

IR DISSOCIATION OF AMMONIA CLUSTERS

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Dissociation spectra of NH_3 clusters have been recorded using a cw CO_2 laser. For the dimer two absorption bands have been found at 979 and 1004 cm^{-1} , which originate from the excitation of two non-equivalent NH_3 molecules. A tunneling motion is held responsible for the observed structure on one of these bands. The symmetry group of the NH_3 dimer is presented considering the tunneling motion solely. Heavier NH_3 clusters dissociate at frequencies between 1020 and 1100 cm^{-1} . The dissociation spectrum of the $\text{SiH}_4\text{-NH}_3$ complex shows one peak centered at 972.3 cm^{-1} .

1. Introduction

Recently, several hydrogen-bonded complexes have been investigated using various experimental methods. Klemperer and co-workers [1] used microwave and infrared spectroscopic techniques to examine a series of complexes containing NH_3 produced in a molecular beam. Pine et al. [2] studied the infrared spectra of $(\text{HF})_2$ and $(\text{HCl})_2$ in a static gas cell using a tunable difference-frequency laser. Equilibrium structures from some complexes could be established and valuable information on the internal motions have been obtained. The most recent theoretical paper predicts for the $(\text{NH}_3)_2$ a dissociation energy of 4.2 kcal/mol [3], in previous works Duquette et al. [4] and Dill et al. [5] calculated a bond energy of 2.8 kcal/mol. Therefore this complex was not expected to dissociate upon excitation with a single $10.2\text{ }\mu\text{m}$ photon. Experiments, however, showed [1,6] that one 970 cm^{-1} photon is sufficient to cause dissociation of this complex.

Howard et al. [6] studied the IR dissociation of $(\text{NH}_3)_n$ complexes. Their spectra show a single broad peak at 977.2 cm^{-1} corresponding to the

dimer dissociation and structure between 1020 and 1060 cm^{-1} due to heavier clusters. A molecular beam electric deflection study [7] demonstrated that the NH_3 dimer has a permanent electric dipole moment. Fraser et al. [1] measured the dipole moment along the axis of smallest moment of inertia, the a axis (0.74 D); moreover, they found two peaks between 970 and 985 cm^{-1} which showed a different behaviour in their IR–microwave double resonance measurements. In a more recent work [8], they suggest that those two peaks correspond with two torsional sublevels of the complex.

Investigations of NH_3 complexes in CO [9] and N_2 [10] matrices demonstrated the existence of two dimer bands of nearly the same intensity separated by 12 (CO) and 17.5 (N_2) cm^{-1} , respectively. This suggests that there also might be two well-separated bands for NH_3 dimers produced in a molecular beam. Indeed, we observed two broad bands ($\text{fwhm} = 14\text{ cm}^{-1}$) in the $(\text{NH}_3)_2$ dissociation spectrum centered at 979 and 1004 cm^{-1} . A structure richer than seen by Fraser et al. [1] emerged in the first band. Dissociation of heavier clusters occurs at frequencies between 1020 and 1100 cm^{-1} , which agrees with the results of ref. [6] and with matrix spectra [10].

In section 2 the experimental apparatus is described briefly. Subsequently the measured spectra

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spectra are presented. Results on the dimers are discussed considering in detail the symmetry of the problem. Results on heavier ammonia clusters, as well as on the $\text{NH}_3\text{-SiH}_4$ dimer, are reported in the last sections of this paper.

2. Experimental apparatus

Since the molecular beam apparatus has been discussed before [11], only a short description will be given. The beam is produced by supersonic expansion of a mixture of NH_3 in He through a 30 μm nozzle into a vacuum chamber. For the reported spectra the stagnation pressure was 5 atm. The temperature of the nozzle can be varied between -50 and 150°C and is stabilized within 0.1°C . A conical skimmer separates the first chamber from the second which is independently pumped. In this chamber the molecular beam is crossed by the radiation from a cw CO_2 laser. This laser with a cavity length of 1.95 m can be operated single-mode with $^{12}\text{CO}_2$, $^{13}\text{CO}_2$ and N_2O gas mixtures, providing more than 250 laser lines between 880 and 1100 cm^{-1} . A piezo-electric transducer, mounted on the laser grating, allows a 75 MHz fine tuning of the laser frequency within each laser line. The gaussian laser beam is focused to a spot of 0.8 mm diameter on the molecular beam axis. The laser power in all the present experiments was 5 W. The molecular beam is detected by a Ge bolometer (Infrared Laboratories) operated at 4.2 K. This very sensitive device is located in a third vacuum chamber, 400 mm from the interaction point.

The larger sensitivity of the bolometer for the detection of heavier clusters relative to the dimers has been stressed in former papers [11,12]. In order to correct for this artifact one needs to know where different clusters absorb [12]. Present data only indicate the spectral region where heavy clusters absorb, therefore no correction procedure has been performed.

The dissociation spectra were obtained working with a continuous molecular beam and modulating the radiation of the laser. The modulated bolometer signal was preamplified, fed into a lock-in amplifier and averaged by a microcom-

puter. For each laser line the bolometer signal due to cluster dissociation was obtained as the difference of the signal with, respectively without molecular beam, both signals averaged for about 1 min, in order to compensate for the straylight from the laser. The reproducibility of the observed spectra was better than 5%.

3. $(\text{NH}_3)_2$ spectra: vibrational interpretation

A mixture of 2% NH_3 in He was expanded from a 294 K nozzle. The dissociation spectrum is displayed in fig. 1b and shows two absorption bands of comparable intensity centered at 979 and 1004 cm^{-1} . The two peaks in the first band, at 977.2 and 980.9 cm^{-1} , correspond to those measured by Fraser et al. [1], the second band has never been observed. Fig. 1a displays a spectrum for a nozzle temperature of 248 K, with the other beam conditions unchanged. The two bands which are due to dimer dissociation remain, but new structures between 1020 and 1100 cm^{-1} appear. As already discussed by Howard et al. [6], those correspond to the dissociation of heavier clusters.

