

Vibrational spectra of ammonia clusters from $n=3$ to 18

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We have calculated the vibrational spectra of the umbrella (ν_2), the symmetric (ν_1), and the asymmetric (ν_3) N–H stretch mode for ammonia clusters from $n=3$ –18. The results are based on recent structure calculations and a molecular perturbation approach that includes the anharmonicities. Clusters with high symmetry exhibit few lines only and show the expected blue shifts for the umbrella and red shifts for the two N–H stretch modes. The calculated frequencies of the umbrella mode agree very well with experimental results for $n=2$ –5 as far as the general shape is concerned, but overestimate the absolute shifts. © 2001 American Institute of Physics.

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I. INTRODUCTION

The structure and dynamical properties of weakly bound clusters are of great interest in a variety of research fields ranging from solvent–solution interactions over atmospheric and stratospheric chemistry to biological applications. One of the standard methods to get the experimental information is still infrared (IR) spectroscopy. The direct absorption methods have been improved by using sensitive detection schemes in the cavity ringdown laser spectroscopy¹ or higher intensities by coupling an intense gas pulse of a slit source with the Fourier transform IR spectroscopy.² The disadvantage of these methods is that no size specific information is obtained. In order to achieve this goal, depletion experiments with size selected clusters generated by the atomic beam deflection method were applied.^{3,4} In favorite cases also high resolution rotational–vibrational–tunneling spectroscopy in the far-IR⁵ was used.

For ammonia, one of the prototype systems for weak interactions, the experimental information is quite rare. Experiments for larger clusters than dimers were only carried out for the umbrella mode using a size distribution^{6,7} and size selected clusters from the dimer to the pentamer⁸ with the help of the atomic beam deflection method.⁹ In no case were the vibrational frequencies calculated in order to compare them with these experimental information.

In the preceding paper, we have determined the minimum energy configurations for ammonia clusters from $n=3$ –18,¹⁰ which will be referred as paper I in the further course of this work. In this paper we present the calculations of the vibrational frequency shifts. In order to get realistic results, we apply an approach based on perturbation theory¹¹ and improved recently by including degenerate states.¹² It takes into account the anharmonicity of the intramolecular force field and couples it to the intermolecular interaction. In this way, we can compare our calculations directly with the experiment for the umbrella mode of the small clusters and will provide realistic predictions for the symmetric and

asymmetric N–H stretch modes for the comparison with measurements that we plan to carry out in our laboratory.

II. THEORETICAL MODEL

For a homogeneous cluster formed of n molecules, the first-order frequency shifts $\Delta\nu_{mi}^{(1)}$ relative to a particular vibrational mode m of the monomer were shown in previous publications^{12,13} to result by solving the eigenvalue problem:

$$\sum_{m' \in \Gamma} \sum_{i'=1}^n \left[\frac{1}{2} \frac{\partial^2 U}{\partial q_{mi} \partial q_{m'i'}} - hc \Delta\nu_{mi}^{(1)} \delta_{mm'} \delta_{ii'} \right] c_{m'i',mi} = 0, \quad i=1,2,\dots,n. \quad (1)$$

The perturbation matrix elements are expressed in terms of the curvature $\partial^2 U / \partial q_{mi} \partial q_{m'i'}$ of the intermolecular potential U . q_{mi} is the normal coordinate associated with normal mode m of molecule i . In the case of a degenerate mode both m and m' belong to the subspace Γ of the considered normal mode, while for a nondegenerate mode $m \equiv m'$.

The second-order line shifts can be explicitly expressed as

$$\Delta\nu_{mi}^{(2)} = \sum_{m',m'' \in \Gamma} \sum_{i',i''} c_{m'i',mi} c_{m''i'',mi}^* \Delta\nu_{m'i',m''i''}^{(2)}, \quad (2)$$

where the coefficients $c_{m'i',mi} c_{m''i'',mi}^*$ are components of the eigenvectors yielded by the eigenvalue problem (1), and the partial contributions $\Delta\nu_{m'i',m''i''}^{(2)}$ are given by

$$\begin{aligned} \Delta\nu_{m'i',m''i''}^{(2)} = & -\frac{\delta_{i'i''}}{2hc} \sum_r \frac{1}{\omega_r} \frac{\partial U}{\partial q_{ri'}} \phi_{m'r''} + \frac{1}{4(hc)^2} \\ & \times \sum_{r \in \Gamma} \sum_j \frac{1}{\omega_m - \omega_r} \frac{\partial^2 U}{\partial q_{m'i'} \partial q_{rj}} \frac{\partial^2 U}{\partial q_{m''i''} \partial q_{rj}} \\ & - \frac{1}{4(hc)^2} \sum_r \sum_j \frac{1}{\omega_m + \omega_r} \\ & \times \frac{\partial^2 U}{\partial q_{m'i'} \partial q_{rj}} \frac{\partial^2 U}{\partial q_{m''i''} \partial q_{rj}}. \end{aligned} \quad (3)$$

