

An infrared–far-infrared double resonance study on $(\text{NH}_3)_2$ in a jet

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An infrared–far-infrared double resonance experiment on $(\text{NH}_3)_2$ in a jet was performed. From the results, the nature of the tunneling splitting detected in former IR and FIR studies was identified. It was found that the $(\text{NH}_3)_2$ complex exhibits the following feasible motions: internal rotation of each monomer, interchange tunneling, and inversion tunneling. The rigid structure was classified in C_s , where a plane of symmetry is assumed. The FIR transitions reported so far and three new bands reported in this work could be assigned within the group G_{144} . It is found that the inversion splitting for some of the bands is almost quenched. Upon excitation of the ν_2 umbrella motion the inversion splitting amounts to 3.7 cm^{-1} .

1. Introduction

The ammonia dimer has been the subject of discussion in the literature for a long time (see, for example, refs. [1–4]). The results of Nelson et al. [5,6], which showed that $(\text{NH}_3)_2$ does not have hydrogen bonding, were surprising in view of former ab initio calculations. The authors also managed to assign their transitions within the group G_{36} [7] which includes the internal rotation of each monomer along the C_3 axis (C_3) and the interchange tunneling between the two nonequivalent NH_3 monomers (I).

The two monomers were found to make different angles with the axis connecting them. It was further assumed that $(\text{NH}_3)_2$ exhibits a plane of symmetry and does not show any inversion splitting, which implies that inversion tunneling is totally quenched. In a later far-infrared study by Havenith et al. [8] several vibration–rotation–tunneling transitions were detected. It was concluded that G_{36} is the smallest

group explaining the observed transitions.

Measurements by Zwart [9] did not fit into this diagram and showed the need for further experiments. He found three bands which were rotationally assigned as $K: 0-0$ and $K: 1-1$ transitions (table 1). The $K: 0-0$ transition at 483 GHz shared the same ground state as the $K: 0-1$ transition assigned as A states [8]. Except for these two bands no other bands shared a common level, so a relative ordering of the states was not possible. It turned out that the tunneling assignment is difficult, but of major importance. We decided to apply a new method to the problem: infrared–far-infrared (IR–FIR) double resonance. This should help to label each state and gain insight into the nature of the splittings. Our measurements are partly based on the results of Fraser et al. [10], who performed an IR–microwave double resonance measurement on the G states. Furthermore we used the results of the measurement on the ν_2 umbrella motion by Snels et al. [11], which was later extended by IR–IR double resonance measurements by Heijmen et al. [12]. The IR spectrum [11] showed two main peaks at 979 and 1004 cm^{-1} , which originate from the excitation of two nonequivalent NH_3 monomers. On one of the bands (at

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Table 1

The observed frequencies and residuals of the fit (in MHz) for three bands of $(\text{NH}_3)_2$

$K=0 \rightarrow 0, \nu_{\text{BO}}=483 \text{ GHz}$				$ K =1 \rightarrow 1, \nu_{\text{BO}}=454 \text{ GHz}$			
J'	J''	frequency	obs. - calc.	J'	J''	frequency	obs. - calc.
8	9	383425.35	0.00	5	6	394443.63	-0.01
7	8	395324.85	-0.01	4	5	404262.96	0.03
6	7	407030.22	0.03	3	4	414075.83	-0.04
5	6	418538.25	0.00	2	3	423900.65	-0.03
4	5	429846.17	-0.02	1	2	433754.32	0.03
3	4	440951.39	-0.01	1	1	453656.39	-0.01
2	3	451851.51	0.01	2	2	453764.64	0.03
1	2	462544.37	0.01	3	3	453913.37	0.03
0	1	473028.10	0.00	2	1	473666.66	-0.05
1	0	493361.85	-0.01	3	2	483777.31	0.04
2	1	503209.32	0.00	4	3	493924.97	-0.03
3	2	512842.51	0.00	5	4	504093.69	0.00
4	3	522260.77	0.00	6	5	514264.15	0.00

