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Proton and fluorine N.M.R. spectra of fluorobenzene†

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Proton and fluorine resonance spectra of fluorobenzene have been obtained under high resolution using a Varian spectrometer operating at 100 Mc/s and 94.1 Mc/s respectively. These have been analysed by treating the molecule as a six-spin system of the type $AB_2C_2X$ with $C_{2v}$ symmetry. The best parameters available were used to solve the secular equation using an IBM 1620 computer. Carbon tetrachloride, chloroform, dioxan and benzene were used as solvents and spectra were obtained at different concentrations. Both $^1H$ and $^{19}F$ spectra show concentration dependence. Splittings of the spectra due to the natural abundance of $^{13}C$ were observed. The coupling constants $J_{13C-H}$ and $J_{13C-F}$ have the values $160.0 \pm 2.0$ c/s and $265.5 \pm 2.0$ c/s respectively.

1. INTRODUCTION

A partial analysis of the nuclear magnetic resonance spectra of fluorobenzene was reported earlier by Fujiwara and Shimizu [1]. Bak, Shoolery and Williams [2] investigated deuterated species of fluorobenzene and particularly analysed the fluorine spectrum of 4-D-fluorobenzene. Since the para H–F coupling is negligibly small, one expects identical fluorine spectra for fluorobenzene and 4-D-fluorobenzene. However Bak et al. obtained, at 30 Mc/s, a fluorine spectrum of fluorobenzene different from that of the 4-D-fluorobenzene and discussed it qualitatively. Fujiwara and Shimizu analysed the proton spectrum of fluorobenzene at 27.03 Mc/s. The present work was undertaken to perform a complete analysis of the spectra at a higher resolution with the hope of getting better parameters. We report here both the proton and fluorine spectra of fluorobenzene at 100 Mc/s and 94.1 Mc/s respectively. In addition to the analysis, solvent effects and $^{13}C$ splittings on both $^1H$ and $^{19}F$ resonances have been observed.

2. EXPERIMENTAL

The spectra were all obtained at room temperature ($25^\circ C$) using a Varian HR–100 spectrometer. The separations of resonance peaks were measured in cycles per second using side band technique. Fluorobenzene was obtained from L. Light and Co. Ltd., England, and had the highest commercially available purity (99 per cent). Nitrogen gas was bubbled through all the samples (before sealing) to remove dissolved oxygen.

† A part of the work reported in this paper was presented at the 1966, Nuclear Physics and Solid State Physics Symposium, held at the Tata Institute of Fundamental Research, Bombay, 21–26 February.
3. DISCUSSION

3.1. Analysis of the spectra

Fluorobenzene is a six-spin system of the type $AB_2C_2X$. It has $C_{2v}$ symmetry. The spin Hamiltonian for the case where a static magnetic field $H_0$ is applied to the system in the $z$ direction, is given by (in units of c/s):

$$\mathcal{H} = \frac{1}{2\pi} \sum_{i=\Lambda}^{x} r_i H_0 (1 - \sigma_i) I_d(i) + \frac{1}{2} \sum_{i,j=\Lambda} J_{ij} (1 - \delta_{ij}) I_i \cdot I_j,$$

where $r$, $\sigma$, $I$, $J$ and $\delta$ are nuclear magnetogyric ratio, nuclear screening constant, nuclear spin, spin coupling constant and Kronecker delta function respectively. This system has sixty-four ($2^6$) basic symmetric functions. These symmetry functions are given by Fujiwara and Shimizu [1] and have been used here. The matrix elements of the Hamiltonian constitute a sixty-fourth order secular equation:

$$|\mathcal{H}_{mn} - \delta_{mn} \lambda_n| = 0,$$

whose solutions are the energies. However, this reduces into four each $1 \times 1$, $2 \times 2$, $3 \times 3$, $4 \times 4$ and $6 \times 6$ dimensional sub-matrices if one considers the symmetry of the molecule and the fact that the $z$ component of the total spin

$$F_z = \sum_i I_d(i)$$

and that of the fluorine spin commute with $H$. The eigenvalues and the eigenvectors cannot be written in explicit analytical form. One has to solve these higher order equations with the help of a computer. The system has a total of 416 transitions of which there are 40 each of $A$ and $X$ transitions and 48 each of $B$ and $C$ transitions and the rest are combination lines almost all of which are very weak in intensity.

The Hamiltonian $H$ of the system is diagonalized by the computer to get its eigenvalues $\lambda_n$ and eigenvectors $\varphi = UX$ where $X$ are the basic symmetry functions and $U$ a unitary matrix which diagonalizes the total Hamiltonian. The intensity is proportional to the elements of the matrix $I_n$ defined by:

$$(I_n)_{ij} = |\langle \varphi_i | I_x | \varphi_j \rangle|^2,$$

where $I_x$ is the sum of $x$ components of all the nuclear spins of the system. Using $\varphi = UX$:

$$(I_n)_{ij} = \left| \sum_{ik} U_{it}^* M_{tk} U_{jk} \right|^2 = |(UMU^t)_{ij}|^2,$$

where $M_{tk} = \langle \chi_t | I_x | \chi_k \rangle$, trace $M = 0$ and $M_{tk} = M_{kt}$.

