MEASUREMENT OF THE $J = 0 \to 1$ TRANSITION FREQUENCY OF $N^{14}H_3$ IN THE SUBMILLIMETER BAND, AND AN IMPROVED DETERMINATION OF THE MOLECULAR STRUCTURE OF AMMONIA

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Radiospectroscopic methods are used to find the lowest rotational transition $J = 0 \to 1$, $K = 0$ of $N^{14}H_3$. The measured transition frequency is 572 499.4 MHz ± 3 MHz ($\lambda \sim 0.53$ mm). The theoretical rotational constant of $N^{14}H_3$ is $B_0 = 298\ 106$ MHz. The molecular structure of ammonia is determined: the N—H bond length $l_0 = 1.0134$ Å, and the H—N—H bond angle $\Theta_0 = 106°36'$.

While the inversion spectrum of ammonia has been fully examined by radiospectroscopic methods [1], its rotational spectrum has so far been studied only by infrared spectroscopy [2] and Raman scattering methods [3], which yield lower accuracy than radio spectroscopy. This situation is due to the fact that the submillimeter band, where the rotational transitions of ammonia lie, is almost inaccessible. It is only for the deuteron form of ammonia $N^{14}D_3$ that a lowest rotational transition $J = 0 \to 1$ has been observed, at a wavelength of roughly 0.97 mm [4].

The present paper describes the first radiospectroscopic measurements to be made of the lowest rotational transition $J = 0 \to 1$ of ordinary $N^{14}H_3$ at a wavelength of roughly 0.53 mm, where the accuracy of measurements of the transition frequency and rotational constant of the ammonia molecule is considerably improved.

1. EQUIPMENT AND METHOD

The experimental equipment consists of two main parts: the spectroscope as such, operating at $\lambda \simeq 0.5$ mm, with a wobbulated signal source, absorbent gas
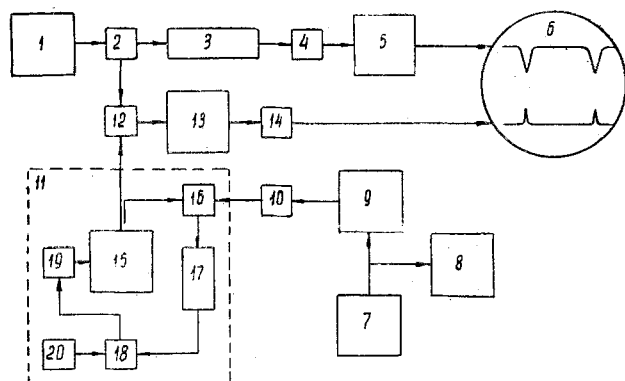

Fig. 1. Block diagram of the experimental equipment. For the meaning of most of the block numbers see text; 16, 17, 18, and 19 are respectively the mixer, intermediate frequency amplifier, phase detector, and video amplifier of the 4 mm klystron PAFC system.

cell and video receiver; and the frequency measurement system, which provided a frequency marker with the stability of a crystal oscillator in the band $\lambda \simeq 0.5$ mm ($f \simeq 600\ 000$ MHz). A block diagram of the equipment is given in Fig. 1.

The monochromatic 0.5 mm signal source 1 of Fig. 1 is the backward-wave tube (BWT) described in [5]. For observation of the fairly narrow (~ 1–10 MHz) spectral lines, parasitic modulation of the BWT output by the power line frequency (50 Hz) and its harmonics had to be minimized. The tube was therefore supplied from an electronically stabilized rectifier with an auxiliary filter, while the residual power line modulation was compensated by application of an auxiliary voltage, at the power line frequency and suitable amplitude and phase, to the BWT supply circuit. By this means a reduction of the frequency deviation to 50–100 MHz was possible. Further reduction of the hum modulation* proved difficult, because of the significant proportion of higher harmonics in the modulation. The residual hum modulation was, in fact, utilized for observing the spectral line by the wobbulation method.

The receiver 4 was type D-407 standard detector, which could operate satisfactorily at a wavelength of 0.5 mm provided that its working point was suitably chosen by displacing the crystal, and that it was matched (slanted relative to the waveguide). The detected signal was applied to the battery-fed amplifier 5 and thence to one set of vertical plates of the double-beam oscilloscope 6.

The high intensity of the observed spectral line ($\gamma_{max} \simeq 0.06$ cm^{-1}) made it possible to restrict the absorption cell 3 to length of 15 cm and a cross section of 1.8×3.6 mm, to suit the BWT and D-407 waveguides. The cell windows were mica plates 0.1 mm thick, the thickness being designed to maximize the transmission at 0.5 mm (the electrical thickness was roughly $\lambda/2$). The coupler 2 split the BWT signal power between the spectroscopic cell and the system for generating the frequency marker. A photograph of the $J = 0 \to 1$, $K = 0$, $N^{14}H_3$ spectral line, obtained in the cell with the D-407 detector, is given in Fig. 2. The line width is on the order of 10 MHz, and the quadrupole structure (around 3 MHz) is not resolved.