$ K =1 \rightarrow 1, \nu_{\text{BO}}=487 \text{ GHz}$							
J'_{K_b, K_t}	J''_{K_b, K_t}	frequency	obs. - calc.	J'_{K_b, K_t}	J''_{K_b, K_t}	frequency	obs. - calc.
6 ₁₆	7 ₁₇	408864.25	0.20	1 ₁₀	1 ₁₁	486433.19	0.61
6 ₁₅	7 ₁₆	409242.96	0.00	1 ₁₁	1 ₁₀	486398.24	0.13
5 ₁₅	6 ₁₆	420725.76	-0.87	2 ₁₁	2 ₁₂	485843.64	-0.08
5 ₁₄	6 ₁₅	421031.29	-0.04	2 ₁₂	2 ₁₁	485744.75	-0.59
4 ₁₄	5 ₁₅	432388.56	0.84	3 ₁₂	3 ₁₃	484980.92	-0.06
4 ₁₃	5 ₁₄	432616.78	0.35	3 ₁₃	3 ₁₂	484798.12	0.03
3 ₁₃	4 ₁₄	443825.84	0.26	2 ₁₂	1 ₁₁	506248.68	-0.35
3 ₁₂	4 ₁₃	443976.91	-0.12	2 ₁₁	1 ₁₀	506339.61	0.07
2 ₁₂	3 ₁₃	455007.43	-0.65	3 ₁₃	2 ₁₂	515553.29	0.25
2 ₁₁	3 ₁₂	455088.46	-0.31	3 ₁₂	2 ₁₁	515718.21	-0.03
1 ₁₁	2 ₁₂	465902.24	-0.04	4 ₁₄	3 ₁₃	524592.01	0.20
1 ₁₀	2 ₁₁	465929.26	0.37	4 ₁₃	3 ₁₂	524838.03	-0.17

979 cm^{-1}) a substructure was detected. The two main peaks at 977.2 and 980.9 cm^{-1} were found to be correlated to the excitation of the G_α and G_β states, respectively [10]. A further peak arising at 970.5 cm^{-1} was interpreted as arising from $K=1$ [11]. The double resonance experiments allow direct access to the nature of the tunneling splitting. In this paper, we conclude that the inversion tunneling is responsible for the observed splitting in the microwave and the IR region. This is in contrast to previous results, where it was assumed that it was the interchange tunneling [10,11]. Furthermore we were able to (re)assign the previous FIR data as well as the new data reported in this work.

2. Experimental details

The $(\text{NH}_3)_2$ complexes were produced in a continuous two-dimensional supersonic jet by expanding a mixture of 2% NH_3 in argon through a 4 $\text{cm} \times 75 \mu\text{m}$ slit nozzle. The FIR radiation was generated with the Nijmegen tunable FIR sideband spectrometer [13] by mixing a fixed FIR laser frequency with tunable microwave radiation generated by a klystron in a Schottky barrier diode. For frequencies in the 300–500 GHz range we used higher harmonics of a 60 or 70 GHz klystron. Radiation generated in this way is focused in the molecular beam and detected by an InSb hot electron bolometer. For the double resonance experiments [14] a second laser beam, generated with a homebuilt CO_2 laser (typical single line

output power of 25 W) is guided anti-parallel to the FIR beam between the latter beam and the nozzle. Because the IR and FIR beams have totally different optical properties, it is not possible to make the laser beams coincide. The double resonances are detected by observing the depletion in a series of FIR transitions by the IR radiation. The frequency of the FIR beam was scanned over the absorption lines. By repeating this measurement for different CO₂-laser lines (10R8-10R32) and correcting for fluctuations in both FIR and IR power, IR-FIR double resonance spectra for the different tunneling states assigned as G_α, G_β, A and E are obtained.

3. Double resonance results and analysis

The results of the double resonance experiment are shown in fig. 1. In order to test the method we first performed double resonance measurements on the G_α and G_β bands, which were also observed by Fraser et al. [10]. Whereas they found that either the 10R22 or 10R28 CO₂ laser frequency is correlated with the G_α or G_β microwave transitions our measurements gave a different result: as can be seen in figs. 1A and 1B, we find a correlation with both peaks for each of the G states. This implies that collisional relaxations in the jet expansion cause a redistribution of the population among the two levels. These relaxations are absent in the collision-free molecular beam experiment. The two IR-FIR double resonance spectra are the same within the experimental uncertainty ($\approx 10\%$) implying that the population is equally distributed among these two states. It is generally assumed that relaxation by collisions can only take place between levels with the same spin state [15].

