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Microwave spectra and nuclear quadrupole structure of the NH_3–N_2 van der Waals complex and its deuterated isotopologues

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The microwave spectrum of the NH_3–N_2 van der Waals complex has been observed in a supersonic molecular jet expansion via broadband (2-8 GHz) chirped-pulse Fourier-transform microwave spectroscopy. Two pure rotational $R(0)$ transitions ($J = 1 - 0$) with different hyperfine structure patterns were detected. One transition belongs to the (*ortho*)-NH_3–(*ortho*)-N_2 nuclear spin isomer in the ground $K = 0$ state reported earlier [G. T. Fraser *et al.*, J. Chem. Phys. **84**, 2472 (1986)], while another one is assigned to the (*para*)-NH_3–(*para*)-N_2 spin isomer in the $K = 0$ state not reported before (K is the projection of the total angular momentum J on the intermolecular axis). The complicated hyperfine structure arising from three quadrupole ^{14}N nuclei of NH_3–N_2 was resolved for both transitions, and the quadrupole coupling constants associated with the NH_3 and N_2 subunits were precisely determined for the first time. These constants provided the dynamical information about the angular orientation of ammonia and nitrogen indicating that the average angle between the C_3 axis of NH_3 and the N_2 axis is about 66°. The average van der Waals bond lengths are slightly different for (*ortho*)-NH_3–(*ortho*)-N_2 and (*para*)-NH_3–(*para*)-N_2 and amount to 3.678 Å and 3.732 Å, respectively. Similar results for the deuterated isotopologues, ND_3–N_2, NHD_2–N_2, and NH_2D–N_2, and their nuclear spin isomers were also obtained thus confirming and extending the analysis for the parent NH_3–N_2 complex. *Published by AIP Publishing.* https://doi.org/10.1063/1.5063346

I. INTRODUCTION

A nuclear hyperfine structure in molecular rotational spectra arises from magnetic and electric interactions of the molecular fields with the nuclear moments. Observation of the resulting splittings of the energy levels into components provides detailed information on the molecular electronic structure and chemical bonds.[1,2] In the case of weakly bound molecular complexes, the hyperfine structure parameters (quadrupole coupling, spin-spin coupling, and spin-rotation constants) might provide additional valuable information about intermolecular dynamics and the interaction potential.[3] Moreover, the hyperfine structure of rotational spectra is so specific that its analysis may help to distinguish the spectra originating from different nuclear spin isomers for those complexes that contain symmetric parent monomer(s). However, the relatively low binding energy of weakly bound complexes can give rise to large amplitude internal motions which complicate the experimental determination of hyperfine parameters, both for problems in resolving hyperfine structure components and the complexity of the hyperfine spectral pattern itself.

The present study demonstrates the successful application of chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy in the study of the NH_3–N_2 van der Waals complex revealing the complicated hyperfine structure arising from three quadrupole ^{14}N nuclei. NH_3–N_2 is of particular interest because molecular nitrogen is the main component of many atmospheres of our solar system and extrasolar planetary systems, and ammonia is the most abundant alkaline gas of these media. High-level spectroscopic information about the structure and intermolecular dynamics of NH_3–N_2 is required in various areas of atmospheric sciences, e.g., atmospheric physics and chemistry.

Spectroscopically, NH_3–N_2 is an interesting case of a weakly bound system that exhibits four nuclear spin isomers, which are formed when *ortho*/*para* (*o*/*p*) NH_3 combines with (*o*/*p*) N_2. Because of the nuclear spin effects, the first excited internal rotor states of both monomers are metastable and are anticipated to be populated in the cold supersonic expansion of the molecules used for the formation of complexes. Rotational transitions originating from these states are therefore also expected in the spectra, besides the ground state transitions, thus probing the angular anisotropy of the intermolecular potential much more extensively.

The spectra of the NH_3–N_2 complex were first studied in the microwave (MW) region by Fraser *et al.* in 1986.[4]

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They found two series of transitions in the 6-27 GHz range using the molecular beam electric resonance (MBER) technique. The main series of four transitions was assigned as having $K = 0$ (the approximate quantum number K is the projection of total angular momentum J on the intermolecular axis), and a second pair of lines was assigned as having $K = 1$. These first observations were followed by more detailed millimeter-wave (mmW) studies.[5,6] As a result, a number of series of pure rotational transitions were assigned in terms of $K = 0$ and $K = 1$ states of NH_3–N_2 involving the possible nuclear spin isomers of the complex.[5] Not all of these assignments were certain however, since the observed mmW series contained transitions only with high J-numbers (larger than 10).

