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# The ammonia dimer: new infrared–far infrared double resonance results

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## Abstract

From the results of an infrared-far infrared double resonance experiment on $(NH_3)_2$ complexes in a supersonic slit nozzle expansion, it was possible to characterize the tunneling dynamics, occurring within the ammonia dimer (Havenith et al., Chem. Phys. Letters 193 (1992) 261). In the current paper we present additional infrared-far infrared double resonance spectra. These confirm the former analysis and give a state specific explanation of the overall infrared spectrum of $(NH_3)_2$ as measured by Snels et al. (Chem. Phys. 115 (1987) 79). The interchange motion is shown to be quenched from 20 $cm^{-1}$ in the ground state to less than 1 $cm^{-1}$ in the infrared excited state. This confirms the assumption of Olthof et al. (J. Mol. Struct. THEOCHEM 307 (1994) 201) that the barrier for interchange tunneling is very small in $(NH_3)_2$.

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## 1. Introduction

In the last years the ammonia dimer has turned out to be a very interesting complex. The results of Nelson et al. in 1985 [1–3] which showed that $(NH_3)_2$ has no hydrogen bonding for the $G{:}K = 0$ state, were surprising in view of most of the earlier ab initio calculations (see, e.g., Refs. [4–7]) that predicted a linear hydrogen bonded structure. From the measured rotational spectrum Nelson and coworkers could deduce the intermolecular distance between the two ammonia monomers, the projection of the electric dipole moment on the dimer axis (0.74 D) and the diagonal component of the quadrupole coupling tensor along the $a$ inertial axis. Under the assumption that $(NH_3)_2$ can be considered as a rigid molecule, they calculated the structure from these values, yielding an equilibrium geometry in which both $NH_3$ monomers are aligned nearly anti-parallel, making polar angles with the intermolecular axis of 49° and 65°. Since the dipole moment of free ammonia amounts to 1.47 D, the sum of the permanent dipoles of both monomers in a hydrogen bonded geometry is estimated to be about 2.0 D. For this reason Nelson et al. excluded the linear $N{-}H\cdots N$ bonding. The only calculation that seemed to support a nearly cyclic structure for $(NH_3)_2$ [8] was shown later [9] to favor in fact a slightly bent hydrogen bonded structure.

In the ensuing debate the assumption was questioned whether $(NH_3)_2$ is a rigid or a rather floppy molecule. In case of large amplitude tunneling motions the structure deduced from the Nelson measurements only reflects a vibrationally averaged

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structure which not necessarily has to coincide with a minimum in the intermolecular potential. However, from the fact that the relevant intermolecular bond angles hardly varied with isotopic substitution Nelson et al. [2,10] concluded that $(NH_3)_2$ is a fairly rigid complex and consequently its equilibrium structure must be nearly cyclic. This conclusion was supported by the observation that the electric dipole moment for $(ND_3)_2$ turned out to be 0.17 D smaller than the value that was found for $(NH_3)_2$. In case of vibrational averaging, this seems to be a contradiction, because the $(ND_3)_2$ is expected to be less influenced by internal motions, i.e. to stay closer to equilibrium, and consequently it should have a larger electric dipole moment [2] if the hydrogen bonded structure is correct.

In the following years the results of detailed infrared [11–13], far infrared [14–17], infrared–far infrared [16], microwave [1] and infrared–microwave [18] studies became available. From these studies, especially those in Refs. [16, 17], it was found that the ammonia dimer is a very floppy molecule, exhibiting large amplitude motions. A result that was also found by a theoretical study by Van Bladel et al. [9]. In addition it became clear that the monomer umbrella inversion is only partly quenched in the complex. This was a rather unexpected result, since the umbrella inversion in most $NH_3$ containing complexes – with the exception of Ar–$NH_3$ [19,20] – is completely quenched. As a consequence the appropriate molecular symmetry group had to be extended from $G_{36}$ to $G_{144}$. Using this group it turned out to be possible to assign all microwave and far infrared data known so far [16,17]. However, none of these studies could provide any structural information that could confirm or disprove the results found by Nelson and that could explain the discrepancy with the conclusions deduced from the $(ND_3)_2$ measurements.

In 1993 dipole measurements on the $G{:}\,|K| = 1$ state by Linnartz et al. [21], explicitly using a Stark treatment in $G_{144}$, gave evidence that the anti-parallel, so-called cyclic structure is indeed more likely than the hydrogen bonded one, although one has to keep in mind that this structure is the consequence of vibrational averaging in a very floppy complex. ''More likely'' in this context means that the complex most of the time will reflect an antiparallel configuration, as an intermediate between several tunneling motions. For this reason a comparison between experiment and theory is difficult. Whereas the electronic structure calculations focus mainly on finding the minimum of the intermolecular potential, the experiment yields a vibration–rotation–tunneling averaged structure. Since the potential surface is very flat, it was a challenge to compute the averaged structure and to explain the results quantitatively. Olthof et al. [22] were able doing so, by solving the full six-dimensional nuclear motion equation for a series of model potentials with different barriers for the interchange motion and for the hindered rotations of the two ammonia monomers around their $C_3$-axes. In this study several measurable quantities were computed; electric dipole moments, energy splittings and nuclear quadrupole splittings. The potential that gave best agreement with the observed quantities has an equilibrium hydrogen bonded structure and a small barrier (24 $cm^{-1}$) for interchange tunneling, but a vibration–rotation–tunneling averaged ground state that is nearly cyclic. Furthermore, Van der Avoird et al. were able to apply this potential to $(ND_3)_2$ [23]. From this it became clear that in terms of localized wave functions it is also possible to explain the decrease of the $G{:}K = 0$ electric dipole moment, when going from $(NH_3)_2$ (0.74 D) to $(ND_3)_2$ (0.57 D), without explicitly demanding a rigid structure. In this study Van der Avoird and co-workers use an even smaller barrier of 7.0 $cm^{-1}$ for the interchange motion. This is less than 1% of the binding energy of the complex, which is estimated to be about 950 $cm^{-1}$ [11]. With this very small barrier height, nearly all experimental data can be reproduced and, especially, the accuracy in predicting the band origins is remarkably good (within 0.25 $cm^{-1}$).

