The Ammonia Dimer Complex Dynamics with a Dynamical Complex

Chemically weak bonds play an important role in many biological and chemical processes. For this reason numerous theoretical and experimental studies have been carried out in recent years in order to gain a better insight into the complex dynamics of weak intermolecular interactions. In the case of a rigid complex, with clearly defined potential minima, it is not a problem to speak of an equilibrium structure. But what can be done with a floppy complex, in which a number of large amplitude motions between several local minima can take place more or less undisturbed? These complexes have their own inter- and intramolecular dynamics and, as will be shown for $(NH_3)_2$, this can result in a very interesting discussion.

Key Words: *spectroscopy, molecular physics, dynamics, weakly bonded complexes, ammonia dimer, hydrogen bonding*

INTRODUCTION

One of the most intriguing bonds in the world of weak intermolecular forces is the hydrogen bond. By hydrogen bond we mean a nearly linear D–H · · · A arrangement which is adopted by a donor bond (D–H) and a molecule (A) that acts as a proton acceptor. The origin of hydrogen bonding is expected to be primarily electrostatic, but with significant contributions arising from short range interactions. In this article we will concentrate on hydrogen bonds and

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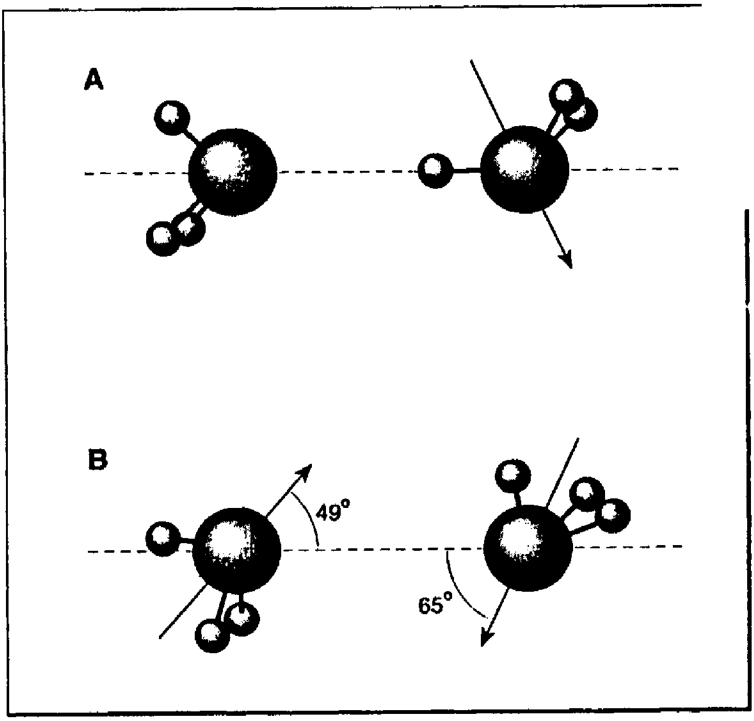

FIGURE 1 Ammonia dimer. A. The classical, hydrogen bonded structure. B. The non-hydrogen bonded, so-called cyclic or anti-parallel structure.

go into detail on what seems to be one of the simplest prototypes for it, the ammonia dimer.

Ammonia, with its lone pair of electrons, is an excellent hydrogen bond acceptor. For a long time it was accepted within chemistry that ammonia can act as a hydrogen donor, too. For this reason the ammonia dimer was expected to have a linear hydrogen bonded structure (see Fig. 1a). In this arrangement one of the H-atoms of a NH_3 monomer forms a linear bridge to the N-atom of the other monomer. However, in a series of papers[1–3] starting in 1985, Nelson, Fraser and Klemperer showed that $(NH_3)_2$ has no linear bonding for the specific tunneling state that was investigated. From the observed microwave spectrum, Nelson and co-workers could deduce the intermolecular distance between the two ammonia monomers, the projection of the electric dipole moment on this axis (0.74 D*) and the diagonal components 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 in which both NH_3 monomers are aligned nearly anti-parallel, making polar angles with the intermolecular axis of 49° and 65° (see Fig. 1b). Since the dipole moment of free ammonia amounts to 1.47 D, the sum of the permanent dipoles of both monomers in a linear hydrogen bonded geometry is estimated to be about 2 D. For this reason Nelson and co-workers excluded the linear structure and questioned the hydrogen bonded character of the complex. This conclusion was surprising in view of the fact that most *ab initio* calculations[4–6] predicted a nearly linear hydrogen bonded structure. The only calculation that seemed to support a nearly anti-parallel structure for the $(NH_3)_2$[7] was shown later[8] to favor in fact a slightly bent structure that is nearly linear, too.

