relation for a given observable according to the sign of the corresponding correlation coefficient. In electron systems, particularly for observables related to distances or angles, qualitative considerations suggest that the correlation is negative. However, positive correlation may occur, for instance in excited states; long range correlation, like the London dispersion forces, is also associated with positive correlation. From a quantitative point of view, absolute values of correlation coefficients for electronic systems are very small, as if the electrons were more or less independent.

The present conclusions depend to a certain extent on the fact that correlation coefficients have been defined through linear functions of the electronic coordinates. It would be worthwhile to investigate by numerical calculations other types of functional dependence. Nevertheless, the coefficients here defined are probably adequate for a quantitative analysis of electronic wave functions in terms of correlation, a field where many concepts still rest on intuitive arguments.

ACKNOWLEDGMENTS

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Hyperfine Structure of $N^{15}H_3$

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Hyperfine structure of the inversion transition for the J-K=4-4, 5-5, 6-6, and 7-7 rotational states of $N^{15}H_3$ was measured with a two-cavity maser spectrometer. Previous data on the J-K=2-2 state and these new data are analyzed including the nitrogen $\vec{I}_N\cdot\vec{J}$ term, the hydrogen $\vec{I}\cdot\vec{J}$ term, the hydrogen-nitrogen spin-spin interaction, the hydrogen-hydrogen spin-spin interaction, and a scalar electron-coupled spin-spin interaction. For the J-K=2-2, 4-4, 5-5, and 7-7 states a consistent set of coupling strengths are found such that the calculated frequencies agree with the data to within the experimental accuracy. There are still large discrepancies between calculated and experimental frequencies for the J-K=1-1, 3-3, and 6-6 states.

INTRODUCTION

In a previous paper,[1] measurements and calculations of transition frequencies for hyperfine structure of inversion transitions in $N^{14}H_3$ and $N^{15}H_3$ were reported. The theoretical expressions for the magnetic hyperfine interactions are given correctly in Ref. 1, but for the $N^{15}H_3$ states the numerical values of the hydrogen-nitrogen spin-spin interaction were not calculated correctly. The previous data for the $N^{15}H_3$ J-K =2-2 state is analyzed along with the new data for the J-K=4-4, 5-5, 7-7 states and for these states a satisfactory fit is obtained with a consistent set of interaction strengths.

ANALYSIS OF DATA

The Hamiltonian for the hyperfine structure is expressed in the form:

$$\mathcal{H} = C_R R + C_S S + C_T T + C_U U + C_V V.$$

The coefficients C_R, C_S, C_T, C_U, and C_V are combinations of 6-j and 9-j symbols containing the quantum numbers J, I_N, F_1, I, and F ($F_1 = I_N + J, F = I + F_1$). Expressions for these coefficients are given in the Appendix and the interactions are discussed in Ref. 1. R, S, T, U, and V are the strengths of the interactions and are related by the following expressions to the parameters used by Gordon[2] and Guther-Mohr, Townes, and VanVleck[3]

$R = a + (b - a)K^2/J(J+1)$ = strength of the magnetic $\vec{I}_N \cdot \vec{J}$ coupling (I_N = nitrogen spin)

$S = A + [CK^2/J(J+1)] + \delta_{K1}(-1)^{J+V}B$ = strength of the $\vec{I} \cdot \vec{J}$ coupling (I = sum of the hydrogen spins)

$T = D_1[1 - 3K^2/J(J+1)] - D_2\delta_{K1}(-1)^{J+V}$ = strength of the hydrogen-nitrogen spin-spin interaction

$U = -\frac{1}{4}D_3[1 - 3K^2/J(J+1)]$ = strength of the hydrogen-hydrogen spin-spin interaction

V = strength of the scalar electron-coupled hydrogen-nitrogen spin-spin interaction

$D_1 = g_H g_N \mu_0^2 \langle V | r_{NH}^{-3}(1 - \frac{3}{2}\sin^2\beta) | V \rangle$, $D_2' = g_H g_N \mu_0^2 \langle V | r_{NH}^{-3}(\frac{3}{2})\sin^2\beta | V \rangle$, $D_3 = (g_H \mu_0)^2 r_{HH}^{-3}$

β is the angle between a hydrogen-nitrogen bond and a line perpendicular to the plane of the hydrogens.

These interaction strengths are treated as adjustable parameters in a least-squares-fit program which determines values for these parameters by fitting the experimental data. Magnetic interactions off-diagonal in F_1 due to the terms S, T, U, and V are included in the analysis. The strength of the scalar electron-coupled interaction V was measured in a NMR experiment.[4] The value was $V = 61$ Hz and this value is used in the following analyses.