From the results obtained in Ref. [23] the splittings due to the hindered umbrella inversions could be computed [24]. Using this semi-empirical potential Olthof et al. calculated very recently the nuclear quadrupole coupling constants for the para–para ammonia dimer [33]. These turned out to be in good agreement with the experimental results (see also Ref. [33]).

From a structural point of view the discussion whether ammonia is hydrogen bonded or not [10,25,26,34,35] comes to an end. The ammonia dimer seems to have an equilibrium hydrogen bonded structure, but this does not represent the actual structure. Due to the low barriers for angular motions all measured quantities retain to an average structure that is nearly anti-parallel. This corresponds to the structure that $(NH_3)_2$ resembles most of the time. The "ammonia dimer riddle" is a consequence of the dynamical character of the complex.

However, there are still some unsolved problems. One of these is the infrared spectrum of $(NH_3)_2$. As an outcome of theoretical work the complex was not expected to dissociate upon excitation with a single 10 $\mu$m photon but experiments [11–13,16] showed that one 970 $cm^{-1}$ photon is sufficient to cause dissociation of the complex. Additional information was found by Bacic et al. [27]. In a scattering experiment with a secondary He beam an average energy of 520 $cm^{-1}$ was transferred to ammonia dimers without causing dissociation. This defines the lower limit for dissociation, whereas the upper limit can be estimated from the experiment of Snels et al. [11] to be about 950 $cm^{-1}$. Snels and co-workers measured the overall infrared spectrum of $(NH_3)_2$ by bolometric detection. Combining the results of this experiment, information from the infrared–microwave double resonance experiment performed by Fraser et al. [18], information from an infrared–infrared double resonance experiment performed by Heijmen et al. [13], the photodissociation of size-selected ammonia clusters as performed by Huisken and Pertsch [12] and the results that are presented here, we are able to give a *state specific* interpretation of the infrared spectrum. We will present the infrared-far infrared double resonance results for the G (band origin 487 and 747 GHz) and $E_{1,2}$ (454 GHz) states. These will be compared with the $G{:}K = 0$ (613/614 GHz) state as was published in Ref. [16]. Finally the $K = 0$–1 and $K = 0$–0 transitions for A symmetry (483 and 734 GHz, resp.) are compared.

## 2. Experiment

The $(NH_3)_2$ complexes are produced in a continuous two-dimensional supersonic jet by expanding a mixture of 2% $NH_3$ in argon through a 4 cm × 75 $\mu$m slit nozzle into vacuum. The pressure is maintained at 50–100 mTorr by a 4000 $m^3/hr$ roots blower pumping system. The experimental mixture is optimized by gas flow controllers. The far infrared radiation is generated with the Nijmegen tunable far infrared sideband spectrometer [28] by mixing an Apollo $CO_2$ laser optically pumped fixed far infrared laser frequency with tunable microwave radiation generated by a klystron, in a Schottky barrier diode. For the measurements in the 700–750 GHz range we used the sideband of the $CH_3I$ 670 463.0 MHz line or the HCOOH 692 951.4 MHz line and a 60 or 70 GHz klystron. For frequencies in the 300–550 GHz range we used higher harmonics of klystrons (50–112 GHz).

The radiation passes the molecular beam and is focussed onto an InSb hot-electron bolometer. For the double resonance experiment an infrared beam, generated by a second Apollo $CO_2$ laser (typical single line output power of 80 W) is guided anti-parallel to the far infrared beam between the nozzle and absorption zone. The double resonance signal is detected by observing the depletion in the far infrared signal for a selected (and assigned) state as function of the infrared radiation (10R8–10R34). In order to achieve this the $CO_2$ laser beam is intensity modulated by a chopper at a frequency of 500 Hz. Consequently the bolometer signal that is lock-in detected, directly reflects the loss in far infrared signal as result of the infrared pumping; this is the double resonance signal. The cluster dissociation versus laser power has been measured for several $CO_2$ laser lines. This showed a linear dependence. No saturation effects have been observed. The reproducibility of the observed spectra was better than 10%, with exception of the $E_{1,2}$ band, where the error is estimated to be smaller than 20%.

## 3. Results

### 3.1. Overview of infrared results

The infrared spectrum measured by Snels et al. [11] shows main bands at 979 $cm^{-1}$, in the range of the $^{12}CO_2$ laser and at 1004 $cm^{-1}$, in the range of the $^{13}CO_2$ laser. The band at 979 $cm^{-1}$ shows a substructure, with peaks at the 10R12 (970.5 $cm^{-1}$), 10R22 (977.2 $cm^{-1}$) and 10R28 (980.9 $cm^{-1}$) $CO_2$

laser line frequencies. Although the results of Snels were very important in providing the first complete infrared spectrum of $(NH_3)_2$, the experiment was not state specific. The infrared depletion signals are obtained from the bolometric detection of the molecular beam. In this beam no state selection is possible and only partial size-selection is achieved. Consequently the measured infrared depletion spectrum shows the overall result of all populated states of the in the expansion formed $(NH_3)_n$ clusters. Using diluted mixtures complex formation is restricted to $n = 2$ and 3 [29], as can be seen in Ref. [11]. From the results of a dissociation experiment on scattered ammonia clusters by Huisken and Pertsch [12], it can be concluded that the band at 979 $cm^{-1}$ completely originates from dimers and that the band around 1004 $cm^{-1}$ is also partly due to trimers. However, the signal to noise ratios of the dissociation signals for dimers in the scattering experiment are too small to fit the dissociation pattern for the 979 $cm^{-1}$ band reliable. In addition this experiment is still not state specific, i.e. the spectrum consists of contributions of all tunneling states (i.e., A, E and G symmetry in $G_{36}$).