In the ensuing debate the assumption was questioned, whether $(NH_3)_2$ is a rigid or a rather floppy molecule. It was argued that in the latter case the Nelson measurements only reflect a vibrationally averaged structure, due to large amplitude tunneling motions, which does not necessarily have to coincide with the minimum in the intermolecular potential. However, from the fact that the relevant intermolecular bond angles hardly varied with isotopic substitution, Nelson *et al.*[2,9] concluded that $(NH_3)_2$ is a fairly rigid complex and consequently its equilibrium structure must be nearly anti-parallel. This conclusion was supported by the observation that the value of the electric dipole moment for $(ND_3)_2$ with 0.57 D turned out to be 0.17 D smaller than the value that was found for

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*1 D = 1 Debye = 3.3358×10^{-30} cm.

$(NH_3)_2$. In the case of vibrational averaging this seems to b tradiction, because the $(ND_3)_2$ is expected to be less influe internal motions, due to its larger mass, and consequently stay closer to equilibrium. This implies that the dipole mom $(ND_3)_2$ should be larger than for $(NH_3)_2$, which obviously the case.

In the years thereafter the results of detailed infrared,[10–] ıaı infrared,[13–16] infrared–far infrared,[15] microwave[1] and infrared–microwave[17] studies became available.

As an outcome of theoretical work[6] the ammonia dimer was no expected to dissociate upon excitation of a single 10 μm photon. From the infrared experiments, however, it was concluded that a single 970 cm^{-1} photon is sufficient to cause dissociation of the complex. Additional information was found by Buck and co-workers.[18] In a scattering experiment with a rare gas beam, an average energy of 520 cm^{-1} was transferred to ammonia dimers without causing dissociation. This gives the lower limits, whereas the upper limit can be estimated from the infrared work to be about 950 cm^{-1}. This is a typical value for a hydrogen bonded system.

From the far infrared studies[15,16] it became clear that the ammonia dimer is a very floppy molecule, exhibiting large amplitude motions. The result was also found by a theoretical study by van Bladel *et al.*[8] In addition it became clear that besides the motions that were proposed in the former microwave studies—rotation of the monomers around their (C_3) symmetry axes and interchange motion which actually exchanges the role of both monomers (se Fig. 2)—the monomer umbrella inversion can also take place. This was a rather unexpected result, since the umbrella inversion—in which the nitrogen atom tunnels through the hydrogen plane—in most NH_3 containing complexes is completely quenched. This means that the motion is hindered in such a way that from a quantum mechanical point of view the tunnel probability is equal to zero. Spectroscopically the corresponding energy levels are degenerate and consequently no tunnel splitting can be observed. Ap-

