

Nuclear Magnetic Hyperfine Spectra of H³⁵Cl and H³⁷Cl

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Citation: *The Journal of Chemical Physics* **49**, 1895 (1968); doi: 10.1063/1.1670322

View online: <http://dx.doi.org/10.1063/1.1670322>

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shown in Fig. 7. WLF³ in proposing their universal equation noted that it did not fit the data below the glass transition but did not consider this discrepancy significant. In addition, the data³² they used were scanty and it was questionable whether the viscosity values represented measurements made on glass in an equilibrium state.

A series of annealing experiments on B_2O_3 glass³³ was undertaken in order to ensure that all viscosity values represented measurements made on glass in equilibrium. Stabilization times at several temperatures through the transformation region were determined by measuring the index of refraction. In turn, these times were used to stabilize the glass in the viscometer before the measurements were started. The results show that the constancy of the activation energy at low temperatures is a true effect and must be taken into account when one proposes a new model.

A naive, yet more significant model for the viscosity of B_2O_3 is one similar to that of Ottar and Ruigh³⁴ in which the liquid has a "disassociated" state at high

temperatures ($T > 800^\circ$) in the Arrhenius region. Then, there is an intermediate region where association takes place, finally, almost completely associated, the liquid again becomes Arrhenius. This model has to be made much more specific in order to explain the distribution of relaxation times.

VI. CONCLUSIONS

The additional viscosity data on B_2O_3 and BSC glass, together with previous work, permitted a critical evaluation of the best known viscosity theories. It was found that the present theories of viscosity are inadequate, in particular, to fit the viscosity data, and, in general, to give physical significance to the calculation of shear relaxation and its spectrum of relaxation times.

ACKNOWLEDGMENTS

The authors wish to thank H. Hagy of the Corning Glass Works for generously donating the BSC glass together with some high-temperature viscosity data. They also wish to thank E. G. Hawkins for fabricating the fibers and making precise viscosity measurements in the 10^{10} – 10^{14} P range.

³² J. P. Poole, J. Am. Ceram. Soc. **32**, 230 (1949).

³³ L. Boesch, A. Napolitano, and P. B. Macedo, J. Am. Ceram. Soc. (to be published).

³⁴ B. Ottar and W. L. Ruigh, Phys. Chem. Glasses **3**, 95 (1962).

Nuclear Magnetic Hyperfine Spectra of $H^{35}Cl$ and $H^{37}Cl^*$

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(Received 20 February 1968)

The nuclear hyperfine spectra of $H^{35}Cl$ and $H^{37}Cl$ have been studied in the limit of zero external magnetic field by a molecular-beam magnetic resonance spectrometer. Thirteen lines of the $H^{35}Cl$ spectrum were observed in the range 20–230 kHz, and eight lines of the $H^{37}Cl$ spectrum were observed in the range 20–140 kHz. The spectra were analyzed by a zero-field magnetic hyperfine Hamiltonian. For each molecule the proton spin-rotation constant c_p and the total tensor spin-spin constant d have been measured, and an upper limit for the magnitude of the scalar part of the electron-coupled spin-spin constant $|\delta|$ has been established. The calculated transition frequencies agree with the observed spectra and the independent determinations of the constants for the two molecules are consistent with the first-order theory of isotopic effects. The measured constants for $H^{35}Cl$ are $c_p = +41.70 \pm 0.10$ kHz and $d = +2.20 \pm 0.04$ kHz; for $H^{37}Cl$ they are $c_p = +41.66 \pm 0.10$ kHz and $d = +1.86 \pm 0.04$ kHz. The upper limits for $|\delta|$ in $H^{35}Cl$ and $H^{37}Cl$ are 0.33 and 0.27 kHz, respectively.

I. INTRODUCTION

Magnetic resonance molecular beam spectroscopy provides an elegant method for the study of nuclear magnetic interactions in free molecules.¹ While many

resonance experiments have been performed to observe these interactions in the presence of a large external magnetic field, very few have been done in the limit of zero external field.^{2–6} The present experiment shows the

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¹ N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1963), Chap. 8.

² W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947).

³ H. J. Zeiger and D. I. Bolef, Phys. Rev. **85**, 788 (1952); D. I. Bolef and H. J. Zeiger, *ibid.* **85**, 799 (1952).

⁴ H. G. Kolsky, T. E. Phipps, Jr., N. F. Ramsey, and H. B. Silsbee, Phys. Rev. **87**, 395 (1952).

⁵ I. Ozier, Ph.D. thesis, Harvard University, 1965 (unpublished).

⁶ P. N. Yi, Ph.D. thesis, Harvard University, 1967 (unpublished).

advantages of zero-field spectroscopy over high-field spectroscopy for the measurement of the internal nuclear magnetic interaction constants in the ground vibrational state of the HCl molecule.