For the reasons mentioned above, the analysis of the infrared spectrum turned out to be very difficult, especially since the correct tunneling motions were not known at that time. However, in a double resonance experiment the infrared information can be coupled to assigned (microwave or far infrared) transitions. This provides a state selective detection scheme from which the analysis of the overall spectrum becomes less ambiguous.

Snels et al. explained the splitting between the 979 and 1004 $cm^{-1}$ band as a consequence of the excitation of the umbrella modes in each of the two non-equivalent $NH_3$ monomers. Similar phenomena were found for other dimers, for example in $(HF)_2$ [30] and $(CH_3OH)_2$ [31] in which the monomers are not equivalent with respect to the intermolecular bond. We will show later that this assumption of Snels is in agreement with our measurements. As was discussed before the $\nu_2$ umbrella motion is only partly quenched in the $(NH_3)_2$ [16] which is reflected in the infrared spectrum by the splitting between the 10R22 (977.2 $cm^{-1}$) and 10R28 (980.9 $cm^{-1}$) $CO_2$ laser line [16] for the $G{:}K = 0$ states. This splitting was explained by Snels as the infrared excited interchange motion, but we will show that the splitting due to interchange motion is actually much smaller.

A major part of our discussion is based on the results of previous double resonance experiments. Fraser et al. [18] performed an IR–MW double resonance experiment which yielded the two infrared transitions at 977.2 and 980.9 $cm^{-1}$ to be correlated with the microwave transitions labeled $G_\alpha$ and $G_\beta$, respectively. An IR–IR double resonance experiment by Heijmen et al. [13] demonstrated that both transitions are indeed mutually uncorrelated. By the following far infrared studies [14,16,17], from which it was concluded that the molecular symmetry group had to be extended from $G_{36}$ to $G_{144}$, these microwave transitions ($G_\alpha$ and $G_\beta$) were assigned as to originate from $G_2^+$ and $G_2^-$ states, i.e. the two umbrella inversion components of the ortho–para ammonia. This explains the result of Heijmen that both states are indeed uncorrelated.

In our experiment the measurements are restricted to the band at 979 $cm^{-1}$ and the attributed substructure, since $^{13}CO_2$ isotope lasers, which are required for the other band around 1004 $cm^{-1}$, yield not enough power to detect a double resonance signal. The infrared spectrum can be labeled by selecting assigned far infrared transitions. This was demonstrated for the $K = 0$ G and A transitions [16], from which it was concluded that the infrared excited monomer umbrella inversion amounts to about 4 $cm^{-1}$ within the ammonia dimer. Another important conclusion was that in contrast to the beam experiments used in previous studies collisional relaxations take place in the jet expansion which complicates the analysis considerably.

Before presenting the different spectra, we will discuss first the splitting between the main bands at 979 and 1004 $cm^{-1}$, followed by a discussion on the substructure of the 979 $cm^{-1}$ band.

### 3.2. Expected interchange splitting in the vibrational excited band

In this subsection we will examine the vibrational dependence of the interchange tunneling in $(NH_3)_2$. The considerations are based on the study of Fraser on $(HF)_2$ and $(HCCH)_2$ [32]. We will further show that this model can be used to explain most of the infrared and IR–MW, IR–IR and IR–FIR double resonance studies published so far. In the study of Fraser model calculations were presented to interpret the observed vibrational dependency on the interchange tunneling of $(HF)_2$ and $(HCCH)_2$. For this purpose effective potentials for the tunneling motion for ground and the excited state were constructed.

For the *ground state* the potential for $(NH_3)_2$ is known from the calculations by Olthof et al. [22]. A schematic cut through the potential surface is shown in Fig. 1a, where the potential energy is plotted as function of $\rho$, the tunneling coordinate. For $(NH_3)_2$ Olthof found the surprising conclusion that there exist two equivalent minima with the proton donor and acceptor configuration separated by a barrier of only 7 $cm^{-1}$. From detailed far infrared studies it is found that the interchange splitting is of the order of 15 to 20 $cm^{-1}$. This implies that we have a situation as drawn in Fig. 1a. The first state lies above the barrier and the interchange splitting does not vary much upon further excitation and is of the order of 20 $cm^{-1}$.

The question that arises by now is "What is the consequence of the excitation of one monomer vibration with respect to the $NH_3$ umbrella motion?" This effect is shown in Fig. 1b, where the effective

