The electric dipole moment of $(NH_3)_2$ for G: $|K| = 1$

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From the results of Stark measurements on the $(NH_3)_2$ van der Waals complex formed in a molecular jet expansion, it was possible to determine the electric dipole moment for the G: $|K| = 1$ state. The partially quenched inversion in the complex gives rise to quadratic Stark effect. We find an electric dipole moment of $|\mu| = (0.10 \pm 0.01)$ D in the ground state and an upper limit of 0.09 D for the dipole moment in the excited state. These small values give evidence that for the G: $|K| = 1–1$ states, the "antiparallel" (cyclic) structure is more likely than the hydrogen bonded one.

INTRODUCTION

In the past 10 years, the ammonia dimer has turned out to be a very interesting van der Waals complex. The results of Nelson, Fraser, and Klemperer[1,2] in 1985, which showed that $(NH_3)_2$ has no hydrogen bonding for the G: $K=0$ state, were surprising in view of former *ab initio* calculations (e.g., Refs. 3–5) that predicted a linear hydrogen bonded structure. They measured the electric dipole moment [0.74(2) D] and quadrupole coupling constants and calculated the structure for the G: $K=0$ state, yielding an equilibrium structure in which both NH_3 monomers are aligned antiparallel, making polar angles with the intermolecular axis of 49° and 65°. They excluded the linear H–N—H bonding, for which a much larger dipole moment (about 2D) is expected. Nelson *et al.* also managed to assign the measured microwave transitions within the group G_{36},[6] which includes the internal rotation of each monomer along the C_3 axis and the interchange tunneling between the two nonequivalent monomer units and in which the umbrella inversion is assumed to be totally quenched.

In 1984, Fraser *et al.* performed an infrared–microwave double resonance experiment, which showed a clear correlation between infrared spectra and the G states G_α and G_β (Ref. 7) within the complex. The total infrared spectrum for $(NH_3)_n$ clusters was measured at the same time in Nijmegen by Snels *et al.*[8] and later extended by an infrared–infrared double resonance experiment on the ammonia dimer by Heijmen *et al.*,[9] who found the same correlations as were found in the infrared–microwave double resonance experiment. A similar experiment to that of Snels was performed in 1987 by Huisken and Pertsch,[10] but with size-selected ammonia clusters, using the scattering of a $(NH_3)_n$ beam by a rare gas beam to produce a well-defined cluster size in the dissociation zone. These IR results were in general agreement with the measurements of Snels.

In 1988, Havenith *et al.*[11] started a far infrared study on several vibration–rotation-tunneling (VRT) transitions. Their work supported the conclusions drawn by Nelson.[2] However, additional far infrared measurements by Zwart *et al.*[12,13] on absorption bands in the 380–520 GHz range did not fit into the G_{36} approach and showed the need for further experiments.

In 1992, three papers on the ammonia dimer were published [an infrared–far infrared double resonance study on $(NH_3)_2$ in a molecular jet expansion;[13] a far infrared study on the complex;[14] and a theoretical study on the six-dimensional VRT dynamics of the dimer,[15]] which came to surprising conclusions.

(i) The umbrella inversion is only partially quenched within the complex, therefore the appropriate symmetry group is G_{144}.[13–15]

(ii) The interchange splitting is rather large (≈ 20 cm^{-1}), which implies that the intramolecular barrier for interchange is quite small. Therefore the molecule is not any longer supposed to exhibit a rigid behavior as was stated in the approach of Nelson *et al.*[13,14]

(iii) The K-type splitting turns out to be very large, which also excludes the high barrier limit.[13]

Concluding that $(NH_3)_2$ exhibits small barriers for internal motion, it is difficult to determine a structure for the molecule, since only vibrationally averaged structures are obtained experimentally. One of the most important measurable quantities is the electric dipole moment. The discussion whether $(NH_3)_2$ is hydrogen bonded or has a cyclic structure is so far based on the measurements of Nelson *et al.* on the dipole moment of $(NH_3)_2$ in one tunneling state—the G: $K=0$ ground state. Since these measurements yield only information on a specific part of the potential surface—with small barriers for internal motions—there is clearly a need for more data. We will present here new Stark measurements on the G $|K| = 1$ states.

