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Measurement of Hyperfine Structure of the $J=3$, $K=2$ Inversion Line of $N^{14}H_3$†

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The magnetic hyperfine structure of the $J=3$, $K=2$ inversion line of $N^{14}H_3$ has been measured in a maser spectrometer employing the method of separated oscillating fields. The molecular-resonance linewidth of this system is 350 cps at 23 kMc/sec. The measured frequencies of the 3-2 inversion-line components are (in cycles/sec): 22 834 247 980±50, 22 834 209 990±50, 22,834,207,230±50, 22 834 185 130 ±20, 22 834 163 020±50, 22 834 160 270±50, 22 834 122 270±50. The pairs of lines adjacent to the main line were unresolved previously.

INTRODUCTION

The NH_3 hyperfine structure produced by the nitrogen quadrupole moment was investigated experimentally by Gordon[1] who used a maser spectrometer. Gordon noted that the nitrogen quadrupole interaction vanishes in first order for the 3-2 line. A calculation with higher order terms included was carried out by Hadley.[2] Shimoda and Kondo[3] measured the structure of the 3-2 line with 6-kc/sec resolution, and found general agreement between measurements and the calculated spectrum, but they were not able to resolve the pairs of lines separated by less than 3 kc/sec on each side of the main line.

EXPERIMENTAL RESULTS

In the present experiment, molecular-resonance patterns of 350-cps linewidth were observed and these pairs of lines were easily resolved. The observed spectrum of the 3-2 line is shown in Fig. 1. The measurements agree with the form of the spectrum calculated by Hadley,[2] and the observed spectrum is symmetrical about the main line. Figure 2 shows the pairs of satellites at 22 834 207.23 and 22 834 209.99 kc/sec which give an indication of the resolution and signal-to-noise ratio of the system. The satellites have lower intensity than the main line by a factor of approximately 30.

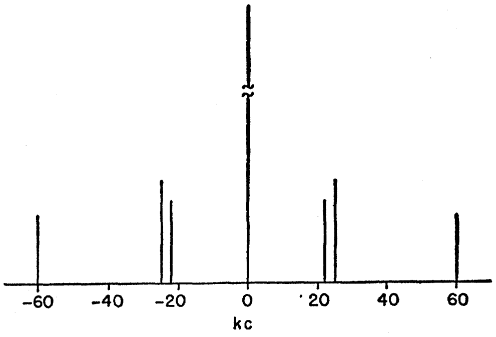

Fig. 1. Measured spectrum of the 3-2 line.

The frequencies of the measured lines are (in cycles/sec):

22 834 247 980±50, 22 834 209 990±50,
22 834 207 230±50, 22 834 185 130±20,
22 834 163 020±50, 22 834 160 270±50,
22 834 122 270±50.

The frequency standard for these measurements was a National 2001 cesium-beam tube. We used the A-1 time scale[4] which locates the zero-field cesium hyperfine resonance at 9 192 631 770 cps. The standard deviation for 10 measurements is approximately one-half of the indicated uncertainty. For all of the magnetic satellites the indicated uncertainty is based on an average value.

The main contribution to systematic errors is a power shift of −20 cps/dB for the satellites and −2 cps/dB for the main line. This is the variation of the resonance frequency as the stimulating power is changed from the optimum value. The dependence of frequency on thermal-cavity tuning is 1 cps/°C and the cavity temperatures are stabilized to better than 1°C. Electric fields in the drift region produce a quadratic frequency shift of approximately 0.12 cps for a 0.1 V/cm field, but the drift region is electrically and magnetically shielded so that stray electric fields should be negligible. The dependence of the measured frequency on focuser voltage, or external magnetic fields, is too small to be significant in any of these measurements.

APPARATUS

The apparatus is basically similar to the original maser spectrometer used by Gordon[1] but employs

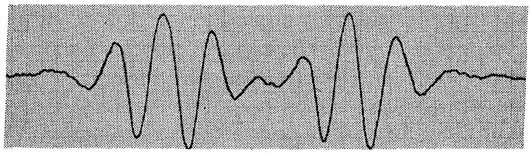

Fig. 2. Resolved pair of satellites at 22 834 207.23 kc/sec and 22 834 209.99 kc/sec.