The cluster dissociation versus the laser power has been measured on all the peaks in fig. 1. Each peak showed the same linear power dependence for the investigated temperature range, which was followed by saturation at ≈ 20 W laser power. Clearly the dissociation of $(\text{NH}_3)_2$ is a one-photon process. Based on our experience the measured spectra correspond to beam temperatures of about 10 K at the end of the expansion. This implies that the rotational energy of 94% of the dimers is less than 16 cm^{-1} . Howard et al. [6] observed that the undissociated fraction of clusters measured on the NH_4^+ mass increased as the beam temperature was reduced. Their explanation for this behaviour was that only the hot fraction of the NH_3 dimers dissociates. We suggest as an alternative explanation that the observed feature of the NH_4^+ mass is due to the fragmentation of heavier clusters. The latter ones contribute to the intensity on this mass, but do not dissociate easily around 980 cm^{-1} . This hypothesis is also supported by the results of Huisken and Pertsch [13] which show that larger clusters preferentially dis-

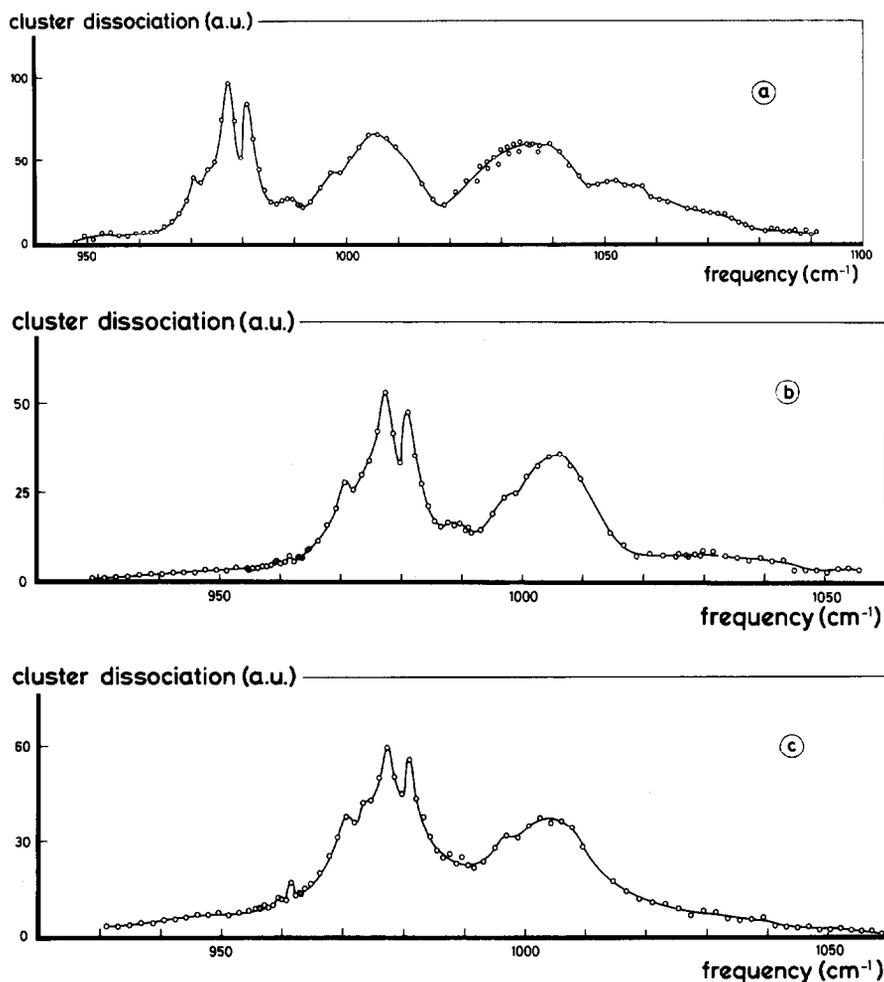


Fig. 1. Cluster spectrum (arbitrary units) for (a) 2% NH_3 in He, nozzle temperature 248 K, (b) 2% NH_3 in He, nozzle temperature 294 K, and (c) 5% NH_3 in He, nozzle temperature 423 K.

sociate at frequencies higher than 1000 cm^{-1} .

Varying the nozzle temperature from room temperature to 423 K (fig. 1c) we noticed that the dimer signal decreased only by a factor of two. In dimers of SF_6 , SiF_4 and SiH_4 a much more drastic dependence has been observed [12]. This observation suggests that the dimer bond in $(\text{NH}_3)_2$ is stronger than in the other complexes. Additional evidence for a rather strong NH_3 dimer bond has been given by Buck and co-workers [14]. In a scattering experiment with a secondary He beam an average energy of 520 cm^{-1} was transferred to NH_3 dimers without causing their dissociation.

Disregarding the rotational energy contribution to the dimer potential, this gives a lower limit of 520 cm^{-1} to the binding energy of $(\text{NH}_3)_2$, from the present results the upper limit is $\approx 950\text{ cm}^{-1}$ (see fig. 1c).

The spectrum displayed in fig. 1c has been recorded for 5% NH_3 in He at a nozzle temperature of 423 K. This spectrum shows a few extra peaks and a broadening of the two dimer bands. Since the two main bands in fig. 1b show the same behaviour on changing the beam conditions (from fig. 1a to fig. 1c their relative strength does not change), both must be due to the same cluster

species, which is shown to be the NH_3 dimer for the band at 979 cm^{-1} [1,6,10].

In order to understand the origin of the two dimer bands we will consider the structure of the $(\text{NH}_3)_2$ complex. Microwave experiments [8] on several isotopic species of $(\text{NH}_3)_2$ have provided constraints on the dimer structure. Six parameters are sufficient to describe the dimer geometry (fig. 2a). Three of them, the distance between the centers of mass of the two molecules, R , and the two angles θ_1 and θ_2 have been fixed by the microwave results. As sketched in fig. 2, θ_1 and θ_2 are the angles between the dimer axis and the symmetry axis of molecules 1 and 2 respectively, χ_1 and χ_2 stand for the rotation of the two molecules around their symmetry axes and ϕ for the rotation of molecule 2 around the N-N axis. The structure suggested by Nelson et al. [8] has $\theta_1 = 48.7^\circ$, $\theta_2 = 115.8^\circ$, $\chi_1 = 0^\circ$, $\chi_2 = 180^\circ$, $\phi = 0^\circ$ and $R = 3.3374\text{ \AA}$. In recent investigations of the electrical influence on monomer orientation in the NH_3 dimer [15,16], experimental results of ref. [8] have been reinterpreted after calculating the induced dipole moment in the dimer with a derivative Hartree-Fock theory. A slightly different structure (fig. 2b), with a total dipole moment of

0.85 D , has been proposed with $\theta_1 = 45^\circ$, $\theta_2 = 105^\circ$, $\chi_1 = 0^\circ$ and $\chi_2 = 0^\circ$ (indicated as "structure 2" in ref. [15]). As well as the structure displayed in fig. 2a, this structure possesses a symmetry plane. The electrostatic energy calculated in ref. [15] for this structure ($F_{\text{el}} = -1128.2\text{ cm}^{-1}$) is not much higher than the expected dimer dissociation energy (lower than 950 cm^{-1}).

The structure first suggested in ref. [8] and shown in fig. 2a will be taken as a starting point for our discussion; the structure from fig. 2b will be referred to explicitly when necessary. However, both structures have the same symmetry. This point will be discussed in somewhat more detail in section 5. The NH_3 dimer contains two non-equivalent molecules; one of them (M_2) is mainly a hydrogen donor, the other (M_1) a hydrogen acceptor. The same nomenclature has been used as for the dimers of HF and HCl [2].

