

## Proton Radio-Frequency Spectrum of HCl<sup>35</sup>†

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The radio-frequency spectrum corresponding to re-orientation of the proton magnetic moment in HCl<sup>35</sup> in the presence of an external magnetic field has been obtained using the molecular beam magnetic resonance method. From the observed resonance shapes and positions, the value of the spin rotational constant of the proton in HCl<sup>35</sup> has been determined to be  $|c_p| = 41 \pm 3$  kc/sec. Due to the large quadrupole interaction in HCl<sup>35</sup>, the perturbation methods of data analysis used with the HF molecule were inapplicable. An approximate theory of the proton spectrum has been developed in detail to aid in the analysis of the experimental data in this case and in cases of similar intermediate coupling. Theoretical spectra were calculated on the UNIVAC computer using this approximate theory and directly compared with the experimental spectrum to estimate the value of  $|c_p|$ . Theoretical spectra were also calculated on the UNIVAC using a direct solution of the Hamiltonian secular equation and were compared with the experimental curves to provide a check on the validity of the approximate theory. The comparisons indicate that the use of the approximate theory will allow the determination of  $|c_p|$  to within 10%.

### I. INTRODUCTION

THE molecular beam magnetic resonance method of studying Zeeman hyperfine structure of molecules furnishes an excellent method of obtaining values of molecular interaction constants such as spin-spin, spin-rotational, and quadrupole interaction constants.<sup>1-3</sup> The analysis of the experimental data to obtain values of the above constants usually involves the construction of several theoretical comparison curves (with different values of the unknown constants) which are compared with the experimental curves until a "best fit" is obtained. High- and low-field perturbation theory are commonly used to calculate these theoretical comparison curves.

However, these perturbation methods proved to be inapplicable to the analysis of the experimental proton spectrum of HCl<sup>35</sup>. Due to the large quadrupole interaction, the HCl molecule in an external magnetic field must be considered an intermediate field problem. The analysis of the experimental data then involves either the direct solution of the secular equations or some approximate method other than the usual perturbation methods.

An approximate theory (using the  $m_p, K, m_k$  representation) of the proton spectrum of HCl<sup>35</sup> is presented in detail in Sec. II to aid in the analysis of experimental data in this case and in cases of similar intermediate coupling. Experimental curves obtained using procedures discussed in Sec. III are compared with theoretical comparison curves calculated using this

approximate theory in Sec. IV. Theoretical curves calculated by a direct solution of the secular equation are also compared with experimental curves to provide a check on the validity of the approximate theory.

### II. APPROXIMATE THEORY

#### Hamiltonian

The interaction energies of the  $^2\Sigma$  HCl molecule in a magnetic field depend on three angular momentum vectors:  $\mathbf{I}_p$  (proton),  $\mathbf{I}_{Cl}$  (chlorine nucleus), and  $\mathbf{J}$  (due to molecular rotation), with corresponding magnetic moments  $\boldsymbol{\mu}_p$ ,  $\boldsymbol{\mu}_{Cl}$ , and  $\boldsymbol{\mu}_J$ . These interactions (omitting that due to the chlorine magnetic octupole moment), for the HCl molecule in an external magnetic field  $\mathbf{H}$ , are described by the following Hamiltonian  $\mathcal{H}$ <sup>3</sup>

$$\begin{aligned} \frac{\mathcal{H}}{h} = & -[1 - \sigma_p(\mathbf{J})]a_p \frac{\mathbf{I}_p \cdot \mathbf{H}}{|\mathbf{H}|} \\ & - [1 - \sigma_{Cl}(\mathbf{J})]a_{Cl} \frac{\mathbf{I}_{Cl} \cdot \mathbf{H}}{|\mathbf{H}|} - [1 - \sigma_J(\mathbf{J})]b \frac{\mathbf{J} \cdot \mathbf{H}}{|\mathbf{H}|} \\ & - c_p \mathbf{I}_p \cdot \mathbf{J} - c_{Cl} \mathbf{I}_{Cl} \cdot \mathbf{J} + \frac{5d_1}{(2J-1)(2J+3)} \\ & \times \left[ \frac{3}{2}(\mathbf{I}_p \cdot \mathbf{J})(\mathbf{I}_{Cl} \cdot \mathbf{J}) + \frac{3}{2}(\mathbf{I}_{Cl} \cdot \mathbf{J})(\mathbf{I}_p \cdot \mathbf{J}) - (\mathbf{I}_p \cdot \mathbf{I}_{Cl})\mathbf{J}^2 \right] \\ & + \frac{5d_2}{(2J-1)(2J+3)} \left[ 3(\mathbf{I}_{Cl} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_{Cl} \cdot \mathbf{J}) - \mathbf{I}_{Cl}^2 \mathbf{J}^2 \right] \\ & - \frac{5f}{3(2J-1)(2J+3)} \left[ \frac{3(\mathbf{J} \cdot \mathbf{H})^2}{|\mathbf{H}|^2} - \mathbf{J}^2 \right] + \delta \mathbf{I}_p \cdot \mathbf{I}_{Cl}. \quad (1) \end{aligned}$$