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

[2] G. F. Hadley, Phys. Rev. **108**, 291 (1957); see especially Fig. 2, p. 291.

[3] K. Shimoda and K. Kondo, J. Phys. Soc. Japan **15**, 1125 (1960).

[4] F. H. Reder, Frequency **1**, 32 (1963).

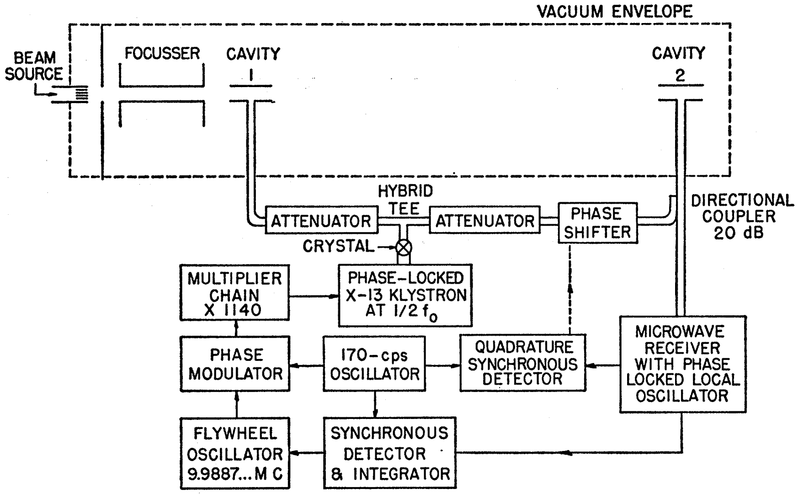

FIG. 3. Diagram of the two-cavity maser.

Ramsey's method[5] of separated oscillating fields to obtain a much narrower molecular-resonance linewidth. A diagram of the present apparatus is shown in Fig. 3. A beam of ammonia molecules in the upper inversion state is directed through the microwave cavities by a four-pole state-selector focuser. The stimulating signal is injected into both cavities and the microwave receiver is connected to the second cavity to observe the resonance. A directional coupler is used at the second cavity to reduce the amount of stimulating power going directly into the receiver.

The cavity separation is 105 cm, and the resulting linewidth is 350 cps. The cavities are each 10 cm long, and operate in the TM_{010} mode with a Q of 1200. For measurements on the main line the cavity diameter is reduced to 0.5 cm for a distance of 1.5 cm from both ends of the cavities. This substantially decreases the rf power radiated out of the ends of the cavities, and reduces the power shift from -20 to -2 cps/dB.

The power level of the stimulating signal in the first cavity is set to produce a transition probability of approximately $\frac{1}{2}$ for molecules leaving the first cavity. The resonance width for this condition is nearly twenty times the Ramsey resonance width, so this condition is nearly constant over the width of the observed resonance. The power delivered to the second cavity is a few dB less than that in the first cavity. This differs from the usual separated-oscillating-field resonance condition,[5] but only reduces the signal intensity. Under these conditions, the power delivered to the second cavity by the molecular system is approximately $W=n\hbar\omega_0(P_{ab}-\frac{1}{2})$ as will be discussed in the last section (n= number of molecules passing through the second cavity $\approx 10^{12}$/sec, $\hbar\omega_0$= inversion energy, P_{ab}= total transition probability for the two-cavity system[5]). The quantity W is measured by the microwave receiver and has nearly the same resonance behavior as P_{ab}.

The stimulating signal is a multiple of the frequency of a stable crystal oscillator near 10 Mc/sec. This signal is phase-modulated with a 170-cps square wave which produces phase deviations of $\pm\frac{1}{2}\pi$ at 23 kMc/sec. The 170-cps square wave then serves as the reference signal for a synchronous detector connected to the microwave receiver. A similar phase-modulation technique has been discussed by Ramsey.[5]

For measurements on the main line the synchronous detector output was used in a servo loop to control the crystal oscillator. This system provides a molecular-resonance clock with an rms frequency deviation of 3 parts in 10^{11} over a 12-h period.