The frequency of the $J = 0 \to 1$ transition was found by comparison with the multiplied frequency of the

*The hum modulation was probably due to the AC heater supply to the BWT; a DC supply shortened the life of the tube.
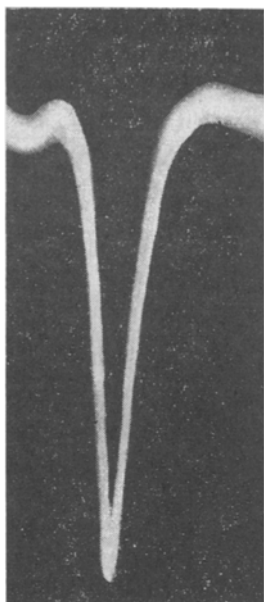
Fig. 2. Spectral line J =
= 0 → 1 of $N^{14}H_3$, λ ~
~ 0.53 mm.

quartz oscillator 7, measured by the type Ch3-9 electronic frequency-meter 8. The crystal oscillator frequency was roughly f_{q1} = 9.126 MHz, since, on the one hand, the operating range of the Ch3-9 is limited to 10 MHz, and on the other, a lower frequency would cause difficulties as regards harmonic filtering in the tube multipliers. In addition, a more precise selection of the crystal oscillator frequency was made to facilitate calibration (see below).

To obtain a frequency marker of crystal stability in the region of 600 000 MHz (λ ~ 0.5 mm), the crystal oscillator frequency was multiplied by means of two series phase-lock automatic frequency control (PAFC) systems. The first system (9 in Fig. 1) stabilized the klystron frequency at f_{kl1} = 872 f_{q1} in the region of λ ≃ ≃ 3.8 cm relative to the crystal oscillator 7. The signal from the first klystron was applied to the crystal frequency multiplier 10, and the ninth harmonic (frequency f_h = 7848 f_{q1}) was utilized as a control signal for the second PAFC system. In the second system (11 in Fig. 1), the frequency of the second klystron 15 (in the range λ ≃ 4.2 mm) was stablizied with respect to the multiplied signal of frequency 7848 f_{q1} and the auxiliary second crystal generator 20 of frequency f_{q2} = 55.13 MHz, so that the frequency of the second klystron was equal to f_{q2} = 7848 $f_{q1} - f_{q2}$.

The second klystron signal was then applied along with the BWT signal to the crystal detector 12, where the klystron frequency is multiplied and its eighth harmonic mixed with the BWT signal in the region of λ ≃ ≃ 0.5 mm. The detector (another D-407) was connected to the input of the intermediate frequency amplifier 13 (IFA), with center frequency f_{if} = 64.4 MHz. When the beat frequency between the BWT and crystal-stabilized signals coincided with the if frequency, the amplifier produced an output which, after detection at detector 14, gave the frequency marker, which was applied to the second set of vertical plates of the double-beam oscilloscope. The two beams scanned in phase. The frequency marker could be displaced from the peak of

the absorption line on the screen of the oscilloscope 6 by adjustment of the crystal oscillator 7.

We usually chose the frequency marker for the case of a BWT signal with lower frequency than the klystron eighth harmonic, so that the final expression relating the frequency of the J = 0 → 1 transition of $N^{14}H_3$ with the crystal oscillator frequency was

$$f_{0-1} = 8(7848 f_{q1} - f_{q2}) - f_{if} \quad . \qquad (1)$$

It is clear from (1) that errors in measuring f_{q2} and f_{if} have a small effect on the measurement results and can in practice be ignored.

In view of the very high (~$6 \cdot 10^4$) factor multiplied by the crystal oscillator frequency, the operation of the frequency measurement system was checked with special attention. The part of the system from the first crystal oscillator and counting frequency-meter to the stabilized klystron operating at λ ~ 3.8 cm, was calibrated by means of a maser using the J = 3, K = 3 inversion transition of $N^{14}H_3$, the frequency of which is known quite accurately.

The frequency of the first crystal oscillator was chosen so that the third harmonic of the first klystron (i. e., the 2616-th harmonic of the crystal 7) was same as the J = 3, K = 3 transition frequency. A check showed that the frequencies of this transition, as measured by us and, for example, in [6], were identical to an accuracy of ~$5 \cdot 10^{-9}$; this indicates that the multiplication factor was correctly determined in the PAFC system, and that the reference crystal oscillator in the Ch3-9 instrument had good accuracy. We then used a 4 mm wavemeter, previously calibrated from the $1_{01} - 0_{00}$ and $5_{14} - 5_{15}$ lines of formaldehyde H_2CO, to check the frequency of the second klystron, and selected the lower of the two possible stabilization frequencies (corresponding to the image channels for reference signal reception). The BWT frequency in the 0.5 mm range crudely determined by a Fabry-Perot wavemeter and from the BWT technical specification.

2. RESULTS AND INTERPRETATION

Our measurements of the J = 0 → 1 transition frequency of $N^{14}H_3$ gave f_{0-1} = 572 499.4 MHz, which corresponds to a frequency of the first crystal oscillator of f_{q1} = 9.126605 MHz; we estimated an experimental error of ±$5 \cdot 10^{-6}$ (±3 MHz at the transition frequency). This result provides a means of calculating the rotational constant and structure of the ammonia molecule.