It has been suggested [6] that the NH_3 dimer might undergo an inversion as in the free molecule. However, in the microwave experiments on $(\text{NH}_3)_2$ [8] no transitions related to (hindered) inversion have been observed. Studies of complexes of NH_3 with other molecules (OCS, CO_2 , N_2O and HCCH) [1] have not given any evidence for this inversion either. Since the hydrogen bond in the latter complexes is certainly weaker than in the ammonia dimer we do not expect inversion to occur in $(\text{NH}_3)_2$. The structure which has been proposed by Nelson et al. [8] possesses a very high barrier for inversion. However, the possibility of an inversion tunneling for the NH_3 dimer with a non-linear open hydrogen bond has been stressed in refs. [15,16]; this point will be discussed in detail in section 5 which deals with the symmetry of the NH_3 dimer.

A strong effect of the resonant dipole-dipole interaction has been observed [12,18], in excited dimers of SF_6 and other high-symmetry molecules. Therefore it is worthwhile to calculate the magnitude of this interaction in the ammonia dimer. The resonant dipole-dipole term in the hamiltonian is

$$H_{\text{dd}} = (\mu_{01}^2 / 4\pi\epsilon_0 R^3) \times [\cos(\theta_1 + \theta_2) - 3 \cos \theta_1 \cos \theta_2].$$

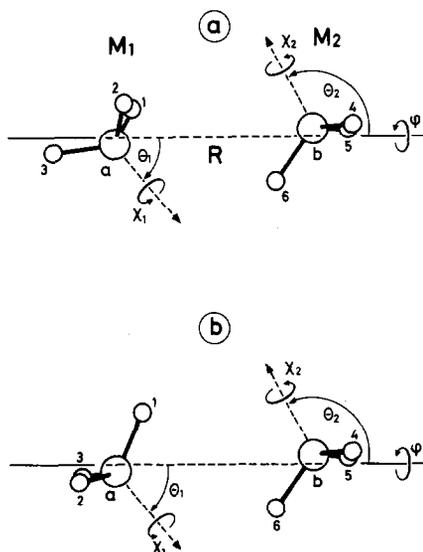


Fig. 2. Possible structure for the NH_3 dimer according to (a) Nelson et al. [8] and (b) Liu et al. [15].

The transition dipole moment of the ν_2 vibration of NH_3 monomer is $\mu_{01} = 0.24$ D [19]. In the dimer with $\theta_1 = 48.7^\circ$, $\theta_2 = 115.8^\circ$ and $R = 3.3374$ Å, H_{dd} takes the value -0.83 cm^{-1} . This value is negligible in comparison with a splitting of 25 cm^{-1} between the two dimer bands at 979 and 1004 cm^{-1} . Considering H_{dd} as a perturbation of two levels which are already 25 cm^{-1} spaced, the additional shift is less than 0.1 cm^{-1} .

Since both the possibilities of inversion and the resonant dipole-dipole interaction are ruled out, we conclude that the two bands in the dimer spectrum originate from the excitation of the two non-equivalent NH_3 molecules in the dimer. Similarly, the two dimer bands observed in matrix experiments [9,10] were explained as excitation of two non-equivalent molecules, assuming, however, that a complex with a linear $\text{N-H}\cdots\text{N}$ hydrogen bond was formed.

A Hartree-Fock calculation [20] gives a splitting of the order of 10 cm^{-1} for the two umbrella vibrations in $(\text{NH}_3)_2$.

4. $(\text{NH}_3)_2$: the electrostatic model

For both of the two different structures proposed in refs. [8,15], the two NH_3 molecules are not equivalent. Hence the excitation of the ν_2 (umbrella) mode in two NH_3 molecules in the dimer produces two different dimer vibrations.

Since no normal mode calculations are available for these structures we attempted to calculate the separation between the two dimer vibrations with a simple model. In first approximation the two NH_3 molecules in the dimer were replaced by two dipole moments, different in the ground and excited state [21]. The difference in dipole-dipole energy between the ground and excited state of the dimer can be expressed as

$$\Delta E = (4\pi\epsilon_0)^{-1} \left[\mu_g (\mu_e - \mu_g) / R^3 \right] \times [3 \cos \theta_1 \cos \theta_2 - \cos(\theta_1 + \theta_2)]. \quad (1)$$

Here μ_g and μ_e are the permanent dipole moments of ground and excited state of the NH_3 monomer, respectively. According to eq. (1) the excitation of either of the NH_3 molecules in the dimer yields the same value for ΔE ($= 4.76$ cm^{-1}), thus there is no splitting. This equation, however, is only valid for ideal dipoles, i.e. point dipoles. This approximation certainly is not valid for physical dipoles ($r_{\text{N-H}} = 1.01$ Å) at short distances ($R = 3.3374$ Å). In that case a modification of the model is necessary. The simplest higher-order approximation is the assumption of a charge distribution for the monomer, which will be different in ground and excited state. The total electrostatic energy of the complex is then obtained by calculating the energy of each of the NH_3 molecules, in the electric field produced by the other NH_3 .

Shimoda et al. [21] obtained dipole moments μ_g

Table 1

Coordinates of the atoms and the molecular parameters of the ammonia molecule for ground and excited (ν_2) state, respectively. Charges of q were put on each H atom and $-3q$ on the N atom, in order to match the experimentally observed dipole moments [12]. For this charge distribution a quadrupole moment has been calculated (Q_{calc})

Ground state				Excited state			
H ₁	H ₂	H ₃	N	H ₁	H ₂	H ₃	N
-0.47335	-0.47335	0.94670	0.00000	-0.47745	-0.47745	0.95491	0.00000
-0.81986	0.81986	0.00000	0.00000	-0.82697	0.82697	0.00000	0.00000
-0.30439	-0.30439	-0.30439	0.06523	-0.29079	-0.29079	-0.29079	0.06231

$\mu_g = 1.47147$ D	$\mu_e = 1.2480$ D
$B_g = 9.9442$ cm^{-1}	$B_e = 9.9802$ cm^{-1}
$C_g = 6.2204$ cm^{-1}	$C_e = 6.1139$ cm^{-1}
$q = 0.2763$ e	$q = 0.2453$ e
$Q_{\text{calc}} = -2.48$ D Å	$Q_{\text{calc}} = -2.34$ D Å
$Q_{\text{exp}} = -2.12$ D Å	

and μ_e as well as accurate values for the rotational constants from high-resolution IR measurements on NH_3 . Those rotational constants were used to calculate the positions of N and H atoms in the NH_3 molecule in ground and excited states. Charges of q and $-3q$ are put on each H atom and N atom, respectively. The values of q were found by matching the resultant dipole moments to the experimental ones. The results for the coordinates of the NH_3 molecule and the corresponding charge q for ground and excited state are given in table 1. The quadrupole moment calculated for this charge distribution agrees rather well with that observed [22]. The dimer is then built from two NH_3 molecules, whose relative orientations are fixed by the six parameters given in ref. [8]. We assume that the N-H distances and HNH angles in each molecule in the complex are the same as in the monomer. The coordinates of the eight atoms of the dimer in the vibrational ground state are listed in table 2.