In fig. 1C the double resonance spectrum of the A state – as assigned in ref. [8] – is displayed. We observe a spectrum which is clearly different from the spectra of the G states: only one peak at 10R22 is obtained. We conclude therefore that in the state probed in fig. 1C one of the two (NH₃) monomers must have a spin which differs from the spins in the G states. This still agrees with the assignment to an A state. For A states both monomers are in an ortho state, in G states one ammonia is in an ortho and the other in a para state.

The two peaks at 10R22 and 10R28, which can be

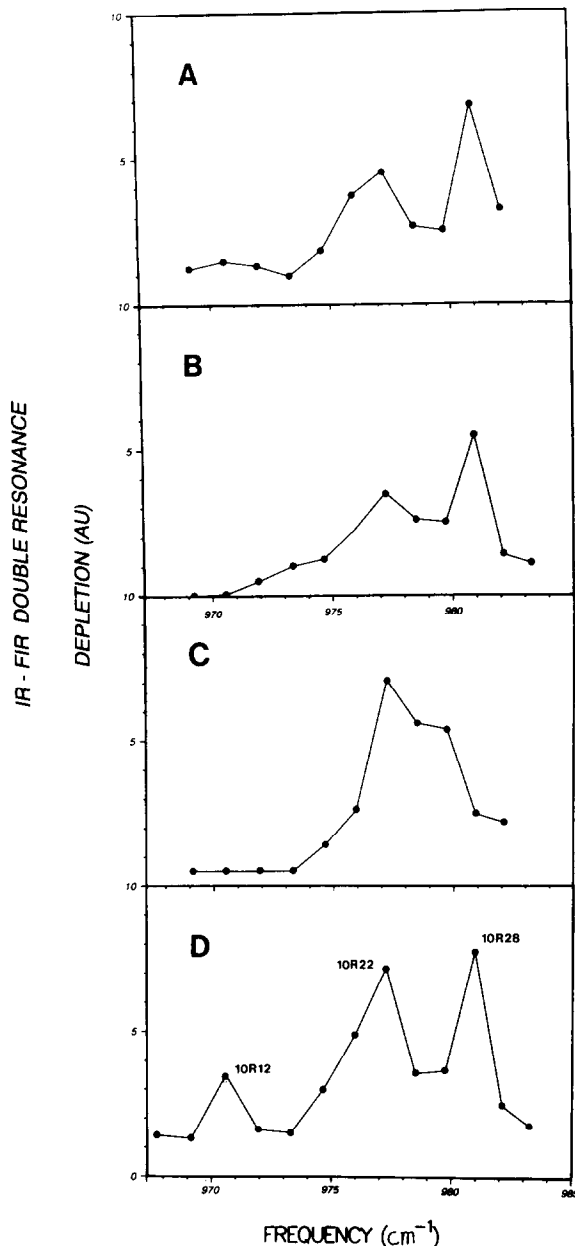


Fig. 1. Double resonance signal of (NH₃)₂ versus the CO₂ laser frequency. The different plots correspond to different FIR transitions as discussed in the text.

seen in figs. 1A and 1B were assigned as the two interchange components before [11]. This can be excluded for the following reason:

In case these are the two interchange components

we would always expect to see two peaks caused by relaxation processes from the other interchange component of the A state. This is in clear disagreement to our measurement, as is shown in fig. 1C. The only exception would be if for *one* state the two interchange components would be separated by a very large energy gap, making relaxation from one interchange component to the other for this state less likely. Since it was found before that relaxation is very effective [15] this would imply that for *one* state (e.g. the A state) the interchange components would be separated by an energy gap of the order of 100 cm^{-1} , whereas the two G states are close in energy as was concluded in this work and in ref. [8]. This would be in contradiction to the assumption that the $(2C_3+I)$ limit is valid as demanded by Nelson et al. [7]. The splitting of 3.7 cm^{-1} observed in the IR spectra can therefore not be due to interchange tunneling but must be due to a different motion. Since the barrier for internal rotation should not be influenced substantially by the umbrella vibration, the splittings for torsional states should not exceed a few GHz. The IR splitting is rather large which excludes that the splitting is due to internal rotation [11]. This would also be in contradiction with the measurements of Fraser et al. [10], where the two peaks were correlated to G_α and G_β . Both states have the same internal rotor description: one internal rotor is active ($j=1$), while for the other monomer $j=0$. From these results we conclude that the splittings observed in the double resonance experiment must be due to an additional motion. We therefore suggest that the splitting observed in the IR-FIR double resonance spectra is due to the (partly quenched) inversion in the NH_3 monomer. This is consistent with the observation that the barrier varies with the excitation of the umbrella vibration. In the following we will verify this assumption. We first discuss the result of a group theoretical calculation, which includes the following motions in the complex: internal rotation (C_3), interchange (I), inversion. It is further assumed that $(\text{NH}_3)_2$ has a plane of symmetry.

The molecule must therefore be classified in the permutation-inversion group G_{144} . The character table including the spin statistical weights was given in ref. [16]. Unfortunately some of the spin statistical weights turned out to be incorrect. The proper results are given in table 2 together with the decom-

Table 2
Decomposition of irreducible representation of G_{36} in irreducible representations of G_{144} . In parentheses are given the spin statistical weights for $(\text{NH}_3)_2$

G_{36}	G_{144}
$A_1(66)$	$= B_2^+(66) \oplus A_1^+(0) \oplus E^-(0)$
$A_2(78)$	$= A_2^-(78) \oplus B_1^-(0) \oplus E^+(0)$
$A_3(66)$	$= B_2^-(66) \oplus A_1^-(0) \oplus E^+(0)$
$A_4(78)$	$= A_2^+(78) \oplus B_1^+(0) \oplus E^-(0)$
$E_1(36)$	$= G_3^-(21) \oplus G_4^+(15)$
$E_2(36)$	$= G_3^+(21) \oplus G_4^-(15)$
$E_3(30)$	$= G_4^+(15) \oplus G_4^-(15)$
$E_4(42)$	$= G_3^+(21) \oplus G_3^-(21)$
$G(144)$	$= G_1^+(0) \oplus G_1^-(0) \oplus G_2^+(72) \oplus G_2^-(72)$

position of irreducible representations of G_{36} in those of G_{144} . We see from table 2 that the G and E states will each be split into two states with a non-zero spin statistical weight, whereas A states correlate to only one state with a non-zero spin statistical weight. The symmetry species for the *rotational* part are A_1^+ (K_c even) or B_2^- (K_c odd). The selection rules are $+$ \leftrightarrow $-$ (i.e. $A_1^+ - A_1^-$).

The spectrum in fig. 1C is assigned as originating from a B_2^+ ground state. This explains the presence of only one peak in this figure (corresponding to only one inversion state). This assignment is consistent with the set of parameters obtained in ref. [8], which indicated a state lacking internal rotation.

We assign the two G states (G_α and G_β) as the G_2^- and G_2^+ states and the splitting of 3.7 cm^{-1} to arise from the inversion in the ν_2 excited state. We can further test this assignment if we compare the intensities of the $K:0-0$ bands of G_α to the $K:0-0$ band, now assigned as the B_2^+ band. Intensity measurements yielded a ratio of 85:100 (error 30%) [9]. Whereas this intensity ratio cannot be explained in the group G_{36} (the intensity ratio of any band compared to the G state is smaller than 1:2) it fits very well with the new assignment in which a ratio of 78:72 or 66:72 is expected. This confirms our initial assumption. Within the group G_{144} , G_2^+ and G_2^- are the only states for which pure rotational transitions are allowed. In order to explain the presence of only two pure rotational transitions in the study of Nelson et al. [5] no further precondition is required, whereas Nelson et al. [7] had to demand that the internal rotation and interchange motion can be sep-

arated and that the $(2C_3+I)$ limit is valid. From our data we cannot decide whether we observe the sum or the difference of the inversion splitting in the ground and the excited state. By inspection of the experimental splittings it can easily be seen that the splittings between these bands can be described by a constant plus a J -dependent part. This leads to the assumption that we observe the sum of the inversion splittings, as indicated in fig. 2, which yields a splitting of approximately 450 MHz in both states. This increases to 3.7 cm^{-1} under excitation of the umbrella vibration. In the absence of any other K : $0-0$, $G_2^+ - G_2^-$ transitions we assign this FIR transition as a transition between the two interchange tunneling states $G_2^+ - G_2^-$, $G_2^- - G_2^+$. The interchange splitting is rather large (610 GHz) compared to what was expected before.

