

## BRIEF COMMUNICATIONS AND LETTERS TO THE EDITOR

### SUBMILLIMETER SPECTRUM OF $\text{NH}_3\text{-H}_2\text{O}$ DIMER IN ITS EQUILIBRIUM GAS PHASE

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*The first observation of the microwave spectrum of the  $\text{NH}_3\text{-H}_2\text{O}$  molecular complex in its equilibrium gas phase is reported. Earlier, the spectrum of  $\text{NH}_3\text{-H}_2\text{O}$  was observed only in nonequilibrium cold supersonic molecular beams. As in the previous paper [1] dealing with the observation of the equilibrium spectrum of  $\text{HF-HF}$  dimer, we use a submillimeter spectrometer with a BWT and acoustic detector and a cooled absorption cell. The submillimeter line frequencies continuing the series known from the beam investigations have been measured. New series, which obviously correspond to the higher states of the dimer, have been detected. The primary results of the analysis of the dimer spectrum together with the earlier data are presented.*

The investigation of the spectra of molecular complexes by microwave methods is a relatively new branch of molecular spectroscopy. The spectra of molecular complexes are most easily observed in cold jets of gases, which leak into the vacuum and experience deep cooling (up to a few degrees Kelvin) under adiabatic expansion. Such a cooling cannot be reached under equilibrium conditions because of the gas condensation. At the same time, the observation of the spectra of molecular complexes makes new investigations possible and enables one to observe these complexes in their higher states and measure their binding energy, line broadening, line shift, etc. At present, observations of the spectra of molecular complexes are rather scanty, and the increase in the number of such complexes observed under equilibrium conditions is of considerable interest. Earlier, we reported on the observation of the first submillimeter equilibrium spectrum of  $\text{HF-HF}$  [1]. In the present paper, we report on the first observation of the equilibrium spectrum of  $\text{NH}_3\text{-H}_2\text{O}$ , which is an important molecular complex composed of widespread components. Owing to the great complexity of the molecules of this complex, the latter undergoes a variety of internal motions of large amplitude. This increases the complexity of the spectrum and decreases the intensity of individual lines, which is seen as "spreading" of the spectrum, and makes its observation and interpretation rather difficult.

The spectra of  $\text{NH}_3\text{-H}_2\text{O}$  were recorded by a RAD spectrometer with a submillimeter frequency synthesizer [2] in the range from 206 to 380 GHz. We used a mixture of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  vapor with total pressure about 1 Torr and  $(\text{NH}_3):(\text{H}_2\text{O})$  proportion from 10:1 to 6:1. The temperature in the cell was maintained at 230 K, and the time constant in the spectrum recording was 3 s. The frequency of the BWT was changed by scanning the frequency of the reference centimeter synthesizer [2]. Marks were put in the spectrum record to indicate fixed frequency intervals. The line frequencies were determined by interpolation. Figure 1 shows part of the record of the  $\text{NH}_3\text{-H}_2\text{O}$  spectrum near 328 GHz. Amplitude modulation was used for recording the spectrum. According to our estimates, the accuracy in measurement was a few megahertz because of the moderate signal-to-noise ratio, the high density of the spectrum (influence of the neighboring line wings), and the large width of the lines themselves.

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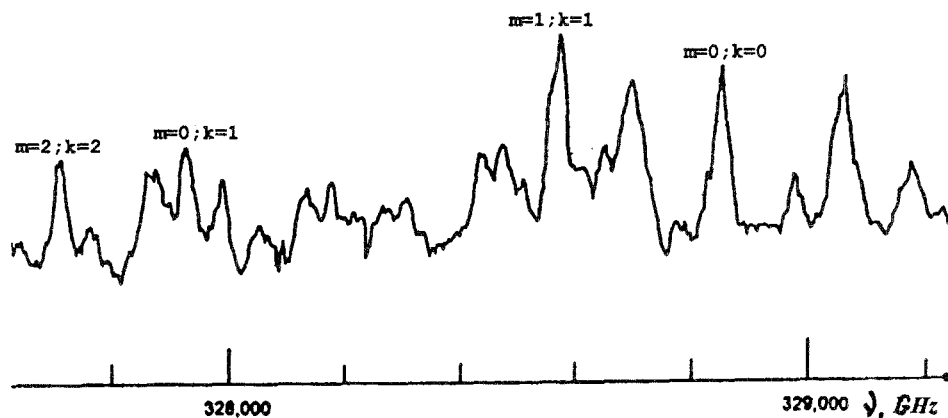


Fig. 1.

The primary proofs of observation of the spectrum of  $\text{NH}_3\text{-H}_2\text{O}$  dimer were the emergence of that spectrum only after the  $\text{NH}_3 + \text{H}_2\text{O}$  mixture was cooled and the characteristic dependences of spectrum intensity and pressure in the gas mixture. Final identification of the observed spectrum as the spectrum of  $\text{NH}_3\text{-H}_2\text{O}$  was obtained by using the results of [3] after measuring the spectral line frequencies.

The recorded spectrum was analyzed on the basis of the results of [4] and [5]. In [4], the authors investigated the microwave and FIR spectra of  $\text{NH}_3\text{-H}_2\text{O}$  in the ranges 36–86 GHz and 520–800 GHz, using a flat cold ultrasonic molecular beam. Seven *a*-type purely rotational microwave lines and almost three hundred of *b*-type FIR rotational–tunnel lines were observed there. The microwave spectrum obtained in [5] consists of a few tens of purely rotational lines in the ground and excited vibrational states.

