# Nuclear Magnetic Resonance Studies of $^{35}Cl$, $^{37}Cl$, $^{79}Br$, and $^{81}Br$ in Aqueous Solution

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The NMR signals of the nuclei $^2H$, $^{35}Cl$, $^{37}Cl$, $^{79}Br$ and $^{81}Br$ have been investigated in aqueous solutions. The concentration dependence of the NMR signals of $^{35}Cl$ and $^{81}Br$ has been determined in solutions of alkali halides and alkali perchlorates in $H_2O$ and $D_2O$ and the large solvent isotope effect on the chemical shift has been established. The ratios of the Larmor frequencies of the halide nuclei relative to $^2H$ have been measured with high accuracy. Using the concentration dependence, the ratios of the Larmor frequencies of the halide nuclei for infinite dilution relative to $^2H$ in pure $D_2O$ are given. From these ratios, magnetic moments for the halide nuclei have been derived.

## Introduction

Alkali metal and halide nuclei in aqueous alkali halide solutions show chemical shifts which vary with concentration [1–4]. In dilute solutions, interaction of the alkali metal or halide ion with surrounding water molecules gives rise to a chemical shift between the free ion and the hydrated ion. This chemical shift will be denoted as the nuclear magnetic shielding constant $\sigma_p(X^{\pm})$ or absolute chemical shift of the alkali metal and halide nuclei in aqueous solution of vanishing concentration. A determination of this quantity would yield an absolute scale for the relative chemical shifts of these nuclei.

Recently, DEVERELL [5] has used various methods for calculating the nuclear magnetic shielding constants of alkali metal and halide ions in aqueous solutions. To proof the usefulness of Deverell's methods, experimental values for the shielding constants would be desirable.

A value for $\sigma_p(F^-)$ has been given by RAMSEY [6]. By comparing the nuclear magnetic moment of the free atom derived from atomic beam magnetic resonance or optical pumping techniques, with NMR measurements of the nuclear magnetic moment of the ion in solution, the nuclear magnetic shielding constants of $^{23}Na$ (see [7]), $^{85}Rb$ (see [8]), $^{87}Rb$ (see [9, 10]), $^{133}Cs$ (see [2]) and $^{207}Pb$ (see [11]) have been determined experimentally. An application of this method to chlorine, bromine and iodine fails, because the nuclear magnetic moments of these halides have not been measured with sufficient accuracy by either of these methods.

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We describe in the following the determination of the nuclear magnetic moments of $^{35}Cl$, $^{37}Cl$, $^{79}Br$ and $^{81}Br$ in the ions for vanishing concentration of aqueous solutions by the nuclear magnetic resonance method.

## Experimental

Our frequency-swept spectrometer, which was described elsewhere [2], was used with some modifications. The frequency range is extended to 6 MHz . . . 32 MHz. The rotation of spherical and cylindrical samples with diameters up to 10 mm is now possible. The magnetic field of 18.07 kOe is held constant by the aid of a $^7Li$ NMR probe [12]. The Larmor frequencies of the investigated nuclei are given in the Table 1.

Table 1. Larmor frequencies of the nuclei studied at a magnetic field of 18.07 kOe.

| Nucleus | $^2H$ | $^{35}Cl$ | $^{37}Cl$ | $^{79}Br$ | $^{81}Br$ |
|---|---|---|---|---|---|
| Larmor frequency in MHz | 11.810 | 7.538 | 6.275 | 19.276 | 20.778 |

The line width due to the inhomogeneity of the magnet was e. g. for the $^2H$ resonance in $D_2O$ in a 10 mm rotating sample about 2 Hz. The range of the line width goes from some Hertz of the deuterium and chlorine resonances to some hundred Hertz of the bromine resonances; therefore appropriate conditions of modulation, radiofrequency field and sweep rates were employed to prevent distortion of the signals.

The chemical shifts were measured relative to an external standard by the probe exchange method. The chemical shift is given by $\delta = \nu_{\text{probe}} - \nu_0$; a positive value means a shift to higher frequency at constant field. Concentrations are given as moles salt per kg solvent or as the mole fraction, i. e. moles salt per moles solvent.

The temperature was $(28 \pm 2)$ °C.