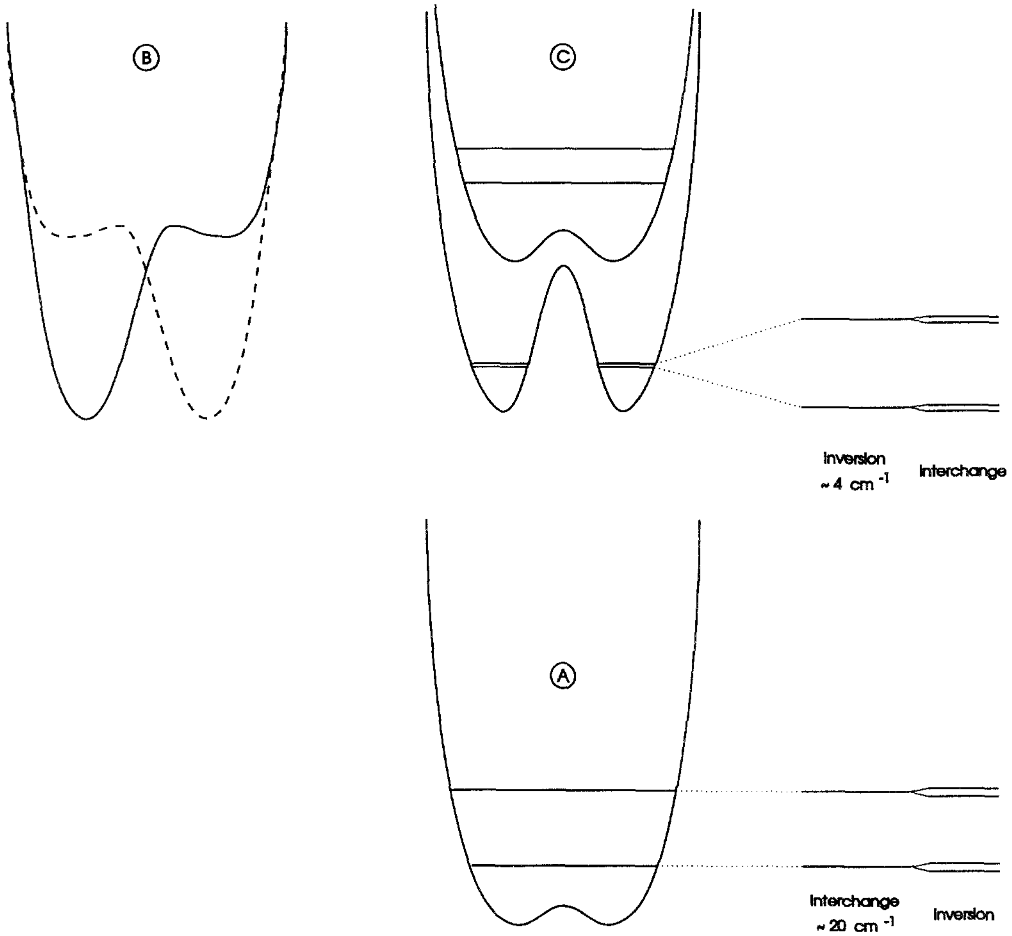

Fig. 1. The potential curves for the ground state (a) and the excited state without (b) and with (c) interaction between the monomeric excitation and the interchange motion. The size of the interchange splitting is strongly affected by the change of the barrier height, due to the excitation of one of the monomers. For the lower band (979 $cm^{-1}$) the interchange is quenched from 20 $cm^{-1}$ in the ground state to less than 1 $cm^{-1}$ in the excited state. For the other band (1004 $cm^{-1}$) the interchange motion is less affected.

potentials are drawn for the *excited state*. In this picture the two potentials correspond to the excitation of either one of the two monomers, with the excitation remaining in one monomer. Due to the excitation of one monomer the potential curve becomes asymmetric with respect to the interchange tunneling coordinate, an effect which is described in the study of Fraser. The increase in the potential on one side will be large compared to the small barrier of 7 $\mathrm{cm}^{-1}$. Therefore we expect a dramatic change of the potential upon vibrational excitation. The splitting between the first two interchange states is expected to increase compared to Fig. 1a and should lie between 20 and 40 $\mathrm{cm}^{-1}$, depending on the increase in potential energy. In Fig. 1c the two potential curves are coupled by an interaction term that allows the vibrational tunneling to be exchanged between the two monomer subunits, thus introducing interchange tunneling. As a result we obtain two symmetric adiabatic potential curves. At $\rho = 0$ the two curves are separated by an energy gap of two times the interaction term. Moreover, the two former energetically degenerate energy levels will split. As is displayed in Fig. 1c for $(NH_3)_2$ we expect now one doublet to be below the barrier, whereas the second doublet should be above the barrier. The absolute size of the tunneling splitting will depend on the interaction term. As can be seen in Fig. 1c the lowest tunneling doublet of the excited state feels a much higher barrier as in the ground state, therefore a dramatic decrease in interchange tunneling frequency compared to the ground state is expected.

Even in $(HF)_2$, where the effective change of the tunneling barrier is negligible (the tunneling barriers for the upper state are 270 and 330 $\mathrm{cm}^{-1}$ compared to the ground state barrier of 300 $\mathrm{cm}^{-1}$), a decrease of a factor of approximately three is found. This decrease is due to the incomplete coupling between the vibration and interchange tunneling. For the upper interchange doublet of $(NH_3)_2$ the barriers for the interchange motion will be small and comparable to the barrier in the ground state. Since this case resembles the situation that was found for $(HF)_2$ we expect the reduction of this tunneling splitting compared to the ground state to be of the same order of magnitude.

To summarize we conclude that we expect to see two main bands corresponding to the excitation of the two non-equivalent monomer subunits, i.e., transitions from the ground state to each of the doublets. These two bands will show a substructure due to the interchange tunneling – as discussed before – and due to the umbrella inversion tunneling. The splitting caused by the interchange motion is expected to be quite different for the two infrared vibrations: whereas for the transitions attributed to the lower band around 979 $\mathrm{cm}^{-1}$ a very small splitting is expected, for the transitions attributed to the other band around 1004 $\mathrm{cm}^{-1}$ a splitting which is smaller