The hyperfine structure arising from the three ^{14}N nuclei was only partially resolved in the first MW study of NH_3–N_2[4] and could not be analyzed. The current paper presents such analysis for the $R(0)$ transition of the (o)-NH_3–(o)-N_2 spin isomer in the ground $K = 0$ state reported earlier[4] and for another $R(0)$ transition assigned to the (p)-NH_3–(p)-N_2 spin isomer in the $K = 0$ state not reported before. The deuterated ammonia species, ND_3–N_2, NHD_2–N_2, and NH_2D–N_2, showing similar hyperfine structure, were also detected, thus confirming the new assignments for the parent species. The resulting quadrupole coupling constants associated with NH_3 (ND_3, NHD_2, and NH_2D) and N_2 were precisely determined for the first time providing the dynamical information about the angular orientation of the ammonia and nitrogen subunits in the complex.

Another important result of the present study is the non-observation of the $K = 0$ state for (p)-NH_3–(p)-N_2 (not the one mentioned above), which was expected based on the earlier analysis[5] and one more $K = 0$ state for (o)-NH_3–(p)-N_2. This fact suggests revision of the assignments in the K numbers for the reported mmW transition series.[5]

II. EXPERIMENTAL DETAILS

The rotational spectra of NH_3–N_2 were detected using a broadband (2-8 GHz) chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer, the details of which are available elsewhere.[7] The microwave excitation pulses (4 μs) are directly generated on an arbitrary waveform generator (AWG), amplified to 300 W, and broadcast into a vacuum chamber where they interact with the cold ensemble of molecules. In order to reduce measurement time and sample consumption, the "fast-frame" scheme was employed.[8] Each sample injection was followed by a pulse train of eight excitation pulses spanning from 2 to 8 GHz. The molecular emission or free induction decay (FID) was then collected in the time domain for 40 μs after each excitation pulse. The Fourier transform of the averaged time trace yielded the frequency domain spectrum after the application of a Kaiser-Bessel window to improve the baseline resolution.

The sample of a gas mixture of 0.5%-1% of NH_3 and few percent of N_2 in Ne was injected through a pulsed pinhole nozzle into an evacuated chamber at a backing pressure in the range of 6-9 bars. The nozzle (General Valve, Series 9) with an orifice of 1 mm diameter was operated at a repetition rate of 9 Hz. The fast-frame scheme yielded an effective repetition rate of 72 Hz. The spectra of the ND_3, ND_2H, and NDH_2 containing complexes were recorded using an isotopically enriched sample of ND_3 (99% D). Partly deuterated species were produced by H/D exchange with remaining H_2O inside the sample system. In all the cases, the final spectra comprised 1.2×10^6 FIDs.

The full width at half-height for each line was about 60 kHz, and the uncertainty in the line center frequencies was estimated to be ≈5 kHz. At a sufficiently high resolution of the CP-FTMW spectrometer, the hyperfine structure due to three ^{14}N nuclei of the N_2 and NH_3 (ND_3, ND_2H, and NDH_2) parts of the complexes was clearly resolved.

III. OBSERVED ROTATIONAL TRANSITIONS AND ANALYSIS

A free internal rotation model provides a useful starting point to consider the energy levels of NH_3–N_2, and the nuclear spin modifications of the parent molecules remain important in the complex. Due to the nuclear spin statistics of N_2, (o)–N_2 complexes with total nuclear spin $I_{N_2} = 0$ and 2 have their lowest internal rotor state with $j_{N_2} = 0$, while (p)-N_2 complexes with $I_{N_2} = 1$ have their lowest internal rotor state with $j_{N_2} = 1$, where j_{N_2} denotes the rotational angular momentum of N_2. Due to the three equivalent protons, the NH_3 part has also two nuclear spin states, (o)-NH_3 ($I_{NH_3} = 3/2$) and (p)-NH_3 ($I_{NH_3} = 1/2$) with the corresponding lowest rotational levels $(j_k)_{NH_3} = 0_0$ and $(j_k)_{NH_3} = 1_1$, where j and k denote the angular momentum of NH_3 and its projection on the symmetry axis. In total, four different nuclear spin species occur for the NH_3–N_2 complex: (o)-NH_3–(o)-N_2, (p)-NH_3–(o)-N_2, (o)-NH_3–(p)-N_2, and (p)-NH_3–(p)-N_2. These spin isomers behave as different molecules because they do not interconvert at the time scale of the experiment, due to quantum-mechanical symmetry rules.