## The Ratios of the Larmor Frequencies

In defined solutions of alkali halides in $D_2O$ (99.75% isotopic purity), the ratios of the Larmor frequencies

$$\nu(\text{halide})/\nu(^2\text{H})$$

were determined. The Larmor frequency of a halide nucleus and the Larmor frequency of $^2H$ were measured alternately in the same probe at constant field only by varying the radio frequency. The radio frequency was controlled by a frequency counter during the registration of the resonance lines. For each halide nucleus about 30 . . . 50 frequency ratios were determined at different runs. The results are given in Table 2.

Table 2. Ratios of the Larmor frequencies $\nu$(halide)/$\nu$($^2$H) in the solutions studied.

| Nucleus | Salt | Concentration $c$ (moles salt/moles $D_2O$) | $\nu$(halide)/$\nu$($^2$H) |
|---|---|---|---|
| $^{35}$Cl | NaCl | 0.090 | 0.638 272 39 (4) * |
| $^{37}$Cl | NaCl | 0.090 | 0.531 294 38 (4) * |
| $^{79}$Br | KBr | 0.080 | 1.632 131 (2) ** |
| $^{81}$Br | KBr | 0.080 | 1.759 331 (2) ** |

* Three times the rms error.
** Three times the rms error and a systematical error due to unsymmetric lines.

From this table, the ratios

$$\nu(^{35}\text{Cl})/\nu(^{37}\text{Cl}) = 0.832\,394\,43(8)$$

and $\nu(^{81}\text{Br})/\nu(^{79}\text{Br}) = 1.077\,934\,9(18)$

can be calculated. These are in excellent agreement with the directly measured ratios of LUTZ [13, 14], which were used for calculating the hyperfine structure anomalies.

No directly measured values for $\nu(^{37}\text{Cl})/\nu(^2\text{H})$, $\nu(^{79}\text{Br})/\nu(^2\text{H})$ and $\nu(^{81}\text{Br})/\nu(^2\text{H})$ are known. The value $\nu(^{35}\text{Cl})/\nu(^2\text{H})$ of PROCTOR and YU [15] is in good agreement within the limits of error of their value, the ratio of WALCHLI [16] was measured in RbCl-solution and lies therefore higher than ours.

NaCl and KBr solutions were chosen because of their small concentration dependence and the small line widths. The other halide solutions showed larger line widths. Only for $NH_4Cl$ and $NH_4Br$ solutions the line widths are smaller for chlorine and bromine resonances respectively. Because of the isotopic exchange of hydrogen and deuterium, the ammonium halide solutions could not be used for measuring the frequency ratios.

For a determination of the Larmor frequencies for vanishing concentration, the concentration dependences of the deuterium and halide resonances had to be studied.

## Concentration Dependence

*a) $^{35}$Cl and $^{81}$Br in Chlorine and Bromine Solutions*

DEVERELL and RICHARD [3] have presented the concentration dependence of $^{35}Cl$ in solutions of the chlorides of Li, Na, K, Rb and Cs in $H_2O$ and of $^{81}Br$ in solutions of the bromides of Na, K, Rb and Cs in $H_2O$.

For an accurate extrapolation to vanishing concentration, proceeding from our values of Table 2, we had to remeasure the concentration dependence for some alkali metal chloride and bromide solutions in $H_2O$ and $D_2O$.

These chemical shifts of $^{35}Cl$ and $^{81}Br$ resonances in aqueous solutions of ammonium and alkali chlorides and bromides are shown in Figures 1 and 2. The shifts are referred to the resonance frequency of the $Cl^-$ and $Br^-$ at infinite dilution in $H_2O$ respectively. The values for $NH_4^+$, and its Goldschmidt ionic radius as well, are situated between $Rb^+$ and $Cs^+$. The large solvent isotope effect is discussed later in this paper. A comparison with the results of DEVERELL and RICHARDS [3] shows good agreement.

The concentration dependence had to be measured only for one isotope. For the second isotope, the chemical shift can be calculated by

$$\delta(^{37}\text{Cl}) = \delta(^{35}\text{Cl}) \cdot [\gamma(^{37}\text{Cl})/\gamma(^{35}\text{Cl})]\,,$$

and correspondingly for $^{79}Br$ and $^{81}Br$.