Here ω_m and $\phi_{m'r''}$ are harmonic frequencies and cubic force constants, respectively. The most significant second-

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TABLE I. Calculated first-order and total (first plus second-order) shifts of the two most intense cluster lines for the most stable $(\text{NH}_3)_n$ clusters. $|\mu_{01}|^2$ is the transition strength in D^2 .

n	$\nu_1 = 3337 \text{ cm}^{-1}$			$\nu_2 = 950 \text{ cm}^{-1}$			$\nu_3 = 3444 \text{ cm}^{-1}$		
	$\Delta\nu^{(1)}$	$\Delta\nu_{\text{tot}}$	$ \mu_{01} ^2$	$\Delta\nu^{(1)}$	$\Delta\nu_{\text{tot}}$	$ \mu_{01} ^2$	$\Delta\nu^{(1)}$	$\Delta\nu_{\text{tot}}$	$ \mu_{01} ^2$
2	-9.4	-54.2	0.002	0.5	42.9	0.22	2.7	-26.3	0.06
	1.7	-29.0	0.002	17.0	65.5	0.30	-15.5	-105.1	0.05
3	-3.7	-78.3	0.003	19.5	110.7	0.39	-23.5	-154.5	0.07
							3.8	-44.1	0.10
4	-7.7	-93.5	0.004	17.1	122.8	0.50	-25.4	-176.9	0.10
							4.8	-46.8	0.11
5	-9.0	-106.3	0.004	20.5	129.3	0.32	-25.2	-184.9	0.09
	-3.3	-78.3	0.003	34.9	150.7	0.38	-5.3	-89.0	0.07
6	-2.8	-107.5	0.004	44.5	166.1	0.49	-20.1	-185.1	0.09
	-0.8	-94.2	0.004	87.3	198.7	0.43	9.5	-99.3	0.08
7	-2.7	-113.3	0.006	12.3	143.9	0.50	-22.7	-191.2	0.08
	-0.5	-107.2	0.001	78.3	213.0	0.59	-3.0	-106.0	0.07
8	-5.9	-133.5	0.005	49.2	198.7	0.49	-13.3	-145.4	0.12
	-1.4	-100.9	0.004	96.9	232.8	0.45	9.3	-108.7	0.09

order contributions are generally due to the first term, coupling the generalized intermolecular forces $-\partial U/\partial q_{ri'}$ with the intramolecular anharmonic force constants $\phi_{m'm''r}$.

The NH_3 - NH_3 intermolecular potential used in our frequency shift calculations is the site-site model of Impey and Klein,¹⁴ already described in paper I and used to determine the geometrical structures of the clusters up to $n = 18$. The NH_3 monomer is considered rigid and its geometry is defined by the nitrogen-hydrogen distance and the angle between the N-H bonds and the C_3 axis of the molecule. The potential features four electrostatic interaction sites (three located at the H atoms and one on the C_3 axis close to the N atom) and also Lennard-Jones interactions implying the N atoms. We assumed this effective two-body potential to be pairwise additive and its appropriateness was proved, at least for sizes up to the heptamer, by the agreement of the obtained cluster structures with the ones reported in the literature.

The intramolecular interactions within the NH_3 monomer are modeled by the anharmonic valence force field of Morino *et al.*¹⁵ As a first step toward incorporating the intramolecular force field into our perturbative frequency shift approach for clusters, the normal mode analysis of the ammonia monomer by the G-F method of Wilson¹⁶ was accomplished. Hereby results, besides the harmonic frequencies, the so-called l matrix of atomic displacements, which is necessary for evaluating the intermolecular potential derivatives with respect to the normal coordinates. The calculation details of these derivatives can be found in previous publications.^{12,13} In a second step, the transformation of the intramolecular force field from valence to normal coordinates was done by the L -tensor formalism of Hoy, Mills, and Strey,¹⁷ yielding the anharmonic monomer frequencies and the transformed cubic force constants $\phi_{m'm''r}$, which couple in the second-order frequency shifts to the intermolecular potential derivatives. Despite the quite elaborate procedure leading from the primary data to the transformed cubic force constants, the force field of Morino *et al.*¹⁵ already causes the anharmonic monomer frequencies to be in error by up to 53 cm^{-1} for the ν_2 mode at 950 cm^{-1} .

III. RESULTS AND DISCUSSION

In this paper we investigate three of the four normal modes of NH_3 : ν_1 —the symmetric stretch at 3337 cm^{-1} , ν_2 —the symmetric bend at 950 cm^{-1} , and ν_3 —the antisymmetric stretch at 3444 cm^{-1} . The first two modes are nondegenerate, while the third one is doubly degenerate. The obtained first-order and total frequency shifts, $\Delta\nu^{(1)}$ and $\Delta\nu_{\text{tot}}$, along with the corresponding transition strengths, measured by the squared transition dipole moment $|\mu_{01}|^2$, are listed in Tables I and II. In case there are more than two lines, only the two most intense lines are presented. As expected, the bending mode exhibits a blue shift, while the two stretching modes are red shifted. We will discuss the size dependence for the modes separately.