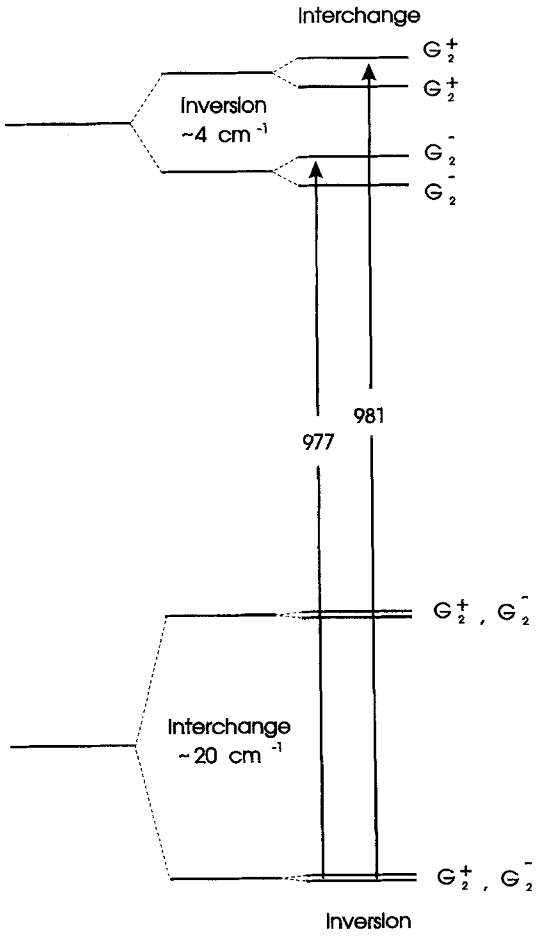

Fig. 2. The energy level scheme for the infrared transitions (in $\mathrm{cm}^{-1}$) starting from the $G{:}K = 0$–$0$ states ($G_\alpha$ and $G_\beta$ in Ref. [18]). The inversion splitting in the infrared excited state amounts to 4 $\mathrm{cm}^{-1}$, whereas the interchange splitting is quenched from 20 $\mathrm{cm}^{-1}$ to less than 1 $\mathrm{cm}^{-1}$. Due to collisional relaxations the overall features of both transitions are found in the IR-FIR double resonance spectra. This is shown in Fig. 3.

but of the order of the interchange splitting in the ground state (20 $cm^{-1}$) is expected. This explains the general features of the overall infrared spectrum as measured by Snels et al. [11].

In the following we will compare this qualitative picture with the double resonance results and from these we will deduce the size of the interchange splitting for both the 979 and 1004 $cm^{-1}$ band.

### 3.3. IR–FIR double resonance spectra

#### 3.3.1. $K = 0$, G ($G_2^{\pm}$ in $G_{144}$), band origin 613 / 614 GHz

We will first discuss the double resonance results on the $K = 0$ $G_2^{+}$ states. These were published before [16] and in combination with the results for the A state it was shown that the monomer umbrella inversion is only partly quenched in the complex. In Fig. 2 we have displayed an energy diagram of the measured infrared transitions, which is based on the model explained above. The ground state is well known from the far infrared studies by Havenith et al. [14,16] and Loeser et al. [17]. The interchange splitting in the ground state amounts to 20 $cm^{-1}$. Each of the interchange components is split by the umbrella inversion which amounts to 3.3 and 2.4 GHz and which for that reason is negligible on the scale of the diagram. In the vibrationally excited state the inversion splitting was determined to be approximately 4 $cm^{-1}$ [16]. Furthermore small splittings due to the interchange motion are expected for the band around 979 $cm^{-1}$, as was discussed in the previous section.

Collisional relaxations in the jet were found to distribute the population equally between the two inversion doublets. This implies that when *one* inversion level is probed all transitions originating from *both* inversion components will appear in the double resonance spectra. This is an important difference to the beam experiments of Fraser et al. that were obtained in the collision-free regime of the expansion. All together we expect to see *four* lines when *one* of the $G_2^{+}$ levels is probed.

The experimental result is given in Fig. 3. We observe only two peaks at 977.2 and 980.9 $cm^{-1}$. This implies that one of the splittings involved, either the inversion or the interchange splitting must be too small to be resolved. Since in a double resonance experiment in a molecular beam collisional relaxations are negligible, it is possible to

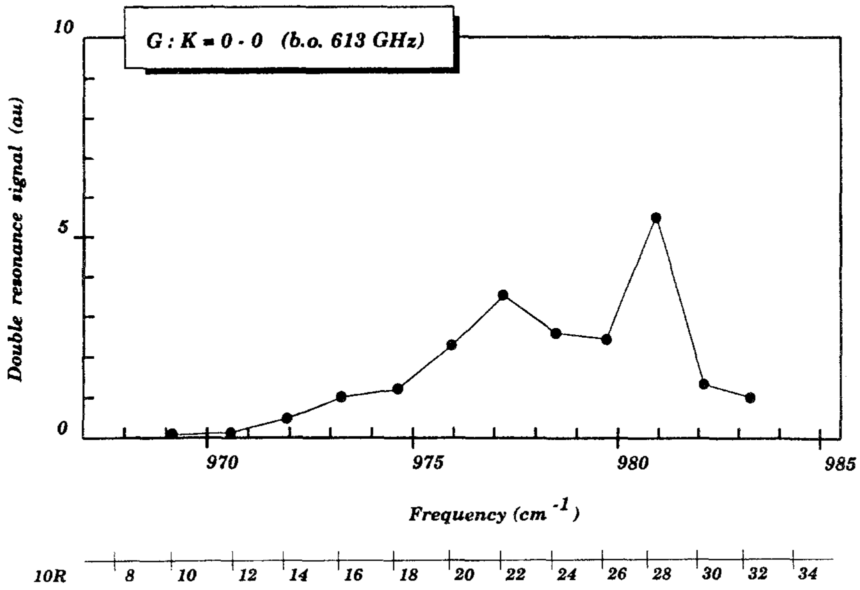

Fig. 3. The IR–FIR double resonance spectrum for the G:$K$ = 0–0 state at 613 GHz ($G_\alpha$). The double resonance spectrum for the other state ($G_\beta$) looks the same (see also Ref. [16]). The line with numbers under the figure indicates the corresponding frequencies in terms of $CO_2$ laser lines.