So far we have demonstrated that, based on our

double resonance, we can conclude that the inversion of the (NH_3) monomer, the interchange and the C_3 rotation are feasible motions. In the following we want to make an assignment of the other bands reported in this work and in ref. [8].

4. Assignment of the FIR transitions

Band 1A (table 1). Using combination differences we assign this band as the $B_2^- - B_2^+$ transition (see fig. 2). We therefore obtain an interchange splitting for the A state of 483 GHz.

Band 1B (table 1). This band was assigned as K : $1-1$ based on the absence of $R(0)$ and $P(1)$ lines. For high J values a small splitting in two lines with different intensities was seen but not fully resolved. Based on the former discussion we expect the split-

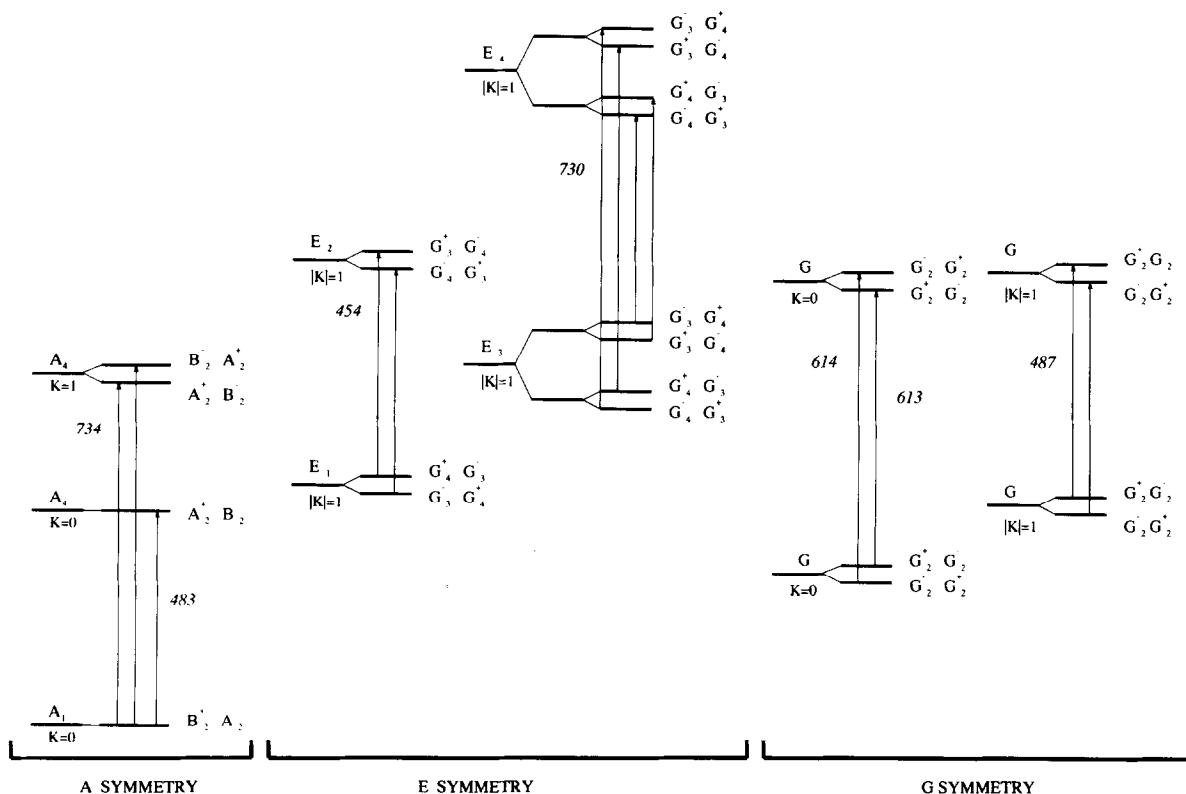


Fig. 2. Energy diagram of the FIR transitions as assigned in this paper. The vertical axes are not on scale. The relative positions of the levels are also not experimentally determined. The indicated labeling on the left-hand sides is in G_{36} , that on the right-hand side in G_{144} for J_{even} and J_{odd} , respectively.