The proton resonance of H^{35}Cl in a large external magnetic field was previously observed by Leavitt, Baker, Nelson, and Ramsey with the same apparatus used in the present experiment.⁷ In their experiment the high-field proton spectrum was symmetric about the Larmor frequency, so that the magnitudes but not the signs of the hyperfine constants could be measured. The lines from different rotational states overlapped in the high-field case, and only the structure on the envelope of the proton spectrum was observed. Attempts made to observe the proton envelope of H^{37}Cl were unsuccessful because the experimental signal to noise level was much lower than it was for H^{35}Cl . The analysis of the envelope of a spectrum is less conclusive than the analysis of a resolved spectrum. Consequently the high-field experiment determined the magnitude of the proton spin-rotation constant in H^{35}Cl to be $|c_p| = 41 \pm 3$ kHz, but failed to determine the total tensor spin-spin constant d or the electron-coupled spin-spin constant δ .

The present experiment which was done in the zero-field limit has determined the algebraic value of c_p for both H^{35}Cl and H^{37}Cl with a 30-fold increase in precision. It has also measured d and given an estimate for δ in both molecules. The zero-field proton spectra have no symmetry, and the relative signs of the hyperfine constants can be determined once the correct identification of a sufficient number of lines has been made. No overlap of lines from different rotational states occurs. Neglecting the Zeeman splittings from the residual magnetic field, most of the lines in the spectra are fully resolved. With the same beam operating conditions, the low signal-to-noise level on the H^{37}Cl lines was sufficient to determine the zero-field proton transition frequencies, although it had not been sufficient to determine the structure on the high-field-proton spectrum envelope in the experiment of LBNR. In addition to the experimental advantages of resolved lines, the analysis of the proton spectra is considerably simplified in the zero-field limit.

The internal nuclear magnetic interactions in molecules explain many phenomena observed in NMR experiments. The spin-rotation and spin-spin interactions make important contributions to the nuclear spin-relaxation times observed in liquid and gaseous HCl ,⁸ in liquid mixtures of HCl and DCl ,⁹ and in liquid HCl and DCl .¹⁰ The electron-coupled spin-spin inter-

action has not been observed directly in a high-resolution NMR experiment on HCl , although the interaction has recently been observed in liquid HF .¹¹ Estimates have been given for the magnitude of δ in HCl ⁸ and DCl ¹⁰ which have been based on the frequency dependence of the relaxation rates T_1^{-1} and T_2^{-1} . The estimate of $|\delta| = 0.352 \pm 0.06$ kHz for H^{35}Cl given by Blicharski and Krynicki⁸ is somewhat larger than the value indicated by the error interval of the present molecular beam measurement of δ .

In Sec. II the theory of the low-frequency part of the zero-field spectrum is presented and the transition frequencies that correspond to a reorientation of the proton spin in the molecular-coupling scheme are calculated. Details of the experimental procedure are given in Sec. III. In Sec. IV the analysis of the observed spectra is outlined, and in Sec. V a discussion of the results is given.

II. THEORY

The nuclear hyperfine Hamiltonian¹ of the $^1\Sigma$ HCl molecule can be written

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{O}(H^2), \quad (1)$$

where \mathcal{H}_0 is independent of the external magnetic field H , \mathcal{H}_1 is linear in H , and terms of higher order in H have been neglected. Expressed in frequency units, \mathcal{H}_0 and \mathcal{H}_1 can be taken as

$$\begin{aligned} \frac{\mathcal{H}_0}{h} = & B_0 J(J+1) + \frac{5d_2}{(2J-1)(2J+3)} \\ & \times [3(\mathbf{I}_{\text{Cl}} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_{\text{Cl}} \cdot \mathbf{J}) - I_{\text{Cl}}(I_{\text{Cl}}+1)J(J+1)] \\ & - c_{\text{Cl}} \mathbf{I}_{\text{Cl}} \cdot \mathbf{J} - c_p \mathbf{I}_p \cdot \mathbf{J} + \frac{5d}{(2J-1)(2J+3)} \\ & \times [\frac{3}{2}(\mathbf{I}_p \cdot \mathbf{J})(\mathbf{I}_{\text{Cl}} \cdot \mathbf{J}) + \frac{3}{2}(\mathbf{I}_{\text{Cl}} \cdot \mathbf{J})(\mathbf{I}_p \cdot \mathbf{J}) \\ & - \mathbf{I}_p \cdot \mathbf{I}_{\text{Cl}} J(J+1)] + \delta \mathbf{I}_p \cdot \mathbf{I}_{\text{Cl}} \\ \frac{\mathcal{H}_1}{h} = & - \frac{g_p \mu_N}{h} \mathbf{I}_p \cdot \mathbf{H} - \frac{g_{\text{Cl}} \mu_N}{h} \mathbf{I}_{\text{Cl}} \cdot \mathbf{H} - \frac{g_J \mu_N}{h} \mathbf{J} \cdot \mathbf{H}, \quad (2) \end{aligned}$$

where the magnetic octupole moment of the chlorine nucleus and the shielding factors of the magnetic moments have been neglected.

The vectors \mathbf{I}_p and \mathbf{I}_{Cl} are the spin angular momenta of the proton and the chlorine nucleus, and \mathbf{J} is the rotational angular momentum of the molecule. The constants c_p , d , and δ have been previously defined. B_0 is the rotational constant of the molecule, d_2 represents the quadrupole interaction of the chlorine nucleus,

⁷ J. A. Leavitt, M. R. Baker, H. M. Nelson, and N. F. Ramsey, Phys. Rev. **124**, 1482 (1961). In the present paper these authors will be referred to as LBNR.

