

INVESTIGATION OF THE HYPERFINE STRUCTURE OF THE
 $J = K = 1$ TRANSITION OF $N^{14}H_3$ AMMONIA FROM
SIMULTANEOUS OSCILLATIONS IN A NUMBER OF
COMPONENTS OF A SPECTRAL LINE

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An investigation was carried out of the hyperfine structure of the $J = K = 1$ transition of $N^{14}H_3$ ammonia by the method of measuring the beats between the line components which oscillate simultaneously in a beam maser. Let us consider the special features of the method. A value of the magnetic constant $B = -14.6$ kHz was obtained.

In the present paper an investigation of the hyperfine structure of ammonia by the method proposed in [1] is described. The method consists in obtaining simultaneous oscillations in a beam maser using a series of components of the hyperfine structure of a line. Under these conditions measurement of the distances between components can be reduced in essence to measurement of the beat frequencies between oscillations which correspond to generation in each component with allowance for certain specifics from the given method of correction. Since in the case given, small frequency differences are measured directly, the equipment and procedure of the experiment can be simplified, high measurement accuracies being attainable in principle. We used this method experimentally for the first time.

We investigated the $J = K = 1$ line of the inversion spectrum of $N^{14}H_3$ ammonia at a frequency 23,694.48 MHz.* The beam maser based on the $J = K = 1$ line had the conventional construction. Measures were merely adopted to increase the intensity of the beam of active molecules: the ammonia was purified by refreezing; cold irises were used on both sides of the sorting system; the sorting system, which could withstand a voltage of up to 42 kV, was carefully fabricated and purified. Because of these measures, oscillation was obtained in four components of the $J = K = 1$ line, which in itself is substantially weaker than the usually employed $J = K = 3$ line. The oscillations of the molecular generator were received by a superheterodyne receiver whose detector produced beats between the oscillations corresponding to generation in the various components of the line. The frequencies of the beats were measured by an electronic-counter 43-9 frequency meter, as well as by a narrow-band receiver with quartz calibration.

1. CALCULATION OF THE OBSERVED HYPERFINE STRUCTURE

Conventional ammonia $N^{14}H_3$ has a quadrupole and magnetic hyperfine structure [3]. A peculiarity of transition with $|K| = 1$ in ammonia lies in the fact that each component of the line, including the central one, splits into two components, due to removal of K-degeneration. The use of the expressions derived in [4, 5] for the energy levels leads to the dependences of the frequencies of the components on the various constants shown in Table 1. We retain the notation of [4, 5], where $(A + 0.5 C)$ and V are constants which describe the magnetic interaction of hydrogen nuclei with the rotation of the molecule and are determined

*In [2] it is mentioned that oscillation in individual components of the $J = K = 1$ line was obtained by A. I. Barchukov and V. V. Savranskii.

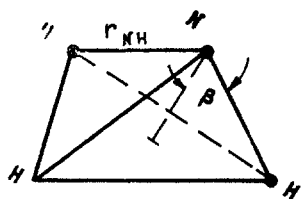


Fig. 1. Structural parameters of the ammonia molecule.

experimentally; D_1 and D_2 are constants which describe the magnetic dipole-dipole interaction of the hydrogen and nitrogen nuclei, calculated according to the expression

$$D_1 = g_H g_N \mu_0^2 \left\langle v \left| r_{NH}^{-3} \left(1 - \frac{3}{2} \sin^2 \beta \right) \right| v \right\rangle, \quad (1)$$

$$D_2 = g_H g_N \mu_0^2 \left\langle v \left| r_{NH}^{-3} \frac{3}{2} \sin^2 \beta \right| v \right\rangle.$$

In Eqs. (1) μ_0 is the nuclear magneton; $g_H = 2 \cdot 2.793$, $g_N = 0.404$, r_{NH} and β are the geometric parameters of the molecule (Fig. 1); the angular bracket denotes averaging over the inversion space. As a first approximation, following [5], we adopt the values of r_{NH} and β averaged over the ground vibrational state. The refined geometric parameters of the ammonia molecule were obtained in [6], whence $r_{NH} = 1.0134 \text{ \AA}$, $\beta = 67^\circ 43'$. Calculation yields $D_1 = -2.35 \text{ kHz}$ and $D_2 = +10.85 \text{ kHz}$. The difference between the quadrupole constants $\Delta(\text{eq } Q) = 3.8 \text{ kHz}$ was refined in [7]. We used these values of the constants thereafter.