Within this model we calculated the electrostatic energy for the ground state (E_0) and for the two different excited states of the dimer (E_1 and E_2). The result is $E_1 - E_0 = 29.6 \text{ cm}^{-1}$ and $E_2 - E_0 = 19.6 \text{ cm}^{-1}$. Our simple model yields a splitting of 10 cm^{-1} , while the peak corresponding to the excitation of molecule (M_2), the hydrogen acceptor, is blue-shifted with respect to the peak corresponding to the excitation of the hydrogen donor (M_1). Note that both dimer frequencies are blue-shifted with respect to the frequency of the monomer vibration. Electrostatic calculations on several other structures with the dipole moment constrained to 0.85 D, $\theta_1 = 45^\circ$ and $\theta_2 = 105^\circ$ have also been performed for different values of χ . Some significant results are listed in table 3. A blue shift and a splitting of the two dimer bands are always obtained. The actual values are espe-

Table 3

Electrostatic energies for $(\text{NH}_3)_2$ in different geometries. Values (in cm^{-1}) have been calculated for the ground and for ν_2 vibrational excitation in monomer 1 and in monomer 2 (angles in degree)

E_0	E_1	E_2	θ_1	θ_2	χ_1	χ_2
-252.0	-222.3	-232.3	48.6	115.5	180	180
-107.2	-93.7	-92.6	45	105	0	0
-406.6	-356.6	-368.0	45	105	0	180
-214.1	-192.8	-186.9	45	105	180	0

cially sensitive to the χ angles. For $\chi_1 = 0^\circ$ and $\chi_2 = 180^\circ$ we find a predicted splitting rather close to the experimental results ($E_1 - E_0 = 38.6 \text{ cm}^{-1}$ and $E_2 - E_0 = 50.0 \text{ cm}^{-1}$ with a splitting of 11.4 cm^{-1}).

In summary, we felt that there is enough evidence to assign the observed two dimer bands to excitation of the umbrella modes in each of the two non-equivalent NH_3 monomers in the non-linear hydrogen-bonded dimer.

5. $(\text{NH}_3)_2$: a tunneling complex

We will now try to give an explanation for the finer details in the spectrum of the two dimer bands. The band at 979 cm^{-1} is very structured, while the other band (at 1004 cm^{-1}) looks rather smooth, as observed with the present sampling. Furthermore, fig. 1 shows that an increase of the nozzle temperature produces a broadening of the bands and a new peak around 961.5 cm^{-1} . In addition, a cooling of the nozzle narrows the band. This observation suggests that the width of the two dimer bands is determined by internal degrees of freedom, which are depopulated in the colder beams.

Table 2

Coordinates of the atoms in the vibrational ground state of the dimer, assuming the structure proposed by Nelson et al. [8]. The corresponding rotational constants are (in GHz): $A = 125.729$, $B = 5.118$ and $C = 5.046$

H ₁	H ₂	H ₃	N _a	H ₄	H ₅	H ₆	N _b
0.5414	0.5414	-0.3977	-0.0489	-0.0710	-0.0710	-0.6823	0.0589
-0.8199	0.8199	0.0000	0.0000	0.8199	-0.8199	0.0000	0.0000
-1.5149	-1.5149	-2.5801	-1.6256	2.2270	2.2270	0.9453	1.6406

In their microwave experiments Nelson et al. [8] observed two vibrational states α and β , whose rotational constants B and C differ by 300 kHz. Double-resonance experiments [1] showed that the two peaks at 977.2 and 980.9 cm^{-1} correspond to excitation to the α and β states. In ref. [8] it was suggested that those states are two torsional sublevels of the NH_3 dimer. From the difference in rotational constants – assuming a threefold barrier for internal rotation – a barrier height of 700 cm^{-1} was calculated, as well as an energy difference of 400 MHz between the two torsional sublevels [8]. This hypothesis, however, does not explain the double-resonance results of ref. [1], since changing the barrier to internal rotation by 10 or 20% for the excited NH_3 complex, we calculated (following the treatment of ref. [8]) that the resulting splittings for the torsional states in the vibrationally excited dimer do not exceed a few GHz, whereas the two peaks observed in the IR absorption differ by about 3.7 cm^{-1} .

The presence of pure torsional motion in NH_3 dimer is also in contradiction with the results of ref. [15], which support the hypothesis of an inversion tunneling of $(\text{NH}_3)_2$ coupled with torsions. In order to explain the observed structures in the IR spectrum we suggest that the NH_3 dimer exhibits a tunneling motion similar as found in the HF dimer [2,23]. Starting from the configuration in fig. 2a with $\theta_1 = 48.7^\circ$, $\theta_2 = 115.8^\circ$, $\chi_1 = 0^\circ$, $\chi_2 = 180^\circ$, $\phi = 0^\circ$ and $R = 3.3374\text{ \AA}$, we can obtain an equivalent situation changing slightly the angles θ_1 , θ_2 , χ_1 and χ_2 to $\theta_1 = 64.8^\circ$, $\theta_2 = 131.4^\circ$, $\chi_1 = 60^\circ$ and $\chi_2 = 120^\circ$. The effect of such an operation is depicted in fig. 3a. The barrier for such a tunneling motion is expected to be rather low, since in this motion the roles of the hydrogen donor and acceptor are gradually interchanged. In ref. [15] a barrier of $\approx 250\text{ cm}^{-1}$ is calculated for the inversion tunneling transforming the structure with $\theta_1 = 45^\circ$, $\theta_2 = 105^\circ$, $\chi_1 = 0^\circ$, $\chi_2 = 0^\circ$ into the one with $\theta_1 = 75^\circ$, $\theta_2 = 135^\circ$, $\chi_1 = 0^\circ$, $\chi_2 = 0^\circ$. A tunneling barrier causes a splitting ΔE_0 of the levels in the ground state and in general different splittings ΔE_i for every vibrationally excited state v_i .

