupling between the 1, 3 fluorine atoms seems highly unlikely.

The spectra of Compounds 12 and 13 are in general broad and only a few coupling constants can be determined. These constants are consistent with coupling constants in similar compounds. Moreover, from the width of the unresolved peaks one can set an upper limit of about 6 cps on all other undetermined coupling constants. From the model discussed here, one would expect near-zero coupling constants for all pairs of fluorines except the 1, 3 axial-axial fluorines. In one of the two canonical chair forms, these fluorines are closer than 2.73 Å, and should give an observable coupling. However, a slight flattening of the ring would rapidly increase the internuclear distance to more than 2.73 Å, corresponding to a near-zero coupling constant.

When the ring is reduced to five members, as in Compound 14, fluorine atoms on adjacent carbon atoms are still not coupled, but fluorine atoms removed by one more bond are capable of getting closer together, and therefore are slightly coupled. The 1, 4 coupling constants across the nitrogen atom between the side chain and ring are quite normal. The 1, 3 coupling constants across the nitrogen atom between the side chain and ring are somewhat smaller than usual, but the geometry of the strained ring system may keep these two sets of atoms further apart than they would be in an unrestrained linear chain. It is reassuring to note that the coupling constants across the nitrogen atom are the same to each of the two sets of ring fluorines adjacent to the nitrogen atom. This would be expected if it is indeed a through-space coupling, since these two sets of atoms occupy similar positions in space with respect to the perfluoroethyl group. However, the electronic structure in the two N-C bonds should be somewhat different.
because of the asymmetrically placed oxygen atom, and hence if the coupling were through the bonds one would expect a different coupling constant between the nonring fluorines and these two sets of ring fluorines.

In Compound 15, the four-membered ring certainly holds the two sets of fluorine atoms far enough apart to yield a near-zero coupling constant, which is observed. It is to be noted that in this case the fluorines are probably locked into the nearly eclipsed configuration whereas, in the six-membered rings, the fluorine atoms are restrained to two of the three staggered configurations. All of these cases result in near-zero coupling constants. It is hard to imagine any kind of function of $J$ vs dihedral angle such that the average of the three staggered configurations would yield zero, the average over the two gauche staggered configurations would yield zero, and the value of the coupling constants corresponding to eclipsed and 120-deg angles would be zero, except for the trivial case in which the coupling constant is zero for all dihedral angles. Therefore, this set of examples implies again that averaging over various dihedral angles has little to do with the near-zero coupling constants.

In Compounds 16 and 17 the 1, 2 coupling constants are nonzero, probably because of shortening of the fluorine-fluorine distance due to steric effects caused by the other halogens present.

The lengths of C-N and C-O bonds are within a few percent of the C-C bond length (7%), while the C-S bond is approximately 20% longer than the C-C bond. However, there is no a priori reason why the interaction between fluorines across a sulfur atom should not show dependence on internuclear distance similar to that exhibited by the other molecules. The coupling constants obtained for Compounds 18 and 19 seem to confirm this. The proton-proton and fluorine-proton coupling constants are comparable to those obtained for other systems.

The $J_{1,3}$ coupling constants, as expected, are larger than the corresponding $J_{1,4}$ constants, although the two $J_{1,3}$ constants differ in absolute value by a factor of about two. Of course, in Compound 19
the $J_{1,3}$ is larger, but it is doubtful that the chlorine atom on the carbon $\beta$ to sulfur is sufficiently bulky to open the S-C-C bond angle enough, and thus throw the 1, 3 fluorines spatially close together, to account for the large increase of $J_{1,3}$ over the corresponding constant in Compound 18.