As a general rule, the components having $\Delta F = \Delta F_1 = \Delta J$ must be the most intense ones; for an inversion transition $\Delta J = 0$. Double application of the well-known procedure for calculating the intensity distribution first over the quadrupole structure and then over the magnetic structure [5] leads to relative intensities I_g (Table 1). Sorting changes the relative intensities of the hyperfine components with respect to the intensities I_g in the gas. Approximate consideration of the sorting is carried out by multiplying I_g by a weighting factor [5]:

$$(2F_1 + 1)^{-1} \sum_{M_J} N(M_J) M_J^2 \quad \text{for the quadratic Stark effect;}$$

$$(2F_1 + 1)^{-1} \sum_{M_J} N(M_J) M_J \quad \text{for the linear Stark effect,}$$

Table 1.

Central line			
Transitions $F_1' F' \rightarrow F_1 F$	Distance of the components from the center of the line, expressed in hyperfine-structure constants	I_g , rel. units	I_s , rel. units
$1 \frac{1}{2} \rightarrow 1 \frac{1}{2}$	$B - 2D_2 - 0,125 \Delta(\text{eq } Q)$	7,93	13,2
$2 \frac{5}{2} \rightarrow 2 \frac{3}{2}$	$1,25(A + 0,5C) + 0,25B + 0,25D_1 + 0,1D_2 - 0,025 \Delta(\text{eq } Q)$	7,1	7,1
$1 \frac{3}{2} \rightarrow 1 \frac{1}{2}$	$0,75(A + 0,5C) + 0,25B - 0,75D_1 - 0,5D_2 - 0,125 \Delta(\text{eq } Q)$	4	6,68
$2 \frac{3}{2} \rightarrow 2 \frac{1}{2}$	$1,5B + 0,6D_2 + 0,025 \Delta(\text{eq } Q)$	64,2	64,2
$1 \frac{1}{2} \rightarrow 1 \frac{3}{2}$	$-0,75(A + 0,5C) + 0,25B + 0,75D_1 - 0,5D_2 - 0,125 \Delta(\text{eq } Q)$	4	6,68
$2 \frac{5}{2} \rightarrow 2 \frac{5}{2}$	$-B - 0,4D_2 + 0,025 \Delta(\text{eq } Q)$	100	100
$1 \frac{3}{2} \rightarrow 1 \frac{3}{2}$	$-0,5B + D_2 - 0,125 \Delta(\text{eq } Q)$	19,8	33,4
$2 \frac{3}{2} \rightarrow 2 \frac{5}{2}$	$-1,25(A + 0,5C) + 0,25B - 0,25D_1 - 0,1D_2 + 0,025 \Delta(\text{eq } Q)$	7,1	7,1
Quadrupole satellites			
Transitions $F_1' F' \rightarrow F_1 F$	Distance Δf from the center of the line, expressed in hyperfine-structure constants	Δf_{meas} , kHz	Δf_{cor} , kHz
$1 \frac{3}{2} \rightarrow 2 \frac{5}{2}$	$-0,15 \text{ eq } Q - (a+b) - 0,25(A + 0,5C) - 0,75B + 0,35D_1 + 0,3D_2 - 0,05 \Delta(\text{eq } Q)$	605,1	617
$1 \frac{3}{2} \rightarrow 0 \frac{1}{2}$	$-0,375 \text{ eq } Q + 0,5(a+b) + 0,25(A + 0,5C) - 0,25B + 0,25D_1 + 0,5D_2 - 0,05 \Delta(\text{eq } Q)$	1531,7	1545,7