That this relation holds very well has been ensured for example by measuring $\nu(^{35}\text{Cl})/\nu(^{37}\text{Cl})$ in $NH_4Cl$ and $NaClO_4$ solutions [14]. This ratio is the same within $1 \cdot 10^{-7}$, although the chemical shift of these solutions is about 1000 ppm. Further, $\sigma_p(^{85}\text{Rb}^+)$ and $\sigma_p(^{87}\text{Rb}^+)$ have been measured independently [8, 10]. The results are

$$\sigma(^{87}\text{Rb}^+) = -2.116(12) \cdot 10^{-4}\,,$$
$$\sigma(^{85}\text{Rb}^+) = -2.11(2) \cdot 10^{-4}\,.$$

There is no difference within the limits of the errors. The error for the extrapolation to infinite dilution was assumed to be $\pm 0.4$ ppm for $^{35}Cl$ and $\pm 0.5$ ppm for $^{81}Br$.

*b) $^{35}$Cl in Perchlorate Solutions*

The $^{35}Cl$ resonance line of the perchlorate ion in $HClO_4$ is situated about 946 ppm to higher frequency than that of the $Cl^-$ ion in HCl [17]. The con-

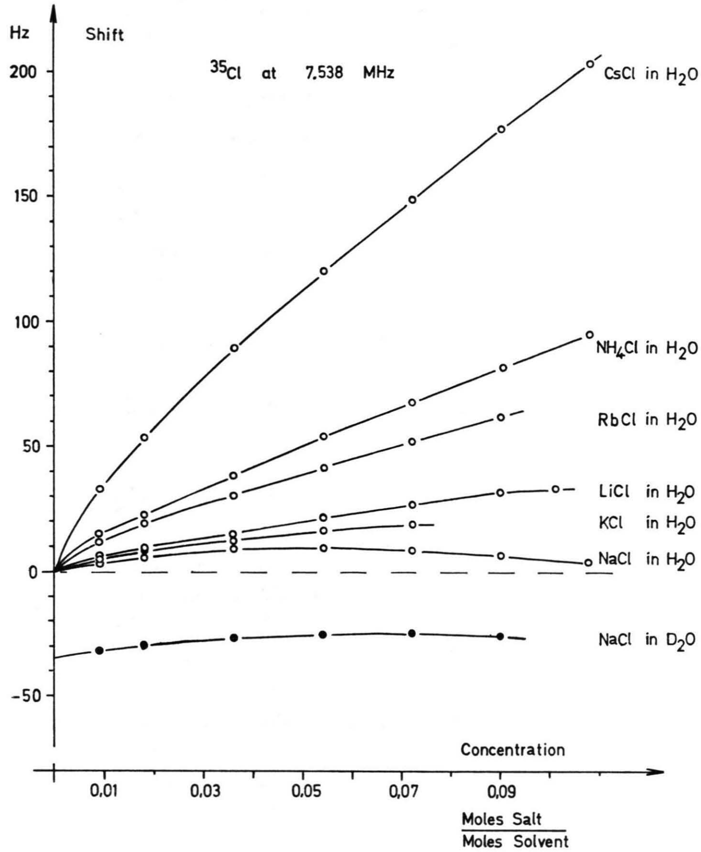


Fig. 1. $^{35}$Cl chemical shifts in solutions of chlorides. Positive values are to higher frequencies. The measured shifts are adjusted so that they refer to the chloride ion at infinite dilution as standard. Rotating cylindrical probes (9 mm inner diameter) were used; no bulk susceptibility correction was made. The errors are smaller than the given circles. The line widths are 15 . . . 25 Hz.