3.2. Proton and fluorine resonance spectra

The proton resonance spectrum (figure 1) spreads over 47 c/s approximately at 100 Mc/s resonance frequency. The zero position on the spectrum corresponds to the ortho protons. The spectrum is extremely complicated and involves a large number of transitions. Bak et al. [2] have observed meta protons at the lowest applied field in 4-D-fluorobenzene. Thus ortho protons occur at a higher applied field. The position of the para proton is found by adjusting the chemical shift parameters. Best fit between the experimental and theoretical lines (figure 2) shows that the chemical shift between ortho and para protons is zero. The
fluorine resonance spectrum spreads over 34 c/s approximately at 94.1 Mc/s resonance frequency. It shows very little similarity with that reported earlier by Bak et al. [2]. This may be due to the low resolution (30 Mc/s) at which they studied. The present spectrum clearly shows asymmetry about the centre
around ±7 c/s and ±14 c/s which arises from combination lines due to the
presence of strong coupling between protons. The observed and the calculated
spectra for fluorine are shown in figures 3 and 4 respectively.

3.3. Signs of the coupling constants

The sense of the asymmetry in the fluorine spectrum depends on the relative
sign of the proton–proton and proton–fluorine couplings. The sense is reversed
in the spectrum by changing the sign of \( J_{0}^{HH} \) and \( J_{m}^{HH} \) and no solution with
\( J_{m}^{HH} \) having a sign opposite to \( J_{0}^{HH} \) fits the spectrum. A similar effect is found
with \( J_{m}^{HF} \) and \( J_{0}^{HF} \) couplings. The H–F couplings are found to have the same
sign as the H–H couplings. Attempts were also made to find out if the values for
the para couplings (\( J_{p}^{HH} = 0 = J_{p}^{HF} \)) are different from zero. It was difficult to
draw conclusions about these coupling constants from the agreement between the
calculated lines with observed spectra since the spectra are complicated. The
final results are given in table 1, for the best fit. These values agree well with
the values obtained by earlier workers [1, 2].

| \( J_{0}^{HH} \) = 8.9 c/s | \( J_{0}^{HF} \) = 9.4 c/s | Chemical shift between ortho and
| \( J_{m}^{HH} \) = 2.2 c/s | \( J_{m}^{HF} \) = 5.8 c/s | meta protons = 18.0 c/s
| \( J_{p}^{HH} \) = 0.0 c/s | \( J_{p}^{HF} \) = 0.0 c/s | Chemical shift between ortho and
| | | para protons = 0.0 c/s

Table 1. The coupling constants and chemical shifts of fluorobenzene.

4. Solvent effect

Carbontetrachloride, chloroform, benzene and dioxan have been used as
solvents. The resonance spectra were obtained at different percentages of
concentration (by volume). The separation of the ortho protons in the proton
spectrum and the centre of gravity of the fluorine spectrum from the respective
reference lines has been taken to be the chemical shift (\( \delta \)). The zero position,
which is approximately 8 c/s up-field from the highest peak in the proton resonance
spectrum in figure 1, corresponds to the ortho protons. The proton shifts were
measured relative to cyclohexane as an internal reference and the fluorine shifts
were measured relative to difluoroacetic acid as an external reference. In both
the cases, the reference signals appeared at higher fields. Figures 5 and 6 show
the variation of chemical shift with dilution for proton and fluorine resonances
respectively. In each case, the plot gives a straight line or a smooth curve which
is extrapolated to give the chemical shift at infinite dilution. The results are
given in table 2.

Contributions to nuclear screening can arise due to (i) bulk diamagnetic
susceptibility of the medium (\( \sigma_{b} \)), (ii) anisotropy in the magnetic susceptibility of
the solvent molecules (\( \sigma_{b} \)), (iii) distortion of the solute molecule by interaction
with the solvent molecules through van der Waals type forces (\( \sigma_{W} \)), (iv) distortion
of the solute molecule by an electric reaction field (polar effect, \( \sigma_{E} \)), (v) hydrogen
bonding and (vi) other molecular association effects. The first four of these
effects have been considered theoretically by Buckingham et al. [3]. The greatest
Table 2. Proton and fluorine chemical shifts at infinite dilution (corrected for bulk susceptibility). Accuracy is within ±0.02 p.p.m. Negative sign indicates the signal occurs at lower field with respect to the reference line.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>Ortho-proton shift p.p.m. from cyclohexane</th>
<th>Fluorine shift p.p.m. from difluoroacetic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorobenzene</td>
<td>Pure</td>
<td>-5.495</td>
<td>-15.445</td>
</tr>
<tr>
<td></td>
<td>CCl₄</td>
<td>-5.755</td>
<td>-17.271</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>-5.760</td>
<td>-16.133</td>
</tr>
<tr>
<td></td>
<td>C₆H₆</td>
<td>-5.365</td>
<td>-15.880</td>
</tr>
<tr>
<td></td>
<td>C₄H₈O₂</td>
<td>-5.680</td>
<td>-15.115</td>
</tr>
</tbody>
</table>

Figure 3. The fluorine resonance spectrum of fluorobenzene at 94.1 Mc/s.