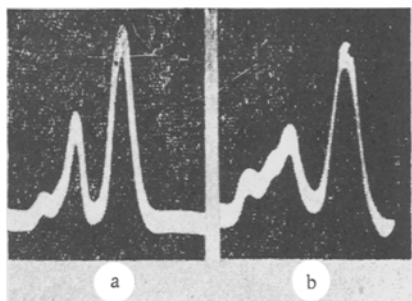


Fig. 2. a) Experimentally observed central line $\Delta F_1 = 0$ of the $J = K = 1$ transitions; b) the same line partially saturated.

constants B and D_2 .^{*} Therefore, it is reasonable to define specifically the constant B , which cannot be calculated. For the quantity $(A + 0.5 C)$, which only slightly affects the frequency of the resultant maxima, the value obtained in [4] for other transitions was taken: namely, $(A + 0.5 C) = -18.3 \pm 0.2$ kHz. The results obtained allow an approach to the interpretation of the experimental data on the central doublet.

Besides the central doublet, we likewise obtained oscillations in the quadrupole satellites situated on the high-frequency side of the line and corresponding to the $\Delta F_1 = \pm 1$, $\Delta F = 0, \pm 1$ transitions, which we identified as $1\frac{3}{2} - 2\frac{5}{2}$ and $1\frac{3}{2} - 0\frac{1}{2}$. These are the most intense satellites, and for them $\Delta F = \Delta F_1$, while the low-frequency satellites were suppressed by the sorting [5]. The expressions for the frequencies of the satellites are given in Table 1. According to the data in [5], the constants corresponding to the magnetic interaction of the nitrogen atom with the rotation of the molecule are $a = 6.66 \pm 0.2$ kHz and $b = 6.66 \pm 0.2$ kHz. For the largest constant eqQ , which determines the quadrupole interaction of the nitrogen nucleus with the field of the molecule, several different values (see below) were cited in [4, 5].

2. EXPERIMENTAL PROCEDURE AND RESULTS

Figure 2a shows the shape of the central line of the $J = K = 1$ transition, observed by the conventional method (with a signal). A comparison of this shape with the calculated line profile (Fig. 3) shows fairly good agreement. Oscillation occurred in the two largest maxima of the lines, which were close to the frequencies of the $2\frac{3}{2} - 2\frac{3}{2}$ and $2\frac{5}{2} - 2\frac{5}{2}$ transitions. Under these conditions, an unexpectedly large (several kHz) dependence of the beat frequency on a number of parameters occurred, i.e., the tuning of the reso-

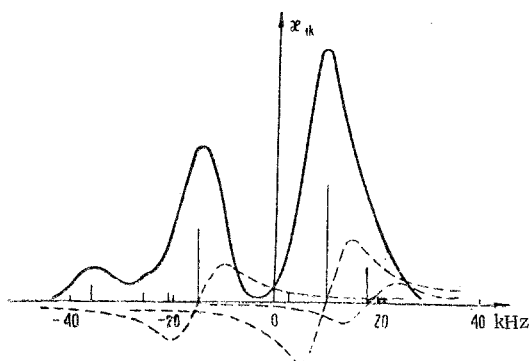


Fig. 3. Calculated profile of the central line of the $J = K = 1$ transition.

where $N(M_J)$ is the number of states of the molecule in a weak field which pass into a state having the given M_J in a strong field. In the case $J = K = 1$, the situation is simplified, due to the fact that only molecules having $M_J = 1$ are sorted, while $N(1)$ is identical for the sorting components $F_1 = 1$ and 2. Then, the weighting factor can be reduced to $(2F_1 + 1)^{-1}$ for any field. The calculated intensities of the components I_c in the sorted beam are likewise presented in Table 1. Let us note that in the working range of sorting voltages the strong-field case is realized throughout; under these conditions the relative intensities of the components (i.e., the shape of the lines) do not depend on the sorting voltage which affects only the total line intensity.