ting to be due to K -type splitting or inversion splitting. Since the splitting is much smaller than what is expected for a K -type doubling, we assign the band as one of the two K -type components, with an inversion splitting smaller than 2 MHz. It was found before in other NH_3 -containing complexes, that for states with at least one active rotor (in G_{36} : G and E states), the K -type splitting is extremely large [17,18]. This splitting increases from the high barrier to the free rotor limit for the ammonia rotation to e.g. several cm^{-1} . Since no other K -type doublet component is found, we conclude that for $(\text{NH}_3)_2$ the high barrier limit is invalid. The differences in spin statistical weights between the two components lead to the assignment of a $G_3^+ - G_3^-$, $G_4^- - G_4^+$ transition, which correlates to the $E_1 - E_2$ transition in G_{36} (see fig. 2). The expected intensity ratio between the two components is 21:15, which is in perfect agreement with our observations (11:7).

Bands E and F (ref. [8]). The double resonance experiment performed for these bands shows two peaks at 10R22 and 10R28, which implies that they must possess a G symmetry in the group G_{144} . In addition we found a third peak at 10R12. Snels et al. [11] found that this peak increases with increasing beam temperature and it was therefore assigned to originate from $K=1$. This was confirmed by Heijmen et al. [12]. We assign the two bands to arise from the two corresponding inversion components. According to the discussion above, the K -type doubling is again expected to be large. Therefore the doubling observed in ref. [8], interpreted as K -type doubling, must have a different physical meaning. In our model the only possible splitting which remains is the interchange splitting. Whereas for the A states the interchange splitting is found to be quite large (480 GHz) in this case the two interchange components are nearly degenerate. If the rotation of the ammonia monomer is described in terms of a nearly free rotation, the $K=1$, E states in group G_{36} can be visualized by the picture that the C_3 axis of each ammonia precesses around the a axis of the complex. The E_1 and E_2 states correspond to an anti-gearred motion of the two monomers, while the E_3 and E_4 states correspond to a geared motion. This is in agreement with the actual wavefunctions of the complex as derived by van Bladel et al. [19]. In the case of a geared motion of the two ammonia monomers,

there should be no potential barrier for the interchange. Therefore the $K=1$ states of E_3 and E_4 are expected to be nearly degenerate, whereas the $K=1$, E_1 and E_2 states will be considerably split. We therefore assign the bands E and F in ref. [8] as $G_4^+ - G_4^-$ or $G_3^+ - G_3^-$ transitions, as displayed in fig. 2. This explains the observed 1:1 intensity ratio between identical $J_{K_a K_c}$ lines of the two inversion components [8] in a more consistent way than was possible before: the states which are only distinguished by + and - have the same spin statistical weight (e.g. G_4^+ and G_4^-). The FIR transition frequency of 730 GHz corresponds then either to the interchange splitting or the " K -type splitting". This latter notation does not make sense anymore in the low-intermediate barrier limit. Based on theoretical calculations [19] it is most likely the first splitting. In order to explain why the inversion splitting is smaller for the band 1B than for the bands E and F [8], we assume that for one band the sum between the inversion splittings was observed (fig. 2), while for the other band it is the difference. It is also likely that inversion is quenched more in the case of an anti-gearred rotation than in the case of a geared rotation. Assuming that the ground state and excited state exhibit nearly the same inversion splitting, the inversion splitting in each $E_{3,4}$ state is estimated to be 19 MHz. (The band origins were separated by 38 MHz [8].)

