

# HALOGEN NUCLEAR MAGNETIC RESONANCE SHIFTS

## Part I. $\text{Cl}^{35}$ Resonance in Alkali Chlorides

BY PUTCHA VENKATESWARLU, F.A.SC. AND B. D. NAGESWARA RAO\*

(*Department of Physics, Muslim University, Aligarh*)

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### ABSTRACT

The nuclear magnetic resonance shifts (chemical shifts) of  $\text{Cl}^{35}$  in aqueous solutions of alkali chlorides were determined using a High Resolution NMR Spectrometer. These small shifts probably represent the effect of the neighbouring atom even in the highly ionic state. A similarity of these results to the quadrupole coupling constants of the halogen atom in these molecules is pointed out.

### INTRODUCTION

DETERMINATIONS of nuclear magnetic resonance shifts (chemical shifts) are of great help in elucidating some of the interesting properties of the electronic distribution in molecules.<sup>1-5</sup> In the present experiments chemical shifts  $\text{Cl}^{35}$  resonance were determined in some compounds, of which the results of alkali chlorides will be presented in this paper. The NMR signals of  $\text{Cl}^{35}$  would, in general, be broad,<sup>6</sup> due to quadrupole interactions. Masuda<sup>7</sup> has determined the chemical shifts in four liquid chlorine compounds  $\text{TiCl}_4$ ,  $\text{VOCl}_3$ ,  $\text{CrO}_2\text{Cl}_2$  and  $\text{SiCl}_4$ , and found the line widths to be proportional to the square of the quadrupole coupling constants, showing that the quadrupole interactions form the dominant relaxation mechanism. But the line widths are less in the case of aqueous solutions of alkali chlorides where these interactions are minimum.

The experimental details and the results obtained are presented in the next two sections. In the last section the results are discussed in comparison with the quadrupole coupling constants of these molecules in gaseous phase.

### EXPERIMENTAL ARRANGEMENT

The chemical shifts were measured on a Varian V-4300 B High Resolution NMR Spectrometer, using a 12" electromagnet. The power supply

\* Senior Research Fellow of the Council of Scientific and Industrial Research.

for the magnet has voltage and current regulation, and the drifts in the field, occurring due to temperature variations, etc., are compensated by a "Superstabilizer". The overall stability and homogeneity of the static magnetic field is roughly 1 part in  $10^7$  or better. The spectrometer essentially consists of 3.6 Mc. fixed frequency transmitter and receiver units with the associated probe, and a sweep unit providing for variable sweep field of adjustable frequency. The corresponding value of the static magnetic field for  $\text{Cl}^{35}$  magnetic resonance is about 8,627 gauss. The frequency stability of the R.F. unit is about 1 part in a million per hour. A Dumont Model 304-AR Oscilloscope is used for visual observation of the resonances, and a Sanborn Model 151-100 A Recorder is employed for recording them. For recording, a "Slow-Sweep Unit" is provided along with the Superstabilizer with which the magnetic field can be varied either way, linearly, at a slow and variable rate. The sample, in liquid form, is contained in a pyrex glass tube of about 13 mm. o.d., with a reference sample in another glass tube of about 7 mm. o.d., placed inside. Thus the signals from the sample and reference are simultaneously observed. The measurement was carried out by the side-band technique,<sup>8</sup> using Hewlett-Packard Model 200 B Audio Oscillator to modulate the sweep voltage. The frequency of the Audio Oscillator is accurately determined by calibrating with the proton resonance spectrum of ethanol at 40 Mc. The error involved in this determination is about  $\pm 2$  cps.

The signals obtained for  $\text{RbCl}$  with  $\text{NaCl}$  as the reference, along with the side-bands separated by 184 cps., on either side, from the main signals, are shown in Fig. 1. Figure 2 shows the signals for  $\text{LiCl}$  and  $\text{CsCl}$ .

The chemical shift is usually expressed as

$$\delta = \frac{H_c - H_r}{H_r} \times 10^5,$$

where  $\delta$  is the chemical shift,  $H_c$  and  $H_r$  are the values of the magnetic field at which the resonance occurs in the compound of interest, and the reference compound respectively.

## RESULTS

The chemical shifts for  $\text{Cl}^{35}$  magnetic resonance in alkali chlorides are shown in Table I.