Figure 4. Calculated fluorine resonance spectrum of fluorobenzene at 94.1 Mc/s.
Figure 5. Solvent-dilution shift of the proton resonance signal of fluorobenzene. Chemical shifts $\delta$ are referred to cyclohexane as an internal reference at 100 Mc/s.

The single uncertainty in the chemical shifts comes from the bulk susceptibility correction. Change in chemical shift due to this is:

$$\Delta \delta = \frac{2\pi}{3} (\chi_v, \text{ref} - \chi_v) = \frac{2\pi}{3} \Delta \chi_v$$

(for cylindrical samples), where $\Delta \chi_v$ = difference in bulk susceptibility of reference and pure liquid. For solutions of varying concentrations, measured with respect to an external reference, the bulk susceptibility required is weighted according to the volume fractions [4] given by:

$$\chi_v, \text{mixture} = \phi_1 \chi_{v1} + \phi_2 \chi_{v2},$$

where $\phi_1$ and $\phi_2$ are the volume fractions of the components and $\chi_{v1}$ and $\chi_{v2}$ are their volume susceptibilities.
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Figure 6. Solvent-dilution shift of the fluorine resonance signal of fluorobenzene. The chemical shifts $\delta$ (corrected for bulk susceptibility) are relative to difluoro-acetic acid as an external reference at 94.1 Mc/s.

Volume susceptibility of CF$_3$HCOOH is not available in the literature. We have determined it experimentally by the Quincke method [5] using an Alpha Scientific Laboratories, Inc., Berkeley, magnet Model AL 7500 with a Varian Model F-8A nuclear fluxmeter. The value is found to be $-0.535 \times 10^{-6}$ as against $-0.464 \times 10^{-6}$ determined by Pascal's constants. The experimental value is used in this paper for bulk susceptibility corrections. Bulk susceptibility correction is zero for proton shifts since cyclohexane is used as an internal reference here. The values for proton and fluorine shifts after these corrections are given in table 2.

Usually contributions to nuclear screening due to $\sigma_b$ and $\sigma_w$ are negative and $\sigma_R$ and $\sigma_a$ can be either positive or negative [3]. Thus the major contribution to the screening is negative and hence resonance occurs at lower applied fields.
with dilution. But the proton resonance shifts to the higher field with respect to pure sample with dilution when benzene is solvent (figure 5). This can be explained by the fact that \( \sigma_a \) is positive for disc shaped solvents like benzene [3] and environment of aromatic molecules tends to lead to an increased solute screening constant in aromatic solvents like benzene [3, 4]. Similarly fluorine resonance shifts to the higher field with dioxan as solvent (figure 6); this is possibly due to positive \( \sigma_E \).

Fluorine resonance shows larger solvent effects. This is probably because distortion due to polarization (and other intermolecular interactions) will have greater effects on the fluorine than on the proton screening constants since more electrons are involved in the former. Also the largest shifts appear with solvents containing heavy halogen atoms as in the case of CCl\(_4\) and CHCl\(_3\) (figure 6). Glick and Ehrenson [6] have also made similar observations in other compounds. These could be approximately correlated with the molecular polarizability of the solvent molecules.

5. \(^{13}\text{C}–\text{H}\) AND \(^{13}\text{C}–\text{F}\) COUPLING CONSTANTS

Splittings of the \(^1\text{H}\) and \(^{19}\text{F}\) resonance spectra due to \(^{13}\text{C}–\text{H}\) and \(^{13}\text{C}–\text{F}\) spin–spin coupling constants are observed due to the natural abundance of \(^{13}\text{C}\) (1\% per cent). These signals are weak due to low abundance and are observed with r.f. fields considerably higher than usual. The values of the coupling constants are found to be \( J_{^{13}\text{C}–\text{H}} = 160 \pm 2 \) \(\text{c/s} \) and \( J_{^{13}\text{C}–\text{F}} = 265.5 \pm 2 \) \(\text{c/s} \). These splittings are due to coupling between \(^{13}\text{C}\) with \(^1\text{H}\) and \(^{19}\text{F}\) in the nearest position. Muller and Pritchard [7] using a semi-empirical formula for \(^{13}\text{C}–\text{H}\) coupling which is given by:

\[
J_{^{13}\text{C}–\text{H}} = J_0 a^2 b^5,
\]

have found the \( J_{^{13}\text{C}–\text{H}} \) constants for aromatic bonds lie in the range 154.0 to 160.0 \(\text{c/s} \). The present result agrees well with this theory.

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References