⁸ J. S. Blicharski and K. Krynicki, Acta Phys. Polon. **22**, 409 (1962).

⁹ K. Krynicki and J. G. Powles, Proc. Phys. Soc. (London) **86**, 549 (1965).

¹⁰ H. Boehme and M. Eisner, J. Chem. Phys. **46**, 4242 (1967).

¹¹ C. MacLean and E. L. Mackor, Proc. Colloq. Ampere 8th Eindhoven, 1962, 571 (1963).

and g_p and g_{Cl} are the "g factors" of the magnetic moments of the proton and chlorine nucleus, and g_J is the "g factor" of the rotational magnetic moment of the molecule, expressed in nuclear magnetons.

The value of the constant d is given by the equation

$$d = d_1 + d_2 = \frac{2}{5} g_p g_{\text{Cl}} (\mu_N/h) \langle 1/R^3 \rangle_{J,v} - \frac{1}{5} b_0, \quad (3)$$

where R is the internuclear distance and $\langle \rangle_{J,v}$ indicates the average value in the J th rotational state and the v th vibrational state. $b_0 = b_{\text{ff}}$ is the diagonal component of the tensor part of the electron-coupled spin-spin interaction taken along the internuclear axis ζ .¹²

The constant d_2 is related to the quadrupole moment of the chlorine nucleus by

$$d_2 = -eqQ/10hI_{\text{Cl}}(2I_{\text{Cl}}+1). \quad (4)$$

The calculation of the zero-field proton spectrum of this Hamiltonian will be done for the rotational states $J=1$ to 5 since these are significantly populated in the experiment. The only interaction of \mathcal{H}_0 observable in the $J=0$ state is the scalar part of the electron-coupled spin-spin interaction. However, the corresponding proton transition is unobservable in this experiment since it lies inside the Rabi linewidth centered at 0 Hz.

Although the first three terms of \mathcal{H}_0 are not directly observed in this experiment, they determine the most convenient representation in which the matrix of \mathcal{H}_0 is written for the calculation of the zero-field proton spectrum.

In H^{35}Cl , the rotational constant $B_0 \approx 313$ GHz is much greater than the quadrupole interaction constant $eqQ \approx -68$ MHz,¹³ so that J can be considered a "good quantum number" and matrix elements nondiagonal in J may be neglected. This procedure is also valid for H^{37}Cl . In this approximation the first terms of \mathcal{H}_0 are diagonal in the $|K m_K\rangle$ representation, where

$$\mathbf{K} = \mathbf{J} + \mathbf{I}_{\text{Cl}}. \quad (5)$$

Since \mathcal{H}_0 is a scalar and commutes with the total angular momentum of the molecule \mathbf{F} , where

$$\mathbf{F} = \mathbf{K} + \mathbf{I}_p = \mathbf{J} + \mathbf{I}_{\text{Cl}} + \mathbf{I}_p, \quad (6)$$

the matrix of \mathcal{H}_0 will be calculated in the $|J, I_{\text{Cl}}, K, I_p; F m_F\rangle$ representation, where the parenthesis indicates the order of coupling in the phase convention of Edmonds.¹⁴

In this representation the last three terms of \mathcal{H}_0 have nondiagonal matrix elements. However, the eigenvalues E_n of \mathcal{H}_0 are dominated by the first three terms which have already been put in diagonal form by the approximation that J is a good quantum number. Furthermore,

¹² N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

¹³ G. Jones and W. Gordy, Phys. Rev. **135**, A295 (1964).

¹⁴ A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N.J., 1965).

TABLE I. Nondiagonal matrix elements of the proton spin-rotation interaction.

J	K'	K	F	$F m_F \langle (J, I_{\text{Cl}}) K', I_p; -c_p \mathbf{I}_p \cdot \mathbf{J} (J, I_{\text{Cl}}) K, I_p; F m_F \rangle$
1	3/2	1/2	1	$5^{1/2}/3 c_p$
1	5/2	3/2	2	$3/5 c_p$
2	3/2	1/2	1	c_p
2	5/2	3/2	2	$(21)^{1/2}/5 c_p$
2	7/2	5/2	3	$2(6^{1/2})/7 c_p$
3	5/2	3/2	2	$2(6^{1/2})/5 c_p$
3	7/2	5/2	3	$3(5^{1/2})/7 c_p$
3	9/2	7/2	4	$5^{1/2}/3 c_p$
4	7/2	5/2	3	$3(5^{1/2})/7 c_p$
4	9/2	7/2	4	$(77)^{1/2}/9 c_p$
4	11/2	9/2	5	$6(2^{1/2})/11 c_p$
5	9/2	7/2	4	$2(2^{1/2})/3 c_p$
5	11/2	9/2	5	$3(13)^{1/2}/11 c_p$
5	13/2	11/2	6	$(105)^{1/2}/13 c_p$