EXPERIMENT

The ammonia dimer complexes are formed in a continuous two-dimensional (4 cm $\times$ 75 μm) supersonic jet expansion of 2% NH_3 in Ar. The spectra are recorded with the tunable far infrared spectrometer in Nijmegen.[16] The radiation used for the dipole measurements is generated

with the seventh harmonic of a 70 GHz klystron and the eight harmonic of a 55 GHz klystron in a Schottky barrier diode and selected using a 0.8 grooves/mm grating. The radiation passes the molecular beam and is focused onto an InSb hot-electron bolometer. The radiation is frequency modulated at 5 kHz and the detector output is monitored at twice this frequency.

For the Stark field, two metal plates ($15 \times 5.4 \times 1$ cm) are used. These are positioned on both sides of the nozzle parallel to the slit, 5 cm apart. The electric field is applied by a stabilized (Fluke 332A) power supply. Due to the relatively large background pressure during jet operation (60–80 mTorr), the highest applicable field, without getting breakdowns, amounts to 43.56 V/cm. It is important to know how much the homogeneity of the electric field is disturbed by the presence of the aluminum nozzle and by the finite dimensions of the Stark plates. Therefore we simulated the setup with "Simion."[17] From this, we concluded that inhomogeneities play only a minor role in the absorption zone, which lies 2.5 cm under the slit. This can also be concluded from the fact that we see no line broadening effects in the electric field. For an applied field of 43.56 V/cm, we calculate an electric field in the absorption zone of (40 ± 1) V/cm.

The polarization of the far infrared radiation is parallel to the electric field.

THEORY

In the G_{36} approach, in which inversion is assumed to be totally quenched, it was shown[15] that the degenerate G and E_3/E_4 ($|K|=1$) states will exhibit a first order Stark effect. We will explain this result and extend these considerations to the group G_{144}, which is applicable here.

A first order Stark effect will occur if two energetically degenerate states ϕ_1 and ϕ_2 have a nonvanishing Stark matrix element $\langle \phi_1 | \mu E | \phi_2 \rangle$. Since the dipole moment operator in G_{36} is of symmetry A_3,[1] first order Stark effects are only expected in two cases, both of which are $K=1$ states.

(1) If the two K-type doubling components for $K=1$ G states are expected to be energetically degenerate, we would obtain a first order Stark splitting, since $\langle G | A_3 | G \rangle \neq 0$ holds. However, since a large K-type splitting for $|K|=1$ G states was found,[14] in G_{36} no observable Stark splitting will be expected.

(2) As was discussed in Refs. 13 and 15, the $|K|=1$ E_3/E_4 states are nearly degenerate, since they represent both geared motions of the NH₃ monomer. The E_3/E_4 states should be split by interchange tunneling, which is quite large for other symmetry states, but since for geared motion no potential barrier for the interchange motion is expected, the two states are degenerate and only split by Coriolis interaction. If the K-type doublet components are also assumed to be energetically degenerate, one can again obtain nonvanishing matrix elements between degenerate states $\langle E_3 | A_3 | E_3 \rangle \neq 0$, but following the assignment as given in Ref. 13 and the energies as given in Ref. 14, the K-type doublet components are separated by 730 GHz. Therefore, no first order Stark effect is expected in G_{36} for these states.