Consideration of the relative intensities of the components shows that almost the entire intensity is concentrated in the components $\Delta F = \Delta F_1 = 0$ whose frequencies depend solely on the con-

stant, the beam intensity, and the magnitude of the starting voltage. Our analysis is evidence of the fact that all of the dependences indicated can be reduced, in the final analysis, to a dependence of beat frequency on the oscillation power, with the beat frequency increasing with increasing power. Figures 4 and 5 show the dependence of the frequency of the beats on the power of the oscillations, the power having been controlled by varying the sorting voltage in the case shown in Fig. 5, while in the case shown in Fig. 5, the intensity of the molecular beam was varied. These dependences, as will be shown further on, can be reduced to the influence of the saturation effect. The average value of the beat frequency, extrapolated to zero amplitude, turned out to equal 24.85 kHz with a mean-square error of 0.12 kHz.

^{*}The constant $\Delta(eq Q)$ is included analogously and with a very small weight.

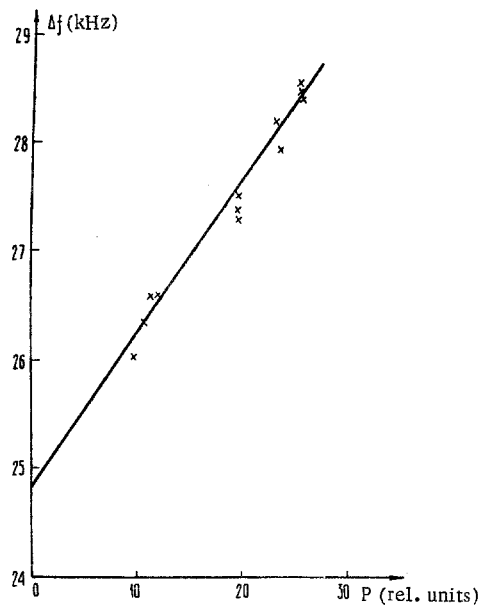


Fig. 4. Dependence of the beat frequency on the oscillation power, for power control by changing the sorting voltage.

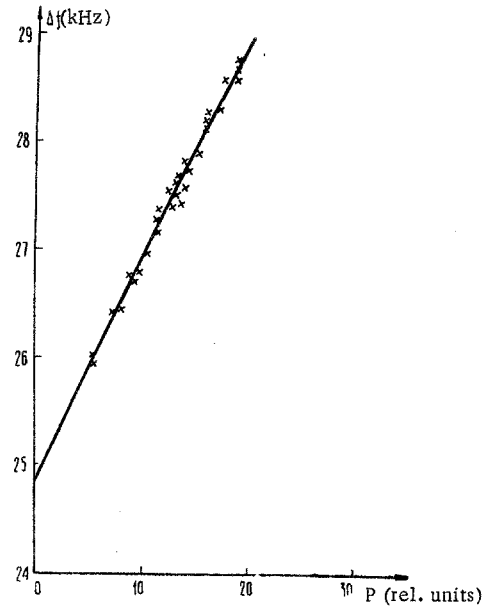


Fig. 5. Dependence of the beat frequency on oscillation power, for power control by changing the beam intensity.

We likewise observe oscillation in two high-frequency quadrupole satellites of the central line. Table 1 presents values of the beat frequencies Δf_{mea} (extrapolated to zero amplitude) for simultaneous oscillation in the quadrupole satellite and in the large peak of the central line near the $2\frac{5}{2} - 2\frac{5}{2}$ transition.

Analysis of the Method and Interpretation of the Results. The principal features of the method given were considered briefly in [1]. In [8] the problem of the biharmonic mode in a molecular generator whose spectral line is split by a magnetic field into two components of equal intensity was solved. As is evident from the analysis, the principal feature of the biharmonic mode is a fairly complex dependence of the beat frequency on the distance between components and the width of the components. In the present paper it is required to find the difference between the components from the frequency of the beats and the width and intensity of the components. However, the distance between the components is simply related to the desired constant B (see Table 1). In connection with the fact that in the problem given it is necessary to consider more than two components of the spectral line, and components having different intensities at that, we shall calculate the beat frequencies in a somewhat different way which allows easier representation of the qualitative picture of the phenomena.