the last three terms are small compared to the first three, so that the eigenvalues of \mathcal{H}_0 can be calculated to sufficient accuracy by second-order perturbation theory and can be labeled by the quantum numbers of this representation, i.e.,

$$E_n = E_{J,K,F}. \quad (7)$$

The low-frequency part of the HCl hyperfine spectrum which is referred to in this paper as the zero-field proton spectrum corresponds to a set of transitions occurring within many isolated "two-level" systems (neglecting the matrix elements nondiagonal in K and the degeneracies in m_F) that exist for each value of J and K . These magnetic dipole transitions represent reorientations of \mathbf{I}_p relative to \mathbf{K} , and obey the selection rules $\Delta K=0$, $\Delta F=\pm 1$, $\Delta m_F=\pm 1, 0$. The transition frequencies can be systematically calculated from the perturbation series

$$\begin{aligned} \Delta W(J, K) &= \Delta W^{(1)}(J, K) + \Delta W^{(2)}(J, K) + \dots \\ &= h^{-1} [E_{J,K,F=K+1/2} - E_{J,K,F=K-1/2}]. \end{aligned} \quad (8)$$

In this representation there are no contributions to the first-order term $\Delta W^{(1)}(J, K)$ from the first three terms of \mathcal{H}_0 . The first-order contributions from the last three terms are easily evaluated. The scalar products in these terms can be replaced by their well-known vector projection values in the coupling schemes (5) and (6) when the diagonal matrix elements are calculated,

$$\mathbf{I}_{\text{Cl}} \cdot \mathbf{J} \approx \frac{1}{2} [K(K+1) - I_{\text{Cl}}(I_{\text{Cl}}+1) - J(J+1)],$$

$$\mathbf{I}_p \cdot \mathbf{J} \approx [(\mathbf{I}_p \cdot \mathbf{K})(\mathbf{K} \cdot \mathbf{J})/K(K+1)],$$

$$\mathbf{I}_p \cdot \mathbf{I}_{\text{Cl}} \approx [(\mathbf{I}_p \cdot \mathbf{K})(\mathbf{K} \cdot \mathbf{I}_{\text{Cl}})/K(K+1)],$$

$$\mathbf{I}_p \cdot \mathbf{K} \approx \frac{1}{2} [F(F+1) - I_p(I_p+1) - K(K+1)]. \quad (9)$$

For example, the first-order contribution of the proton spin-rotation interaction to (8) is

$$\begin{aligned} & \langle (J, I_{Cl}) K, I_p; F m_F | -c_p \mathbf{I}_p \cdot \mathbf{J} | (J, I_{Cl}) K, I_p; F m_F \rangle \\ & - \langle (J, I_{Cl}) K, I_p; F-1 m_F | -c_p \mathbf{I}_p \cdot \mathbf{J} | (J, I_{Cl}) K, I_p; F-1 m_F \rangle \\ & = -c_p \{ [K(K+1) + J(J+1) - I_{Cl}(I_{Cl}+1)] [F]/2K(K+1) \}. \quad (10) \end{aligned}$$

The first-order contributions from the dipole-dipole and electron-coupled spin-spin interactions are similarly evaluated, and the resulting equations for $\Delta W^{(1)}(J, K)$ are

$$\begin{aligned} \Delta W^{(1)}(J, J+\frac{3}{2}) &= -c_p \frac{2J(J+2)}{(2J+3)} + d \frac{15J(J+2)}{(2J+3)^2} + \delta \frac{3(J+2)}{(2J+3)}, \\ \Delta W^{(1)}(J, J+\frac{1}{2}) &= -c_p \frac{2(J+1)(2J^2+3J-3)}{(2J+1)(2J+3)} + d \frac{5(J+1)(2J^2-9J-27)}{(2J+1)(2J+3)^2} + \delta \frac{(J+1)(2J+9)}{(2J+1)(2J+3)}, \\ \Delta W^{(1)}(J, J-\frac{1}{2}) &= -c_p \frac{2J(2J^2+J-4)}{(2J-1)(2J+1)} - d \frac{5J(2J^2+13J-16)}{(2J-1)^2(2J+1)} - \delta \frac{J(2J-7)}{(2J-1)(2J+1)}, \\ \Delta W^{(1)}(J, J-\frac{3}{2}) &= -c_p \frac{2(J-1)(J+1)}{(2J-1)} - d \frac{15(J-1)(J+1)}{(2J-1)^2} - \delta \frac{3(J-1)}{(2J-1)}. \quad (11) \end{aligned}$$

Since both ^{35}Cl and ^{37}Cl have nuclear spin $\frac{3}{2}$, $\Delta W^{(1)}(J, J-\frac{3}{2})$ is not defined for the $J=1$ case.