The resonance pattern is shifted if the rf fields in the two cavities are out of phase. The dependence on phase shift is $\delta\omega_L T=\delta\phi$, where $\delta\omega_L$ is the resonance shift, and T is the transit time for a molecule to pass between the two cavities.[5] The dependence of this shift on cavity tuning has been considered elsewhere.[6] An additional synchronous detector operating 90° out of phase with the 170-cps modulation signal was used to detect a phase difference between the two cavities.[7] The cavities were thermally stabilized at the inversion frequency, and any residual phase error was corrected manually with a phase shifter.

For measurements on the magnetic satellites the signal-to-noise ratio was not sufficient to use this servo system, so the stimulating frequency was slowly swept through resonance and the asymmetry of the resonance pattern was used to detect the cavity phase difference.

THEORY OF THE TWO-CAVITY MASER

An arbitrary state of the two-level ammonia inversion system may by represented as a linear combination of the upper- and lower-state eigenfunctions u_a and u_b ($\psi=au_a+bu_b$, where a and b are complex and subject

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[5] N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956), Chap. 5.

[6] S. G. Kukolich, Proc. IEEE 52, 211; 437 (1964).

[7] R. S. Badessa, V. J. Bates, and C. L. Searle, Quarterly Progress Report No. 72, Research Laboratory of Electronics, MIT, Cambridge, Massachusetts, 1964, pp. 1–11 (unpublished).

to the condition $a^*a+b^*b=1$). It is convenient to use the spinor representation $\psi=\begin{bmatrix} a \\ b \end{bmatrix}$, since the resulting Schrödinger equation will be the same as that for spin-$\frac{1}{2}$ particles in a magnetic field.[8] Then the Hamiltonian for this system when no external fields are present is $\mathcal{H}_0=\frac{1}{2}(\hbar\omega_0)\sigma_z$ and $\psi^*\mathcal{H}_0\psi=\frac{1}{2}(\hbar\omega_0)(a^*a-b^*b)$, where $\hbar\omega_0$ is the energy separation between the inversion levels, and σ_z is a Pauli spin matrix. An applied rf field provides a perturbation of the form

$$V_I=\begin{pmatrix} 0 & \frac{1}{2}(\hbar\omega_1)e^{-i\omega t} \\ \frac{1}{2}(\hbar\omega_1)e^{i\omega t} & 0 \end{pmatrix},$$

and the Schrödinger equation $i\hbar(\partial/\partial t)\psi=\mathcal{H}\psi$ is

$$i\frac{\partial}{\partial t}\begin{pmatrix} a \\ b \end{pmatrix}=\begin{pmatrix} \frac{1}{2}\omega_0 & \frac{1}{2}(\omega_1)e^{-i\omega t} \\ \frac{1}{2}(\omega_1)e^{i\omega t} & -\frac{1}{2}\omega_0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix},$$

where $\hbar\omega_1=\mu_{ab}\mathcal{E}_0$, μ_{ab} is the dipole matrix element between the upper and lower states, and $\mathcal{E}_0$ is the magnitude of the rf field ($\mu_{aa}=\mu_{bb}=0$). If we make the substitution

$$\begin{pmatrix} a \\ b \end{pmatrix}=\begin{pmatrix} a' & e^{-i(\omega/2)t} \\ b' & e^{i(\omega/2)t} \end{pmatrix},$$

the Schrödinger equation becomes

$$i\frac{\partial}{\partial t}\begin{pmatrix} a' \\ b' \end{pmatrix}=\begin{pmatrix} \frac{1}{2}(\omega_0-\omega) & \frac{1}{2}\omega_1 \\ \frac{1}{2}\omega_1 & -\frac{1}{2}(\omega_0-\omega) \end{pmatrix}\begin{pmatrix} a' \\ b' \end{pmatrix}.$$

