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$J=3$, $K=2$ Line in the Inversion Spectrum of $N^{14}H_3$

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The coupling scheme used by Gunther-Mohr to study the hyperfine structure in the spectrum of $N^{14}H_3$ breaks down when there is no first-order quadrupole splitting, i.e., for $J=3, K=2$. This occurs because to neglect matrix elements off-diagonal in F_1 it is necessary to have a quadrupole splitting considerably larger than the other interactions being considered. This special case is treated here by including the elements off-diagonal in F_1. The energy splittings, frequencies, and relative intensities are found. The numerical constants used in the evaluation are taken from the work of Gordon. It should be possible to observe the details of this line with the maser.

INTRODUCTION

THE hyperfine structure in the microwave inversion spectrum of the $N^{14}H_3$ molecule, occurring at a wavelength of about 1.25 cm, has been given a rather thorough theoretical and experimental treatment by Gunther-Mohr[1,2] and Gordon.[3] Gunther-Mohr first investigated the hyperfine structure with a resolution of about 40 kc/sec. He found a splitting of the quadrupole lines for $K=1$. This splitting was explained theoretically in terms of the interaction of the magnetic moments of the protons with the molecular magnetic field and the spin-spin interactions between the nitrogen nucleus and the protons. The theory predicted a number of magnetic satellites that were not resolved. However, a short time later, Gordon using an instrument giving a remarkable resolution of something like 5 kc/sec resolved the magnetic satellites predicted by Gunther-Mohr. When terms were included giving the spin-spin interactions between the protons, there was essentially complete agreement between the theory and the experimental results.

There is one particular line in the ammonia spectrum which is not included in the above theoretical analyses. This is the $J=3, K=2$ line. For these values of J and K the nitrogen quadrupole interaction vanishes in first order and the coupling scheme assumed by the above authors breaks down. The difficulty lies in the fact that matrix elements off-diagonal in F_1 were neglected in their treatment. This was a valid approximation so long as the nitrogen quadrupole splitting was considerably larger than any of the other interactions being considered. When the quadrupole splitting vanishes, this approximation is no longer valid and elements off-diagonal in F_1 must be included.

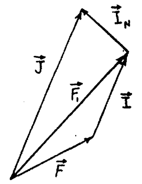

FIG. 1. Coupling scheme in the molecular frame.

THEORY

As was shown by Gunther-Mohr, matrix elements off-diagonal in $|K|$ can be neglected; only those connecting K and $-K$ need be considered. These elements exist only for the special case of $K=1$. $K=2$ is a special case of $K=3q\pm1$; for these K values the total proton spin $I=\frac{1}{2}$. For $K=3q$ the spin $I=\frac{3}{2}$. Because of the restriction that elements off-diagonal in $|K|$ are negligible, there are no elements connecting $I=\frac{1}{2}$ and $I=\frac{3}{2}$. The coupling scheme in the molecular frame[4] is shown in Fig. 1, where $\mathbf{J}$ = angular momentum exclusive of spin, $\mathbf{I}=-\mathbf{I}'=\mathbf{I}_1+\mathbf{I}_2+\mathbf{I}_3$ = total spin angular momentum of the three protons, $\mathbf{I}_i$ = spin of ith proton, $\mathbf{I}_N=-\mathbf{I}_N'$ = nitrogen spin, $\mathbf{F}$ = total angular momentum, and $\mathbf{F}_1=\mathbf{I}_N+\mathbf{J}=\mathbf{F}+\mathbf{I}'$. It should be noted that in the molecular coupling scheme $\mathbf{I}_N'$ commutes with $\mathbf{I}'$, $\mathbf{F}_1$, and $\mathbf{F}$. The nitrogen quadrupole term which involves only $3(I_{Nz}')^2-(\mathbf{I}_N')^2$ is rigorously diagonal in F_1.

Gunther-Mohr showed that the spin-spin interactions between the protons vanished by symmetry for $I=\frac{1}{2}$. Hence they do not appear. The spin interactions between the protons and the nitrogen nucleus give a pseudo-quadrupole type of interaction and hence this term vanishes for $J=3, K=2$. The interaction of the

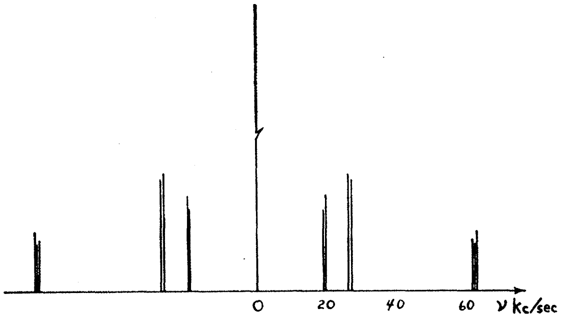

FIG. 2. $J=3, K=2$ line of $N^{14}H_3$ (approximately to scale except for main line intensity).