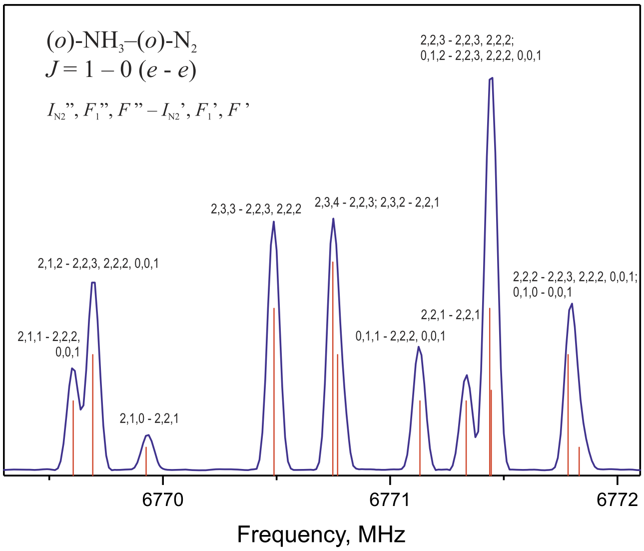

FIG. 1. Nuclear hyperfine structure of the $R(0)$ pure rotational transition of (o)-NH_3–(o)-N_2. The stick spectrum is simulated from the nuclear quadrupole coupling constants obtained from a fit of the respective transitions.

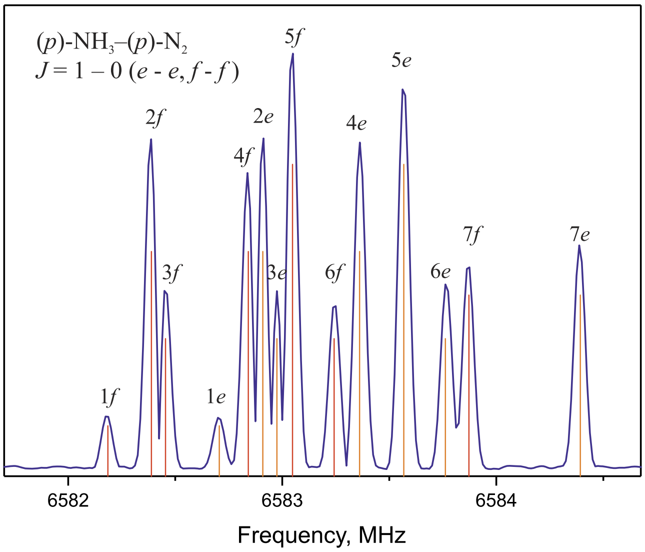

FIG. 2. Nuclear hyperfine structure of the $R(0)$ pure rotational transition of (p)-NH$_3$–(p)-N$_2$. The hyperfine pattern consists of two similar groups of seven peaks, designated by spectroscopic parity e and f correspondingly. The stick spectrum is simulated from obtained nuclear quadrupole coupling constants.

TABLE II. Observed hyperfine structure of the $R(0)$ rotational transition of (p)-NH$_3$–(p)-N$_2$ and (p)-ND$_3$–(p)-N$_2$ complexes (in MHz).

I_{N2}'', F_1'', F''–I_{N2}', F_1', F'	pNH$_3$–pN$_2$ e/f	pND$_3$–pN$_2$ e/f
1,1,0–1,1,1	6582.705/6582.182	5767.774/5767.725
1,1,2–1,1,2	6582.912/6582.388	5767.974/5767.913
1,1,1–1,1,2, 1,1,0	6582.974/6582.456	5768.023/–
1,2,2–1,1,1	6583.363/6582.840	5768.362/5768.302
1,2,3–1,1,2	6583.565/6583.047	5768.536/5768.487
1,2,1–1,1,1, 1,1,0	6583.762/6583.244	5768.724/5768.675
1,0,1–1,1,2, 1,1,1, 1,1,0	6584.391/6583.877	5769.248/5769.199