This equation has been solved by Abragam[9]:

$$\begin{pmatrix} a'(t) \\ b'(t) \end{pmatrix}=\Omega\begin{pmatrix} a(0) \\ b(0) \end{pmatrix}=\begin{bmatrix} \cos\alpha t-i\left(\dfrac{\omega_0-\omega}{2\alpha}\right)\sin\alpha t & -i\dfrac{\omega_1}{2\alpha}\sin\alpha t \\ -i\left(\dfrac{\omega_1}{2\alpha}\right)\sin\alpha t & \cos\alpha t+i\left(\dfrac{\omega_0-\omega}{2\alpha}\right)\sin\alpha t \end{bmatrix}\begin{pmatrix} a(0) \\ b(0) \end{pmatrix},$$

where $\alpha^2=(\frac{1}{2}(\omega_0-\omega))^2+(\frac{1}{2}\omega_1)^2$. The initial state selected by the focuser is $\psi_0=\begin{bmatrix} 1 \\ 0 \end{bmatrix}$. The state produced by an rf field that is on for a time τ is

$$\begin{pmatrix} a' \\ b' \end{pmatrix}=\begin{bmatrix} \cos\alpha\tau-i\left(\dfrac{\omega_0-\omega}{2\alpha}\right)\sin\alpha\tau & -\dfrac{i\omega_1}{2\alpha}\sin\alpha\tau \\ -i\dfrac{\omega_1}{2\alpha}\sin\alpha\tau & \cos\alpha\tau+i\left(\dfrac{\omega_0-\omega}{2\alpha}\right)\sin\alpha\tau \end{bmatrix}\begin{pmatrix} a(0) \\ b(0) \end{pmatrix}.$$

For the first cavity we define

$$\cos\alpha\tau-i((\omega_0-\omega)/2\alpha)\sin\alpha\tau\equiv\beta_{\mathrm{I}},\quad -i(\omega_1/2\alpha)\sin\alpha\tau\equiv\gamma_{\mathrm{I}},$$

so

$$\begin{pmatrix} a' \\ b' \end{pmatrix}_I=\Omega_I\begin{pmatrix} a(0) \\ b(0) \end{pmatrix}=\begin{pmatrix} \beta_I & \gamma_I \\ \gamma_I & \beta_I^* \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}=\begin{pmatrix} \beta_I \\ \gamma_I \end{pmatrix}.$$

In the two-cavity maser the level of ω_1 in the first cavity is adjusted so that $\omega_1\approx\pi/2\tau$, where τ is the average time that the molecules spend in the first cavity. The resonance width $\Delta\omega$ for the validity of this condition is approximately $\Delta\omega=\omega_1=\pi/2\tau$. This produces a transition probability $b^*b=\frac{1}{2}$, and the wave function

$$\begin{pmatrix} a' \\ b' \end{pmatrix}_I=\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}\quad\text{so}\quad\begin{pmatrix} a \\ b \end{pmatrix}_I=\frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i(\omega_0/2)t} \\ -ie^{i(\omega_0/2)t} \end{pmatrix}.$$

The average energy is

$$E_{\mathrm{I}}=\tfrac{1}{2}(\hbar\omega_0)\langle\sigma_z\rangle=\tfrac{1}{2}(\hbar\omega_0)(a^*a-b^*b)=0,$$

and there is an oscillating polarization

$$P=P_0\langle\sigma_x\rangle=P_0(a^*b+b^*a)=P_0\sin\omega_0 t.$$

In the region between the cavities the rf fields are very small, and the matrix is

$$\Omega_{II}=\begin{pmatrix} e^{-i\frac{1}{2}(\omega_0-\omega)T} & 0 \\ 0 & e^{i\frac{1}{2}(\omega_0-\omega)T} \end{pmatrix},$$

where T is the time spent by molecules in the region between the cavities.

The final wave function, after the molecules have passed through the two-cavity system, is

$$\begin{pmatrix} a' \\ b' \end{pmatrix}_{\mathrm{III}}=\Omega_{\mathrm{III}}\Omega_{\mathrm{II}}\Omega_{\mathrm{I}}\begin{pmatrix} a(0) \\ b(0) \end{pmatrix},$$

where Ω_{I} represents the effect of the first cavity, Ω_{II},

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[8] R. P. Feynman, F. L. Vernon, and R. W. Hellwarth, J. Appl. Phys. **28**, 49 (1957).