The constants  $a_p$  and  $a_{Cl}$  represent the interaction of the proton and chlorine magnetic moments with the external field, the constant  $b$  represents the interaction of the rotational magnetic moment with the external field, the spin rotational constants  $c_p$  and  $c_{Cl}$  represent the interaction of the respective nuclear moments with

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<sup>1</sup> M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, *Phys. Rev.* **121**, 807 (1961).

<sup>2</sup> H. M. Nelson, J. A. Leavitt, M. R. Baker, and N. F. Ramsey, *Phys. Rev.* **122**, 856 (1961).

<sup>3</sup> N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956).

the magnetic fields due to the rotation of the molecule at the nuclear positions, the constant  $d_1$  represents the direct dipole-dipole interaction of the two nuclear moments, the constant  $d_2$  represents the interaction of the quadrupole moment with the non-uniform electric field of the molecule, the constant  $f$  represents the orientation-dependent part of the molecular diamagnetic interaction with the external field, the constant  $\delta$  represents the scalar part of the electron coupled spin-spin interaction (the tensor part makes a contribution to  $d_1$ ), and  $\sigma_i(\mathbf{J})$  are magnetic shielding constants.

### Choice of Representation

Using the above Hamiltonian, approximate expressions for the energy levels of the HCl molecule in an external field may be obtained and the allowed transition frequencies calculated using the selection rules. The method used in making this approximate calculation depends on the relative magnitudes of the interaction energies of the separate terms of the Hamiltonian. The usual perturbation methods (both strong- and weak-field perturbation theory) are inappropriate for the calculation of the HCl energy levels. The large chlorine quadrupole interaction [ $eqQ \approx 67$  Mc/sec ( $d_2 = 2.24$  Mc/sec), measured<sup>4</sup> for Cl<sup>35</sup> in DCI<sup>35</sup>] invalidates the condition (strong-field perturbation theory) that the internal interactions be small compared to the interactions of the nuclear moments with the external field. The condition necessary for the weak-field perturbation method is also violated (at the fields used) since the internal interactions, in the case of the proton, are small compared to the interaction of the proton moment with the external field.

In this case, for an accurate calculation of the proton spectrum of HCl, the HCl molecule in a magnetic field must be considered an intermediate field problem, and the secular equation for each value of  $J$  must be solved. This procedure was carried out and the results are presented in the last section. However, an approximate first-order method of solution can be developed which is adequate to allow the determination of the spin rotational constant of the proton. This method utilizes the  $m_p, K, m_k$  representation, which takes into account the experimental evidence of the large quadrupole interaction and assumes that the  $\mathbf{I}_p$  coupling is a strong-field case, while the  $\mathbf{I}_{Cl}$  and  $\mathbf{J}$  couplings are weak-field cases. This method has the advantage over the solution of the secular equation that results can be obtained with a much shorter computer time.

The significance of the notation used in this section is:  $I_p(I_p+1)$ ,  $I_{Cl}(I_{Cl}+1)$ ,  $J(J+1)$ ,  $K(K+1)$  are the eigenvalues of the angular momentum operators  $\mathbf{I}_p^2$ ,  $\mathbf{I}_{Cl}^2$ ,  $\mathbf{J}^2$ ,  $\mathbf{K}^2$ ;  $m_p, m_{Cl}, m_J, m_k$  are the eigenvalues of the operators  $I_z^p, I_z^{Cl}, J_z, K_z$  (components of  $\mathbf{I}_p, \mathbf{I}_{Cl}, \mathbf{J}, \mathbf{K}$