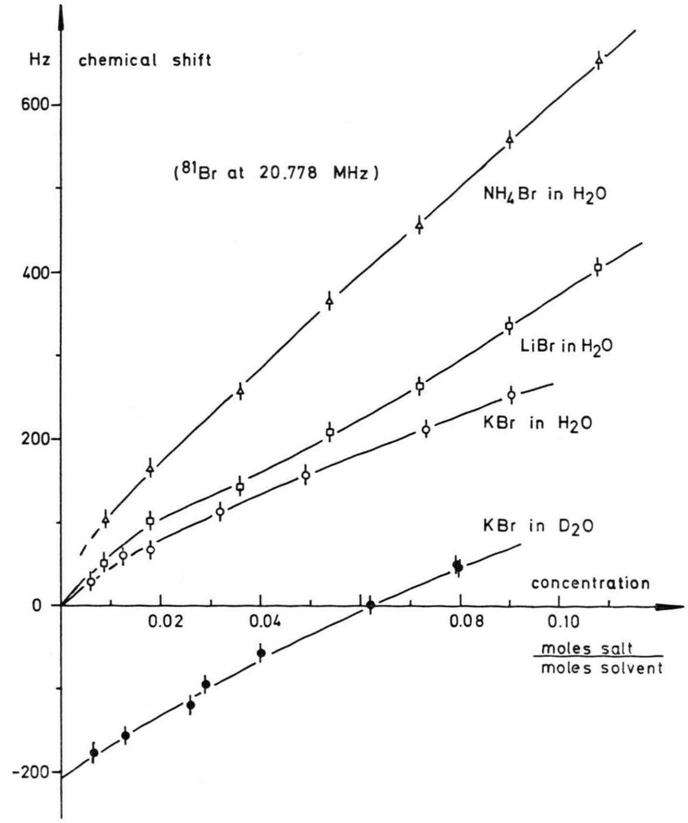


Fig. 2. $^{81}$Br chemical shifts in solutions of bromides. Positive values are to higher frequencies. The measured shifts are adjusted so that they refer to the bromide ion at infinite dilution in $H_2O$ as standard. Cylindrical probes (9 mm inner diameter) were used; no bulk susceptibility correction was made. The line widths are 350 . . . 750 Hz.
350 . . . 750 Hz.

centration dependence of alkali perchlorates has not been studied before. Our measured shifts are shown in Figure 3. They are very small and to increasingly lower frequency with increasing concentration. Similar shifts to lower frequency have also been found for the $^{55}Mn$ resonance line of alkali permanganates [18] in aqueous solution. Nearly the same shift for $NaClO_4$ and $LiClO_4$ in $H_2O$ and of $LiClO_4$ in $D_2O$ has been found. This reveals the small influence of the surrounding on the perchlorate ion. The chemical shift of $^{35}Cl$ in the $Cl^-$ ion and in the

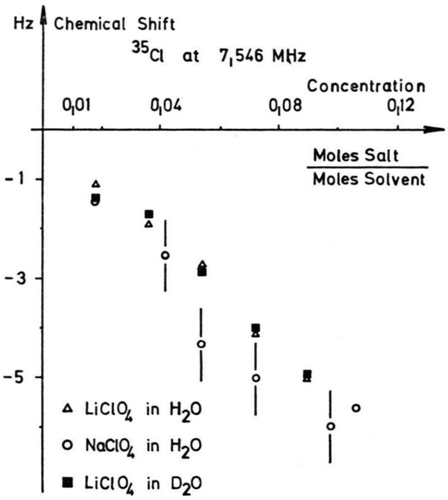


Fig. 3. $^{35}Cl$ chemical shifts of solutions of $LiClO_4$ in $H_2O$ and $D_2O$ and $NaClO_4$ in $H_2O$. Rotating spherical probes of inner diameter of about 9 mm were used. Typical errors only for a few points are drawn. The line widths of the $^{35}Cl$ resonances in the $ClO_4^-$ ion are smaller than in the $Cl^-$ ion: line widths of 3 . . . 5 Hz were found; they are partly due to the inhomogeneity of the magnetic field.

$ClO_4^-$ ion at infinite dilution respectively is

$$\nu_{ClO_4^-} - \nu_{Cl^-} = (7563.4 \pm 3)\ \text{Hz}$$

referred to the Larmor frequency of the hydrated $Cl^-$:

$$\sigma = (1003.3 \pm 0.4)\ \text{ppm}.$$

### c) $^2H$ *in Alkali Halide Solutions*

For the extrapolation of the ratio of the Larmor frequencies, the influence of the alkali metal halides on the $^2H$ resonance line in $D_2O$ had to be measured also. The $^2H$ resonance is shifted to lower frequency for NaCl and KBr in $D_2O$. The shift is small; $(-3.3 \pm 1.0)$ Hz for the KBr and $(-2.2 \pm 0.5)$ Hz for the NaCl solutions quoted in Table 2, referred to pure $D_2O$.

## Ratios of the Larmor Frequencies for Infinite Dilution

The ratios of the Larmor frequencies, which have been measured in somewhat arbitrary solutions (Table 2), are now transferred to a general base by using the dependence on concentration. As the common base, the ratio of the Larmor frequency of the halide nucleus at vanishing concentration to the Larmor frequency of $^2H$ in pure $D_2O$ is chosen:

$$[\nu(\text{halide})/\nu(^2\text{H})]_{\text{extrapol.}}\,.$$

Table 3 shows these ratios resulting from the values of Table 2 and the concentration dependence. The errors arise from the extrapolation to zero concentration.