Without going in full detail we will now discuss the consequences of this tunneling motion on the

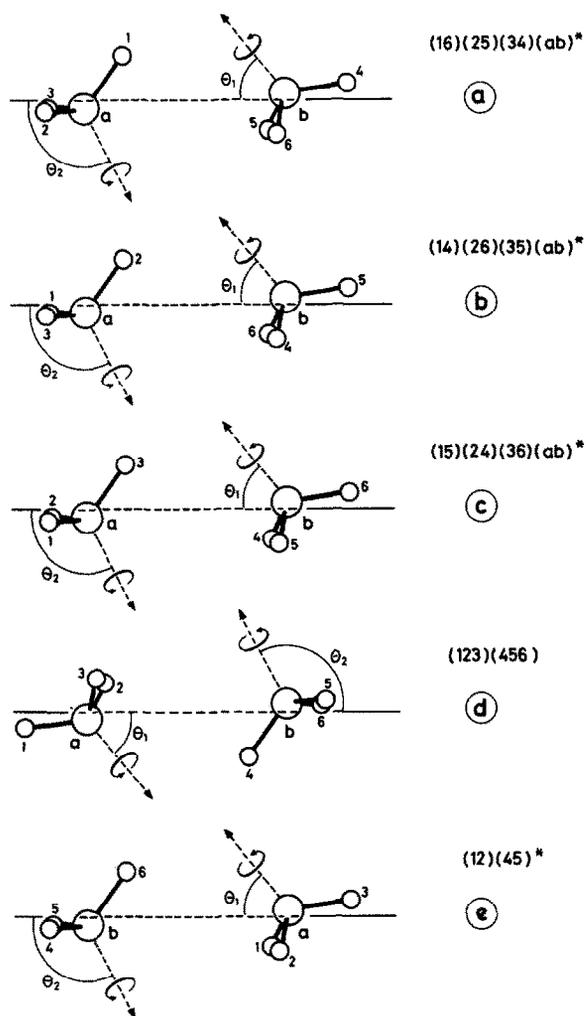


Fig. 3. The result of various symmetry operations on the reference configuration of fig. 2a.

symmetry of the NH_3 dimer. Only feasible operations will be considered. This implies that none of the hydrogens of one NH_3 molecule can be interchanged with those of the other one in the cluster. Although, as we will show below, the full symmetry group for $(\text{NH}_3)_2$ contains many elements, we will try to find the group which is minimally necessary to explain our experimental data and to get insight into the effects of the various different possible internal motions in the complex. Odutola et al. [7] presented the results for the permutation inversion group G_{72} . We will

demonstrate, however, that the group containing all the feasible operations for the dimer can be reduced.

There are three equivalent configurations starting from the reference configuration of fig. 2a that can be reached, for which the roles of the two NH_3 molecules in the complex are interchanged. These configurations are depicted in figs. 3a–3c. They can be written in the notation of permutation inversion operators as (16)(25)(34)(ab)*, (14)(26)(35)(ab)* and (15)(24)(36)(ab)*. It is worthwhile to remember that this notation only describes what the position of the atoms is after they have undergone the tunneling motion. No statement is made about the actual pathway. The discussion below will elucidate the relevance of this remark. It should further be noted that we have chosen as reference configuration that of fig. 2a. It can be easily seen that for the other structure (fig. 2b) the same definition of the tunneling operators can be used and that we will find the same symmetry group. We have, however, decided to use the structure from fig. 2a as starting position, since it is easier to distinguish the resulting positions of the various atoms after a symmetry operation has been applied on the dimer.

In order to determine the full symmetry group for the NH_3 dimer, allowing only the tunneling motion, we have to include all the products generated from the three basic tunneling operators defined in the previous paragraph. This yields another two operations: (123)(456) and (132)(465). The first one is depicted in fig. 3d. The second one is very similar. Although the two latter operations suggest that we have included the “geared” part of the torsional motion, i.e. the rotation of the two NH_3 molecules relative towards each other, this is

not necessarily the case. The reason is that those two operations describe a symmetry operation on the complex which can be reached by two consecutive tunneling operations. At this point it is clear that it is important to be very explicit about the pathways of the different symmetry operations.

The five symmetry operations discussed above form together with the unity operator E a group of order 6, G_6 . It can be shown that this group is isomorphic with C_{3v} (and also with D_3). The group G_6 is the symmetry group for the tunneling dimer if in the equilibrium configuration the symmetry axes of the NH_3 molecules are not in a plane, i.e. $\phi \neq 0$. However, the equilibrium structures of fig. 2 possess an additional symmetry. As it is obvious from fig. 2, the plane containing the two nitrogen atoms and the hydrogen atoms H_3 and H_6 is a symmetry plane. The corresponding symmetry operation is (12)(45)* (fig. 3e). The full symmetry group, which is obtained by making all the products of this reflection with the elements of G_6 is a group of order 12, G_{12} . This group is isomorphic with D_{3h} and D_{3d} . Table 4 displays the character table for G_{12} . We have chosen to adopt the D_{3d} nomenclature for the irreducible representations. The reason is that in that case the translational species T_z and (T_x, T_y) in G_{12} transform according to the same representations as they do in D_{3d} . The z axis is defined to lie along the axis of least moment of inertia (a axis) of the complex. In $(\text{NH}_3)_2$ this is approximately the N---N axis. The y axis is chosen to be perpendicular to the symmetry plane (fig. 2). For completeness table 4 also presents the nuclear spin statistical weights.

Until now we have only discussed the tunneling motion. In this complex one also has to consider

Table 4
Character table for the NH_3 dimer

C_s	G_{12}	E	(123)(456)	(12)(45)*	(14)(25)(36)(ab)	(162435)(ab)	(14)(26)(35)(ab)*	Nuclear spin statistics
A'	A_{1g}	1	1	1	1	1	1	99
A''	A_{2g}	1	1	-1	1	1	-1	15
	E_g	2	-1	0	2	-1	0	93
A'	A_{1u}	1	1	1	-1	-1	-1	81
A''	A_{2u}	1	1	-1	-1	-1	1	T_z 21
	E_u	2	-1	0	-2	1	0	(T_x, T_y) 88

the low-barrier rotation over 120° of each NH_3 molecule independently. The group generated by including these torsional motions is of order 36 and isomorphous with G_{36} given by Bunker [24]. The torsional selection rules [25] allow no change in symmetry during the IR transition. For this reason only the difference in torsional splittings between the ground and the vibrationally excited state will appear in the spectra. The low intradimer vibrational frequencies calculated in ref. [20], suggest a low barrier for the torsion. A barrier of 8 cm^{-1} is calculated in ref. [15] for the structure with $\theta_1 = 45^\circ$, $\theta_2 = 105^\circ$, $\chi_1 = 0^\circ$, $\chi_2 = 0^\circ$ corresponding with a χ_2 rotation, a much larger barrier (657 cm^{-1}) corresponds to a χ_1 rotation. In the structure of ref. [8], by using the simple electrostatic model introduced in section 4 we have calculated a barrier of 104 cm^{-1} for χ_1 rotation and of 227 cm^{-1} for χ_2 rotation. Assuming an average value of 100 cm^{-1} for the torsional barrier and a change of 20% in the barrier height in the excited state, differences of $\approx 1\text{ cm}^{-1}$ have been calculated for the $(\text{NH}_3)_2$. The present low-resolution data, in any case, do not show any significant effect ascribable to torsional splitting. As we will see below, the situation is different for the effects of the tunneling motion on the splittings in the IR spectrum of the dimer. It is therefore that we consider the discussion of the group G_{36} beyond the scope of the present work. Nelson [26] has recently presented a discussion of G_{36} in order to explain the observed rotational spectrum [1].

