INFRARED (9-11 μm) DISSOCIATION OF THE HYDROGEN BONDED CLUSTERS $(NH_3)_n$ ($n \geq 2$) DETECTED BY BOLOMETRIC TECHNIQUE

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ABSTRACT. Predissociation of NH_3 clusters has been induced by a CW CO_2 laser and detected by a semiconducting bolometer. For the dimer two absorption bands have been found at 979 cm^{-1} and 1004 cm^{-1}, which originate from the excitation of two non-equivalent NH_3 molecules. Heavier NH_3 clusters dissociate at frequencies between 1020 cm^{-1} and 1100 cm^{-1}. A simple electrostatic model can account qualitatively for the observed features.

1. INTRODUCTION

Recently many theoretical and experimental studies on the subject of hydrogen bonded clusters have been carried out.

Equilibrium structures for some complexes could be established and valuable information on internal motions has been obtained. The IR dissociation of $(NH_3)_n$ complexes has been first investigated by Howard et al. [1], who observed a broad dimer band centered at 977.2 cm^{-1} and dissociation of heavier clusters between 1020 cm^{-1} and 1060 cm^{-1}. A molecular beam electric deflection study [2] investigating small clusters, from dimers to hexamers, has shown that only dimers posses a permanent electric dipole moment larger than 0.3 D. A dipole moment of 0.74 D was indeed measured [3] for $(NH_3)_2$ along the dimer axis.

Investigations of NH_3 complexes in CO and N_2 matrices [4] demonstrated the existence of two dimer bands of nearly the same intensity separated by 12 cm^{-1} (CO) and 17.5 cm^{-1} (N_2), respectively.

In the molecular beam machine described in the next section we observed two broad bands (FWHM $\cong$ 14 cm^{-1}) in the $(NH_3)_2$ dissociation spectrum centered at 979 cm^{-1} and 1004 cm^{-1}. A structure richer than previously [1,3] emerged in the first band. Dissociation of heavier

clusters occurred at frequencies between 1020 cm^{-1} and 1100 cm^{-1}, which agrees with the results of [2] and with matrix spectra [4].

2. EXPERIMENTAL APPARATUS

The molecular 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°C 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 can be operated single-mode with $^{12}CO_2$, $^{13}CO_2$ and N_2O gasmixtures, providing more than 250 laserlines between 880 cm^{-1} and 1100 cm^{-1}. The gaussian laser beam is focussed 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 [5]. 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 microcomputer. The reproducibility of the observed spectra was better than 5%. A discussion about the use of the bolometer for the cluster dissociation spectra can be found in [5].

3. RESULTS AND DISCUSSION

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 cm^{-1} and 1004 cm^{-1}. The two peaks in the first band, at 977.2 cm^{-1} and 980.9 cm^{-1}, correspond to those measured by Fraser et al. [3], the second band has never been observed before. Figure 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 cm-1 and 1100 cm-1 appear which correspond to the dissociation of heavier clusters [1].

The cluster dissociation versus the laser power has been measured on all the peaks shown in Fig. 1. The same linear dependence was observed for the investigated temperature range, followed by saturation at about 20 W laser power. Clearly the dissociation of $(NH_3)_2$ is an one-photon process.

Varying the nozzle temperature from room temperature to 150°C (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 [5]. This observation suggests that the dimer bond in $(NH_3)_2$ is stronger than in the other complexes. A lower limit of 520 cm^{-1} to the binding energy of $(NH_3)_2$ was given by Buck et al. [6],

the present results yield the upper limit of about 950 cm^{-1} (Fig. 1c).

The spectrum displayed in Fig. 1c has been recorded fro 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 in Fig. 1 the two main bands show the same behaviour when we change the beam conditions 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} [1,3].

In order to understand the origin of the two dimer bands we have to consider the structure of the $(NH_3)_2$ complex. The structure suggested by Nelson et al. [3] for the NH_3 dimer (θ_1=48.7°, θ_2= 115.8°, χ_1= 0°, χ_2= 180°, ϕ= 0° and R= 3.3374 A) accounts for the experimental