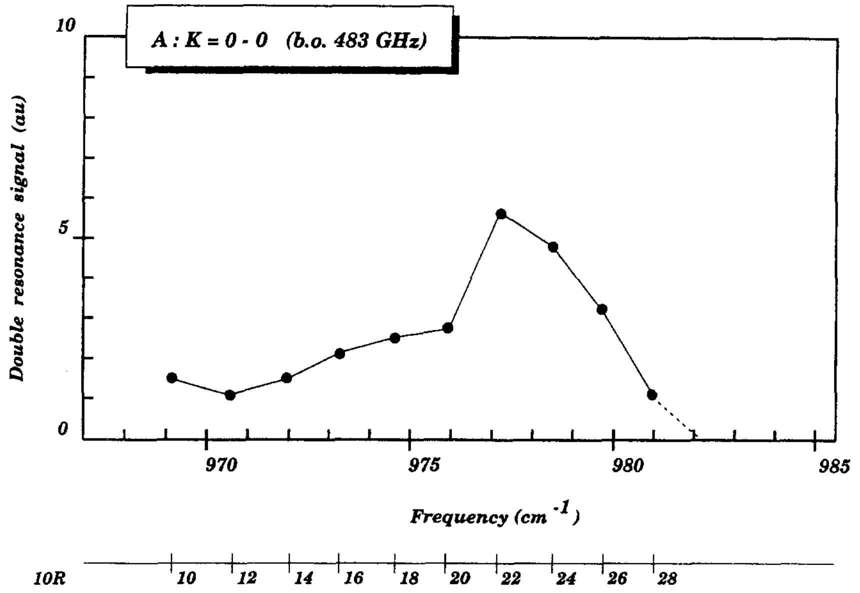

Fig. 4. The IR–FIR double resonance spectrum for the A: $K = 0$–0 state with band origin at 483 GHz.

distinguish in those experiments between transitions originating from different inversion components in the ground state. The experiment by Fraser [18] proved that the lines at 977.2 and 980.9 cm$^{-1}$ originate from different inversion components. Probing a specific inversion doublet yields one single double resonance in the IR–MW spectrum. From this we conclude that the interchange splitting in the vibrationally excited state is too small to be resolved and must be smaller than 1 cm$^{-1}$. This estimate is given by the resolution of the double resonance spectra which is limited by the line tunable character of the

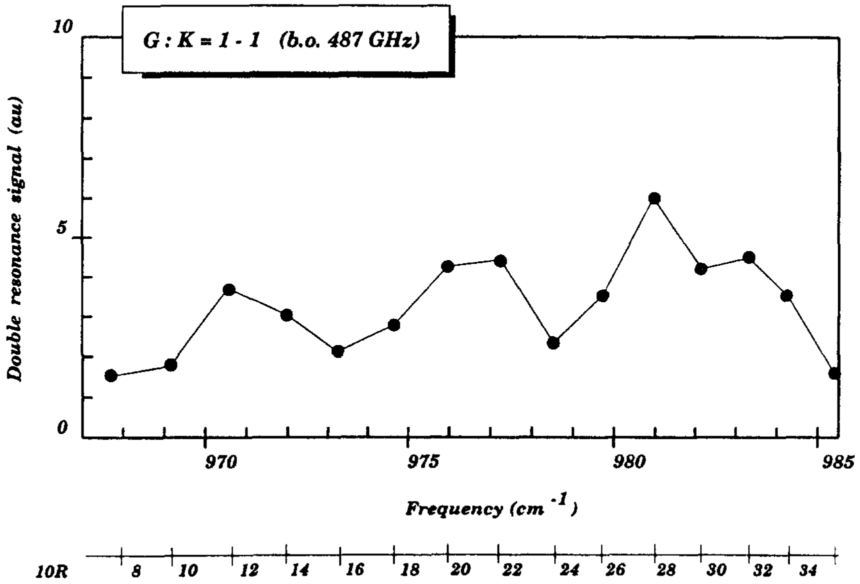

Fig. 5. The IR–FIR double resonance spectrum for the G: $K = 1$–1 state with band origin at 487 GHz.

$CO_2$ laser. The interchange splitting is reduced by at least a factor of 20 upon vibrational excitation from the ground state. This decrease is substantially larger as the values that were found until now for Van der Waals complexes. As was shown before, the decrease is a consequence of the very small barrier upon interchange tunneling. This confirms the assumption of a very small barrier between the two minima in the potential surface as stated in Ref. [22]. In the IR–FIR double resonance spectrum only the splitting induced by the inversion motion remains. This latter splitting amounts to 4 $cm^{-1}$, as was concluded before [16].

### 3.3.2. $K = 0$, A ($B_2^+/A_2^-$), band origin 483 GHz

For states of A symmetry only one inversion component has a non-zero spin statistical weight. Since the interchange splitting is not expected to affect the infrared spectrum a single line is expected in the IR–FIR double resonance spectrum. The corresponding experimental result of the $K = 0$ A state is displayed in Fig. 4. This spectrum shares the same features as the $K = 0$–1 transition with the band origin at 734 GHz [16], as is expected for transitions sharing the same ground state. The absence of other peaks is explained in [16].

### 3.3.3. $|K| = 1$, G ($G_2^\pm$), band origin 747 and 487 GHz

The IR–FIR double resonance spectrum of the $G_2^+$ $K = 1$ state is shown in Figs. 5 and 6. The two spectra show different FIR transitions. The band origin for the corresponding subbands is 487 and 747 GHz, respectively. It is clear from the experimental result that more than two lines appear in the double resonance spectrum. An explanation for this observation is given in Fig. 7. The energy level diagram for the ground state is well known. For the $K = 1$ state two so called "K-type doubling components" have been assigned that are separated by 4 $cm^{-1}$ [17]. Because $K_c$ is not a good quantum number in such floppy molecules labeling of levels as K-type doubling components is strictly speaking incorrect. We will only use it to label the energy levels.