In second order, only the proton spin-rotation interaction is large enough to produce observable contributions to $\Delta W(J, K)$. The matrix elements nondiagonal in K can be easily evaluated in the vector algebra formalism of Edmonds¹⁴ using published tables of the 6- j symbols,¹⁵

$$\begin{aligned} & \langle (J, I_{Cl}) K', I_p; F m_F | -c_p \mathbf{I}_p \cdot \mathbf{J} | (J, I_{Cl}) K, I_p; F m_F \rangle \\ & = c_p (-1)^{F+2K+J+I_{Cl}+I_p} [I_p(I_p+1)(2I_p+1)(2K'+1)(2K+1)J(J+1)(2J+1)]^{1/2} \\ & \quad \times \begin{pmatrix} F & I_p & K' \\ 1 & K & I_p \end{pmatrix} \times \begin{pmatrix} J & K' & I_{Cl} \\ K & J & 1 \end{pmatrix}. \quad (12) \end{aligned}$$

The second-order corrections to the transition frequencies due to the proton spin-rotation interactions are given by

$$\begin{aligned} \Delta W^{(2)}(J, K) &= \frac{-\sum_{K'} | \langle (J, I_{Cl}) K', I_p; F=K+\frac{1}{2} | -c_p \mathbf{I}_p \cdot \mathbf{J} | (J, I_{Cl}) K, I_p; F=K+\frac{1}{2} \rangle |^2}{(E_{J,K^0} - E_{J,K^0})/\hbar} \\ &+ \frac{\sum_{K''} | \langle (J, I_{Cl}) K'', I_p; F=K-\frac{1}{2} | -c_p \mathbf{I}_p \cdot \mathbf{J} | (J, I_{Cl}) K, I_p; F=K-\frac{1}{2} \rangle |^2}{(E_{J,K'^0} - E_{J,K^0})/\hbar}. \quad (13) \end{aligned}$$

The frequency denominators were calculated from the quadrupole splittings of the chlorine nucleus,¹⁶ neglecting the chlorine spin-rotation constant. Although c_{Cl} is unknown, it is expected to be much smaller than d_2 , and since $\Delta W^{(2)}(J, K)$ is small compared to $\Delta W^{(1)}(J, K)$ the error introduced by this approximation is negligible. The off-diagonal matrix elements of the proton spin-rotation interaction are given in Table I for $J=1$ to 5. The numerical values of $\Delta W^{(2)}(J, K)$ for H^{35}Cl and H^{37}Cl are given in Tables II and III, respectively. Although these second-order corrections are the same order of magnitude as the statistical errors in the

observed frequencies, they are significant in determining upper limits for the electron-coupled spin-spin interactions in the two molecules.

Since the proton spectra were observed in the limit of zero external magnetic field, there is the possibility of a residual field removing the m_F degeneracies in the hyperfine energy levels. The Zeeman corrections to the energy eigenvalues of \mathcal{H}_0 are given by the diagonal matrix elements of \mathcal{H}_1 in this representation,

$$E_{J,K,F,m_F} = E_{J,K,F} + \langle (J, I_{Cl}) K, I_p; F m_F | \mathcal{H}_1 | (J, I_{Cl}) K, I_p; F m_F \rangle, \quad (14)$$

which can be calculated from vector projections similar to Eqs. (9). It will be shown in sec. IV that the residual magnetic field was sufficiently small that individual Zeeman transitions were not resolved and field-depend-

¹⁵ M. Rotenberg, N. Metropolis, R. Bivins, and J. K. Wooten, Jr., *The 3-j and 6-j symbols* (M.I.T. Press, Cambridge, Mass., 1959).

¹⁶ These were calculated from tables of quadrupole splittings given by J. Bardeen and C. H. Townes, *Phys. Rev.* **73**, 97 (1948): assuming $eqQ = -68$ MHz for H^{35}Cl and $eqQ = -53$ MHz for H^{37}Cl .

TABLE II. Spectrum of H^{35}Cl .

J, K	Intensity (arbitrary units)	Linewidth (kHz)	Completely resolved?	$\Delta W^{(1)}(J, K)^a$ (kHz)	$\Delta W^{(2)}(J, K)^a$ (kHz)	$\Delta W(J, K)^a$ (kHz)	Observed frequency (kHz)
1, 1/2	27	3.1	No	+31.530	+0.032	+31.562	32.04±0.10
1, 3/2	27	3.1	No	-32.141	-0.005	-32.146	32.04±0.10
1, 5/2	24	3.1	Yes	-46.008	-0.037	-46.045	46.07±0.10
2, 1/2	5	3.1	No	-94.425	+0.102	-94.323	94.10±0.50
2, 3/2	11	3.1	Yes	-75.491	+0.222	-75.269	75.34±0.10
2, 5/2	23	3.1	Yes	-83.563	+0.070	-83.493	83.56±0.10
2, 7/2	34	3.1	Yes	-89.857	-0.050	-89.907	89.88±0.10
3, 3/2	5	3.1	Yes	-144.031	+0.098	-143.933	143.83±0.15
3, 5/2	20	3.5	No	-129.239	+0.300	-128.939	129.30±0.10
3, 7/2	20	3.5	No	-129.831	+0.145	-129.686	129.30±0.10
3, 9/2	21	3.1	Yes	-132.820	-0.057	-132.877	132.76±0.10
4, 5/2	4	3.1	Yes	-188.849	+0.094	-188.755	188.57±0.15
4, 7/2	18	3.6	No	-176.219	+0.371	-175.848	174.75±0.15
4, 9/2	18	3.6	No	-174.217	+0.216	-174.001	174.75±0.15
4, 11/2	18	3.6	No	-175.349	-0.061	-175.410	174.75±0.15
5, 7/2	-232.211	+0.091	-232.120	...
5, 9/2	2	3.1	No	-220.918	+0.441	-220.477	220.50±1.0
5, 11/2	6	4.0	No	-217.694	+0.286	-217.408	217.00±0.50
5, 13/2	6	4.0	No	-217.634	-0.064	-217.698	217.00±0.50