By choosing as a reference configuration the one shown in fig. 2, dimer vibrations can be classified under the C_s point group – the σ plane is the xz plane, the operation σ_h in C_s corresponds with $(12)(45)^*$ in G_{12} (already shown in fig. 3e). The correlation between G_{12} and C_s is also given in table 4. We can classify the eighteen dimer vibrations as in ref. [20], grouping six stretchings and six bendings, which are symmetric (A') and antisymmetric (A'') monomer-like vibrations. Furthermore we have six intermolecular (intradimer) vibrations which depend on the dimer coordinates defined in fig. 2a. In total the species of the eighteen normal modes in C_s are $11A' + 7A''$. As noted by Mills [23] for $(\text{HF})_2$, the dimer vibra-

tions are better labelled in C_s ; under this group T_x and T_y transform as A' , while T_z transforms as A'' . The umbrella symmetric deformation localized on each of the monomer subunits can be written in terms of the displacement angle $\Delta\alpha_i$ for each hydrogen, as in NH_3 [27]. With respect to $(12)(45)^*$ in G_{12} (i.e. to σ_h in C_s) the in-phase umbrella vibration in the dimer $[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) + (\Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6)]$ is symmetric (A' species in C_s), the out-of-phase umbrella vibration $[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6)]$ is antisymmetric (A'' species in C_s). Thus a different ordering of the tunneling sublevels will occur in these vibrations and will give rise to different splittings [23] in vibro-tunneling transitions from the ground state (of A' vibrational symmetry). This has been shown schematically in fig. 4 in the simple case of $J = 0$ and $K = 0$ rotational sublevels.

Because of the selection rules for the IR vibro-tunneling transitions in the dimer one of the bands is predominantly determined by the difference in the change of the tunneling splittings in the ground and the vibrationally excited states, while the other one is measuring the sum of this change. On basis of this picture we tentatively assign the structured low-frequency dimer band (at $\approx 975.5\text{ cm}^{-1}$) as

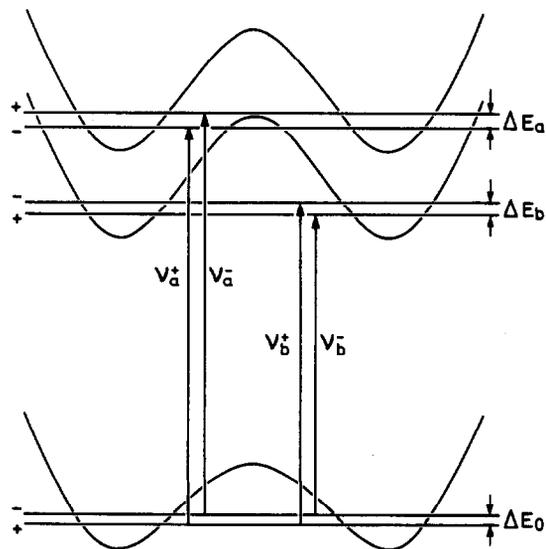


Fig. 4. IR transitions in the NH_3 dimer in the presence of a tunneling barrier.

the ν_b^+ and ν_b^- transitions (fig. 4). The smooth high-frequency dimer band (at $\approx 1004.5 \text{ cm}^{-1}$) corresponds to the ν_a^+ and ν_a^- transitions (fig. 4). As shown in the figure the tunneling splittings in ν_b transitions are summed, in contrary they are subtracted in ν_a transitions.

Although in the light of the above discussion this seems quite a plausible explanation for the observed IR dimer spectrum, the resolution of the present experiment does not allow an unambiguous statement. As another hypothesis we would like to mention a "mode-specific" predissociation rate similar to that observed by Pine et al. [2] in the HF dimer. In this case the linewidth for the 975 cm^{-1} NH_3 dimer band could be smaller than for the 1004 cm^{-1} band, thus revealing more structure in the low-resolution spectrum.

6. Heavier clusters: $(\text{NH}_3)_n$ ($n = 3, \dots, 6$)

For very cold beam conditions (fig. 1a) a broad band is observed, which corresponds to heavier clusters. Comparison of spectra measured at different beam temperatures showed that the broad band between 1020 and 1100 cm^{-1} (fig. 1a) emerges bit by bit. Initially (at 270 K) only a band around 1045 cm^{-1} was observed, but the reduction of the beam temperature produced dissociation signals for higher and higher laser frequencies. Apparently the absorption bands shift to the blue for heavier clusters. This is consistent with the results of Pimentel et al. [10] who observed $(\text{NH}_3)_n$ complexes ($n > 2$) in a N_2 matrix at frequencies from 1015 to 1065 cm^{-1} . Peculiar of the cluster spectra of NH_3 is that dimers and heavier clusters produce well-separated absorption bands.

In the electric beam deflection experiment by Odutola et al. [7] it has been observed that the permanent dipole moment of the NH_3 clusters is smaller than 0.3 D , for all the heavy complexes from the trimers to the hexamers. The constraint of an almost zero permanent dipole moment is fulfilled by a symmetric cyclic geometry. In order to obtain the minimum of electrostatic energy for each complex, θ and χ angles have been optimized. These angles are defined analogously to the dimer case. θ is the angle between the NH_3 sym-

metry axis of each monomer and the N---N axis with the right-hand adjacent monomer. χ stands for the rotation around the symmetry axis for each monomer. The lack of a true repulsive term in the model prohibits an optimization of the bond distance, which has been fixed equal to that of the dimer for all the heavier clusters. Results are shown in fig. 5 and in table 5). It should be noticed that all the heavier clusters considered are blue-shifted with respect to the dimer and the blue shift increases with the cluster size. Although the absolute value for the blue shift is by far overestimated, the trend toward increasing blue shift with the cluster size is in agreement with the experimental findings.

This calculation shows also that the most stable structure corresponds to the tetramer. Preliminary results obtained by Huisken and Pertsch [13] in a scattering experiment showed the presence of tetramers in the band centered at 1045 cm^{-1} . The energy per bond calculated in the present model is roughly about 700 cm^{-1} for all the small clusters, which fits exactly between the lower (520 cm^{-1} [14]) and upper (950 cm^{-1}) experimental limits obtained for the dimers.