along the field direction). The operator  $\mathbf{K}$  is defined as

$$\mathbf{K} = \mathbf{I}_{Cl} + \mathbf{J}. \quad (2)$$

In the  $m_p, K, m_k$  representation, it is assumed that  $\mathbf{I}_{Cl}$  and  $\mathbf{J}$  are strongly coupled together (by the large quadrupole interaction) to form the resultant vector  $\mathbf{K}$ , which precesses about the external field, while  $\mathbf{I}_p$  also precesses about the external field. Since  $\mathbf{I}_{Cl}$  and  $\mathbf{J}$  precess about their resultant  $\mathbf{K}$ ,  $m_{Cl}$  and  $m_J$  are not good quantum numbers. It is assumed that the  $\mathbf{I}_{Cl} \leftrightarrow \mathbf{J}$ ,  $\mathbf{K} \leftrightarrow \mathbf{H}$ , and  $\mathbf{I}_p \leftrightarrow \mathbf{H}$  couplings are strong enough to cause  $I_z^p, K^2, K_z$  to be well defined, and hence to make  $m_p, K, m_k$  the good quantum numbers for the problem.

### Approximate Hamiltonian

Equation (1) may be approximately expressed in terms of the operators  $\mathbf{I}_p^2, \mathbf{I}_{Cl}^2, I_z^p, \mathbf{K}^2$ , and  $K_z$  only. The matrix of this approximate Hamiltonian is then diagonal in the  $m_p, K, m_k$  representation and the approximate energy levels are then simply the eigenvalues of this Hamiltonian.

The coupling between  $\mathbf{I}_{Cl}$  and  $\mathbf{J}$  is assumed to be so strong that the weak field approximation<sup>3</sup> applies in the case of the  $\mathbf{J} \cdot \mathbf{H}$  and  $\mathbf{I}_{Cl} \cdot \mathbf{H}$  terms of Eq. (1). Only the components of  $\mathbf{I}_{Cl}$  and  $\mathbf{J}$  along  $\mathbf{K}$  are effective since the perpendicular components average to zero. Therefore:

$$\mathbf{J} \cdot \mathbf{H} \approx \frac{\mathbf{J} \cdot \mathbf{K} \mathbf{K} \cdot \mathbf{H}}{|\mathbf{K}| |\mathbf{K}|}; \quad \mathbf{I}_{Cl} \cdot \mathbf{H} \approx \frac{\mathbf{I}_{Cl} \cdot \mathbf{K} \mathbf{K} \cdot \mathbf{H}}{|\mathbf{K}| |\mathbf{K}|}. \quad (3)$$

In the case of the  $\mathbf{I}_p \cdot \mathbf{J}$  term, it is assumed that only the component of  $\mathbf{J}$  along  $\mathbf{K}$  is effective:

$$\mathbf{I}_p \cdot \mathbf{J} \approx \frac{\mathbf{I}_p \cdot \mathbf{K} \mathbf{K} \cdot \mathbf{J}}{|\mathbf{K}| |\mathbf{K}|}. \quad (4)$$

The  $\mathbf{I}_p \cdot \mathbf{I}_{Cl}$  term may be expressed as

$$\mathbf{I}_p \cdot \mathbf{I}_{Cl} = \mathbf{I}_p \cdot (\mathbf{K} - \mathbf{J}) \approx (\mathbf{I}_p \cdot \mathbf{K})(1 - \mathbf{J} \cdot \mathbf{K} / |\mathbf{K}|^2). \quad (5)$$

It should be noted that the  $\mathbf{I}_p \cdot \mathbf{J}$  and  $\mathbf{I}_{Cl} \cdot \mathbf{J}$  approximations give a  $d_1$  term in the approximate Hamiltonian which agrees with a simplified version of the  $d_1$  term given in the literature<sup>5</sup> for NH<sub>3</sub> in a case of similar coupling.

In the case of the coupling between  $\mathbf{I}_p$  and  $\mathbf{K}$  it is assumed that the strong-field approximation<sup>3</sup> applies;

$$\mathbf{I}_p \cdot \mathbf{K} \approx \frac{\mathbf{I}_p \cdot \mathbf{H} \mathbf{K} \cdot \mathbf{H}}{|\mathbf{H}| |\mathbf{H}|} = I_z^p K_z. \quad (6)$$

Using the above approximations and Eq. (1), the

<sup>4</sup> C. A. Burrus, J. Chem. Phys. 31, 1270 (1959).