Band 1C (table 1). The band at 486 GHz shows a resolvable splitting, which is assumed to be the inversion splitting. In order to fit the data the following expression was used:

$$E = E_0 + BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 \\ \pm [aJ(J+1) - dJ^2(J+1)^2 + hJ^3(J+1)^3].$$

The fact that so many parameters are required indicates perturbations by Coriolis interaction. a , d and h describe the Coriolis interaction and distortion effects herein. The results of the fit for all three bands, reported in this work, are given in table 3. The ratio between the intensities of the two inversion components are found to be 1:1. This means that the band must originate from states correlating to G or $E_{3,4}$ states in G_{36} . We therefore assign them as the $G_2^+ - G_2^-$ transitions, as indicated in fig. 2. Comparing the intensity ratio of the 1C band (G_2^+) with the 1B band (G_4^+ and G_3^-) a ratio of 59:30 was found

Table 3
 Constants for the three bands in table 1 obtained from the fit ^{a)}

	$K=0 \rightarrow 0$	$ K =1 \rightarrow 1$	$ K =1 \rightarrow 1$
ν_{BO}	483301.067(54)	453599.485(96)	486731.35(35)
B''	5136.601(13)	4974.023(24)	5125.409(53)
D''	58.53(34)	-191.7(1.3)	58.8(1.5)
H''		-605(20)	
a''			0.491(12)
B'	5030.494(13)	5002.952(12)	4966.441(95)
D'	48.47(50)	46.71(24)	-428.2(5.2)
H'			-2498(73)
a'			8.345(35)
d'			111.7(3.1)
h'			857(53)
σ	0.01	0.03	0.38

^{a)} ν_{BO} is the band origin; σ is the standard deviation of the fit. All constants are in MHz, except D and d in kHz and H and h in Hz. Between parentheses we list either the errors, calculated from the estimated 0.10 MHz frequency uncertainties (first two columns) or the standard deviations (last column), whichever are larger.

[9]. Based on our assumption, a ratio of 72: (21+15) = 72:36 (since the two lines were not resolved) is expected. This is in perfect agreement. The FIR transition is either a transition to the other "K-type" component or to the other interchange component. Like for the E and F bands the latter case is most likely.

A possible candidate responsible for the observed perturbation in the upper state can be the upper state of the $K: 0 \rightarrow 0$, $G_2^+ - G_2^-$ band. It should be mentioned at this point that the B values found for the upper interchange component of the G_2^- , $K=0$ state are too large compared e.g. the unperturbed A states (and all other states). One might speculate whether this is a consequence of the interaction between these states.

Band D (ref. [8]). The double resonance spectrum of this state is shown in fig. 1D. From the presence of two peaks we conclude that the band is of G symmetry. The small splitting, which was attributed to K-type splitting in ref. [8], is assigned here as an inversion splitting. Since the two components were found to have identical spin statistical weights [8], they will be due to states correlating with $E_{3,4}$ or G states in G_{36} . In a check of the combination differences we were not able to find any coincidences with bands assigned so far. Therefore the band must originate from an upper G_2^{+-} level or the assignment as

a $K: 1 \rightarrow 1$ transition has to be checked. Since, for example, the R(0) line is very close to a water absorption it is possible that lines were missed. At the moment no definite assignment of this band can be given.

5. Conclusion

We have demonstrated that IR-FIR double resonance experiments are a powerful tool for revealing the nature of the tunneling splittings observed in the FIR spectrum. We have proved that the ammonia dimer exhibits an inversion motion, which was assumed in former papers to be quenched. It was possible to assign the bands published so far within the group G_{144} . It was also shown that the ammonia rotation cannot be described within the high-barrier limit. The interchange splitting was found to be large. Similar conclusions are also drawn from a recent theoretical study [19]. Whereas further FIR measurements will provide additional information on energy spacing, the splitting due to the internal rotation can only be provided by ab initio calculations, since transitions between different internal rotor states are not allowed.

Further experiments to label the bands detected around 500 GHz are in progress. For that purpose we will install a second Apollo high-power CO_2 laser as IR-pump laser. Since no saturation effect from the CO_2 laser power could be found so far, an increase in power by a factor of five should allow a probing of weak lines. Since the IR absorption frequencies of the ammonia trimer differ by $\approx 50 \text{ cm}^{-1}$ from those of the dimer [11,12], this method will also allow us to distinguish between dimer and trimer transitions in the FIR.

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