Due to the resolution of the infrared experiment the inversion splitting in the ground state can be neglected. In the excited state we expect an inversion splitting and two "K-type" components for each inversion state. Collisional relaxation will take place between the two inversion components in the ground state. If we neglect the small inversion splitting in the ground state, the selection rules allow a total of four transitions starting from each of the two K-doubling components in the ground state. This has been

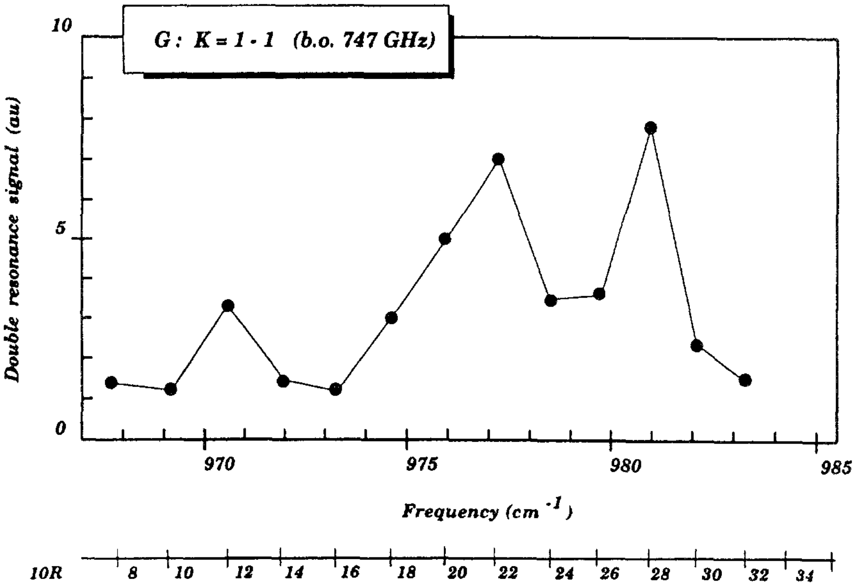

Fig. 6. The IR–FIR double resonance spectrum for the G:$K = 1$–1 state with band origin at 747 GHz.

depicted in the diagram of Fig. 7. From this figure it can be seen that the current model predicts the observation of all IR transitions of Fig. 5 (FIR 487 GHz, lower $K$-doubling component) to be present in the spectrum of Fig. 6 (FIR 730 GHz, upper $K$-doubling component), however, shifted by 4 cm$^{-1}$. The latter value corresponds to the energy difference between the two $K$-doubling ground states. For this reason the quartets in the double resonance transitions in Figs. 5 and 6 are assigned as follows:

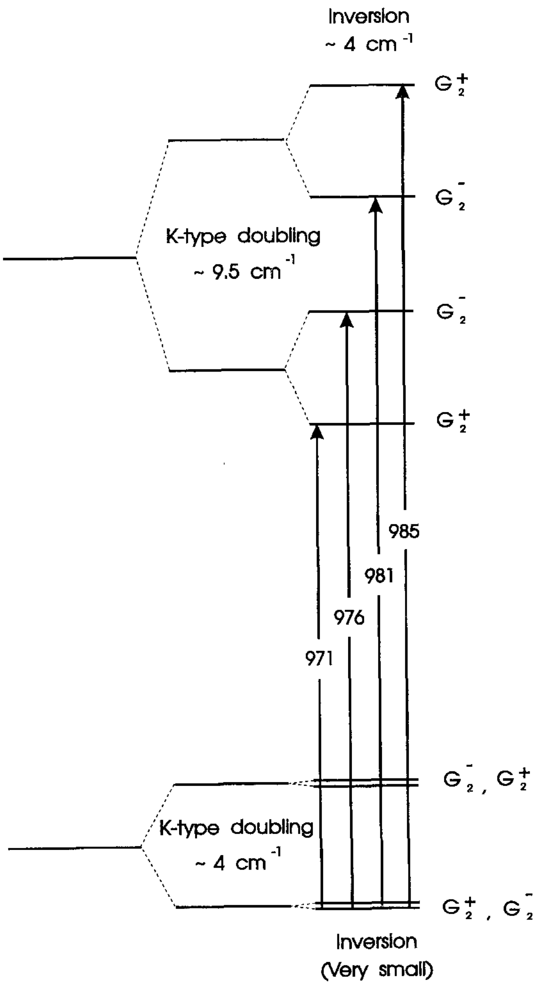

Fig. 7. The energy level scheme for the infrared transitions (in cm$^{-1}$) starting from the G:$K = 1$–$1$ state with band origin at 487 GHz. Due to collisional relaxations the overall features are found in the double resonance spectra. These have to be the same as those found for the infrared transitions starting from the 747 GHz band – the upper $K$-type component – but shifted by 4 cm$^{-1}$.

Fig. 5 (band origin 487 GHz): 971, 975.5, 981 and 984.5 cm$^{-1}$,
Fig. 6 (band origin 747 GHz): 967 (not measured), 971.5, 977 and 980.5 cm$^{-1}$,
which is consistent with the 4 cm$^{-1}$ shift. Based on this assignment the separation between the two $K$-type doubling components in the vibrational excited level is estimated to be approximately 9.5 cm$^{-1}$ and the inversion splitting to be about 4 cm$^{-1}$, as indicated in Fig. 7.