<sup>5</sup> G. R. Gunther-Mohr, C. H. Townes, and J. H. Van Vleck, Phys. Rev. 94, 1191 (1954).

approximate Hamiltonian  $\mathcal{H}'$  may be written:

$$\begin{aligned} \frac{\mathcal{H}'}{h} = & -[1-\sigma_p(\mathbf{J})]a_p I_z^p - [1-\sigma_{Cl}(\mathbf{J})]a_{Cl} K_z \frac{\mathbf{I}_{Cl} \cdot \mathbf{K}}{|\mathbf{K}|^2} \\ & - [1-\sigma_J(\mathbf{J})]b K_z \frac{\mathbf{J} \cdot \mathbf{K}}{|\mathbf{K}|^2} - c_p I_z^p K_z \frac{\mathbf{J} \cdot \mathbf{K}}{|\mathbf{K}|^2} - c_{Cl} \mathbf{I}_{Cl} \cdot \mathbf{J} \\ & + \frac{5d_1 \mathbf{I}_z^p K_z}{(2J-1)(2J+3)} \left[ 3 \frac{(\mathbf{J} \cdot \mathbf{K})^2}{|\mathbf{K}|^2} - \frac{2\mathbf{J}^2(\mathbf{J} \cdot \mathbf{K})}{|\mathbf{K}|^2} - \mathbf{J}^2 \right] \\ & + \frac{5d_2}{(2J-1)(2J+3)} \left[ 3(\mathbf{I}_{Cl} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_{Cl} \cdot \mathbf{J}) - \mathbf{I}_{Cl}^2 \mathbf{J}^2 \right] \\ & - \frac{5f}{3(2J-1)(2J+3)} \left[ 3K_z^2 \frac{(\mathbf{J} \cdot \mathbf{K})^2}{|\mathbf{K}|^4} - \mathbf{J}^2 \right] \\ & + \delta I_z^p K_z \left( 1 - \frac{\mathbf{J} \cdot \mathbf{K}}{|\mathbf{K}|^2} \right). \quad (7) \end{aligned}$$

In the above form,  $\mathcal{H}'$  involves only the operators  $I_z^p, I_{Cl}^2, J^2, K^2, I_z^p, K_z$ , since

$$\begin{aligned} \mathbf{I}_{Cl} \cdot \mathbf{J} &= \frac{1}{2}[\mathbf{K}^2 - \mathbf{I}_{Cl}^2 - \mathbf{J}^2], \\ \mathbf{I}_{Cl} \cdot \mathbf{K} &= \frac{1}{2}[\mathbf{K}^2 + \mathbf{I}_{Cl}^2 - \mathbf{J}^2], \\ \mathbf{J} \cdot \mathbf{K} &= \frac{1}{2}[\mathbf{K}^2 - \mathbf{I}_{Cl}^2 + \mathbf{J}^2]. \end{aligned} \quad (8)$$

### Approximate Energy Levels

The approximate energy levels of the HCl molecule in a magnetic field are the energy eigenvalues of  $\mathcal{H}'$ :

$$\begin{aligned} E(I_p I_{Cl} J; m_p K m_k) &= -[1-\sigma_p(\mathbf{J})]a_p m_p - [1-\sigma_{Cl}(\mathbf{J})]a_{Cl} m_k L_2 \\ & - [1-\sigma_J(\mathbf{J})]b m_k L_3 - c_p m_p L_3 - c_{Cl} L_1 \\ & + d_1 m_p m_k L_4 + d_2 L_5 - f L_6 + \delta m_p m_k (1-L_3), \quad (9) \end{aligned}$$

where

$$\begin{aligned} L_1 &= \frac{1}{2}[K(K+1) - I_{Cl}(I_{Cl}+1) - J(J+1)], \\ L_2 &= \frac{K(K+1) + I_{Cl}(I_{Cl}+1) - J(J+1)}{2K(K+1)}, \\ L_3 &= \frac{K(K+1) + I_{Cl}(I_{Cl}+1) + J(J+1)}{2K(K+1)}, \\ L_4 &= \frac{5}{(2J-1)(2J+3)} [3L_3^2 K(K+1) \\ & \quad - 2J(J+1)L_3 - J(J+1)], \quad (10) \\ L_5 &= \frac{5}{(2J-1)(2J+3)} [3L_1^2 - \frac{3}{2}L_1 - I_{Cl}(I_{Cl}+1)J(J+1)], \\ L_6 &= \frac{5}{3(2J-1)(2J+3)} [3m_k^2 L_3^2 - J(J+1)], \end{aligned}$$

and the allowed values of  $m_p, K, m_k$  are half-integral

values with limits:

$$|J - I_{Cl}| \leq K \leq (J + I_{Cl}); \quad -K \leq m_k \leq K; \\ -I_p \leq m_p \leq I_p. \quad (11)$$