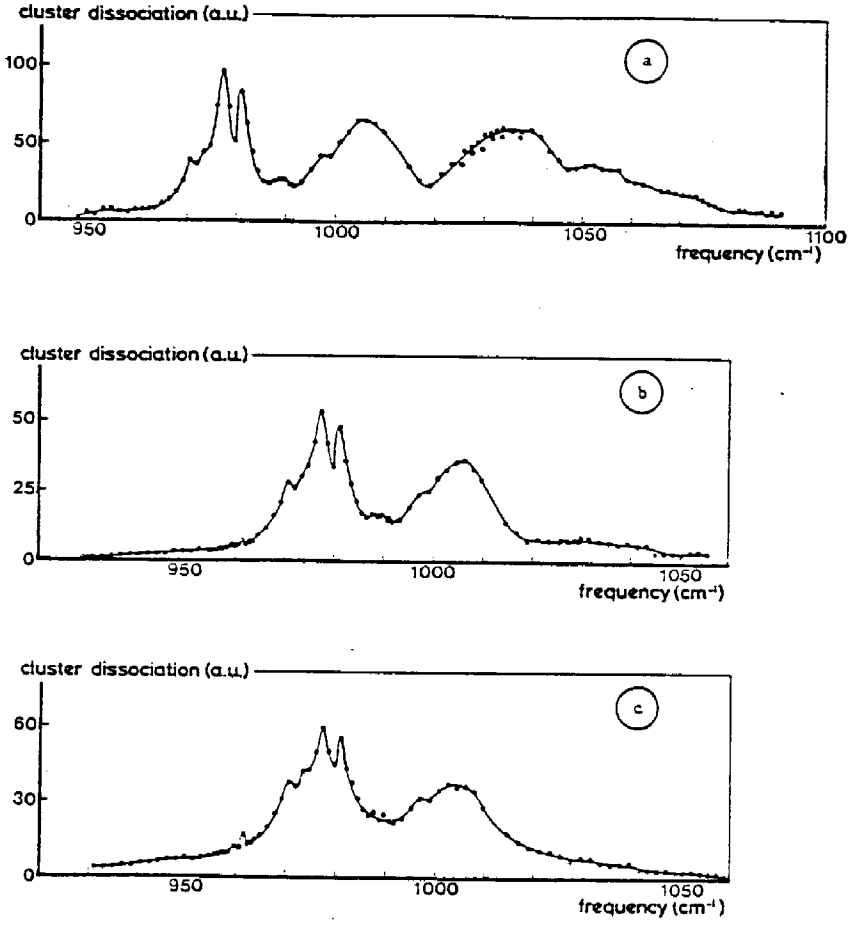

Figure 1. a,b) Cluster spectrum for 2% NH_3 in He, nozzle temperature 248 K (a), 294 K (b); c) Cluster spectrum for 5% NH_3 in He, nozzle temperature 423 K.

data measured in the microwave region (below 22 GHz). This structure contains two non-equivalent molecules; one of them (M_2) is mainly a hydrogen donor, the other (M_1) a hydrogen acceptor (see Fig. 2a). No evidence for NH_3 molecule inversion in the dimer was obtained [3]. A resonant dipole-dipole interaction, observed in excited dimers of SF_6 [5], could give rise only to a splitting of 0.83 cm^{-1} in the case of $(NH_3)_2$.

It can be concluded that the two bands with a splitting of 25 cm^{-1} 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 were explained as excitation of two non-equivalent molecules, assuming, however, that a complex with a linear N-H--N hydrogen bond was formed.

In order to check this hypothesis for the structure of Ref. [3] we have perfomed a simple calculation of the electrostatic energy. A charge distribution, yielding the correct dipole moments for the NH_3 monomers both in the ground and in the excited state was assumed.

The total electrostatic energy of the complex is obtained by calculating the energy of one of the NH_3 molecules, in the electric field produced by the other NH_3. The electrostatic energy has been calculated for groundstate (E_0) and for two different excited states of dimer (E_1 and E_2). We find $E_1-E_0 = 29.6$ cm^{-1} and $E_2-E_0 = 19.6$ cm^{-1}. Our simple model yields a splitting of 10 cm^{-1}; the peak corresponding to the excitation of the hydrogen acceptor molecule (M_2), 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. We will now try to find an explanation for the different spectral appearance of the two dimer bands. The band at 979 cm^{-1} is structured within 1 cm^{-1} resolution, the other band (at 1004 cm^{-1}) looks rather smooth. Furthermore, Fig. 1 shows that increasing the nozzle temperature leads to a new peak around 961.5 cm^{-1}. In addition, cooling the nozzle narrows the bands. This observation suggests that the width of the two dimer bands is determined by internal degrees of freedom, which become depopulated for colder beams. In order to explain the observed spectral structures we suggest that the NH_3 dimer exhibits a tunneling motion as observed for the HF dimer [7]. Starting from the configuration in Fig. 2a with $\theta_1 = 48.7°$, $\theta_2 = 115.8°$, $\chi_1 = 0°$, $\chi_2 = 180°$, $\phi = 0°$ and R= 3.3374 Å, we can obtain an equivalent situation changing slightly the angles θ_1, θ_2, χ_1 and χ_2 to $\theta_1 = 64.8°$, $\theta_2 = 131.4°$, $\chi_1 = 60°$ and $\chi_2 = 120°$. The barrier for this tunneling motion is expected to be rather low, since in this motion the roles of the hydrogen-donor and -acceptor is gradually interchanged. A tunneling barrier causes a splitting ΔE_i for every vibrationally excited state v_i. We can classify the 18 dimer vibrations in 6 stretchings and 6 bendings, three of each mainly localized on monomer M_1 and three of each on monomer M_2. More precisely these are symmetric and antisymmetric conbinations of monomer-like vibrations. Furthermore we have six intermolecular (intradimer) vibrations which depend on the dimer coordinates defined in Fig. 2a. A pictorial sketch of the vibrational levels (J=0, K=0) with the tunneling sublevels is shown in Fig. 2b. In general selection rules for tunneling [7] require