[9] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. 2.

the field-free drift space between the cavities, and Ω_{III}, the effect of the second cavity.

$$\Omega_{\text{III}}=\begin{pmatrix}\beta_{\text{III}} & \gamma_{\text{III}}\\ \gamma_{\text{III}} & \beta_{\text{III}}^*\end{pmatrix}=\begin{bmatrix}\cos\alpha'\tau-i\left(\dfrac{\omega_0-\omega}{2\alpha'}\right)\sin\alpha'\tau & -\left(i\dfrac{\omega_1'}{2\alpha'}\right)\sin\alpha'\tau\\ -i\left(\dfrac{\omega_1'}{2\alpha'}\right)\sin\alpha'\tau & \cos\alpha'\tau+i\left(\dfrac{\omega_0-\omega}{2\alpha'}\right)\sin\alpha'\tau\end{bmatrix}$$

which is the same form as Ω_{I}, but the field strength ω_1 may be different. For the initial condition $\psi_0=\begin{bmatrix}1\\0\end{bmatrix}$,

$$\begin{pmatrix}a'\\b'\end{pmatrix}_{\text{III}}=\begin{pmatrix}\beta_{\text{III}} & \gamma_{\text{III}}\\ \gamma_{\text{III}} & \beta_{\text{III}}^*\end{pmatrix}\begin{pmatrix}e^{-i\frac{1}{2}(\omega_0-\omega)T} & 0\\ 0 & e^{i\frac{1}{2}(\omega_0-\omega)T}\end{pmatrix}\begin{pmatrix}\beta_{\text{I}} & \gamma_{\text{I}}\\ \gamma_{\text{I}} & \beta_{\text{I}}^*\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}$$

$$\begin{pmatrix}a'\\b'\end{pmatrix}_{\text{III}}=\begin{pmatrix}\beta_{\text{III}}\beta_{\text{I}}e^{-i\frac{1}{2}(\omega_0-\omega)T}+\gamma_{\text{III}}\gamma_{\text{I}}e^{i\frac{1}{2}(\omega_0-\omega)T}\\ \gamma_{\text{III}}\beta_{\text{I}}e^{-i\frac{1}{2}(\omega_0-\omega)T}+\beta_{\text{III}}^*\gamma_{\text{I}}e^{i\frac{1}{2}(\omega_0-\omega)T}\end{pmatrix}.$$

The total transition probability for the two-cavity system is

$$(b^*b)_{\text{III}}=(b'^*b')_{\text{III}}=\tfrac{1}{2}(a^*a+b^*b)-\tfrac{1}{2}(a^*a-b^*b)=\tfrac{1}{2}-\tfrac{1}{2}\langle\sigma_z\rangle_{\text{III}}$$

$$b'=\cos\tfrac{1}{2}(\omega_0-\omega)T[(\gamma_{\text{III}}\beta_{\text{I}}+\beta_{\text{III}}^*\gamma_{\text{I}})]-i\sin\tfrac{1}{2}(\omega_0-\omega)T[(\gamma_{\text{III}}\beta_{\text{I}}-\beta_{\text{III}}^*\gamma_{\text{I}})]$$

$$\begin{aligned}(b^*b)_{\text{III}}=&-\cos^2\tfrac{1}{2}(\omega_0-\omega)T[(\gamma_{\text{III}}\beta_{\text{I}}^*+\beta_{\text{III}}\gamma_{\text{I}})(\gamma_{\text{III}}\beta_{\text{I}}+\beta_{\text{III}}^*\gamma_{\text{I}})]-\sin^2\tfrac{1}{2}(\omega_0-\omega)T[(\gamma_{\text{III}}\beta_{\text{I}}^*-\beta_{\text{III}}\gamma_{\text{I}})(\gamma_{\text{III}}\beta_{\text{I}}-\beta_{\text{III}}^*\gamma_{\text{I}})]\\&+i\cos\tfrac{1}{2}(\omega_0-\omega)T\sin\tfrac{1}{2}(\omega_0-\omega)T[2\gamma_{\text{I}}\gamma_{\text{III}}(\beta_{\text{I}}\beta_{\text{III}}-\beta_{\text{I}}^*\beta_{\text{III}}^*)].\end{aligned}$$

(Note that the minus sign occurs because the γ are pure imaginary.)