### Proton Transition Frequencies

With the above expression for the energy levels and the selection rules:

$$\Delta m_p = \pm 1; \quad \Delta K = \Delta m_k = 0, \quad (12)$$

the general expression for the allowed frequencies corresponding to re-orientation of the proton magnetic moment is

$$\nu(JK m_k) = [1-\sigma_p(\mathbf{J})]a_p + c_p m_k L_3 \\ - d_1 m_k L_4 - \delta m_k [1-L_3]. \quad (13)$$

### Calculation of the HCl Proton Spectrum

The final proton spectrum is obtained by substituting appropriate values of the constants  $a_p, c_p, d_1$ , and  $\delta$  into the above expression for the allowed transition frequencies, assigning appropriate shapes and intensities to the individual lines, and adding the individual curves together to obtain the spectrum.

The line shapes assigned to the proton lines are Rabi curves for a single rf coil. The full width  $\Delta\nu$  at half intensity for the Rabi curve is given by

$$\Delta\nu = (1.072)\alpha/l, \quad (14)$$

where  $l$  is the length of the rf coil and  $\alpha$  is the most probable velocity of the molecules in the source.

The relative intensities assigned to the proton lines are proportional to the relative numbers of beam molecules in the states between which the transitions take place. The rotational energy states of diatomic molecules are populated according to

$$n_J = \frac{(2J+1)e^{-(\beta/T)J(J+1)}}{\sum_{n=0}^{\infty} (2n+1)e^{-(\beta/T)n(n+1)}}, \quad (15)$$

where  $\beta$  is a constant which depends only on the moment of inertia of the molecule. For HCl<sup>35</sup>,  $\beta = 14.8^\circ\text{K}$ .<sup>6</sup>

TABLE I. Relative state populations (in % of total number of beam molecules).

$J$	200°K	300°K
0	0.91	0.63
1	0.78	0.57
2	0.58	0.46
3	0.37	0.33
4	0.21	0.22
5	0.10	0.14
6	0.04	0.07

<sup>6</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

Assuming equal populations for all states of the same  $J$ , the relative populations are tabulated in Table I.

The constants  $a_p$  and  $d_1$  are known. For a particular value of the magnetic field  $H$ , the constant  $a_p$  may be calculated from

$$a_p = \mu_p H / I_p h. \quad (16)$$

The constant  $d_1$  may be calculated<sup>8</sup> with values of the appropriate constants obtained from Herzberg.<sup>6</sup> The variation of  $d_1$  with  $J$  is quite small, so the value  $d_1 = 2230$  cps, corresponding to  $J=3$ , was used in all UNIVAC calculations. In the calculations, the value of  $\delta$  was chosen to be 69 cps. This value was selected somewhat arbitrarily as the value<sup>7</sup> of  $\delta$  for HF ( $\delta_{\text{HF}} = 615$  cps) scaled down according to the ratio of the chlorine-to-fluorine gyromagnetic ratios. The contribution of this  $\delta$  to the line shape is negligibly small. The constant  $c_p$  is then the only unknown constant appearing in Eq. (13), and may be determined by choosing the value that produces the best agreement between calculated and experimental curves.