An investigation of the stability of HF trimers, performed in refs. [16,28], has also shown that the cyclic structure with no dipole moment corresponds with a local minimum in the potential surface and that the energy of this structure is largely dominated by the electrostatic term that we have considered in the present analysis of NH_3 clusters. It is interesting to notice that the θ angles we obtained at the energy minimum of the $(\text{NH}_3)_n$ complexes ($n = 3, \dots, 6$), are showing exactly the same behaviour as those obtained for the corresponding HF complexes [28]. The present calculation of cyclic structures for $(\text{NH}_3)_n$ ($n = 3, \dots, 6$)

Table 5
Cyclic structure for $(\text{NH}_3)_n$ in the electrostatic model

n	Energy per bond (cm^{-1})	Optimum θ (degree)	Vibrational shift with respect to ν_2 (cm^{-1})
3	686	40	174
4	765	21	197
5	760	10	199
6	737	2	195

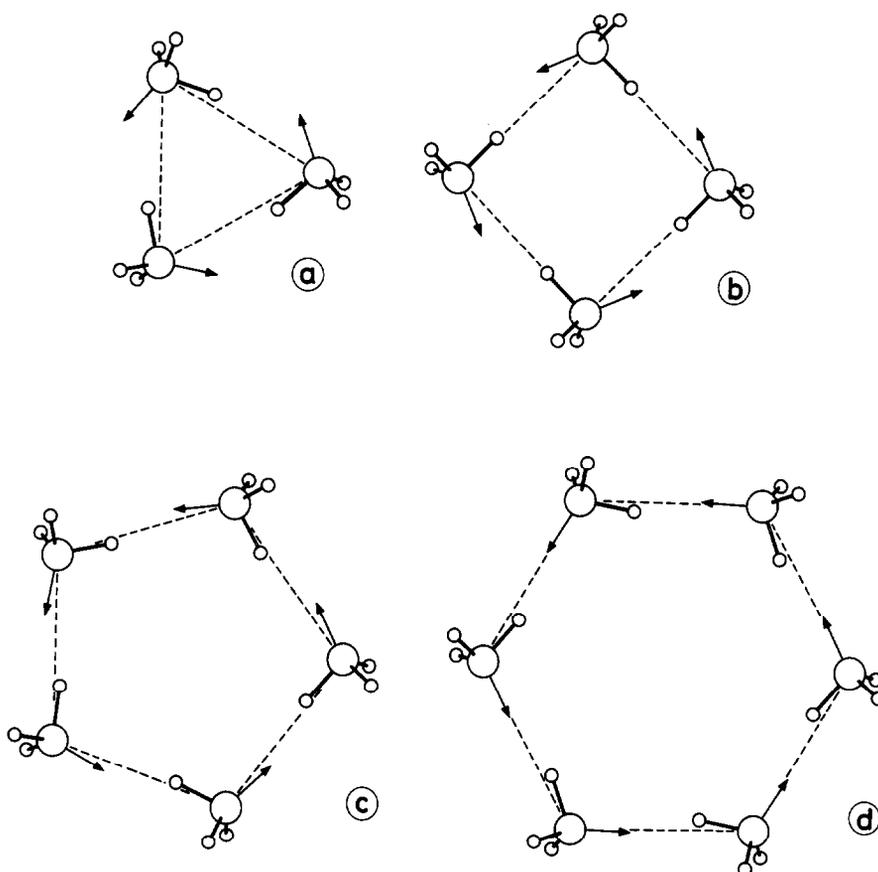


Fig. 5. Optimized (angles) geometry for higher ammonia clusters: (a) trimer, (b) tetramer, (c) pentamer, (d) hexamer.

shows also that a larger non-linearity of the hydrogen bond does not necessary correspond with a weakening of the cluster bond itself. Analogous results obtained on $(\text{HF})_3$ have been stressed in ref. [16].

7. $\text{SiH}_4\text{-NH}_3$

Mixed clusters containing NH_3 have been investigated both experimentally [1,29] and theoretically [5,30,31]. Theoretical results [20] for dimers formed by identical molecules indicate that the hydrogen bond is peculiar of the first-row hydride clusters, while hydrides of the second row tend to form van der Waals complexes in which the electrostatic interaction plays a minor role. The role of electrostatic interactions in hydrogen-bonded and

non-hydrogen-bonded NH_3 hetero-dimers is investigated in detail in ref. [31].

We expanded a mixture of 1% NH_3 and 1% SiH_4 in He through a 30 μm nozzle at room temperature. The spectral region between 880 and 1020 cm^{-1} has been investigated. Because the bolometer is not mass-selective, several different clusters may contribute to the spectrum. Contributions due to $(\text{NH}_3)_2$ and $(\text{SiH}_4)_2$ were subtracted after normalization. The SiH_4 dimer spectrum has been taken from ref. [12].

After subtraction of the other contributions only one single peak at 972.3 cm^{-1} , due to the mixed cluster $\text{SiH}_4\text{-NH}_3$, remained (fig. 6). Since the ν_2 vibration in SiH_4 (970.9 cm^{-1}) is only very weakly allowed, the observed peak must be due to excitation of the strong ν_2 (umbrella) vibration in the NH_3 molecule. The blue shift of the observed

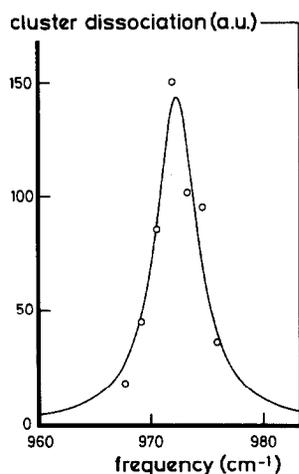


Fig. 6. Dissociation spectrum for 1% SiH₄, 1% NH₃ in He, nozzle at room temperature. Contributions of (SiH₄)₂ and (NH₃)₂ have been subtracted. Error bar is ± 30 arbitrary units for each point.

structure with respect to the NH₃ monomer frequency is comparable to that in other NH₃ complexes [1]. It is remarkable that the blue shift is observed also for non-hydrogen-bonded complexes.

No evidence for a second peak which could be related to NH₃ inversion has been found; the inversion should be rather unlikely if the bond involves the N lone pair.

A spectral feature corresponding to the excitation of the ν_4 mode in SiH₄ has not been observed. This might imply that such a peak was either too narrow to be resolved or too broad to be distinguished from the SiH₄ dimer spectrum. Also a large red shift on the SiH₄ ν_4 vibration in the NH₃-SiH₄ dimer can be responsible for our observation.