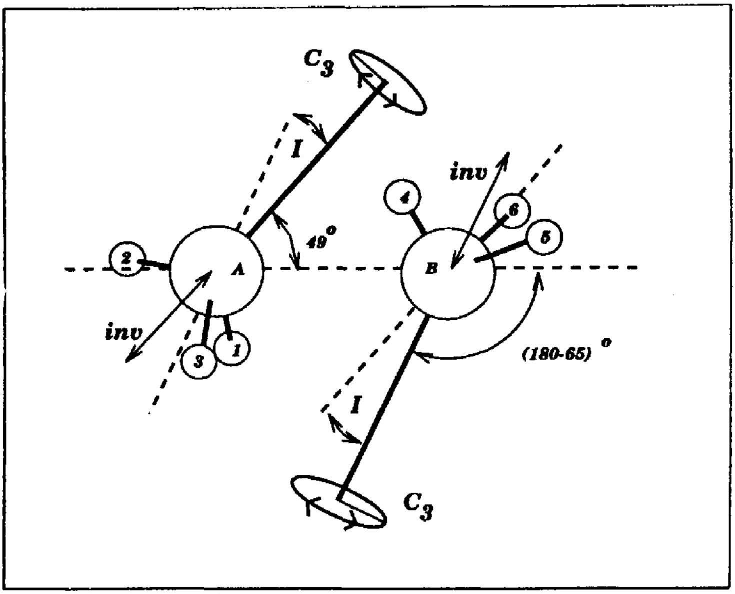

FIGURE 2 Feasible motions for $(NH_3)_2$ between equivalent structures: rotation around the C_3 axes, interchange of both monomers (I) and monomer umbrella inversion (inv).

parently, since inversion splittings are found, this probability is non-zero for the umbrella inversion in the case of $(NH_3)_2$. Although the complex is relatively strongly bonded, internal motions can take place more or less undisturbed. These motions can be classified by group theory.

GROUP THEORY

With group theory it is possible to construct an energy level diagram without actually knowing anything quantitatively about the molecule.[19] The idea behind this is to look at all possible transitions between non-distinguishable configurations. For these transitions it is necessary to tunnel through a barrier, and it is not very hard to imagine that in a floppy complex this will be easier than in a fairly rigid complex. From a spectroscopic point of view this means that tunneling splittings will be large or small, respectively. The group of all feasible motions, i.e., all motions that can be observed experimentally and consequently do not correspond to very unlikely motions (as breaking up internal bonds), is called the molecular symmetry group. Under the operations described by this group, the Hamiltonian is invariant and each energy level can b labeled according to an irreducible representation of the symmetry group. Furthermore it is possible to determine selection rules and spin statistical weights.

If we exclude any element which corresponds to unfeasible motions, such as any motion which involves the breaking of the N–H bonds, and if we exclude in the first instance the monomer umbrella inversions, only 36 permutation-inversion motions are left (see Fig. 2): the permutation of the hydrogen nuclei on each NH_3 subunit [(123) and (456)], the interchange of all nuclei on one subunit with those on the other subunit [(14)(25)(36)(AB)], the inversion of all particle coordinates in the center-of-mass followed to preserve the handedness of the monomers [(23)(56)*] and the products of all these motions with each other. These motions form the molecular symmetry group G_{36}. It is important to remember that this notation only describes the position of the atoms before and after they have undergone the tunneling motion. No statement is made about the actual pathway.

Due to the Pauli exclusion principle, the NH_3 monomers have a total nuclear spin either of 3/2 (ortho) or 1/2 (para) which results in two series for the overall molecular momentum K of $K_{\mathrm{ortho}} = 0, 3, 6, \ldots$ and $K_{\mathrm{para}} = 1, 2, 4, 5, \ldots$. Using G_{36} and assuming a plane of symmetry, we therefore expect each rotational level to split in eight tunneling states: 2A (ortho-ortho NH_3), 2G (ortho-para and para-ortho NH_3) and 4E (para-para NH_3) states, which correspond to the different combinations of nuclear spin. For this reason interchange motion, for example, is forbidden for G states since it is not possible to exchange different nuclear spins.

In the case that the umbrella monomer inversion is also taken into account, the number of feasible permutation-inversion motions increases by a factor of 4. This results in even more tunneling splittings, which are described by the molecular symmetry group G_{144}.