However, due to the inversion of the monomer units, each rotational level for these states will split in two components with different symmetry in G_{144}. The symmetry of the dipole moment operator in G_{144} is A_1^-. This means that nonvanishing matrix elements are obtained between the two inversion components of the G states ($\langle G_2^+ | A_1^- | G_2^- \rangle \neq 0$) and the two inversion components of the former E_3 states ($E_3 = G_4^+ + G_4^-$) and the E_4 states ($E_4 = G_3^+ + G_3^-$). If the zero field splitting is large compared to the term describing the Stark interaction between these levels, applying an electric field will yield a quadratic Stark effect. A Stark splitting is now expected for all K values, where the observed splitting will depend on the size of the inversion splitting, the J level involved, and the Q or P, and R character of the transition. Each J level will split in $J+1$, $|M|$ components. Because the polarization direction is parallel to the electric field, only $\Delta M = 0$ transitions are allowed. For Q transitions, the intensities are proportional to (M^2); for P and R transitions the intensities are proportional to $(J^2 - M^2)$.

In contrast to the E states, the hyperfine structure for the G states cannot be resolved in our experiment. Therefore for G states, the electric dipole moment can be calculated by diagonalizing

$$\left\{ \begin{array}{cc} E_{01} & -(\mu \epsilon KM)/[J(J+1)] \\ -(\mu \epsilon KM)/[J(J+1)] & E_{02} \end{array} \right\},$$

$$(1)$$

where μ is the electric dipole moment, ϵ is the applied electric field, and $K=1$. From Ref. 13, it can be concluded that the energy difference between two inversion levels $\Delta E_{\text{int}} = E_{01} - E_{02}$ is given by

$$\Delta E_{\text{inv}} = 2 [\tfrac{1}{4}(B-C)J(J+1) - dJ^2(J+1)^2 + hJ^3(J+1)^3],$$

$$(2)$$

with

	Initial state	Final state
$B-C$	1.965(46) MHz	33.38(14) MHz
d		111.7(3.1) kHz
h		857(53) kHz

For $J = 1 \leftarrow 1$ transitions, only $\Delta M = 0$ for $|M| = 1$ is observable. In this case, the shift (δ) in the presence of an electric field is directly correlated to the value of the electric dipole moment.

RESULTS AND DISCUSSION

In Fig. 1, the energy level scheme is drawn for $J = 1$ and $J = 2$ in the ground and excited state. The small splittings are due to the umbrella inversion in the complex, the large transitions are due to interchange motion. The dotted lines indicate the observed shifts and splittings in the presence of an electric field.

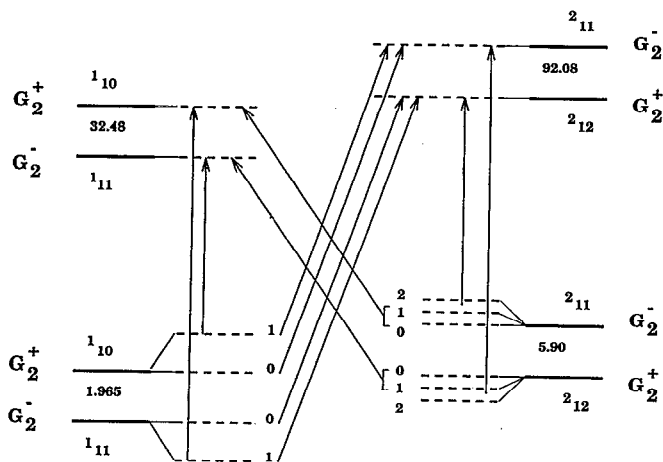We measured the line positions for the four Q transitions and the two P and R transitions without electric field

FIG. 1. The energy level scheme for the G: $|K|=1$–1 states for $J=1$ and 2 of $(NH_3)_2$. The small splittings are due to inversion; the large splittings are due to interchange motion. The dotted lines indicate the M components in the presence of an electric field. The arrows show the observed transitions.

FIG. 2. The G: $|K|=1$–1, $1_{11}\leftarrow 1_{10}$ transition in zero electric field and in a field of 40 V/cm.

and with an electric field of (40 ± 1) V/cm in the absorption zone. The results are listed in Table I. For the $Q(1)$ transitions, the measurement is repeated for (30 ± 1) V/cm, which is almost a factor $\sqrt{2}$ smaller. The shift turns out to be a factor of 2 smaller, which proves that the Stark effect is indeed quadratic.