A strong feature at 6.77 GHz was observed as expected for the $R(0)$ transition of the (o)-NH$_3$–(o)-N$_2$ spin isomer in the ground $K = 0$ state.[4] In contrast to the previous MW study,[4] the hyperfine structure was now clearly resolved representing nine peaks spread over a 2.5 MHz region, as shown in Fig. 1. Another strong feature consisting of 14 peaks distributed also within 2.5 MHz was found at lower frequencies around 6.58 GHz, as shown in Fig. 2. In fact, looking closely, one can see that these 14 peaks consist of doublets, that is, they represent two similar series of seven lines, shifted relative to each other by approximately 0.5 MHz. For clarity, the paired components in Fig. 2 are numbered as 1e and 1f, 2e and 2f, etc. For the isoelectronic NH$_3$–CO complex,[9,10] similar doubling of rotational transitions was associated with (p)-NH$_3$ and its absence with (o)-NH$_3$, and it was also assumed[5] that NH$_3$–N$_2$ behaves in a similar fashion. Our hyperfine structure analysis confirmed this fact and showed that the observed pattern at 6.58 GHz corresponds to the $R(0)$ transition of the (p)-NH$_3$–(p)-N$_2$ nuclear spin isomer. Here in Fig. 2, we use the spectroscopic parity labels e ($\varepsilon = +1$) and f ($\varepsilon = -1$) to assign the parity p of individual levels according to the relation $p = \varepsilon(-1)^J$, and the e/f ordering was assumed to be the same as for (p)-NH$_3$–CO.[10] In case of (o)-NH$_3$–(o)-N$_2$, only e-symmetry refers to all $K = 0$ levels, therefore we omitted parity labels in Fig. 1. The $R(0)$ transition of (p)-NH$_3$–(p)-N$_2$ was not observed in the earlier MW study[4] and was also not expected from available mmW data.[5,6] Indeed, from the mmW series of the four $R(11)$-$R(14)$ transitions assigned to the $K = 0$ state of (p)-NH$_3$–(p)-N$_2$,[5] the $R(0)$ line of this spin isomer was predicted at 6.69 GHz, but no feature was detected at this frequency.

An additional criterion for assigning the observed nuclear spin isomers of NH$_3$–N$_2$ is relative intensities of their transitions. On the basis of nuclear spin statistics, we expect an intensity ratio of 2:1 for complexes composed of (o)- and (p)-N$_2$, respectively. For NH$_3$, the spin statistics are also 2:1 for *ortho/para*, but in spite of the higher multiplicity of the *ortho* nuclear spin states, the larger number of the *para* rotational levels results in approximately equal populations of the (o)- and (p)-NH$_3$ species. The observed intensity ratio of (o)-NH$_3$–(o)-N$_2$ to (p)-NH$_3$–(p)-N$_2$ for $J = 1 - 0$ transitions is 2.4. This value agrees reasonable with the above consideration taking into account the variations of the spectrometer response over the frequency range.

The resolved individual hyperfine components of the (o)-NH$_3$–(o)-N$_2$ and (p)-NH$_3$–(p)-N$_2$ $R(0)$ transitions are given in Tables I and II, respectively. The assigned quantum numbers correspond to the coupling scheme: $\mathbf{I}_{N_2} = \mathbf{I}_1 + \mathbf{I}_2$, $\mathbf{F}_1 = \mathbf{I}_{N_2} + \mathbf{J}$, and $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_N$, where $\mathbf{I}_1$ and $\mathbf{I}_2$ are the nuclear spins of two identical ^{14}N nuclei ($I_1 = I_2 = 1$), $\mathbf{I}_{N_2}$ is their sum ($I_{N_2} = 0, 1, 2$), and $\mathbf{I}_N$ is the nuclear spin of the ^{14}N nucleus ($I_N = 1$) in the ammonia molecule.

TABLE I. Observed hyperfine structure of the $R(0)$ rotational transition of (o)-NH$_3$–(o)-N$_2$ and its deuterated isotopologues (in MHz).