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[1] Gunther-Mohr, White, Schawlow, Good, and Coles, Phys. Rev. 94, 1184 (1954).

[2] Gunther-Mohr, Townes, and Van Vleck, Phys. Rev. 94, 1191 (1954).

[3] J. P. Gordon, Phys. Rev. 99, 1253 (1955).

[4] J. H. Van Vleck, Revs. Modern Phys. 23, 213 (1953).

Table I. Hyperfine energy levels for $J=3$, $K=2$ line of $N^{14}H_3$ (symmetric top energy not included).

$E(9/2)\ =-\ 7.02$ kc/sec;	$E(7/2+)=\ 55.4$ kc/sec;	$E(7/2-)=-33.0$ kc/sec
$E(5/2+)=\ 28.6$ kc/sec;	$E(5/2-)=-52.8$ kc/sec;	$E(3/2)\ =\ 9.36$ kc/sec

Table II. Frequencies and relative intensities for $J=3$, $K=2$ line of $N^{14}H_3$. (Origin of frequencies is main line.)

	ΔF	Frequency (kc/sec)	Relative intensity
$3/2\ \rightarrow 3/2$	0	0	100
$5/2\ -\rightarrow 5/2-$			
$5/2\ +\rightarrow 5/2+$			
$7/2\ -\rightarrow 7/2-$			
$7/2\ +\rightarrow 7/2+$			
$9/2\ \rightarrow 9/2$			
…			
$7/2\ +\rightarrow 9/2$	+1	−62.4	0.853
$7/2\ -\rightarrow 9/2$		+26.0	1.695
$5/2\ +\rightarrow 7/2+$		+26.8	1.601
$5/2\ +\rightarrow 7/2-$		−61.6	0.750
$5/2\ -\rightarrow 7/2+$		108.2	~0
$5/2\ -\rightarrow 7/2-$		19.8	1.385
$3/2\ \rightarrow 5/2+$		19.2	1.180
$3/2\ \rightarrow 5/2-$		62.2	0.681

nitrogen magnetic moment with the molecular magnetic field involves only I_N and J and hence has no elements off-diagonal in F_1. It does have diagonal elements, however; these were evaluated by Gunther-Mohr and can be carried over directly. An order of magnitude estimate shows that the second-order quadrupole effects should contribute less than 0.1 kc/sec to the energy and hence can be neglected. Thus the only term which yields elements off-diagonal in F_1 is the term representing the interaction energy between the proton spins and the molecular magnetic field. The details of evaluating the elements off-diagonal in F_1 are given in the Appendix.

For $J=3$, $I_N=1$, the allowed values of F_1 are 4, 3, 2. With $I=\frac{1}{2}$, the possible values of F are 9/2, 7/2, 5/2, 3/2. The following combinations can then occur:

F	F_1	F	F_1
9/2	4	5/2	3
7/2	4	5/2	2
7/2	3	3/2	2

Thus for $F=9/2$ or 3/2, the secular equation will be of first order, i.e., no off-diagonal elements in F_1 appear. For $F=\frac{7}{2}$ or $\frac{5}{2}$, the secular equations will be quadratic, i.e., an off-diagonal element in F_1 appears.

RESULTS

The energy levels are given in Table I. Where there are two energies for a given F value, they are denoted by plus and minus signs. The zeroth-order wave functions are

$$\begin{aligned}
&\Psi(9/2)=\psi(9/2,4)=\psi(F,F_1),\\
&\Psi(7/2+)=(7.61)^{-1}[\psi(7/2,3)+7.53\psi(7/2,4)],\\
&\Psi(7/2-)=(7.61)^{-1}[7.53\psi(7/2,3)-\psi(7/2,4)],\\
&\Psi(5/2+)=6^{-1}[5.92\psi(5/2,3)+\psi(5/2,2)],\\
&\Psi(5/2-)=6^{-1}[\psi(5/2,3)-5.92\psi(5/2,2)],\\
&\Psi(3/2)\ \ =\psi(3/2,2).
\end{aligned}$$

By using these wave functions, the relative intensities can easily be evaluated from the matrix elements in Condon and Shortley.[5] Table II gives a listing of the allowed frequencies and the relative intensities for the $J=3$, $K=2$ line of $N^{14}H_3$. A plot of the line is given in Fig. 2. It will be noted that the splittings and intensities are such that not too much difficulty should be encountered in investigating the line structure by means of the maser.

ACKNOWLEDGMENT

The author would like to express his appreciation to Professor J. H. Van Vleck for his encouragement and his suggestions regarding the writing of this paper.