### III. EXPERIMENTAL PROCEDURE

The experimental radio-frequency spectrum corresponding to reorientation of the proton moment in HCl<sup>35</sup> was obtained using the new molecular beam apparatus at Harvard University. A description of this apparatus has previously appeared in the literature.<sup>1,8</sup> Experimental curves were taken at three different magnetic fields (480, 885, 3400 gauss) and two different source temperatures ( $\approx 200^\circ\text{K}$ ,  $\approx 300^\circ\text{K}$ ) using a single oscillatory field region initially  $\frac{3}{4}$  in. long ( $\Delta\nu = 17.1$  kc/sec, 21.0 kc/sec at  $T = 200^\circ\text{K}$ ,  $300^\circ\text{K}$ ). On-off modu-

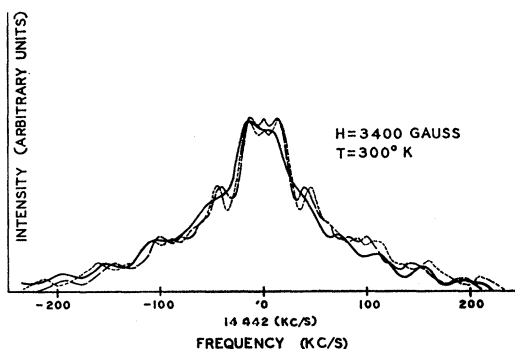


FIG. 1. Comparison of calculated and experimental proton spectra for HCl<sup>35</sup>. The theoretical curves were calculated using the approximate theory of Sec. II. — Experimental curve (using  $\frac{3}{4}$ -in. rf coil). - - - Theory 1 (calculation parameters:  $c_p = 41$  kc/sec,  $\delta = 69$  cps,  $\Delta\nu = 21.0$  kc/sec,  $d_1 = 2.230$  kc/sec). - - - Theory 3 (calculation parameters:  $c_p = 45$  kc/sec,  $\delta = 69$  cps,  $\Delta\nu = 21.0$  kc/sec,  $d_1 = 2.230$  kc/sec).

<sup>7</sup> I. Solomon and N. Bloembergen, J. Chem. Phys. **25**, 261 (1956).

<sup>8</sup> Details on construction methods, dimensions, and circuitry can be found in H. M. Nelson, thesis, Harvard University, 1959 (unpublished); J. A. Leavitt, thesis, Harvard University, 1960 (unpublished); M. R. Baker, thesis, Harvard University, 1960 (unpublished).

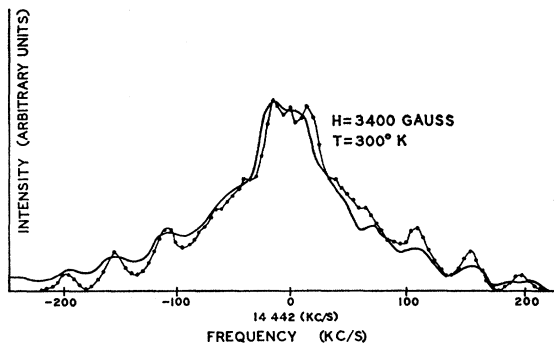


FIG. 2. Comparison of calculated and experimental proton spectra for HCl<sup>35</sup>. — Experimental curve (using  $\frac{3}{4}$ -in. rf coil). - - - Theoretical curve calculated using UNIVAC solution of secular equation. Calculation parameters:  $\Delta\nu = 21.0$  kc/sec,  $a_p = 14320$  kc/sec,  $a_{c1} = 1410$  kc/sec,  $b = 1397$  kc/sec,  $c_{c1} = -10.48$  kc/sec,  $c_p = 41$  kc/sec,  $d_1 = 2.230$  kc/sec,  $d_2 = -2.24$  Mc/sec,  $\delta = 69$  cps.

lation of the oscillatory field was used; the time constant of the phase sensitive detector was 8 sec. The signal-to-noise ratio (near maximum signal) was about 10 to 1. The curves produced on the recorder chart were reduced to smooth curves by drawing lines through the tops and bottoms of the noise peaks and plotting points midway between these extremes. The final data were plotted on the same scale as the UNIVAC print-out, thus allowing direct comparison between experimental and calculated curves. The experimental curve for  $H = 3400$  gauss and  $T = 300^\circ\text{K}$  is shown in Figs. 1 and 2.

Several months after the above observations with a  $\frac{3}{4}$ -in. long oscillatory field coil, the experimental spectrum was run again with a 3-in. oscillatory field ( $\Delta\nu = 4.3$  kc/sec at  $200^\circ\text{K}$ ). An experimental curve ( $H = 1810.5$  gauss,  $T = 220^\circ\text{K}$ ) taken using this increased resolution is shown in Fig. 3.