I_{N_2}'', F_1'', F''–I_{N_2}', F_1', F'	oNH$_3$–oN$_2$	NH$_2$D–oN$_2$	NHD$_2$–oN$_2$	oND$_3$–oN$_2$
2,1,1–2,2,2, 0,0,1	6769.601	6493.175	6243.261	6015.663
2,1,2–2,2,3, 2,2,2, 0,0,1	6769.695	6493.264	6243.327	6015.738
2,1,0–2,2,1	6769.935	6493.498	6243.574	6016.000
2,3,3–2,2,3, 2,2,2	6770.487	6494.000	6244.014	6016.388
2,3,4–2,2,3; 2,3,2–2,2,1	6770.750	6494.263	6244.289	6016.675
0,1,1–2,2,2, 0,0,1	6771.128	6494.588	6244.577	6016.925
2,2,1–2,2,1	6771.336	6494.802	6244.790	6017.138
2,2,3–2,2,3, 2,2,2; 0,1,2–2,2,3, 2,2,2, 0,0,1	6771.445	6494.911	6244.899	6017.238
2,2,2–2,2,3, 2,2,2, 0,0,1; 0,1,0–0,0,1	6771.797	6495.273	6245.273	6017.625

TABLE III. Molecular parameters of (*o*)-NH_3–(*o*)-N_2, (*o*)-ND_3–(*o*)-N_2, NHD_2–(*o*)-N_2, and NDH_2–(*o*)-N_2 complexes.

	oNH_3–*o*N_2	NH_2D–*o*N_2	NHD_2–*o*N_2	*o*ND_3–*o*N_2
B, MHz	3385.65389 (84)	3247.3904 (12)	3122.3858 (14)	3008.5583 (14)
D, kHz	111.4101 (47)	103.8[a]	97.2[a]	91.5[a]
H, Hz	−7.7682 (83)			
$eQq(N_2)$, MHz	1.7236 (43)	1.6142 (65)	1.5248 (71)	1.4524 (72)
$\langle P_2(\cos\theta_{N_2})\rangle$	−0.3208	−0.3005	−0.2838	−0.2704
θ_{N_2} (deg)	69.8	68.6	67.7	67.0
$eQq(NH_3)$, MHz	−1.1546 (96)	−1.173 (13)	−1.192 (14)	−1.203 (14)
$\langle P_2(\cos\theta_{NH3})\rangle$	0.2823	0.2868	0.2915	0.2946
θ_{NH_3} (deg)	43.8	43.6	43.4	43.3

[a] Fixed to the value scaled from (*o*)-NH_3–(*o*)-N_2.

The change of NH_3 for ND_3 in the gas mixture allowed the observation of similar $R(0)$ transitions for (*o*)-ND_3–(*o*)-N_2 and (*p*)-ND_3–(*p*)-N_2 as well as partly deuterated NHD_2–(*o*)-N_2 and NDH_2–(*o*)-N_2 species. They could be easily assigned due to the expected line positions and hyperfine patterns analogous to those of the parent isotopologue. The partial substitution in the case of NHD_2 and NDH_2 reduces the symmetry of the ammonia monomers and, although two nuclear spin isomers remain, there is no metastable excited internal rotor state (similar to (*p*)-NH_3 and (*p*)-ND_3) associated with them. The corresponding levels cannot be populated at the low rotational temperature of the jet (1-3 K) and only transitions correlating with the (*o*)-NH_3–(*o*)-N_2 spin isomer were detected for NHD_2–(*o*)-N_2 and NDH_2–(*o*)-N_2.

Inversion tunneling splitting was expected in the ground internal rotor state for the (*o*)-ND_3-, NHD_2-, and NDH_2-containing complexes with relative spin statistical weights for symmetric and asymmetric components of 10:1, 6:3, and 1:3, respectively, in contrast to the spectrum of the (*o*)-NH_3–(*o*)-N_2 isotopologue in which the symmetric inversion component has a nuclear spin weight of zero. Probably this separation of inversion components was too small to observe, and it was also not detected for the related (*o*)-ND_3–CO, NHD_2–CO, and NDH_2–CO complexes.[4] Also no additional D (I_D = 1) hyperfine splittings for all deuterated isotopologues could be resolved, which can be expected to be below the FWHM linewidths of about 60 kHz.[11]

TABLE IV. Molecular parameters of (*p*)-NH_3–(*p*)-N_2 and (*p*)-ND_3–(*p*)-N_2 complexes.[a]

	pNH_3–*p*N_2 *e*/*f*	*p*ND_3–*p*N_2 *e*/*f*
B, MHz	3291.804 31 (16)	2884.376 48 (45)
D, kHz	111.4[b]	91.5[b]
$eQq(N_2)$, MHz	1.713 5 (27)	1.391 (15)
$\langle P_2(\cos\theta_{N_2})\rangle$	−0.319 0	−0.258 9
θ_{N_2} (deg)	69.7	66.4
$eQq(NH_3)$, MHz	−1.160 5 (40)	−1.145 (19)
$\langle P_2(\cos\theta_{NH_3})\rangle$	0.283 7	0.280 4
θ_{NH_3} (deg)	43.7	43.8

[a] The mean center frequencies were used in the fitting procedure.