The equation for the oscillations in a molecular generator has the form

$$\frac{d^2 E}{dt^2} + \frac{\omega_r}{Q_r} \frac{dE}{dt} + \omega_r^2 E = -4\pi \frac{d^2 \langle P \rangle}{dt^2}, \quad (2)$$

where E is the field in the resonator; Q_r , ω_r are the Q and frequency of the resonator. The beam polarization $\langle P \rangle$ averaged over the resonator in the presence of several components of the spectral line may be represented as

$$\langle P \rangle = \sum_k \langle P_k \rangle = \sum_k (\langle x_{1k} \rangle + i \langle x_{2k} \rangle) E. \quad (3)$$

Table 2.

Velocity distribution of the molecules in the beam	K_1	K_2
Monokinetic beam	1,07	0,38
$\tau_0^{-1} \exp(-\tau \tau_0^{-1})$	1	0,5
Maxwellian beam	0,86	0,39

The polarization $\langle P_k \rangle$ of each component may be calculated, for example, from the general solution of the equations which describe the state of a two-level system in the presence of a harmonic perturbation [9]. Stipulating the existence of a biharmonic mode in advance (the components are allowed [8]), we seek the solution of (2) in the form

$$E = E_1 \exp(i\omega_1 t) + E_2 \exp(i\omega_2 t). \quad (4)$$

Substituting (3), (4) into (2), separating the real and imaginary parts, and setting terms having identical frequencies equal to one another, we have the following equations for the oscillation frequencies ω_1 and ω_2 :

$$\begin{aligned} \frac{\omega_1 - \omega_1}{2\pi\omega_1} &= \sum_k \langle \kappa_{1k}(\omega_1) \rangle, \\ \frac{\omega_2 - \omega_2}{2\pi\omega_2} &= \sum_k \langle \kappa_{1k}(\omega_2) \rangle. \end{aligned} \quad (5)$$

In the particular case of two fairly distant components having the same order of intensity, the frequency of the beats is

$$F = \Delta - K_1 \Delta \frac{Q_r}{Q_l} - K_2 \Delta \frac{\Delta_l}{\Delta} \left[1 + \frac{(I_2 - I_1)^2}{2I_1 I_2} \right], \quad (6)$$

where Δ is the distance between the lines; Δ_l is the width of the component at the half-intensity level; I_1 , I_2 are the intensities of the components; K_1 , K_2 depend on the shape of the components (on the form of the velocity distribution of the molecules) and are given in Table 2.

A rough estimate of the role played by the terms in the right side of Eq. (5) (for $\Delta_l = 9 \cdot 10^3$ Hz, $Q_r Q_l^{-1} = 2.3 \cdot 10^{-3}$) shows that in the case of oscillations in the quadrupole satellite and one of the central components, the principal role in noncoincidence of the beat frequency with the frequency interval between components ($\Delta = 6 \cdot 10^5$ and $1.5 \cdot 10^6$ Hz) is played by conventional oscillation-frequency pulling by the resonator. The last term, however, is the principal one, as far as affecting the beat frequency between the components of the spectral line is concerned; this term describes the effect of the dielectric constant of neighboring components. Neglecting the effects of the resonator, we have from (4) the following conditions governing the oscillation frequency in the first approximation:

$$\begin{aligned} \sum_k \langle \kappa_{1k}(\omega_1) \rangle &= 0, \\ \sum_k \langle \kappa_{1k}(\omega_2) \rangle &= 0. \end{aligned} \quad (7)$$

The form of $\kappa_{1k}(\omega)$ for the three most intense components of the central line (in the absence of saturation) is shown by the dashed line in Fig. 3. Thus, the oscillation frequency is found in the first approximation as the frequency at which the algebraic sum of the real parts of the dielectric susceptibilities of the different components of the spectral line is equal to zero. Such a treatment allows easy qualitative representation (and easy numerical solution) of the dependence of the beat frequency on the number, position, width, and intensity of the components.