EXPERIMENTAL WORK

Infrared–Far Infrared Double Resonances

The vibration-rotation-tunneling motions occurring in the $(NH_3)_2$ are typically associated with energy differences corresponding to the far infrared region of the electromagnetic spectrum (3–40 cm^{-1}). In our laboratory at Nijmegen we generate tunable far infrared radiation by mixing a CO_2 laser pumped fixed far infrared laser frequency with tunable microwave radiation generated by klystrons in a Schottky barrier diode and subsequently selecting the (tunable) sidebands.[20] The $(NH_3)_2$ complexes are generated in a two-dimensional supersonic jet by expanding a mixture of about 2% NH_3 in Ar through a 4 cm × 75 μm slit nozzle into a vacuum chamber that is maintained at low pressure by a roots blower pumping system. The sidebands are focussed in the jet expansion and detected by an InSb hot electron bolometer. In this way in several laboratories some hundreds of $(NH_3)_2$ absorption lines have been found (see, e.g., Refs. 13 and 14), but only some of them could be assigned. Therefore we started an infrared–far infrared double resonance experiment.[15] In this experiment a line tunable CO_2 laser is guided anti-parallel to the far infrared beam between the nozzle and absorption zone. The double resonance signal for a selected state is detected by observing the depletion in far infrared signal as a function of the infrared frequency, which occurs when both transitions share the same initial state.

The first goal of this experiment was to correlate the overall infrared spectrum, as measured by Snels *et al.*[10] to the state-resolved far infrared information, in that way introducing a labeling technique. As a result it turned out to be possible to show that the monomer umbrella inversion is only partly and not completely quenched within the complex.[15] As was mentioned before, this was quite a surprising conclusion that was also confirmed by an extended set of new infrared data reported by Loeser *et al.*[16] As a consequence, group theoretical considerations had to be extended from G_{36} to G_{144}. Within this new molecular symmetry group, all microwave and far infrared data known at that time could be (re)assigned. This is illustrated in Fig. 3. In this figure several states with different symmetries are shown. On the left and right sides of each state the G_{36} and G_{144} symmetry labels are shown, respectively. The splittings correspond to the possible tunneling motions. Starting with the G:K = 0 ground states, (G_2^+, G_2^-)—denoted as G_α and G_β in Ref. 1—where K stands for the projection of the overall angular momentum, one of the important consequences of the introduction of the umbrella inversion becomes clear. The splitting between G_α and G_β that was recorded in the microwave by Nelson and coworkers was assigned to the G_{36} approach as interchange splitting. Since this splitting is small (450 MHz), the barrier for interchange was assumed to be rather large, suggesting a rigid structure. From the infrared–far infrared[15] and far infrared[16] measurements, it became clear that this splitting is due to the umbrella inversion motion and that the interchange splitting, in fact, is much larger (typically 20 cm^{-1}) which also holds for most of the other states. Only for the E_3 and E_4 bands is this incorrect. Here the two interchange components are nearly degenerate. If the rotation of the ammonia monomer is described in terms of a nearly free rotation, the E:|K| = 1 states in G_{36} can be visualized by the picture that the C_3 axis of each ammonia processes around the *a*-axis of the complex. The E_1 and E_2 states correspond to an anti-geared 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