^a The spectrum of H^{35}Cl was calculated assuming $c_p = +41.698$ kHz, $d = +2.198$ kHz, and $\delta = +0.041$ kHz. The sign convention and notation are defined in Eq. (8) of the text.

ent shifts of less than 0.25 kHz occurred in the envelopes of the zero-field hyperfine transitions.

III. EXPERIMENTAL CONDITIONS

The apparatus used in this experiment has been previously described in the literature,¹⁷ and was also used in the high-field proton experiment of LBNR. Although many of the experimental conditions in the two experiments were similar, the important difference in procedure was the demagnetization of the resonance region in the "C" magnet prior to the observation of the zero-field spectra.

Normal demagnetization techniques¹⁸ were not sufficient, since a residual magnetic field of approximately 10 G could not be eliminated. However, this residual

field could be cancelled over the resonance region by using a small current in the magnet windings to add an opposite field in the magnet gap and remove the Zeeman splittings of the two hyperfine transitions of molecular hydrogen in the $I_R = J = 1$ state.¹⁹ In a weak field the $F = 0 \leftrightarrow 1$ and the $F = 1 \leftrightarrow 2$ transitions of H_2 have the frequencies $(546.437 \pm 2.465H)$ and $(54.795 \pm 2.465H)$ kHz, respectively, for H measured in gauss. From shifts in the envelopes of these hyperfine transitions, the magnitude and drift rate of the field in the resonance region could be measured, with the conclusion that the external magnetic field during the observations of the HCl hyperfine spectra was less than 50 mG. This method of demagnetization has been described in detail by Ozier⁵ and Yi.⁶

TABLE III. Spectrum of H^{37}Cl .

J, K	Intensity (arbitrary units)	Linewidth (kHz)	Completely resolved?	$\Delta W^{(1)}(J, K)^a$ (kHz)	$\Delta W^{(2)}(J, K)^a$ (kHz)	$\Delta W(J, K)^a$ (kHz)	Observed frequency (kHz)
1, 1/2	6	3.1	No	+30.984	+0.041	+31.025	30.57±0.20
1, 3/2	6	3.1	No	-30.545	-0.006	-30.551	30.57±0.20
1, 5/2	11	3.1	Yes	-46.514	-0.047	-46.561	46.55±0.10
2, 1/2	1	3.1	No	-92.676	+0.131	-92.545	92.10±1.0
2, 3/2	3	3.1	Yes	-74.059	+0.284	-73.775	93.70±0.50
2, 5/2	6	3.1	Yes	-82.685	+0.090	-82.595	82.58±0.20
2, 7/2	11	3.1	Yes	-90.538	-0.064	-90.602	90.71±0.20
3, 3/2	-142.304	+0.125	-142.179	...
3, 5/2	3	4.0	No	-127.923	+0.383	-127.540	128.40±0.50
3, 7/2	3	4.0	No	-129.243	+0.185	-129.058	128.40±0.50
3, 9/2	3	3.1	Yes	-133.568	-0.073	-133.641	133.65±0.50

^a The spectrum of H^{37}Cl was calculated assuming $c_p = +41.655$ kHz, and $d = +1.860$ kHz, $\delta = +0.069$ kHz. The sign convention and notation are defined in Eq. (8) of the text.

¹⁷ M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, Phys. Rev. **121**, 807 (1961).

¹⁸ H. B. Silbsee, Ph.D. thesis, Harvard University, 1950 (unpublished).

¹⁹ N. F. Ramsey, Phys. Rev. **85**, 60 (1952).

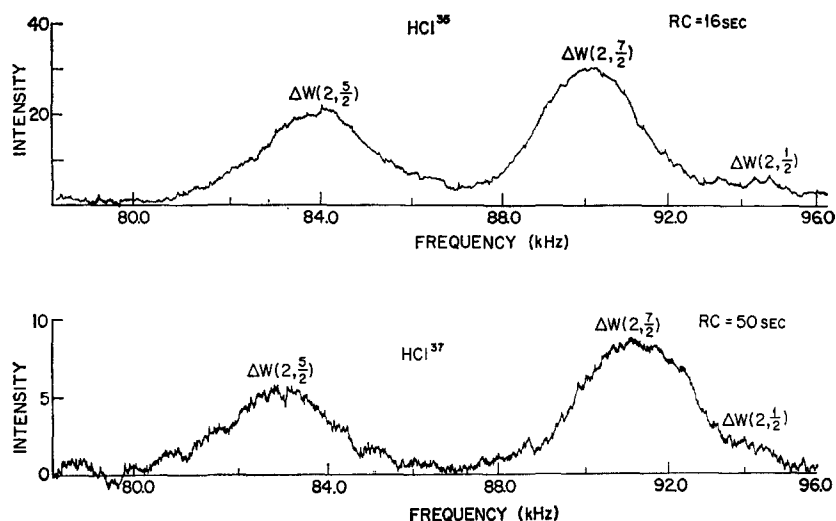


FIG. 1. A comparison of part of the spectrum of H^{35}Cl with the corresponding part of the spectrum of H^{37}Cl . Both scans were taken as the oscillator frequency increased with time.