Measurements were made on the aqueous solutions of these compounds. The values are given with respect to sodium chloride as the reference. The shifts in the case of  $\text{LiCl}$  and  $\text{KCl}$  were not measured with  $\text{NaCl}$  as the reference, but they were measured with respect to  $\text{CsCl}$  and the values were finally

TABLE I

Compound	Chemical shift $\delta$	Observed $eQq_{\text{molecule}}^{17}$ in Mc.	$(D - i) \beta$ $eQq_{\text{atom}}^{17}$ in Mc.
LiCl ..	$-0.31 \pm 0.1$	..	..
NaCl ..	0	<1	..
KCl ..	$-0.18 \pm 0.1$	0.04	0.51
RbCl ..	$-1.05 \pm 0.1$	0.774	1.24
CsCl ..	$-2.32 \pm 0.1$	3.00	3.00

reduced to NaCl as the reference. The bulk diamagnetic susceptibility correction was not applied.\* All the measurements were carried out at room temperature. Measurements were done with different concentrations of the solutions, but the shifts were found to be independent of the concentration, within the experimental accuracy of about  $\pm 0.1$  in the chemical shift.

#### DISCUSSION

Ramsey<sup>9</sup> has shown that the chemical shift arises due to interaction between the molecular electrons and the external magnetic field. The interaction would, in turn, produce a small magnetic field at the site of the nucleus in opposition to the external field. The magnitude of this shielding field is different in different molecules due to variations in electronic structure.

If the alkali halides are 100% ionic, the shielding field for the halogen nucleus or the alkali nucleus, according to Ramsey's theory, would not vary from molecule to molecule, and hence no chemical shift would be observed between these molecules. However, Gutowsky and MacGarvey<sup>10</sup> have observed chemical shifts between the solid Rubidium and Cesium halides for Rb<sup>87</sup> and Cs<sup>133</sup> resonances. Recently, Bloembergen and Sorokin<sup>11</sup> have observed the shifts for both halogen and alkali nuclei in the case of solid Cesium halides. Kanda<sup>12</sup> has also observed halogen resonance shifts in certain solid metal halides. In all these cases, the observed shifts were explained by attributing a certain amount of covalent character to the crystalline bonds in these halides.<sup>10-13</sup> The present work shows the occurrence of the shifts in Cl<sup>35</sup> resonance in aqueous solutions of alkali chlorides

\* The correction will not bring any significant difference in the results, as it would be within the experimental error involved in the measurements.

where crystalline fields are not expected. The shifts observed here are much smaller in magnitude than those in solid samples mentioned above.

Shoolery and Alder<sup>18</sup> observed the proton magnetic resonance shifts in various aqueous electrolytes, and the fluorine magnetic resonance in aqueous potassium fluoride solutions at several concentrations. They found concentration dependence of these shifts and explained on the basis of solvent-ion interactions. The overall effect of these interactions, if any, are probably negligible in the alkali chloride solutions worked out in the present experiments, as the shifts are found, within experimental errors, to be independent of concentration.

It is interesting to note the similarity of the nuclear magnetic resonance shifts in the present experiment to the known quadrupole coupling constants of these molecules in gaseous phase. The similarity can be expected<sup>7, 14</sup> as both these depend upon the fraction of unbalanced *p*-character about the atom in question. The quadrupole coupling constant for a halogen atom forming a hybrid bond, with a negative ionic character of amount  $\beta$  is given by<sup>15</sup>

$$eQq_{\text{molecule}} = (-1 + \alpha - S^2)(1 - \beta) eQq_{\text{atom}}$$

where  $\alpha$  is the hybridization,  $S$  is the overlap factor and  $eQq_{\text{atom}}$  is known from atomic data.<sup>16</sup> It can be seen from this expression that  $eQq_{\text{molecule}}$  would be zero if the ionic character is 100%. The observed values of the quadrupole coupling constants, in the gaseous phase, of KCl, RbCl, and CsCl, were explained by Vankateswarlu and Jaseja<sup>17</sup> by modifying the above expression as

$$eQq_{\text{molecule}} = [(-1 + \alpha - S^2)(1 - \beta) + (D - i)] \beta eQq_{\text{atom}}$$

where  $D$  represents the effect on quadrupole coupling constant due to distortion of the closed shells of the halogen atom, and  $i$  represents the effect due to presence of adjacent ions or atoms in the molecule. The contribution of this term,  $(D - i) \beta eQq_{\text{atom}}$ , to the  $eQq_{\text{molecule}}$  as given by Venkateswarlu and Jaseja<sup>17</sup> is given in the fourth column of Table I.

It may be noted that the chemical shift for LiCl with reference to NaCl is towards the same direction as that for KCl, RbCl and CsCl. For comparison of this behaviour, the quadrupole coupling constant is not known for LiCl and it is not correctly found for NaCl. A similar behaviour can, however, be noted in the case of quadrupole coupling constants of bromine and iodine in the bromides and iodides of Lithium, Sodium and Potassium.<sup>17</sup>

The concentration independence of the observed nuclear magnetic resonance shifts, and the similarity of the trend of variation of these shifts to that of the corresponding nuclear quadrupole coupling constants, suggest the need of a quantitative explanation of these two effects on similar grounds in these molecules. However, more concrete conclusions would be attempted after the data on the other halides are collected.

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