In our analysis of the spectrum, we used the microwave transition frequencies in the ground vibrational state from [5] and the FIR data from [4]. For identification of the spectrum, we processed the frequencies of the submillimeter purely rotational transitions, measured in the present paper, together with the transition frequencies for different bands in the FIR spectrum from [4]. The latter differ in quantum numbers *K* (projection of the angular momentum of the dimer onto the *a* axis) and *m* (projection of the angular momentum of internal rotation of  $\text{NH}_3$  onto the symmetry axis of ammonia). Each FIR band was processed using eight parameters, including three constants, *B*, *D*, and *H*, for the upper and lower states and two frequencies, which correspond to the beginning of the bands for ortho states and para states with respect to water tunneling in  $\text{NH}_3\text{-H}_2\text{O}$ . Only in one band was the agreement within the experimental error in each case. Thus, the observed series were identified on a data agreement basis (Table 1).

The results of spectrum processing of  $\text{NH}_3\text{-H}_2\text{O}$  are presented in Table 1, and the spectroscopic data obtained are given in Table 2. It is seen from these tables that the above constants are sufficient for band-by-band processing of the measured spectrum within the experimental accuracy.

In analyzing the spectrum, we discovered a few successions of spectral lines with *B* and *D* constants, which are close to the constants of the  $\text{NH}_3\text{-H}_2\text{O}$  dimer in its ground state. We think that we are dealing with purely rotational transitions, which are similar to those already identified but which correspond to the higher excited states (with larger *m* and *K*.) Unfortunately, neither our analysis nor the analysis performed in [4] make identification of these transitions possible at present. Such an analysis will be the object of further investigation.

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T a b l e 1  
Observed purely rotational transitions of ammonia-water dimer  
in different states of internal rotation ( $m, K$ ) in [MHz]

Exper. frequency	Exper.- Theor.	$J'$	$J''$	Exper. frequency	Exper.- Theor.	$J'$	$J''$
State (0,0)				State (0,-1)			
208132.0	-8.8	17	16	207549.0	10.6	17	16
220294.0	0.9	18	17	219640.0	-16.8	18	17
232426.0	-3.4	19	18	231770.0	10.4	19	18
244548.0	-1.1	20	19	243832.0	-14.1	20	19
268753.0	18.0	22	21	267965.0	-1.1	22	21
280811.0	11.7	23	22	279992.0	-5.9	23	22
292849.0	5.8	24	23	292014.0	4.2	24	23
304867.0	1.2	25	24	304000.0	-0.5	25	24
316871.0	4.8	26	25	315970.0	0.5	26	25
328850.0	6.6	27	26	327923.0	7.5	27	26
340795.0	-1.4	28	27	339832.0	-5.7	28	27
352729.0	4.4	29	28	351739.0	3.7	29	28
364631.0	4.4	30	29	363618.0	10.9	30	29
376493.0	-8.5	31	30	375448.0	-4.2	31	30
State (0,1)				State (1,0)			
233029.0	-17.8	19	18	207763.0	6.2	17	16
245211.0	12.8	20	19	219850.0	8.2	18	17
269441.0	-5.9	22	21	231912.0	8.5	19	18
293616.0	-1.6	24	23	279902.0	12.5	23	22
317710.0	7.2	26	25	291804.0	-10.3	24	23
329705.0	-5.9	27	26	303684.0	-23.6	25	24
341698.0	3.1	28	27	315577.0	8.9	26	25
353654.0	0.3	29	28	327397.0	2.4	27	26
365588.0	1.6	30	29	339195.0	9.5	28	27
375505.0	13.1	31	30	350930.0	-9.5	29	28
				362666.0	10.7	30	29
				374320.0	-11.6	31	30
State (1,1)				State (2,2)			
207941.0	-2.9	17	16	219442.0	-19.9	18	17
220075.0	-11.3	18	17	231563.0	3.2	19	18
232197.0	-16.1	19	18	243642.0	0.0	20	19
244330.0	6.5	20	19	279800.0	13.8	23	22
280541.0	-5.5	23	22	291804.0	6.9	24	23
292585.0	2.7	24	23	303790.0	2.3	25	24
304593.0	-3.5	25	24	315760.0	2.8	26	25
316583.0	-5.8	26	25	327709.0	4.4	27	26
328570.0	11.9	27	26	339622.0	-6.8	28	27
340500.0	-3.3	28	27	351523.0	-6.0	29	28
352427.0	3.3	29	28	363407.0	2.8	30	29
364316.0	-2.0	30	29	375251.0	-2.0	31	30
376188.0	2.5	31	30				

T a b l e 2

Spectroscopic constants of ammonia–water dimer  
for different states ( $m, K$ )

$m, K$	$B$ [MHz]	$D$ [kHz]	$H$ [Hz]
(0,0)	6142.6458(10)	35.720(41)	-0.509(37)
(1,1)	6136.4124(88)	35.09(44)	-0.526(39)
(0,1)	6159.1137(72)	36.27(35)	-0.297(33)
(0,-1)	6124.5499(38)	35.258(38)	-0.397(39)
(1,0)	6141.584(40)	53.66(49)	-0.302(43)
(2,2)	6117.65(53)	32.7(10)	-0.783(83)
(2,1)	6141.56(26)	53.5(25)	

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