Let us consider the qualitative effect of saturation on the frequency of the beats. In the presence of saturation the curve $\kappa_1(\omega)$ becomes wider and flatter, with the height of the maxima decreasing to a greater extent than does the height of the wings. Therefore, it is qualitatively evident that under saturation the effect of neighboring lines will increase. In our case a nonuniform saturation of components having $F_1 = 1$ and 2 is also added to this effect. Transitions having $F_1 = 2$ have a larger average matrix element of the dipole moment than do transitions having $F_1 = 1$. In accordance with this, it is evident from Fig. 3 that

with increasing saturation the frequency of the beats (and the distance between the maxima of the central line) must increase, due to the increase in the role played by components having $F_1 = 1$ (basically $1\frac{3}{2} - 1\frac{3}{2}$), which are further from the center of the line. Figure 2b shows the partially saturated line observed, whose shape substantiates the notion expounded above (and is evidence of the correct identification of the components). In our experiment the effect of saturation was eliminated by extrapolation of the beat frequency to zero amplitude.

In order to solve the system (4), it is also necessary to know the shape and width of the spectral components. Finding these parameters was achieved by constructing the profile of the resultant line using a computer for linear models corresponding to the velocity distributions indicated in Table 2 and a component width of 6-10 kHz. The best coincidence was obtained for the line shape $x^{-2} \sin^2 x$ (corresponding to a monokinetic beam) and a component width 9 kHz at the half-intensity level. Under these conditions $x^{-2} \sin^2 x$, we considered only the central maximum (the side maxima are "smeared" for a certain velocity spread of the molecules). The shape obtained for the line is shown in Fig. 3. The construction of the profile of the resultant line showed, in addition, that while the shape of the line on the wings depends essentially on the choice and width of the components (it is easy to distinguish the curves for a change in line width by 0.5 to 1 kHz), the distance between the central maxima is insensitive to the model.

Thus, we found the magnitude of the constant B for a line width of 9 kHz with allowance for only the three most intense components $2\frac{3}{2} - 2\frac{3}{2}$, $2\frac{5}{2} - 2\frac{5}{2}$, and $1\frac{3}{2}$ of the line. The magnitude of the constants determined in this fashion was $B = -14.6$ kHz. This value lies within the limits of the error given in [4], but is beyond the limits of the error in the value given in [5].

The difference between the beat frequency and the distance between the components (i.e., the magnitude of the correction calculated) is about 2.5%. Likewise considering the weak dependence of the correction on the choice of the shape of the spectral line (see Table 2), it may be said that the error in the distance between components is basically determined by the experimental error. Let us likewise note that the distance between the maxima of the resultant line is determined basically by the components B and D; the resultant contribution of the other components to this distance does not exceed 3%, and the errors in the other constants may likewise be neglected.

The data obtained for oscillation in the quadrupole satellites of the line were processed similarly. The magnitude of the distance Δf_{cor} from the center of the line is given in Table 1. Our measurements for the inner quadrupole satellite yielded the value $\text{eq } Q = -4083.7$ kHz for the magnitude of the quadrupole constants, while for the outer quadrupole satellite the value $\text{eq } Q = -4094.7$ kHz was obtained. These results do not allow a choice to be made between the values of $\text{eq } Q$ in [4, 5]. For $J = K = 1$ [4] gave $\text{eq } Q = -4085.4 \pm 0.3$ kHz, while [5] gave two values $\text{eq } Q = -4090 \pm 1.5$ kHz and $\text{eq } Q = -4092.8 \pm 1.5$ kHz for $\text{eq } Q$. It should be noted that the values themselves given in [4] and [5] differ by more than the limits of the error indicated by the authors. The causes of such a discrepancy are at present unclear.

In conclusion, let us note that for an investigation using conventional equipment only fairly intense lines are adequate, but the results obtained for one line are applicable to the calculation of other lines of the substance considered. An easing of the conditions governing self-excitation in such a radio-spectroscope (for example, the use of a superconducting resonator) would considerably expand the range of substances suitable for investigation by this method and would in our case permit the experimental error to be reduced severalfold.

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