The hyperfine spectra of H^{35}Cl and H^{37}Cl were observed with a single rf coil $3\frac{5}{8}$ -in. long, having a sinusoidal magnetic induction field approximately 1.3 G in magnitude. The temperature of the source oven was 200°K . The Rabi linewidth was $\Delta\nu = 3.0$ kHz. The rf field was "chopped" at 17 Hz and the "flop-out" resonance signal was synchronously detected.

Commercial grade, anhydrous hydrogen chloride gas (Matheson Company) was used in this experiment. H^{35}Cl and H^{37}Cl were present in the sample in a ratio of 3:1. The spectra for H^{35}Cl and H^{37}Cl were taken by setting the mass spectrometer of the electron bombardment detector at mass 36 and 38, respectively. Resonances were observed in H^{35}Cl that corresponded to rotational states up to $J = 5$. States with higher J values were not observed because of their low statistical weight at 200°K . The intensities of the proton resonances in H^{37}Cl were approximately three times weaker than those observed in H^{35}Cl . This reduced the total number of lines observed for H^{37}Cl , but did not prevent analysis of the H^{37}Cl spectrum as it did in the high-field experiment of LBNR.

IV. ANALYSIS OF THE SPECTRA

The observed spectra for H^{35}Cl and H^{37}Cl are presented in Tables II and III. The transition frequencies were determined from averages of the line centers of three or more pairs of scans taken in opposite directions over the frequency interval. The errors quoted are statistical uncertainties in the line centers. In Fig. 1 a typical scan of a portion of the H^{35}Cl spectrum is compared with the corresponding portion of the H^{37}Cl spectrum.

The analysis of the spectra was based on the assumption that the hyperfine constants c_p , d , and δ were independent of the quantum number J . There was not sufficient data for these three constants to be measured independently for each J state. The spectral assignment

was easily made from preliminary calculations of the spectra using estimates of the hyperfine constants obtained from the experiment of LBNR.

The hyperfine constants for both molecules were determined by independent least-squares regression analyses²⁰ of the fully resolved lines in the two spectra. Since the intensities and line shapes of the hyperfine transitions were not discussed in the theory presented in Sec. II, no additional information about the hyperfine constants could be determined from the envelopes of the unresolved transitions. The sign of c_p was determined relative to the sign of d , which is known from the sign of the dominant direct spin-spin interaction term in Eq. (3).

Errors in measuring the hyperfine constants may have originated from systematic errors in determining the line centers and from Zeeman shifts caused by the residual magnetic field as well as from random errors in the data. Bias in determining the line centers was estimated by comparison of the results of several observers. Instrumental asymmetries in the line shapes were estimated by comparison of the observed line shapes with those of the strong proton resonances in H_2 taken under the same conditions. The systematic errors introduced by these two sources were estimated to be less than the random errors in the data. However, the errors introduced by Zeeman shifts were significant and limited the accuracy of the zero-field experiment. The relevant Zeeman transitions had the selection rules $\Delta F = \pm 1$, $\Delta m_F = \pm 1, 0$, but since the direction of the residual external field relative to the oscillatory field was not known, the transition probabilities were uncertain. Furthermore, certain Zeeman transitions produced only a small net change of magnetic moment in the deflecting magnets and were not observed in this experiment. The effects of the Zeeman transitions on the

²⁰ D. A. S. Fraser, *Statistics, An Introduction* (John Wiley & Sons, Inc., New York, 1960), Chap. 12.

envelopes of the hyperfine transitions could only be estimated from the diagonal matrix elements of \mathcal{H}_1 as indicated in Eq. (14),

$$\begin{aligned} & \langle (J, I_{Cl}) K, I_p; F m_F | \mathcal{H}_1 / h | (J, I_{Cl}) K, I_p; F m_F \rangle \\ &= \frac{-\mu_N}{h} \left\{ g_p \left[\frac{\mathbf{I}_p \cdot \mathbf{F}}{\mathbf{F} \cdot \mathbf{F}} \right] + g_{Cl} \left[\frac{(\mathbf{I}_{Cl} \cdot \mathbf{K})(\mathbf{K} \cdot \mathbf{F})}{(\mathbf{K} \cdot \mathbf{K})(\mathbf{F} \cdot \mathbf{F})} \right] \right. \\ & \quad \left. + g_J \left[\frac{(\mathbf{J} \cdot \mathbf{K})(\mathbf{K} \cdot \mathbf{F})}{(\mathbf{K} \cdot \mathbf{K})(\mathbf{F} \cdot \mathbf{F})} \right] \right\} m_F H_z. \end{aligned}$$