The coupling constants reported for Compound 20, finally, seem to confirm again the importance of through-space coupling between fluorines. Gauche fluorine atoms are closer spatially than trans atoms, and therefore they interact more strongly. These results are in contradistinction to the established mechanism between protons.24
IV. SUMMARY

The spectra of fluorine-substituted saturated organic compounds have been investigated. It has been found that the coupling constants between 1, 2 fluorine atoms are usually near zero. The coupling constants between 1, 3 fluorine atoms in a free chain are usually between 7 and 10 cps if all of the intermediate skeletal atoms are carbon atoms. If one of the intermediate skeletal atoms is a nitrogen atom, these coupling constants go up to between 10 and 17 cps. The coupling constants between 1, 4 fluorine atoms are usually in the range 2 to 7 cps when a nitrogen atom is in the intermediate skeletal chain.

A critical examination of the "long range" mechanism (more than two chemical bonds intervening) of spin-spin interaction between fluorine atoms is given. For the coupling between protons it has been shown by many authors that only the Fermi-content interaction is important, and that magnetic dipolar and electron orbital interactions may be neglected. Moreover, "long range" coupling has been considered generally to take place through the bonds—actually the interaction being "telegraphed" through the cooperative coupling of bonding electrons. Although no real progress has been made in the discussion of the coupling mechanism between fluorines, it is generally assumed to resemble closely the coupling mechanism between protons. However, in this work, data are presented to support the notion that magnetic dipolar and electron orbital terms must play an important part in the coupling mechanism between fluorines, and that "long range" coupling takes place directly through space rather than through the bonds. Atomic p orbitals centered on F atoms are generally assumed to contribute greatly to the bonding, and the large excursions of these p electrons make it reasonable that direct through-space coupling could be significant in F-F coupling constants and not significant in H-H coupling constants.
Effectively, then, long-range coupling may be considered as the formation of a long bond between the two nuclei A and B, and the greater the spatial proximity the stronger the coupling. Indeed, the F-F experimental coupling constants from various unrelated structural systems diminish smoothly with internuclear distance, and vanish at about the sum of the van der Waals' radii of the interacting fluorines.

It is shown that direct through-space coupling can explain a series of hitherto anomalous coupling constants. For example, coupling through five chemical bonds in perfluoroethyl dimethyl amine is greater than coupling through three chemical bonds. However, substitution of bulkier groups throws the normally distant fluorines closer together through steric interference, and causes the coupling constants to become larger. Direct through-space coupling is also shown capable of explaining "anomalous" coupling constants in other structurally unrelated systems, and reveals why in compounds with the general formula CF₂X-CFYZ the two coupling constants between the gem-fluorines and the third fluorine atom are almost the same. Finally, direct through-space coupling seems capable of being extended with ease to other systems where angle-dependent orbitals may contribute appreciably to the bonding.
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FOOTNOTES AND REFERENCES

8. See also for a discussion of Ramsey's mechanism: A. Abragam,
   Nuovo cimento Suppl. 6, 1015 (1957).
9. J.A. Pople, W.G. Schneider, and J.H. Berstein, High-Resolution
   Nuclear Magnetic Resonance (McGraw-Hill Book Company, Inc.,
   New York, 1959), Chap. 8.
10. H.A. Bethe, in Handbuch der Physik, Vol. 24/1 (Verlag von
11. N.F. Ramsey, Nuclear Moments (John Wiley and Sons, Inc.,
     New York, 1953).
    and Solids, (Associated Students, University of California, 1959).
    135 (1951).
    (1959); 34, 1049 (1961).
18. H.M. McConnell, J. Chem. Phys. 24, 460 (1956); ibid. 33, 720
    (1960); J. Mol. Spectroscopy 1, 11 (1957).
32. Henceforth all compounds will be referred to by their serial numbers as listed in Part I of this thesis, Table IV.
35. Pople, Schneider, and Bernstein: Ref. 9, p. 333.
45. All bond distances and angles have been obtained from Tables of Interatomic Distances and Configurations in Molecules and Ions, Special Publication No. 11, The Chemical Society, London, (1958).
48. There is some evidence that these configurations are not the stable ones, but the structural data are not sufficient to warrant their use over the tetrahedral assumption — G. W. Bunn and G. R. Howells, Nature 174, 549 (1954).
50. R. K. Harris, (University Chemical Laboratory, Cambridge, England), private communication.
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