The ammonia molecule is a symmetric top, and its rotational spectrum consists of a series of lines with the frequencies

$$f_{J, J+1} = 2(J+1)(B_0 - D_{JK}K^2) - 4D_J(J+1)^3, \qquad (2)$$

where B_0 is the rotational constant, and D_J, D_{JK} are the centrifugal perturbation constants, equal to 19 MHz and −28 MHz respectively for ammonia. Every rotational level of ammonia is split as a result of inversion, so that (2) defines the mean frequency of the inversion doublet (see Fig. 3).* The magnitude of the

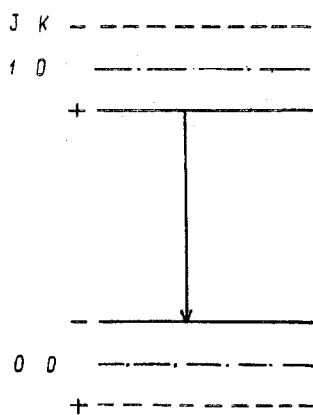*We ignore the quadrupole structure, which was not resolved in this work.

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J  K  _  _ _ _ _ _ _ _ _
1  0     ___ _ ___ _ _ ___
   +     _____
                │
                │
                │
                │
                ▼
   _     _____
0  0     _ _____ _ _ _ _ _
   +  _ _ _ _ _ _ _ _
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Fig. 3. Arrangement of the lower ro-
tational transition J = 0 → 1, K = 0
of $N^{14}H_3$: Solid lines are resolved
levels, dashed lines are absent inver-
sion levels, dot-dash lines show the
position of the center of the inver-
sion doublet, and the arrow indicates
the observed transition. The inversion
splitting is greatly exaggerated.

inversion splitting ν_{JK} is obtained from an empirical
formula [1].

The lower rotational transition J = 0 → 1, K = 0 on
which the measurements were made has a property
related to the half-integer spin of the H nucleus. In
fact, the requirement that the total wave function of a
molecule with three H nuclei at K = 0 be antisymmetric
implies that one of the inversion levels is absent: the
lower (+) for J = 0, and the upper (−) for J = 1 [1].
Only one (the low-frequency) component of the inver-
sion doublet is thus observed in the rotational transi-
tion; to evaluate the positions of the unsplit levels (the
dot-dash lines in Fig. 3), we have to add to the mea-
sured transition frequency half the sum of the inversion
splitting of the J = 0, K = 0 and J = 1, K = 0, levels,
i.e., $(\nu_{00} + \nu_{10})/2$ = 23 636.8 MHz [1]. Finally, we have

$$B_0 = \frac{1}{2}\left(f_{0-1} + 4D_J + \frac{\nu_{00} + \nu_{10}}{2}\right) = 298106 \text{ MHz} \quad (3)$$

The ammonia molecule is well known to have a pyr-
amid shape, with the nitrogen nucleus at the vertex.
Its structure is fully defined by two parameters, usually
the length l_0 of the N—H bond and the H—N—H bond angle
Θ_0. The structural parameters are related to the ro-
tational constant by [1]

$$\frac{\hbar}{4\pi B_0} = m_1 l_0^2 (1 - \cos\Theta_0) +$$

$$\frac{m_1 m_2 l_0^2}{3m_1 + m_2}(1 + 2\cos\Theta_0), \quad (4)$$

where m_1 and m_2 are the masses of the H and N nuclei
respectively.

Notice that the zero subscript indicates averaging
over the fundamental (zero) oscillatory state. To ob-
tain the set of two equations giving l_0 and Θ_0 in terms
of B_0, we have to measure B_0 for two isotopic combi-
nations of the molecule (the structural parameters are
assumed identical here, as usual). Hence the exact
value B_0 = 154 162.7 MHz for the deuteron form of am-
monia [4] does not of itself provide accurate informa-
tion on the structural parameters. Erlandsson and
Gordy [4] were forced to combine their data with less
accurate results of infrared measurements [2]; they
also took Θ_0 = 107° and on this assumption obtained l_0 =
= 1.0144 Å. With our present results it is now possible
to calculate both structural constants. For the values
of the other required constants we used the data given
in [1]. The same values are obtained for the structural
parameters of ammonia from our measurements as
were obtained from [4]:

$$l_0 = 1.0134 \text{ Å},$$
$$\Theta_0 = 106°36'.$$

The authors thank A. I. Naumov, A. G. Kislyakov,
Yu. A. Dryagin, L. I. Fedoseev, and N. I. Furashov
for making available some of the equipment and for
valuable consultations, and B. V. Gromov for assis-
tance with the experimental work.

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Note added in proof. The picture of the J = 1-2, K = 0, and K = 1
transitions of ND_3 observed by us in the region of 0.5 mm differed from
the theoretical (inversion doublet for each K) in that there was a cen-
tral undisplaced line of lower intensity at the frequency of the rota-
tional transition unaccompanied by inversion transition. It is possible
that such transitions are resolved in the case of the deuteron form of
ammonia when K = 1.