For the $J=1\leftarrow1$ transitions, the only component that can be seen is $\Delta M=0$ for $|M|=1$. This component shifts 420 ± 30 kHz. The observed Stark shifts of Table I lead to the conclusion that the shift in the $Q(1)$ transitions is completely determined by the energy shift in the ground state. This is supported by the following arguments:

(1) For the $R(1)$ transitions, we see two components (Fig. 2)—one for $M=0$ and one for $|M|=1$ with an intensity ratio of 4 to 3. The $M=0$ transition coincides wi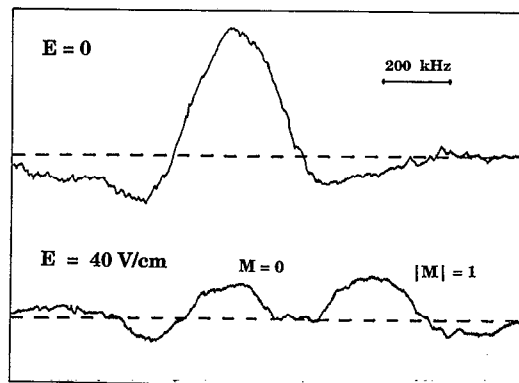th the zero field transition. The shift of the $|M|=1$ component is equal to the shift measured for the $|M|=1$ component of the $Q(1)$ transition.

(2) We observe one component of the $Q(2)$ transition, shifted by (70 ± 30) kHz. We expect two components ($|M|=1$ and $|M|=2$) with an intensity ratio of 1 to 4. Taking into account the different values for J and ΔE_{inv}, we calculate the expected shift of these components from the shift of the $|M|=1$ $Q(1)$ transition. The Stark shifts for the $|M|=1$ and $|M|=2$ components are smaller by factors of 27 and 6.8, respectively, yielding 15 and 60 kHz. Within the Doppler limited linewidth of 200 kHz, a single transition shifted by 50 kHz is expected. This is consistent with our measurements.

(3) For the $P(1)$ transitions, we observe a single component that is not shifted. We expect a $M=0$ component—that will not shift—and a $|M|=1$ component that almost coincides (15 kHz shift) with intensity ratios of 4 to 3, which is again in agreement with the observation.

From the shift measured for the $Q(1)$ transitions, we calculate the (absolute value of the) electric dipole moment of (0.10 ± 0.01) D for the ground state. For the ex-

TABLE I. Observed Stark shifts for G: $|K|=1$ transitions in $(NH_3)_2$.

$J'_{K'_a,K'_c}\leftarrow J''_{K''_a,K''_c}$	ν_0 (MHz)	Observed shift (kHz) $\epsilon=(40\pm1)$ V/cm	$|M|$	Experimental uncertainty (kHz)
$1_{10}\leftarrow 1_{11}$	486 433.22	+420	1	30
$1_{11}\leftarrow 1_{10}$	486 398.33	−420	1	30
$2_{12}\leftarrow 1_{11}$	506 248.67	−20	0	30
		+430	1	30
$2_{11}\leftarrow 1_{10}$	506 339.63	+10	0	30
		−420	1	30
$2_{11}\leftarrow 2_{12}$	485 843.64	+70	1+2	30
$2_{12}\leftarrow 2_{11}$	485 744.81	−70	1+2	30
$1_{11}\leftarrow 2_{12}$	465 902.29	+10	0+1	30
$1_{10}\leftarrow 2_{11}$	465 929.30	0	0+1	30