The energy level diagram for one of the inversion levels of the 2-2 state is shown in Fig. 1. All states with $K \neq 1$ or $3n$ have this same general form of energy level diagram. The observed spectrum for the 2-2 state is shown in Fig. 2. The resonance linewidth in these experiments is 350 Hz. The level diagram for the upper and lower inversion levels is the same so the spectrum is symmetric about the strong central component. The two transitions in each pair are identified by their relative intensity which agrees quite well (±10%) with the calculated values.

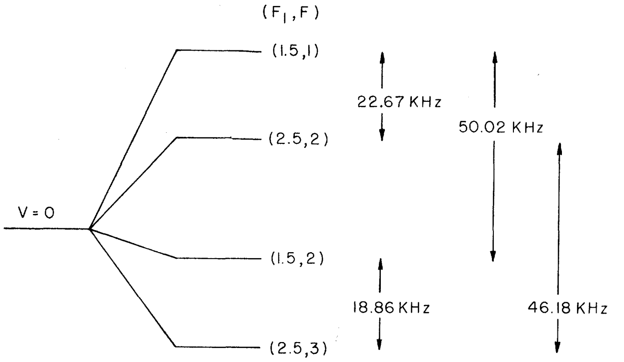

FIG. 1. Energy level diagram for one inversion level of the 2-2 rotational state in $N^{15}H_3$.

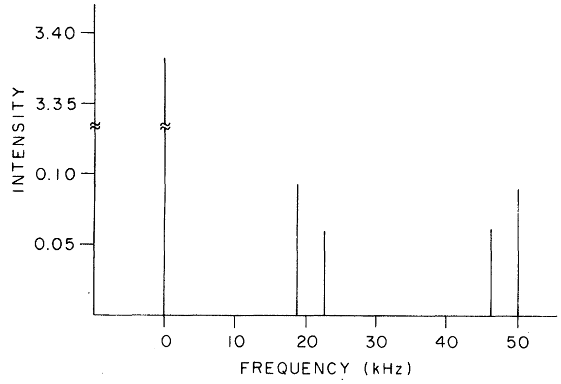

FIG. 2. Measured spectrum of the 2-2 rotational state in $N^{15}H_3$. Spectrum is symmetric about strongest line at 0. kHz. Frequencies relative to 22 649 843.407 kHz.

The results of the fit program for J-K = 2-2, 4-4, 5-5, and 7-7 are shown in Tables I, II, III, and IV. The standard deviation for the fit is probably a good indication of the experimental accuracy, since there are more lines than adjustable parameters. The experimental standard deviation indicates the width of the distribution of measured frequencies. The interaction strengths obtained from these fits are listed in Table V. The spin-rotational interactions R and S may be analyzed to fit a rotational dependence of the form[3] $R = a + (b - a)K^2/J(J+1)]$ and $S = A + CK^2/J(J+1)$. We find $a = -6.06$ kHz, $(b - a) = -3.70$ kHz (using J-K = 2-2, 4-4, 5-5, and 7-7), and $A = -17.735$ kHz, $C = -1.215$ kHz (using J-K = 2-2, 3-3, 4-4, 5-5, 6-6, and 7-7). The values of R, S, and D_1 calculated from $N^{14}H_3$ data are $R = -9.3$ kHz, $S = -18.6$ kHz, and $D_1 = 3.42$ kHz. D_1 may also be calculated from bond angles and lengths[5] and nuclear moments,[6] and this gives $D_1 = 3.33$ kHz. For these rotational states we are able to fit the data with a reasonable and consistent set of coupling parameters.

The measured frequencies and the results of the fit program for the 6-6 state are shown in Table VI.

Similar results are obtained for J-K = 1-1 and 3-3. For these cases we are not able to fit the data using the Hamiltonian given above. Deviations between calculated and experimental frequencies are 1 kHz or greater for some of the transitions in each case while experimental errors are 0.1 kHz or less. In addition the coupling parameters obtained (see Table V) are not consistent with calculated values or those obtained from the states discussed above.

TABLE I. Results of N^{15} 2-2 line measurements and calculations. Frequencies in kHz relative to 22 649 843.407. $R = -8.506\,28$, $S = -18.552\,82$, $T = 3.363\,50$, and $V = 0.061$. Standard deviation for fit = 0.0228; experimental standard deviation = 0.0739.