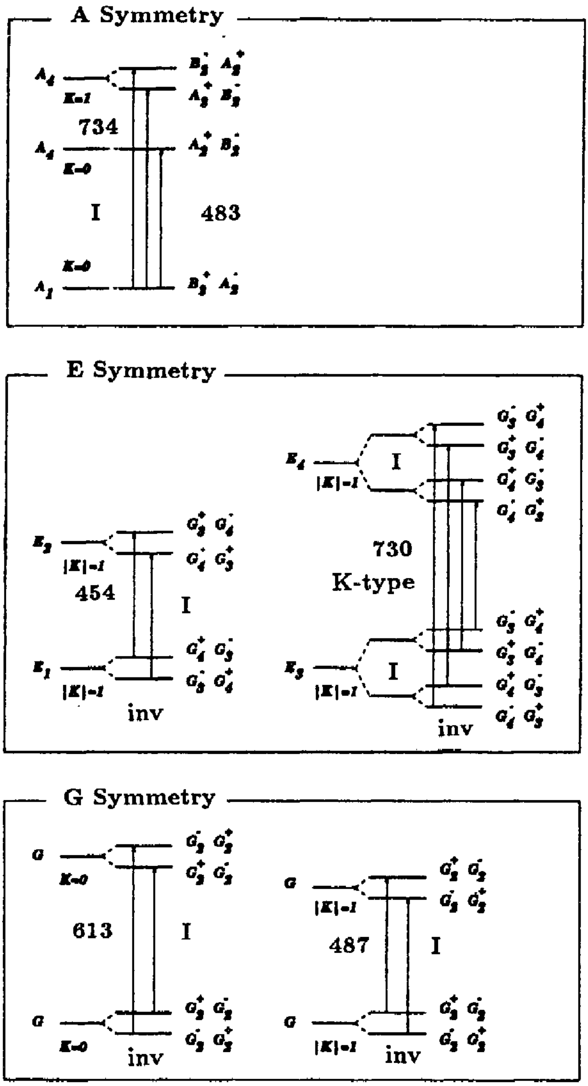

FIGURE 3 Energy diagram of the FIR transitions as assigned in Ref. 15. The vertical axes are not to scale. The indicated labeling on the left-hand side is in G_{36} and that on the right-hand side in G_{144} for J_{even} and J_{odd}, respectively. In the picture the nature of the tunneling splitting is indicated. The splittings are given in GHz (1 $\text{cm}^{-1} \approx 30$ GHz).

of the complex as derived by van Bladel *et al.*[8] In the case of a geared motion of the two ammonia monomers, there should be no potential barrier for interchange. Therefore the |K| = 1 states of E_3 and E_4 are nearly degenerate, whereas the |K| = 1 E_1 and E_2 states will be considerably split.

With the infrared–far infrared double resonance method, it furthermore turned out to be possible to assign the overall infrared spectrum as measured by Snels *et al.*[10] These infrared data were very important in providing the first complete infrared informatio on $(NH_3)_2$, but the experiment was not state specific. The infrared depletion signals were recorded by bolometric detection of the molecular beam. In this beam no state selection is possible. Consequently the measured infrared depletion spectrum shows the overall result of all populated states. This problem can be overcome by the infrared–far infrared double resonance experiment. From this it is found that the infrared excited umbrella splitting for the G states amounts to 3.9 cm^{-1} (36 cm^{-1} in free ammonia)[15] and that the infrared excited interchange splitting is of the same order of magnitude as in the ground state.[21]

Although all these measurements provided insight into the tunneling dynamics taking place in the complex, no structural information was obtained that could confirm or disprove the results found by Nelson and explain the discrepancy with the conclusions deduced from the $(ND_3)_2$ measurements. Furthermore it became clear that the Nelson measurements probed a small part of a shallow potential surface. For these reasons there was need for more structural information.

Stark Measurements

One possibility to attack the structural problem would be to construct a potential surface that fits the experimental data and as such directly reflects the molecular structure. But this is a very hard job and until very recently it was not met with success. However, experimentally it is possible to gain additional structural information in a relatively easy way using the Stark effect.