### 3.3.4. $|K| = 1$, $E_{1,2}$ $(G_3^-, G_4^+)$, band origin 454 GHz

The IR–FIR double resonance spectrum of the E states at 454 GHz is shown in Fig. 8. Due to the low intensity it was difficult to obtain reliable double resonance spectra for this state. The experimental uncertainty in the intensities was large (20%). Furthermore only for one E state double resonance spectra were obtained. A comparison between several different E states could not be made. We will therefore renounce an assignment for these lines. We only want to note that the data seem to indicate that the inversion splitting in the vibrationally excited state for the $K = 1$ E symmetry is approximately 7 cm$^{-1}$, which is larger than in the states with $G$ symmetry. This is concluded from the fact that no smaller splittings are present in this spectrum. This splitting is at first sight surprising, since in the ground state the inversion splitting for the E states was found to be smaller than for the G states. Clearly, the splitting of 7 cm$^{-1}$ cannot be found in the infrared spectrum of Snels, probably because the transitions are too weak to affect the overall spectrum substantially. Because of its lower statistical weight the E state contributes little to the infrared spectrum. One may hazard to guess whether this structure becomes visible in the case of a heated nozzle and a less diluted mixture [11], i.e. beam conditions for which the population of higher $K$ states is increased.

### 3.4. Implications for the infrared data

In the IR–IR double resonance studies of Heijmen et al. all symmetries are probed. The interchange splitting is negligible for the low frequency infrared transition at 979 cm$^{-1}$ and therefore the transitions in the different tunneling symmetries

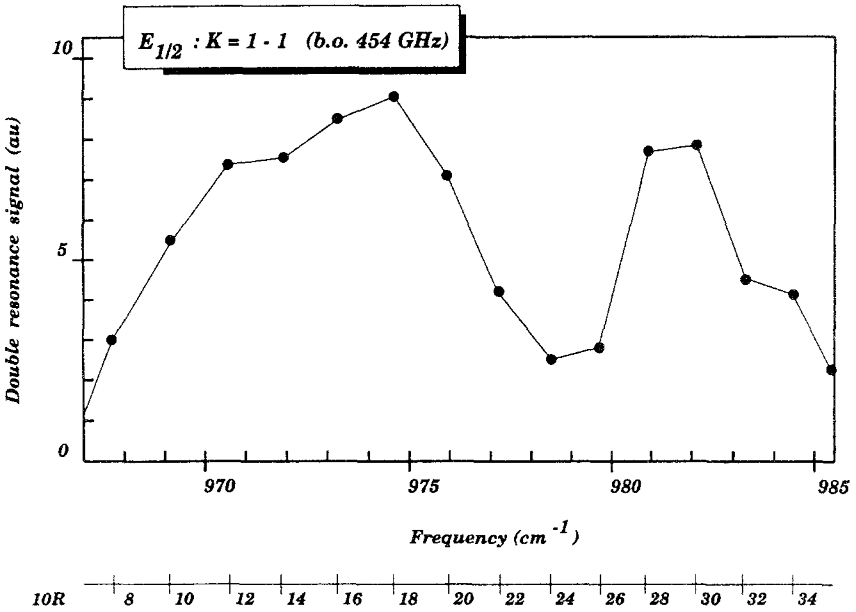

Fig. 8. The IR–FIR double resonance spectrum for the $E_{1,2}$:$K$ = 1–1 state with band origin at 454 GHz.

overlap in frequency in the infrared spectrum. Consequently, the inversion splitting is observable in those spectra. Based on the present model the other band at 1004 cm$^{-1}$ corresponds to a transition from the ground state to levels of the upper potential surface as is indicated in Fig. 1c. The corresponding interchange splitting in this transition is therefore expected to be larger than in the 979 cm$^{-1}$ transition. It should be noted that the size of the interchange splitting may differ for different symmetries. We predict the peak at 1004 cm$^{-1}$ to consist of several lines split by interchange tunneling, which is in agreement with the experimental result of Snels et al. showing a single broad peak around 1004 cm$^{-1}$. From the above presented model it also follows that because several lines are overlapping no substructure due to inversion is resolved. An estimate of the actual size of the interchange splitting for this blue shifted infrared transition can be obtained from the measurements of Heijmen et al. [13]. In these IR–IR double resonance spectra a substructure can be observed. Based on these observations, we tentatively assign the broad peak at 1004 cm$^{-1}$ to consist of two peaks separated by approximately 10 cm$^{-1}$. The latter splitting can be considered as an estimate of the interchange tunneling splitting in the second vibrational excited band.

The present model also explains other details of the IR–IR double resonance study of Heijmen. If one of the lines at 977.2 or 980.9 cm$^{-1}$ is probed a broad substructure around 1004 cm$^{-1}$ is found in the double resonance spectra. This can be assigned to distinct transitions that originate from one inversion component in the ground state.

Besides the features that are assigned above the overall infrared spectrum shows a small structure around 990 cm$^{-1}$ in between both main bands. Since we were not able to perform a double resonance experiment at this frequency a definitive assignment is not possible.

## 4. Summary

Using an IR–FIR double resonance set-up it was possible to obtain state selective infrared information. The study of states with different symmetries yielded information on the monomer umbrella inversion and the interchange tunneling. Using the model as proposed by Fraser [32] the splittings for the interchange motion are expected to be different for the two infrared bands observed in the overall spectrum as measured by Snels et al. [11]. These bands originate from the different positions that both monomers have within the complex. For the lower band around 979 $cm^{-1}$ the interchange splitting is quenched upon infrared excitation from about 20 $cm^{-1}$ in the ground state to less than 1 $cm^{-1}$ in the excited state. This confirms that the barrier for the interchange motion is very small. For the other band around 1004 $cm^{-1}$ the effective quenching will be much less, since the corresponding energy levels are positioned above the barrier. We estimate this splitting to be about 10 $cm^{-1}$. The inversion splitting amounts to about 4 $cm^{-1}$, as was concluded in Ref. [16]. For the $E_{1,2}$ states the monomer inversion is about a factor two larger.

Summarizing we conclude that the IR–FIR double resonance data presented here, give new insight in the tunneling dynamics of the $(NH_3)_2$ and that they explain most of the infrared data found so far.

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