F_1'	F_1	F'	F	Data	Calculated	Deviation	Experimental standard deviation
1.5	2	1.5	1	−50.041	−50.022	−0.008	0.062
2.5	3	2.5	2	−46.184	−46.178	0.006	0.092
2.5	2	1.5	1	−22.682	−22.671	0.011	0.092
2.5	3	1.5	2	−18.793	−18.827	−0.034	0.047
1.5	1	1.5	1	−0.050	−0	0.050	0.056
1.5	2	2.5	3	18.855	18.827	−0.028	0.059
1.5	1	2.5	2	22.666	22.671	0.005	0.089
2.5	2	2.5	3	46.178	46.178	−0.000	0.083
1.5	1	1.5	2	50.024	50.022	−0.002	0.069

TABLE II. Results of N^{15} 4-4 line measurements and calculations. Frequencies in kHz relative to 23 046 015.781. $R = -9.0671$, $S = -18.7456$, $T = 4.6559$, and $V = 0.061$. Standard deviation for fit = 0.0528; experimental standard deviation = 0.0621.

F_1'	F'	F_1	F	Data	Calculated	Deviation	Experimental standard deviation
3.5	4	3.5	3	−87.738	−87.819	−0.081	0.057
4.5	5	4.5	4	−83.080	−82.981	0.099	0.090
4.5	4	3.5	3	−43.008	−42.992	0.015	0.063
4.5	5	3.5	4	−38.130	−38.155	−0.024	0.052
3.5	3	3.5	3	0.020	0.	−0.020	0.013
3.5	4	4.5	5	38.149	38.155	0.006	0.040
3.5	3	4.5	4	43.007	42.992	−0.015	0.043
4.5	4	4.5	5	82.912	82.981	0.069	0.108
3.5	3	3.5	4	87.868	87.819	−0.050	0.037

TABLE III. Results of N^{15} 5-5 line measurements and calculations. Frequencies in kHz relative to 23 421 982.366. $R = -9.1634$, $S = -18.7654$, $T = 5.0469$, and $V = 0.061$. Standard deviation for fit = 0.0581; experimental standard deviation = 0.1402.

F_1'	F'	F_1	F	Data	Calculated	Deviation	Experimental standard deviation
4.5	5	4.5	4	−106.607	−106.676	−0.069	0.132
5.5	6	5.5	5	−101.463	−101.500	−0.037	0.146
5.5	5	4.5	4	−52.923	−52.821	0.102	0.168
5.5	6	4.5	5	−47.626	−47.645	−0.019	0.156
4.5	4	4.5	4	−0.047	0	0.047	0.081
4.5	5	5.5	6	47.618	47.645	0.027	0.141
4.5	4	5.5	5	52.766	52.821	0.056	0.107
5.5	5	5.5	6	101.582	101.499	−0.083	0.130
4.5	4	4.5	5	106.699	106.676	−0.023	0.176

TABLE IV. Results of N^{15} 7-7 line measurements and calculations. Frequencies in kHz relative to 24 553 425.048. $R = -9.25163$, $S = -18.77749$, $T = 5.68193$, and $V = 0.061$. Standard deviation for fit = 0.0234; experimental standard deviation = 0.1824.

F_1'	F'	F_1	F	Data	Calculated	Deviation	Experimental standard deviation
6.5	7	6.5	6	−144.382	−144.362	0.019	0.305
7.5	7	6.5	6	−72.214	−72.193	0.020	0.205
7.5	8	6.5	7	−66.402	−66.434	−0.032	0.181
7.5	7	7.5	7	0.015	−0	−0.015	0.039
6.5	7	7.5	8	66.466	66.434	−0.032	0.184
6.5	6	7.5	7	72.173	72.193	0.020	0.070
6.5	6	6.5	7	144.343	144.362	0.019	0.158

TABLE V. Strength of interactions in kHz as obtained from fit programs.

J-K	R	S	T	D_1
2-2	−8.506	−18.553	3.364	−3.364
4-4	−9.067	−18.746	4.656	−3.326
5-5	−9.163	−18.765	5.047	−3.347
7-7	−9.252	−18.778	5.682	−3.497
1-1	−8.238	−15.790	−1.876	
3-3	−6.824	−18.605	−1.220	
6-6	−9.428	−18.751	−6.573	

TABLE VI. Results of N^{15} 6-6 line measurements and calculations. Frequencies in kHz relative to 23 922 313.218. $R = -9.4277$, $S = -18.7510$, $T = -6.5732$, $U = 13.5340$, and $V = 0.061$. Standard deviation for fit = 1.9521; experimental standard deviation = 0.0765.