8. Conclusions

The (NH₃)₂, as well as heavier clusters (NH₃)_n ($n = 3, \dots, 6$) dissociate after absorption of one photon in the 9–10 μm region. The order of magnitude of the energy per bond in these complexes is about 700 cm^{-1} , as the simple electrostatic model predicts.

In the IR dissociation spectra of the NH₃ dimer

two bands have been observed. These dimer bands are due to two different dimer vibrations, which correspond to non-equivalent NH₃ molecules in the dimer. The spectral structures have been explained in terms of a tunneling motion. More detailed information can be obtained in microwave experiments. In high-resolution spectra also torsional splitting might appear. It would be also interesting to study the dimer bands in the 3 μm region, where higher resolution sources are available. Since the NH₃ dimer bond energy is comparable to that of the HCl dimer, their spectra might be obtained using a cooled cell. Of course monomer lines will partly obscure the dimer spectrum, but, e.g., the spectral region between the aR(1,1) transition (971.88 cm^{-1}) and the aR(2,2) transition (987.63 cm^{-1}) is completely free from monomer absorption.

The laser-induced predissociation technique at 9–10 μm may be effectively used to identify spectral features belonging to dimers or heavier clusters in a two-frequency excitation. The assumption of a cyclic configuration for the (NH₃)_n ($n = 3, \dots, 6$) clusters, in which the electrostatic interactions play a dominant role, is in agreement with all the experimental results.

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References

- [1] G.T. Fraser, D.D. Nelson Jr., A. Charo and W. Klemperer, *J. Chem. Phys.* 82 (1985) 2535.

- [2] A.S. Pine, W.J. Lafferty and B.J. Howard, *J. Chem. Phys.* 81 (1984) 2939;
N. Ohashi and A.S. Pine, *J. Chem. Phys.* 81 (1984) 73.
- [3] Z. Latajka and S. Scheiner, *J. Chem. Phys.* 84 (1986) 341.
- [4] G. Duquette, T.H. Ellis, G. Scoles, R.O. Watts and M.L. Klein, *J. Chem. Phys.* 68 (1978) 2544.
- [5] J. Dill, L.C. Allen, W.C. Topp and J.A. Pople, *J. Am. Chem. Soc.* 97 (1975) 7220.
- [6] M.J. Howard, S. Burdinski, C.F. Giese and W.R. Gentry, *J. Chem. Phys.* 80 (1984) 4137.
- [7] J.A. Odutola, T.R. Dyke, B.J. Howard and J.S. Muenter, *J. Chem. Phys.* 70 (1979) 4884.
- [8] D.D. Nelson Jr., G.T. Fraser and W. Klemperer, *J. Chem. Phys.* 83 (1985) 6201.
- [9] W. Hagen and A.G.G.M. Thielens, *Spectrochim. Acta* 38 A (1982) 1203.
- [10] G.C. Pimentel, M.O. Bulanin and M. van Thiel, *J. Chem. Phys.* 36 (1962) 500;
G. Ribbegard, *Chem. Phys.* 8 (1975) 185.
- [11] M. Snels, R. Fantoni, M. Zen, S. Stolte and J. Reuss, *Chem. Phys. Letters* 124 (1986) 1.
- [12] M. Snels and R. Fantoni, *Chem. Phys.* 109 (1986) 67.
- [13] F. Huisken and T. Pertsch, to be published.
- [14] Z. Bacic, U. Buck, H. Meyer and R. Schinke, *Chem. Phys. Letters* 125 (1986) 47.
- [15] S.-Y. Liu, C.E. Dykstra, K. Kolenbrander and J.M. Lisy, *J. Chem. Phys.* 85 (1986) 2077.
- [16] S.-Y. Liu and C.E. Dykstra, *Chem. Phys.* 107 (1986) 343.
- [17] P.A. Kollmann and J.C. Allen, *J. Am. Chem. Soc.* 93 (1971) 4991;
Z. Latajka and S. Scheiner, *J. Chem. Phys.* 81 (1984) 407.
- [18] J. Geraedts, S. Stolte and J. Reuss, *Z. Physik A* 304 (1982) 167.
- [19] T. Shimizu, F.O. Chimizu, R. Turner and T. Oka, *J. Chem. Phys.* 55 (1971) 2822.
- [20] M.J. Frisch, J.A. Pople and J.E. Del Bene, *J. Phys. Chem.* 89 (1985) 3664;
J.E. Del Bene, private communication.
- [21] K. Shimoda, Y. Ueda and J. Iwahori, *Appl. Phys.* 21 (1980) 181.
- [22] S.G. Kukolich, *Chem. Phys. Letters* 5 (1970) 401.
- [23] I.M. Mills, *J. Chem. Phys.* 88 (1984) 532.
- [24] P.R. Bunker, in: *Molecular symmetry* (Academic Press, New York, 1979).
- [25] C.C. Lin and J.D. Swalen, *Rev. Mod. Phys.* 31 (1959) 841.
- [26] D.D. Nelson, G.T. Fraser Jr. and W. Klemperer, in: *Structure and dynamics of weakly bound molecular complexes*, ed. A. Weber (Reidel, Dordrecht, 1986).
- [27] G. Herzberg, *Molecular spectra and molecular structure. Vol. 2* (Van Nostrand-Reinhold, New York, 1945).
- [28] S.Y. Liu, D.W. Michael, C.E. Dykstra and J.M. Lisy, *J. Chem. Phys.* 84 (1986) 5032.
- [29] G.T. Fraser, F.J. Lovas, R.D. Suenram, D.D. Nelson Jr. and W. Klemperer, *J. Chem. Phys.* 84 (1986) 5983;
G.T. Fraser, D.D. Nelson Jr., K.I. Peterson and W. Klemperer, *J. Chem. Phys.* 84 (1986) 2472;
G.T. Fraser, K.R. Leopold and W. Klemperer, *J. Chem. Phys.* 80 (1984) 1423;
G.T. Fraser, K.R. Leopold, D.D. Nelson Jr., A. Tung and W. Klemperer, *J. Chem. Phys.* 80 (1984) 3073;
G.T. Fraser, K.R. Leopold and W. Klemperer, *J. Chem. Phys.* 81 (1984) 2577;
G.T. Fraser, D.D. Nelson Jr., G. Gerfen and W. Klemperer, *J. Chem. Phys.* 83 (1985) 5442;
P. Herbine and T.R. Dyke, *J. Chem. Phys.* 83 (1985) 3768.
- [30] A.-M. Sapse, D.C. Jain, *Chem. Phys. Letters* 124 (1986) 517.
- [31] A.E. Reed, F. Weinhold, L.A. Curtiss and D. Pochatko, *J. Chem. Phys.* 84 (1986) 5687.