Table 3. Ratios of the Larmor frequencies for infinite dilution of halide salts in $D_2O$. The errors result from the uncertainty of the extrapolation to vanishing concentration. (In Physics Letters **32 A**, 403 [1970], there is a printing error in the value $\nu(^{37}Cl)/\nu(^2H)$.)

| Nucleus | $[\nu(\text{halide})/\nu(^2\text{H})]_{\text{extrapol.}}$ |
|---|---|
| $^{35}Cl$ | 0.638 271 6 (3) |
| $^{37}Cl$ | 0.531 293 7 (3) |
| $^{79}Br$ | 1.632 111 (3) |
| $^{81}Br$ | 1.759 309 (3) |

## The Magnetic Moments

From the ratios of the Larmor frequencies of Table 3, nuclear magnetic moments can be derived, using $\nu(^2H)/\nu(^1H) = 0.153\,506\,083(60)$ of SMALLER [19] and the uncorrected magnetic moment of the proton in water $\mu_p = 2.792\,709(17)\ \mu_N$ of TAYLOR et al. [20]. The so calculated nuclear magnetic moments are listed in Table 4. All moments are affected by the uncertainty of the magnetic moment of the proton and are not corrected for the ionic diamagnetism. Because a crossed-coil type spectrometer was used, the sign of the magnetic moments is also given.

These values of the magnetic moments are influenced only by the electrons of the ion itself and by the surrounding water molecules, which interact

Table 4. Nuclear magnetic moments of the halide nuclei in the halide ions, which are hydrated by $D_2O$.

| Nucleus | $\mu(\text{halide})_{\text{uncorr.}}$ |
|---|---|
| $^{35}Cl$ | $+\,0.820\,876\,9\,(5)\ \mu_N$ |
| $^{37}Cl$ | $+\,0.683\,293\,3\,(5)\ \mu_N$ |
| $^{79}Br$ | $+\,2.099\,047\,(4)\ \mu_N$ |
| $^{81}Br$ | $+\,2.262\,636\,(4)\ \mu_N$ |

with the ion. If such magnetic moments could be compared with magnetic moments of free ions, the effect of the water molecules could be evaluated, the shielding constant calculated and compared with the results of DEVERELL [5]. Further, an absolute scale for the relative chemical shifts could be established and e. g. the arbitrary zero of Fig. 1 of the paper of HALL [21] could be replaced.

## Solvent Isotope Effect

The Larmor frequencies of nuclei of ions in aqueous solutions depend on the isotopic composition of the solvent. Solvent isotopic shifts in water have been found for several nuclei [11, 18, 22–26], the size of the shift ranges up to 31 ppm in the case of $^{207}Pb$ (see [11]) and is always to lower frequencies, going from $H_2O$ to $D_2O$.

Solvent isotope shifts of $^{35}Cl$ and $^{81}Br$ as a function of concentration are shown in Figs. 1 and 2 for NaCl and KBr. The shift of $^{81}Br$ in KBr was different from that of LOEWENSTEIN et al. [23] for Br in RbBr. We have therefore measured the difference in the Larmor frequencies i. e. the solvent isotope effect in solutions of the alkali bromides and chlorides with a constant mole ratio of $c = 0.009$ in $H_2O$ and $D_2O$. We use this assignment for the concentration because the ratio of the number of ions to the number of solvent molecules is a constant also for the isotopic change. The results are given in Table 5. Within the limits of error, no cation dependence of the solvent isotope effect for the anionic nuclei was established. The value of LOEWENSTEIN et al. [23] for $^{81}Br$ is not in agreement with ours. Recently, $\sigma_{H_2O} - \sigma_{D_2O}$ for $^{81}Br$ in RbBr solutions with $c = 0.009$ was measured more accurately by A. UHL in this laboratory with our new Fourier transform NMR spectrometer [8]. The result was $9.4 \pm 0.3$ ppm.