[b] Fixed to the value from (*o*)-NH_3–(*o*)-N_2.

The assigned individual hyperfine components of the $R(0)$ transitions for (*o*)-ND_3–(*o*)-N_2, NHD_2–(*o*)-N_2, and NDH_2–(*o*)-N_2 are listed in Table I. The assigned hyperfine components for the $J = 1 - 0$ transition of (*p*)-ND_3–(*p*)-N_2 are given in Table II.

The transitions of NH_3–N_2 and deuterated isotopologues assigned in this work were fitted using the PGOPHER program, which is open to the public.[12] All complexes in the $K = 0$ state were treated as a linear molecule, and two ^{14}N nuclei of the nitrogen molecule were considered as identical in hyperfine structure analysis according to the coupling scheme mentioned above: $\mathbf{I}_{N_2} = \mathbf{I}_1 + \mathbf{I}_2$, $\mathbf{F}_1 = \mathbf{I}_{N_2} + \mathbf{J}$, and $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_N$. In the case of the (*o*)-NH_3–(*o*)-N_2 spin isomer, the previously observed mmW transitions[5,6] were also included in the fitting procedure with a weight of 0.1 relative to our measurements in accordance with their experimental accuracy. The MW data from Fraser *et al.*[4] were not used in the fits because of their unclear/unresolved hyperfine/splitting structure. Since we have only one transition for (*p*)-NH_3–(*p*)-N_2 and each deuterated complex, their centrifugal distortion parameters D were fixed to quantities that were obtained by scaling corresponding values for the main isotopologue using relations for reduced masses. For the (*p*)-NH_3–(*p*)-N_2 and (*p*)-ND_3–(*p*)-N_2 transitions exhibiting doubling, the mean center frequencies were used in the fit analysis. The results of the fits are given in Tables III and IV. The weighted value of the root mean squared deviation is σ_{fit} = 78 kHz for (*o*)-NH_3–(*o*)-N_2.

IV. DISCUSSION AND CONCLUSIONS

The determined rotational constant B and centrifugal distortion parameter D for (*o*)-NH_3–(*o*)-N_2 (Table III) agree well with the previous mmW results, B = 3385.634 91(910) MHz and D = 111.3343(368) kHz.[6] These values can be also compared with those of the closely related (*o*)-NH_3–CO complex in the ground $K = 0$ state: B = 3485.762 76(63) MHz and D = 110.4157(450) kHz.[10] Overall, the B values of NH_3–(*o*)-N_2 are lower than those of (*o*)-NH_3–CO by about 100 MHz, indicating a slightly longer effective intermolecular distance. The obtained rotational constant B for the new $K = 0$ state of (*p*)-NH_3–(*p*)-N_2 (Table IV) is 94 MHz less than the corresponding value for (*o*)-NH_3–(*o*)-N_2. In the case of NH_3–CO, such difference is only 8 MHz[10] considering that the (p)-NH_3–CO (j_{N_2}, j_{CO}) = (1, 1) state is analogous to the (p)-NH_3–(p)-N_2 (j_{NH_3}, j_{N_2}) = (1, 1) state.

Dynamical information about the orientation of the ammonia and nitrogen units within the van der Waals complex can be obtained from the determined quadrupole coupling constants using the expression, $eqQ = (eqQ)_0 \langle P_2(\cos\theta_{NH3/N2})\rangle$, where $(eqQ)_0$ is the quadrupole coupling constant for the free NH_3 (ND_3) molecule, −4.0898 MHz[13] (−4.0831 MHz[14]), or the N_2 molecule, −5.372 MHz,[15] and θ_{NH_3/N_2} is the angle between the intermolecular axis and the C_3 axis of NH_3 (ND_3) or the N_2 axis, respectively. This expression assumes that complexation has little effect on the electron distribution around the ^{14}N nuclei and that the angular brackets represent averaging over the internal motions of NH_3 (ND_3) or N_2 in the complex. We assume also that the weighted average of the free NH_3 and ND_3 $(eqQ)_0$ values is a suitable approximation for the $(eqQ)_0$ values of NDH_2 and ND_2H. Solving this expression for θ_{NH_3} and θ_{N_2} yields two possible angles 43.8°/136.2° for NH_3 and 69.8°/110.2° for N_2 in (o)-NH_3–(o)-N_2. From the *ab initio*[10] and experimental[4] studies of the related NH_3–CO complex, it was found that in the ground state it has a T-shaped structure with the N atom closest to the CO subunit. Assuming a similar geometry for NH_3–N_2, the first two values $\theta_{NH3} = 43.8°$ and $\theta_{N2} = 69.8°$ were chosen as shown in Fig. 3, resulting in the angle between the C_3 axis of NH_3 and the N_2 axis of 66.4°.