F_1'	F'	F_1	F	Data	Calculated	Deviation	Experimental standard deviation
5.5	5	5.5	4	−136.432	−139.069	−2.637	0.084
5.5	6	5.5	5	−132.222	−131.739	0.483	0.049
6.5	7	6.5	6	−127.805	−124.218	3.587	0.073
6.5	8	6.5	7	−115.086	−116.035	−0.949	0.049
5.5	7	5.5	6	−104.927	−105.618	−0.691	0.030
6.5	8	5.5	7	−55.482	−57.764	−2.282	0.149
6.5	6	5.5	5	−54.594	−54.869	−0.274	0.110
6.5	7	5.5	6	−49.860	−47.347	2.512	0.065
6.5	6	6.5	6	−0.041	−0	0.041	0.027
5.5	6	6.5	7	49.803	47.347	−2.456	0.129
5.5	5	6.5	6	54.786	54.869	0.083	0.026
5.5	7	6.5	8	55.436	57.764	2.329	0.101
5.5	6	5.5	7	104.920	105.618	0.698	0.074
6.5	7	6.5	8	115.055	116.035	0.980	0.028
6.5	6	6.5	7	127.748	124.218	−3.530	0.084
5.5	5	5.5	6	132.131	131.739	−0.392	0.028
5.5	4	5.5	5	136.574	139.069	2.496	0.028

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APPENDIX

$$C_R = (-1)^{I_N + J + F_1} [I_N(I_N+1)(2I_N+1)J(J+1)(2J+1)]^{\frac{1}{2}} \begin{Bmatrix} F_1 & I_N & J \\ 1 & J & I_N \end{Bmatrix}$$

$$C_S = (-1)^{1 + J + I_N + I + F + 2F_1} [J(J+1)(2J+1)(2F_1+1)(2F_1'+1)I(I+1)(2I+1)]^{\frac{1}{2}} \begin{Bmatrix} J & F_1' & I_N \\ F_1 & J & 1 \end{Bmatrix} \begin{Bmatrix} F & I & F_1' \\ 1 & F_1 & I \end{Bmatrix}$$

$$C_T=(-1)^{F+I+F_1'+1}\sqrt{30}\,J(J+{}_1)(2J+1)\left[\frac{(2I_N+1)(I_N+1)I_N(2I+1)I(I+1)(2F_1'+1)(2F_1+1)}{J(J+1)(2J+1)(2J+3)(2J-1)}\right]^{1/2}$$

$$\times\begin{Bmatrix} I & F_1' & F\\ F_1 & I & 1\end{Bmatrix}\begin{Bmatrix} F_1' & F_1 & 1\\ I_N & I_N & 1\\ J & J & 2\end{Bmatrix}$$

$$C_U=(-1)^{J+I_N+F_1'+F_1+F+3I}\sqrt{2}\;J(J+1)(2J+1)\left[\frac{(2F_1'+1)(2F_1+1)}{J(J+1)(2J+1)(2J+3)(2J-1)}\right]^{1/2}[I(I+1)(2I+1)]$$

$$\times\begin{Bmatrix} F_1' & J & I_N\\ J & F_1 & 2\end{Bmatrix}\begin{Bmatrix} I & F_1' & F\\ F_1 & I & 2\end{Bmatrix}\left[\frac{(2I+3)(2I-1)}{2I(I+1)(2I+1)}\right]^{1/2}$$

$$C_V=(-1)^{I_N+J+F_1+F_1'+I+F+1}[I(I+1)(2I+1)I_N(I_N+1)(2I_N+1)(2F_1+1)(2F_1'+1)]^{\frac{1}{2}}\begin{Bmatrix} J & I_N & F_1'\\ 1 & F_1 & I_N\end{Bmatrix}\begin{Bmatrix} I & F_1' & F\\ F_1 & I & 1\end{Bmatrix}.$$

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Nuclear Radio-Frequency Spectra of a Series of Tetrahedral Molecules*

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The molecular-beam magnetic-resonance method has been applied to a series of tetrahedral molecules. In each case, the radio-frequency spectrum was observed which corresponds to the reorientation of the total nuclear spin with respect to a large external magnetic field. In order to analyze these spectra, the energy levels of the complete spin-rotation interaction and the direct dipole-dipole interaction have been calculated to first order in high-field perturbation theory by applying the recent group-theoretical treatment of Yi, Ozier, and Anderson. On the basis of these energy levels, the theoretical spectrum for each molecule has been constructed on a high-speed digital computer. By fitting this theoretical spectrum to the data, it has been found that:

for	CH_4	$c_a = (10.4 \pm 0.4)$ kHz	$c_d = (21 \pm 8)$ kHz
	SiH_4	(3.88 ± 0.23)	(9.0 ± 3.5)