An upper limit to the Zeeman shifts was given by this expression using the limit of 50 mG for the residual magnetic field in the resonance region that was established in Sec. III. The value of g_J has been estimated for H³⁵Cl as 0.2 nuclear magnetons (μ_N) from precise infrared spectroscopy.²¹ The nuclear "g factors" for ³⁵Cl and ³⁷Cl are known to be $0.5479\mu_N$, and $0.4561\mu_N$, respectively.²² Since the angular factors are of the order of unity, the Zeeman splittings are dominated by the large value of $g_p = 5.586\mu_N$, and are less than 0.25 kHz for all of hyperfine transitions observed. For most of the transitions, the maximum Zeeman splittings are of the order of 0.05 kHz.

The values of the hyperfine constants c_p and d and the estimates of δ for both molecules are presented in Table IV. A weighted least-squares fit of seven resolved lines was used for H³⁵Cl, and a similar fit of five resolved lines was used for H³⁷Cl. The errors quoted account for random errors in the data and the estimates of the other sources of error in the experiment.

V. DISCUSSION OF THE RESULTS

The agreement between the calculated spectra and the observed spectra in Tables II and III indicates that the assumption of the hyperfine constants being independent of J is valid for the analysis of this experiment. The independent determinations of these constants for the two molecules can be compared by well-known theories of isotope effects.²³ To first order, c_p is inversely proportional to the moment of inertia of the molecule, and d and δ are directly proportional to the nuclear "g factors" of the chlorine isotopes. Smaller second-

TABLE V. Calculated values of the direct (unshielded) spin-spin interaction constant d_1 in H³⁵Cl and H³⁷Cl.

J	d_1 (H ³⁵ Cl) (kHz)	d_1 (H ³⁷ Cl) (kHz)
0	2.239	1.864
1	2.238	1.863
2	2.237	1.862
3	2.235	1.860
4	2.232	1.858
5	2.229	1.855

order corrections arise from changes in the averages over the vibrational wavefunction, but since the difference of the reduced masses of the molecules is approximately 0.2%, this effect is unobservable in this experiment, as are the centrifugal, or J -dependent effects. Using first-order isotopic corrections the following values for the hyperfine constants of H³⁷Cl can be calculated from the analysis of the H³⁵Cl hyperfine spectrum:

$$c_p \approx +41.63 \pm 0.10 \text{ kHz},$$

$$d \approx +1.83 \pm 0.04 \text{ kHz},$$

$$\delta \approx +0.03 \pm 0.10 \text{ kHz}.$$

These values are in excellent agreement with the values obtained from the H³⁷Cl hyperfine spectrum that are shown in Table IV.

The experimental measurements of d can be expressed equivalently as estimates of the tensor part of the electron-coupled spin-spin constant d_E in the two molecules. The values of the direct spin-spin constant d_1 have been calculated²⁴ for several J states in H³⁵Cl from constants obtained by infrared spectroscopy²³ and are given in Table V. The values of d_1 in H³⁷Cl given in the same table were calculated from those of H³⁵Cl using the ratio of the magnetic moments of the chlorine nuclei. The average values of d_1 in the rotational states used for the analysis of the data are 2.236 kHz in H³⁵Cl and 1.861 kHz in H³⁷Cl. Therefore, from Eq. (3) in H³⁵Cl $d_E = -0.04 \pm 0.04$ kHz and in H³⁷Cl $d_E = 0.00 \pm 0.04$ kHz. Since these constants are related in first order by the ratio of the chlorine moments, the upper limits on the magnitude of d_E in H³⁵Cl and H³⁷Cl are 0.12 and 0.10 kHz, respectively.

The ratio of the experimental estimates of δ for the two molecules cannot be expected to agree with the ratio of the chlorine magnetic moments as the errors are roughly twice as large as the magnitudes of these constants. However, the largest experimental estimate (given for δ in H³⁷Cl) yields upper limits to the magnitude of δ that are 0.33 kHz in H³⁵Cl and 0.27 kHz in H³⁷Cl. These limits are slightly smaller than expected from the NMR experiments of Blicharski and Krynicky.⁸

TABLE IV. Hyperfine constants of HCl determined from the zero-field spectra.

	H ³⁵ Cl	H ³⁷ Cl
c_p (kHz)	$+41.70 \pm 0.10$	$+41.66 \pm 0.10$
d (kHz)	$+2.20 \pm 0.04$	$+1.86 \pm 0.04$
δ (kHz) (estimate)	$+0.04 \pm 0.10$	$\pm 0.07 \pm 0.10$

²¹ D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Opt. Soc. Am. **52**, 1 (1962).

²² G. H. Fuller and V. W. Cohen, *Nuclear Moments* (Nuclear Data Project, Oak Ridge, Tenn., 1965).

²³ N. F. Ramsey, Phys. Rev. **87**, 1075 (1952).

²⁴ D. H. Rank, B. S. Rao, and T. A. Wiggins, J. Mol. Spectry. **17**, 122 (1956).