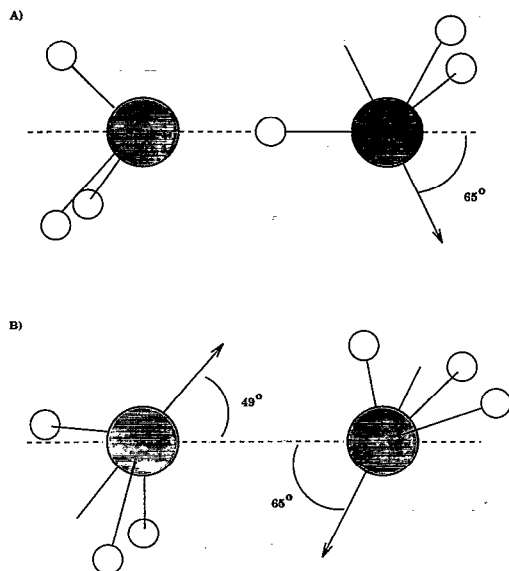| $J'_{K'_a,K'_c}\leftarrow J''_{K''_a,K''_c}$	ν_0(MHz)	Observed shift (kHz) $\epsilon=(30\pm1)$ V/cm	$|M|$	Experimental uncertainty (kHz)
$1_{10}\leftarrow 1_{11}$	486 433.22	+200	1	40
$1_{11}\leftarrow 1_{10}$	486 398.15	−180	1	40

FIG. 3. The classical hydrogen bonded structure (upper) and the cyclic (antiparallel) structure, as predicted by Nelson et al. (lower).

cited state, we can only determine an upper limit. Taking into account an inversion splitting that is about 16 times larger than in the ground state and assuming an uncertainty of 30 kHz in the measurements (a shift larger than this value can be resolved), we calculate an upper limit of approximately 0.09 D.

STRUCTURAL IMPLICATIONS

The dipole moment of the complex can be calculated according to[1]

$$\mu_a = \mu_a^{ind} + \mu^{NH_3} \langle \cos \theta_1 + \cos \theta_2 \rangle, \qquad (3)$$

where θ_1 and θ_2 form the angles between the C_3 axis and the a inertial axis of the complex.

A dipole moment as small as 0.10 D implies that for the $|K| = 1$ G state, the projection of the C_3 axis of the ammonia monomers onto the a axis will be of equal size, but opposite in direction. This means that the angles θ_1 and θ_2 form nearly complementary angles. However, we cannot determine the two angles independently without knowledge of the hyperfine splitting, which is not resolved in our experiment. Moreover, vibrational averaging effects, as discussed by van Bladel et al.,[15] might also be a principal problem when trying to deduce the structure.

In the following, we will compare the measured dipole moment with the dipole moments as expected for the two structures discussed in literature—the classical hydrogen bonded structure and the cyclic (antiparallel) structure. For the hydrogen bonded structure, one of the ammonia monomers acts as a proton donor, whereas the other acts as a proton acceptor. For this structure, $\theta_1 = 0°$ and $\theta_2 = 68°$. For the cyclic structure, as was proposed by Nelson et al. for the G: $K=0$ ground state, these angles amount to 48.6° and 115.5° respectively (Fig. 3).

The electric dipole moment of a hydrogen bonded structure is estimated by van Bladel et al.[15] to be -1.6 D. In this theoretical study, vibrational averaging effects based on the potential calculated by Sagarik, Ahlrichs, and Brode[18] were examined, but the electric dipole moment, measured by Nelson et al., and especially the value obtained in this paper are too small to be explained as a vibrational averaging effect. Our measurements therefore support the conclusion that $(NH_3)_2$ is not a hydrogen bonding system.

Furthermore, our measurements confirm that the ammonia dimer van der Waals complex is a nonrigid molecule. A remarkable variation of μ with K (K being the projection of the overall angular momentum, including internal rotation) is found. For $K=0$, $|\mu| = 0.74$ D and for $|K| = 1$, $|\mu| = 0.10$ D. This gives evidence that $(NH_3)_2$ has a shallow potential, so that different K levels probe different parts of the potential.

Further Stark measurements[19] and studies of the hyperfine structure in different tunneling levels will be of great interest in clarifying the structure of this important molecule.

ACKNOWLEDGMENTS

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