Table 5. Solvent isotope effect of $^{35}Cl$ and $^{81}Br$ in solutions of alkali halides in $H_2O$ and $D_2O$ with a constant concentration of $c = 0.009$, given as the difference in the shielding constants in ppm.

| Salt | $\sigma(H_2O) - \sigma(D_2O)$ | Salt | $\sigma(H_2O) - \sigma(D_2O)$ |
|---|---|---|---|
| LiBr | $-9.2 \pm 1.0$ | LiCl | $-4.7 \pm 0.3$ |
| NaBr | $-10.3 \pm 1.0$ | NaCl | $-4.6 \pm 0.3$ |
| KBr | $-9.9 \pm 0.5$ | KCl | $-4.8 \pm 0.3$ |
| RbBr | $-10.1 \pm 1.0$ | RbCl | $-4.7 \pm 0.3$ |
| CsBr | $-9.6 \pm 1.0$ | CsCl | $-4.4 \pm 0.3$ |
| RbBr * | $-8.3 \pm 0.3$ | NaCl * | $-4.7 \pm 0.3$ |

* Ref. [23].

With increasing concentration, the solvent isotope effect decreases, a fact which Halliday et al. have also found for $^{133}Cs$. For $^{133}Cs$ and $^{87}Rb$, the solvent isotope effect is 0.35% and 0.14% of the total absolute shielding of the nuclei of the ions by water [2, 9]. If a similar fraction for the halides is assumed, the absolute shielding of the chloride and bromide ion by water would be about some $10^{-4}$ to some $10^{-3}$, which is larger than the calculated value of IKENBERRY and DAS [27, 28]. But for Rb and Cs, the calculated shielding constants [27–29] are also in disagreement with the experimental ones [2, 9, 10].

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1 C. DEVERELL and R. E. RICHARDS, Mol. Phys. **10**, 551 [1966].
2 O. LUTZ, Z. Naturforsch. **23 a**, 1202 [1968].
3 C. DEVERELL and R. E. RICHARDS, Mol. Phys. **16**, 421 [1969].
4 J. D. HALLIDAY, R. E. RICHARDS, and R. R. SHARP, Proc. Roy. Soc. London A **313**, 45 [1969].
5 C. DEVERELL, Mol. Phys. **16**, 491 [1969].
6 M. R. BAKER, C. H. ANDERSON, and N. F. RAMSEY, Phys. Rev. **A 133**, 1533 [1964].
7 S. PENSELIN, Fachberichte der 35. Physikertagung in Hannover, Hannover 1970, p. 45.
8 O. LUTZ and A. NOLLE, to be published.
9 O. LUTZ, Phys. Letters **25 A**, 440 [1967].
10 C. W. WHITE, M. W. HUGHES, G. S. HAYNE, and H. G. ROBINSON, Phys. Rev. **174**, 23 [1968].
11 O. LUTZ and G. STRICKER, Phys. Letters **35 A**, 397 [1971].
12 J. KAUFMANN and A. SCHWENK, Z. Angew. Phys. **21**, 527 [1966].
13 O. LUTZ, Phys. Letters **31 A**, 384 [1970].
14 O. LUTZ, Phys. Letters **31 A**, 528 [1970].
15 W. G. PROCTOR and F. C. YU, Phys. Rev. **77**, 716 [1950].
16 H. E. WALCHLI, ORNL-1775 [1954].
17 K. J. JOHNSON, J. P. HUNT, and H. W. DODGEN, J. Chem. Phys. **51**, 4493 [1969].
18 O. LUTZ and W. STEINKILBERG, Phys. Letters **30 A**, 183 [1969], and to be published.
19 B. SMALLER, Phys. Rev. **83**, 812 [1951].
20 B. N. TAYLOR, W. H. PARKER, and D. N. LANGENBERG, Rev. Mod. Phys. **41**, 375 [1969].
21 C. HALL, Quart. Rev. Chem. Soc. London **25**, 87 [1971].
22 C. DEVERELL, K. SCHAUMBURG, and H. J. BERNSTEIN, J. Chem. Phys. **49**, 1276 [1968].
23 A. LOEWENSTEIN, M. SHPORER, P. C. LAUTERBUR, and J. E. RAMIREZ, Chem. Comm. 214 [1968].
24 J. HALLIDAY, H. D. W. HILL, and R. E. RICHARDS, Chem. Comm. 219 [1969].
25 B. W. EPPERLEIN and O. LUTZ, Z. Naturforsch. **23 a**, 1413 [1968].
26 O. LUTZ, Phys. Letters **29 A**, 58 [1969].
27 D. IKENBERRY and T. P. DAS, Phys. Rev. **138 A**, 822 [1965].
28 D. W. HAFEMEISTER and W. H. FLYGARE, J. Chem. Phys. **44**, 3584 [1966].
29 D. IKENBERRY and T. P. DAS, J. Chem. Phys. **45**, 1361 [1966].