The Legendre polynomial factor $\langle P_2(\cos\theta_{NH_3/N_2})\rangle$ in the above equation will be zero if the ammonia or nitrogen subunit undergoes free internal motion. For (o)-NH_3–(o)-N_2, $\langle P_2(\cos\theta_{NH_3})\rangle$ is 0.2823, a value that is remarkably large in magnitude compared to −0.066 for the (o)-NH_3–Ne[16] and −0.086 for the (o)-NH_3–Ar[17] complexes. The $\langle P_2(\cos\theta_{N_2})\rangle$ value for (o)-NH_3–(o)-N_2 is −0.3208, that is, only slightly larger in magnitude than −0.2189 for the N_2–Ne[15] and −0.2997 for N_2–Ar[18] complexes. This suggests a significantly hindered internal motion of the NH_3 moiety and a similar degree of hindered motion of the N_2 monomers in (o)-NH_3–(o)-N_2 as compared to their complexes with rare gas atoms. The same sign of the $\langle P_2(\cos\theta_{N_2})\rangle$ values assumes an "on average" more perpendicular orientation of N_2 to the intermolecular axis in (o)-NH_3–(o)-N_2 similar to N_2–Ne and N_2–Ar. The different sign of $\langle P_2(\cos\theta_{NH_3})\rangle$ as compared to complexes of NH_3 with rare gas atoms assumes an "on average" more parallel orientation of NH_3 to the intermolecular axis, in contrast to a more perpendicular arrangement in case of Ar– and Ne–(o)-NH_3. Indeed, the $\langle P_2(\cos\theta_{NH_3})\rangle$ value is very close to the value of (o)-NH_3–(o)-H_2 (0.306),[19] for which the equilibrium structure was found to be axial, with the C_3 symmetry axis of ammonia collinear with the intermolecular axis.[20] The magnitude of $\langle P_2(\cos\theta_{NH_3})\rangle$ slightly increases with increasing deuterium substitution. For (o)-N_2 paired with NH_3, NDH_2, ND_2H, and ND_3, the corresponding values are 0.2824, 0.2868, 0.2915, and 0.2941. This can be attributed to the larger tunneling mass and lower zero-point energies of the heavier complexes, resulting in stronger localization of the ammonia unit.

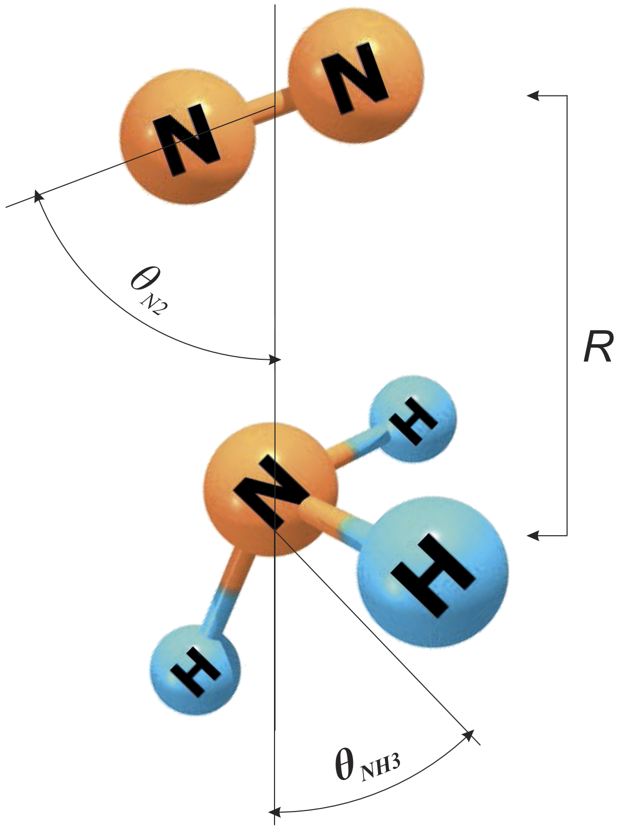

FIG. 3. The angular orientation of the NH_3 (θ_{NH_3} = 43.8°) and N_2 (θ_{N_2} = 69.8°) monomers in the (o)-NH_3–(o)-N_2 complex as determined from the nuclear quadrupole structure analysis. The average van der Waals bond length R was estimated to be 3.678 Å.