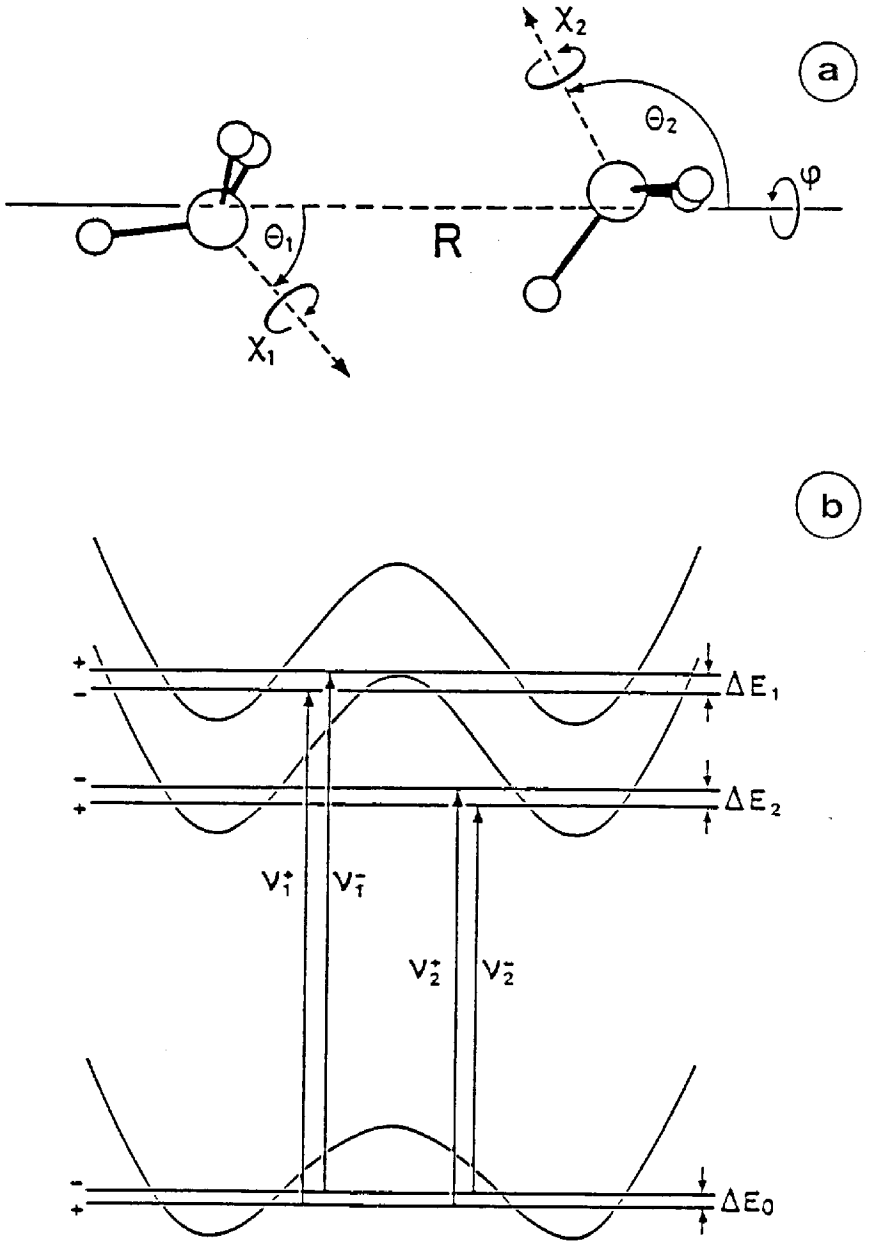

Figure 2. a) NH_3 dimer, structure according to Nelson et al. /3/; b) Tunnelling splitting in the NH_3 dimer ground state (ΔE_0) and in the symmetric (ΔE_1) and antisymmetric (ΔE_2) umbrella vibrations. Allowed transitions between J=0, K=0, sublevels are shown.

a change of symmetry in the tunneling species during the transition. The symmetry group of the NH_3 dimer, including the possibility of tunneling will be presented in a forthcoming paper [8] where a complete discussion of vibro-rotational-tunneling selection rules will be given.

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 reducing the beam temperature produced a dissociation signal at higher laser frequencies. Apparently, the absorption bands shift to the blue for heavier clusters. The constraint of an almost zero permanent dipole moment for all the heavy complexes from the trimers to the hexamers is fulfilled by a symmetric cyclic geometry [2]. In order to obtain the minimum of electrostratic 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 symmetry axis of each monomer and the N--N axis with the right hand adjacent monomer. χ stands for the rotation around the symmetry axis each monomer. The simple electrostatic model, previously applied for the trimer, yields in this case a large blue shift (from 174 cm^{-1} for the dimer to 195 cm^{-1} for the hexamer) with respect to the ν_2 in NH_3 monomer. The trend is in qualitative agreement with the experiment. The energy per bond calculated in the present model is roughly about 700 cm^{-1} for all the small clusters, which falls within the lower and upper experimental limits obtained for the dimer.

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