In the G_{36} approach, in which inversion is assumed to be totally quenched, it was shown[8] that only states with $|K| = 1$ exhibit a first order Stark effect when an electric field is applied. This effect is expected in the case that two energetically degenerate states have a non-vanishing Stark matrix element. However, if two $|K| = 1$ states are not degenerate anymore, but split by a large energy gap, due to internal motions as was found for $(NH_3)_2$, no observable Stark splitting is expected.[22] But within G_{144} each rotational level of G nd E symmetry in G_{36} splits into two additional components with different symmetry due to the umbrella inversion. If the zero field splitting is large compared to the term describing the Stark interaction between these levels, applying an electric field yields a quadratic Stark effect. For $(NH_3)_2$ this was verified in Ref. 22. The Stark splittings depend on the size of the inversion splitting, the rotational quantum number J, the Q, P or R character of the transition and the polarization of the far infrared radiation compared to that of the electric field. Using two Stark plates around the slit nozzle the electric dipole for the $G{:}|K| = 1$ state is determined to be (0.10 ± 0.01) D.[22] A dipole as small as this implies that the anti-parallel, so-called cyclic structure is indeed more likely than the linear one. For the anti-parallel structure the two dipole moments are also anti-parallel. Therefore, the two projections onto the axis have to be subtracted, whereas in the linear structure they add up. However, one has to keep in mind that this structure is the consequence of vibrational averaging in a very floppy complex. "More kely" in this context means that the complex most of the time will reflect an anti-parallel configuration, as an intermediate between several tunneling motions. Furthermore, these measurements confirm that the ammonia dimer is a non-rigid molecule. A remarkable variation of the electric dipole moment with K is found. For the $G{:}K = 0$ state, Nelson *et al.*[1] found a value of $|\mu| = 0.74$ D and for $G{:}|K| = 1$ it is found in Ref. 22 that $|\mu| = 0.10$ D. This gives evidence that $(NH_3)_2$ has a shallow potential and that different K levels probe different parts of the potential.

COMPARISON TO THEORY

Summarizing, it can be concluded that the $(NH_3)_2$ is strongly bound in radial direction, but that angular motions, including the monomer umbrella inversion, can take place relatively easily. As a consequence it is very hard to speak of a structure, and 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 is quite a challenge to compute the average structure and to explain the results quantitatively. Olthof, van der Avoird and Wormer[23] were able to do so by solving the full six-dimensional nuclear motion equation for a series of model potentials, with different barriers for interchange motion and hindered rotation of the monomers along their symmetry axes. In this study several measurable quantities were calculated—energy splittings, dipole moments, nuclear quadrupole splittings and the amount of quenching of the monomer umbrella inversions—and compared with the experimental data. The potential that gave best agreement with the observed quantities has a nearly linear hydrogen bonded equilibrium structure, small barriers for interchange motion (24 cm^{-1}), but a vibration-rotation-tunneling averaged ground state structure that is nearly cyclical. Furthermore van der Avoird *et al.*[24] were able to extend the use of this potential to $(ND_3)_2$. From this it became clear that it is also possible to explain the decrease of the G:K = 0 dipole moment when going from $(NH_3)_2$ (0.74 D) to $(ND_3)_2$ (0.57 D), without explicitly demanding a rigid structure. This can be understood in terms of localized wavefuntions.

As one would expect (the "rigid structure" argument), the wavefunction of $(ND_3)_2$ compared to $(NH_3)_2$ has a larger amplitude near its equilibrium position. This results in an increase of the average dipole moment. However, there is a second phenomenon with an opposite effect. Due to the ortho-para difference, the G state wavefunction is mainly localized on one side of the two (equivalent) minima. This effect will be less for $(ND_3)_2$ than for $(NH_3)_2$, due to the smaller rotational constant. As a consequence the contribution of the wavefunction of $(ND_3)_2$ at the other minimum will be substantially larger, which implies a decrease of the average dipole moment. Apparently, the second effect dominates the first, which explains the decrease in dipole moment, without assuming a near rigidity of the complex.

In the most recent study Olthof *et al.*[25] use an even smaller barrier of 7.5 cm^{-1} for the interchange motion. With this very small barrier height, nearly all experimental data can be reproduced. This opens the door to the next stage. Since $(ND_3)_2$ measurements in the far infrared are very expensive, good predictions are necessary to make these experiments possible. They would provide a sensitive test for the potential surface that now seems to have found a solution for the ammonia dimer riddle.

CONCLUSION

From a structural point of view the discussion of whether the ammonia dimer is hydrogen bonded or not should both experimentally[9,26–28] and theoretically[24,29–31] come to an end. The ammonia dimer seems to have a linear hydrogen bonded equilibrium structure, but this does not represent the actual structure. Due to the low barriers for angular motions all measured quantities retain 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 dynamic character of the complex. Taking this explicitly into account it is possible to understand what is going on in the complex.

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