The hydrogen chloride gas (commercial grade, anhydrous, Matheson Company) used in these experi-

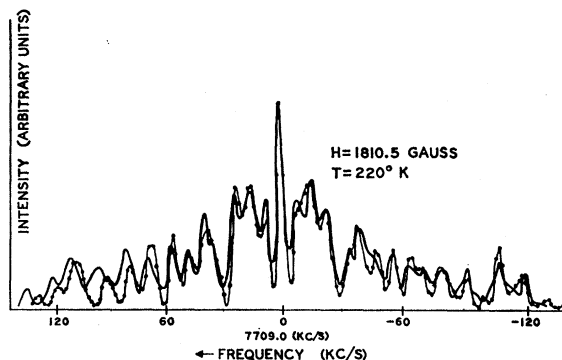


FIG. 3. Comparison of calculated and experimental proton spectra for HCl<sup>35</sup>. — Experimental curve (using 3-in. rf coil). - - - Theoretical curve calculated using UNIVAC solution of secular equation. Calculation parameters:  $\Delta\nu = 4.5$  kc/sec,  $a_p = 7709$  kc/sec,  $a_{c1} = 756$  kc/sec,  $b = 753$  kc/sec,  $c_{c1} = -10.48$  kc/sec,  $c_p = 41$  kc/sec,  $d_1 = 2.230$  kc/sec,  $d_2 = -2.24$  Mc/sec,  $\delta = 69$  cps.

ments contained  $\text{HCl}^{35}$  and  $\text{HCl}^{37}$  in the naturally occurring isotopic abundances (about 75%  $\text{HCl}^{35}$ ). The  $\text{HCl}^{37}$  proton spectrum was observed (by tuning the mass spectrometer to mass 38) but the signal-to-noise ratio was too poor for meaningful interpretation of the spectrum.

#### IV. INTERPRETATION AND RESULTS

The interpretation of the experimental resonance curves shown in Figs. 1-3 was carried out by direct comparison of the experimental curves with theoretical curves calculated using the UNIVAC computer. The theoretical curves were calculated using two different programs devised by one of the authors (N.F.R.). The program for the approximate method (Fig. 1) of Sec. II was considerably simpler and involved less machine time than the program for direct solution of the secular equations (Figs. 2 and 3). All calculations were carried out through all significant orders of  $J$  (through  $J=5$ ). Parameters used in the calculations are given in the figure captions.

Figure 1 shows the comparison of the low-resolution ( $\Delta\nu=21$  kc/sec) experimental curve with the corresponding theoretical curves calculated using the approximate theory of Sec. II. The agreement is not expected to be perfect since the approximate theory gives a symmetrical curve whereas the experimental curve is somewhat asymmetrical. An analysis of the positions and separations of the side peaks indicates that the value of  $|c_p|$  for best fit is

$$|c_p| = 43 \pm 4 \text{ kc/sec.}$$

The rather large uncertainty is due to the use of the approximate theory and to the uncertainty in the knowledge of  $\delta$ .

Figure 2 shows the comparison of the same low-resolution experimental curve with the corresponding

theoretical curve calculated by solving the secular equation. The value of  $|c_p|$  for best fit is judged to be

$$|c_p| = 41 \pm 3 \text{ kc/sec.}$$

The assigned uncertainty is due to uncertainty in the knowledge of the calculation parameters  $c_{Cl}$ ,  $b$ , and  $\delta$ .

Figure 3 shows the comparison of the high-resolution ( $\Delta\nu=4.5$  kc/sec) experimental curve with the corresponding theoretical curve calculated by solving the secular equation. The agreement is good but not perfect. The value of  $|c_p|$  for best fit is judged to be

$$|c_p| = 41 \pm 3 \text{ kc/sec.}$$

The discrepancies between the calculated and experimental curve are probably due to a combination of experimental noise; uncertainty in the parameters  $c_{Cl}$ ,  $b$ , and  $\delta$ ; and a modification of the transition intensities of different states by such experimental factors as the collisions of some molecules with the magnet poles.

The sign of  $c_p$  is not determined by this analysis, since a change in the sign of  $c_p$  produces only small changes in the calculated curves.

The final conclusions are:

(1) The approximate theory developed in Sec. II is adequate to allow the determination of  $|c_p|$  to within 10%. This theory should also be valid for cases of similar coupling.

(2) The absolute value of the spin rotational constant of the proton in  $\text{HCl}^{35}$  is

$$|c_p| = 41 \pm 3 \text{ kc/sec.}$$

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