APPENDIX

Computational Details

The Hamiltonian and the matrix elements diagonal in F_1 have been given by Gunther-Mohr[2] and will not be repeated here because of their length. The part of the effective Hamiltonian which has off-diagonal elements in F_1 is

$$H_{\text{eff}}=-\{2\sigma(\mathbf{J}\cdot\mathbf{I}')+(\gamma-2\sigma)J_zI_z'\}.$$

By using the matrix elements in Condon and Shortley, one obtains

$$\begin{aligned}
&(JKF_1I_N'I'F\cdots|J_zI_z'|JKF_1+1I_N'I'F\cdots)\\
&\quad=(JKF_1I_N'I'F\cdots|J_z|JKF_1I_N'I'F\cdots)(JKF_1I_N'I'F\cdots|I_z'|JKF_1+1I_N'I'F\cdots)\\
&\quad=\left[\frac{(F_1+1-I+F)(F_1+1+I-F)(I+F+2+F_1)(I+F-F_1)}{4(F_1+1)^2(2F_1+1)(2F_1+3)}\right]^{\frac{1}{2}}\frac{[P(J+1)Q(J-1)]^{\frac{1}{2}}}{2J(J+1)}K^2,\\
&P(J+1)\equiv(J+1-I_N+F_1)(J+2+I_N+F_1),\\
&Q(J-1)\equiv(I_N+F_1-J+1)(J+I_N-F_1).
\end{aligned}$$

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[5] E. U. Condon and G. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953).

Now consider $(F_1|\mathbf{J}\cdot\mathbf{I}'|F_1+1)$.

$$\mathbf{J}\cdot\mathbf{I}'=\mathbf{I}_N'\cdot\mathbf{I}'+\mathbf{F}_1\cdot\mathbf{I}'.$$

Since $\mathbf{F}_1$ and $\mathbf{I}'$ each satisfy the vector commutation relation with respect to $\mathbf{F}_1$, $\mathbf{F}_1\cdot\mathbf{I}'$ is diagonal in F_1. Therefore

$$(F_1|\mathbf{J}\cdot\mathbf{I}'|F_1+1)=(F_1|\mathbf{I}_N'\cdot\mathbf{I}'|F_1+1)=\tfrac{1}{2}[(J+F_1+1-I_N)(J+I_N-F_1)(J+I_N+F_1+2)(I_N+F_1+1-J)]^{\frac{1}{2}}$$
$$\times\left[\frac{(F_1+1-I+F)(F_1+1+I-F)(I+F+2+F_1)(I+F-F_1)}{4(F_1+1)^2(2F_1+1)(2F_1+3)}\right]^{\frac{1}{2}}$$

from the matrix elements of $\mathbf{P}\cdot\mathbf{Q}$ given in Condon and Shortley.

The values of the constants, in Gunther-Mohr's notation, are those given by Gordon[3]:

$$a=6.66\pm0.2\ \text{kc/sec},\qquad b-a=0\pm0.4\ \text{kc/sec},$$
$$2\sigma=-17.3\pm0.5\ \text{kc/sec},\qquad \gamma-2\sigma=-2.0\pm1\ \text{kc/sec}.$$

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Scattering Cross Sections and Interaction Energies of Low-Velocity He^+ Ions in Helium*

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It is pointed out that the determination of ion-molecule forces from results of measurements of scattering of low-velocity ion beams in gases can be seriously in error unless some *a priori* knowledge of the nature of the forces is available. The scattering of He^+ in He is chosen as an illustration. The elastic and charge exchange cross sections calculated from Moiseiwitsch's theoretical force laws are shown to be in good agreement with the experimental values of Cramer and Simons. The force law determined by the latter authors directly from their measurements is in error because of the assumption of an incorrect form and the failure to consider the two interaction states involved.

A NUMBER of careful measurements of the elastic and inelastic scattering cross sections of low-velocity ions in gases have been reported by Simons and co-workers.[1] These results can lead to valuable information about ion-molecule forces, but do not in themselves give unambiguous information. In particular, the measurements cannot distinguish between attractive and repulsive forces, nor can they show how many interaction states contribute appreciably to the cross sections.

The purpose of this note is to show, by an example, that some *a priori* knowledge of the forces is necessary to avoid possible serious errors in the interpretation of the measurements. The example chosen is the work of Cramer and Simons[1] on the scattering of He^+ in He, for which independent quantum-mechanical calculations of the interaction energies have been made by Moiseiwitsch.[2] This case is a good illustration because two interaction states are involved.

The interaction energies of the $^2\Sigma_u$ and $^2\Sigma_g$ states of He_2^+ calculated by Moiseiwitsch are shown in Fig. 1 as a function of internuclear separation. The dashed lines correspond to the interaction energy calculated by Cramer and Simons from their elastic cross-section measurements on the assumption of forces of pure attraction. The discrepancy is obvious.

It is possible to show that the measured cross sections are actually in good agreement with Moiseiwitsch's calculations. Moiseiwitsch[2] has already calculated the inelastic (charge-exchange) cross sections by an impact parameter method,[3,4] with the results shown in Fig. 2 as solid lines, one for each of two somewhat different wave functions. The agreement with the experimental points is very good. Moiseiwitsch has justified his neglect of polarization in the calculation.

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[4] Bates, Massey, and Stewart, Proc. Roy. Soc. (London) **A216**, 437 (1953).