The first two terms are both symmetric functions of $(\omega_0-\omega)$, and the last term is the product of two antisymmetric functions and thus is also symmetric. This means that the resonance peak at ω_0 will not be shifted if the two rf fields have different strengths ($\omega_1\neq\omega_1'$ and $\gamma_{\text{I}}\neq\gamma_{\text{III}}$), since the resonance pattern will be modified in a symmetrical way. This problem has also been considered by Ramsey.[10]

For conditions near the center of the resonance $(\omega_0-\omega<1/T)$

$$\beta_{\text{I}}\cong\cos\tfrac{1}{2}(\omega_1\tau)\qquad\gamma_{\text{I}}\cong-i\sin\tfrac{1}{2}(\omega_1\tau)$$

$$\beta_{\text{III}}\cong\cos\tfrac{1}{2}(\omega_1'\tau)\qquad\gamma_{\text{III}}\cong-i\sin\tfrac{1}{2}(\omega_1'\tau),$$

and the last term in $(b^*b)_{\text{III}}$ vanishes. If the rf field strengths are equal, the second term vanishes also, and

$$(b^*b)_{\text{III}}=\sin^2\omega_1\tau\cos^2\tfrac{1}{2}(\omega_0-\omega)T$$

(see Ramsey[11]).

For the two-cavity maser, conditions in the first cavity are nearly such that $\beta_{\text{I}}=1/\sqrt{2}$, $\gamma_{\text{I}}=-i/\sqrt{2}$, and the average energy just before the second cavity is

$$E_{\text{II}}=\tfrac{1}{2}(\hbar\omega_0)\langle\sigma_z\rangle_{\text{II}}=0.$$

After the second cavity, the average energy is

$$E_{\text{III}}=\tfrac{1}{2}(\hbar\omega_0)\langle\sigma_z\rangle_{\text{III}}=\hbar\omega_0[\tfrac{1}{2}-(b^*b)_{\text{III}}].$$

If there are n molecules per sec, the power delivered to the second cavity is

$$W=n(E_{\text{II}}-E_{\text{III}}),$$

$$W=n\hbar\omega_0[(b^*b)_{\text{III}}-\tfrac{1}{2}],$$

and the resonance behavior will be determined by $(b^*b)_{\text{III}}[(b^*b)_{\text{III}}\equiv P_{ab}]$. For these conditions,

$$\begin{aligned}(b^*b)_{\text{III}}\cong&\tfrac{1}{2}+\sin\tfrac{1}{2}(\omega_1'\tau)\cos\tfrac{1}{2}(\omega_1'\tau)\\&\times[\cos^2\tfrac{1}{2}(\omega_0-\omega)T-\sin^2\tfrac{1}{2}(\omega_0-\omega)T],\end{aligned}$$

$$(b^*b)_{\text{III}}\cong\tfrac{1}{2}+\tfrac{1}{2}\sin(\omega_1'\tau)[\cos(\omega_0-\omega)T].$$

The velocity distribution in the beam will provide a distribution of transit times T, and reduce the amplitude of other maxima relative to the central maximum at $(\omega_0-\omega)=0$.[5] The factor $\sin(\omega_1'\tau)$ reduces the resonance signal if the rf field is less than the optimum value $(\omega_1\tau=\frac{1}{2}\pi)$.

ACKNOWLEDGMENTS

The author would like to express his appreciation to V. J. Bates and R. S. Badessa for supplying the reference signal used in this measurement. Professor J. R. Zacharias and Professor J. G. King provided many helpful discussions during the course of this experiment.

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[10] N. F. Ramsey, *Recent Research in Molecular Beams*, edited by I. Estermann (Academic Press Inc., New York, 1959), Chap. 6.

[11] N. F. Ramsey, Ref. 5, cf. Eq. (V. 44a).