As can be seen from Tables III and IV, the determined quadrupole coupling constants and the Legendre polynomial factors for (p)-NH_3–(p)-N_2 are very similar to those of (o)-NH_3–(o)-N_2. This fact suggests a similar angular orientation of the two spin isomers with a slightly different intermolecular distance. From the derived molecular constants, the average van der Waals bond lengths $\langle R\rangle$ were calculated to be 3.678 Å and 3.732 Å for (o)-NH_3–(o)-N_2 and (p)-NH_3–(p)-N_2, respectively, using the formula,[21]

$$I_b = M\left\langle R^2\right\rangle + \frac{I_\perp^{NH_3}}{2}\left(1+\left\langle \cos^2\vartheta_{NH_3}\right\rangle\right) + \frac{I_\parallel^{NH_3}}{2}\left\langle \sin^2\vartheta_{NH_3}\right\rangle + \frac{I_{N_2}}{2}\left(1+\left\langle \cos^2\vartheta_{N_2}\right\rangle\right),$$

where I_b is the moment of inertia of the complex obtained from the experimental rotational constant, $M = \frac{m_{NH_3} m_{N_2}}{(m_{NH_3}+m_{N_2})}$ is the pseudodiatomic reduced mass, and $I_\parallel{}^{NH_3}$, $I_\perp{}^{NH_3}$, and I_{N_2} are the effective moments of inertia of the free ammonia (perpendicular and parallel to C_3 axis)[22] and molecular nitrogen.[23]

From a previous mmW study of NH_3–N_2,[5] we could expect the observation of one more $K = 0$ state for (p)-NH_3–(p)-N_2 as well as the $K = 0$ state for (o)-NH_3–(p)-N_2 spin isomers. Both these states were not detected in spite of significant resource in sensitivity as can be seen from the signal to noise ratio for the measured NH_3–N_2 transitions. No corresponding features were found also in the spectra of complexes containing the ND_3–N_2 isotopologues. Analyzing the results obtained earlier for the NH_3–CO complex[10] and considering that the (p)-NH_3–CO (j_{NH_3}, j_{CO}) = (1, 1) state is analogous to the (p)-NH_3–(p)-N_2 (j_{NH_3}, j_{N_2}) = (1, 1) state, we can suppose that the observed series[5] for the latter belongs to the $K = 2$ state, located quite closely (1.12 cm^{-1} in case of (p)-NH_3–CO) to the $K = 0$ state. For the (o)-NH_3–CO $(j_{NH_3}, j_{CO}) = (0, 1)$ state, correlating to the (o)-NH_3–(p)-N_2 $(j_{NH_3}, j_{CO}) = (0, 1)$ state, no $K = 0$ levels were detected at all and according to the *ab initio* calculations,[10] such levels would be located at 24.13 cm^{-1} above the lowest $K = 1$ state of this spin isomer. This results in very low population of the expected $K = 0$ levels and makes some doubt in the correct assignment of the corresponding mmW transition series[5] to the (o)-NH_3–(p)-N_2 spin isomer.

In summary, from high-resolution rotational spectroscopy of the weakly bound NH_3–N_2 complexes and their deuterated isotopologues, hyperfine interactions of ammonia and nitrogen and their angular orientation and internal rotational dynamics within the complexes have been revealed. The earlier mmW study of NH_3–N_2[5] reported a number of series of pure rotational transitions tentatively assigned in terms of $K = 0$ and $K = 1$ states of the possible nuclear spin isomers of the complex. Two expected $K = 0$ states for (p)-NH_3–(p)-N_2 and (o)-NH_3–(p)-N_2 were not detected in our experiment, thus calling the proposed assignments in K of these series[5] into question. Future observations of low-J transitions, e.g., the $R(1)$ and $R(2)$ transitions, as well as theoretical studies of the potential energy surface and bound state calculations will definitively establish the K values for all observed series of four different NH_3–N_2 spin isomers.

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