A. The symmetric bending (umbrella) mode

The results are presented in Fig. 1. The symmetric angle bend or umbrella mode ν_2 at 950 cm^{-1} is the only mode for which size-selected measurements are available (Huisken and Pertsch⁸), and this is the reason why we will report in more detail the results that refer to it. Since it is nondegenerate and the molecules occupy nonequivalent positions in the dimer, the calculated dimer spectrum shows two lines. While for the line at 992.9 cm^{-1} the major contributions come from the acceptor molecule, the donor molecule is mainly responsible for the more blue shifted line at 1015.5 cm^{-1} . In fact, the donor contributes by about 80% to the stronger blue shifted line, but only by about 25% to the less shifted one. This can be easily understood since the acceptor is essentially free to rotate about its C_3 axis, while the donor is somewhat more locked in position. Consequently, a stronger perturbation of the intramolecular force field of the donor is expected. The same qualitative reasoning also applies for understanding the other vibrational modes of the dimer. We note that this picture is a bit simplified, since in reality the roles of donor and acceptor molecules in the dimer are per-

TABLE II. Calculated first-order and total (first plus second-order) shifts of the two most intense cluster lines for the most stable $(\text{NH}_3)_n$ clusters. $|\mu_{01}|^2$ is the transition strength in D^2 .

n	$\nu_1 = 3337 \text{ cm}^{-1}$			$\nu_2 = 950 \text{ cm}^{-1}$			$\nu_3 = 3444 \text{ cm}^{-1}$		
	$\Delta\nu^{(1)}$	$\Delta\nu_{\text{tot}}$	$ \mu_{01} ^2$	$\Delta\nu^{(1)}$	$\Delta\nu_{\text{tot}}$	$ \mu_{01} ^2$	$\Delta\nu^{(1)}$	$\Delta\nu_{\text{tot}}$	$ \mu_{01} ^2$
9	-8.7	-128.7	0.006	10.3	143.7	0.36	-13.8	-160.3	0.09
	-1.3	-105.4	0.005	94.6	240.2	0.55	-4.0	-109.3	0.11
10	-8.9	-138.8	0.004	46.0	207.9	0.44	-6.1	-146.9	0.11
	-2.7	-104.6	0.007	84.5	229.1	0.44	-6.6	-121.9	0.09
11	-10.8	-135.4	0.005	-21.4	132.6	0.40	5.9	-128.1	0.07
	-3.9	-115.5	0.008	86.3	239.7	0.50	-4.1	-125.3	0.09
12	-5.3	-133.9	0.008	-18.1	146.4	0.40	-6.5	-141.0	0.15
				96.5	256.1	0.62	-11.2	-132.9	0.17
13	-5.3	-134.5	0.007	65.9	215.0	0.47	-12.8	-168.3	0.13
	-8.0	-127.1	0.007	99.9	259.6	0.46	-6.6	-147.1	0.13
14	-9.7	-139.9	0.008	81.5	242.4	0.48	13.5	-162.8	0.13
	-6.4	-128.7	0.007	58.2	232.4	0.50	-6.0	-119.3	0.12
15	-8.8	-137.7	0.007	85.4	240.8	0.81	-8.1	-159.7	0.14
	-6.1	-121.6	0.007	89.6	257.6	0.90	-3.7	-139.8	0.18
16	-9.7	-141.8	0.009	87.8	241.2	0.77	-3.9	-145.5	0.13
	-7.1	-129.0	0.008	90.9	268.9	0.71	-0.1	-145.0	0.14
17	-5.5	-131.6	0.007	66.7	221.0	0.58	-8.5	-148.0	0.10
	-7.1	-126.8	0.006	83.7	236.7	0.81	-0.8	-131.2	0.10
18	-12.2	-146.9	0.006	46.1	212.5	0.77	-13.4	-163.1	0.10
	-5.6	-136.9	0.005	78.5	245.0	0.60	-3.5	-136.7	0.20

manently interchanged. In spite of this interchange tunneling, we still have two different dimer configurations that contribute to the lineshift in a different way.

The calculated trimer spectrum contains a single doubly degenerate line at 1060.7 cm^{-1} , which is allowed in the first order of the theory due to the nonvanishing transition strength. This is understandable, having in view the planar cyclic C_{3h} structure of the most stable trimer, with all monomers in equivalent positions.

Due to its D_{4h} symmetry, the vibrational spectrum of the most stable tetramer is again simple, consisting of a doubly degenerate line at 1072.8 cm^{-1} and a nondegenerate line of much smaller intensity at 1096.9 cm^{-1} . In the case of the second lowest tetramer, having C_{4h} symmetry, with all four ammonia molecules in equivalent positions, the spectrum reduces to a single doubly degenerate line at 1072.1 cm^{-1} .

The total lack of symmetry of the pentamer brings about a spectrum composed of as many as five lines, with one line of considerably lower intensity (due to the near pyramidal structure of the pentamer). The larger shift, as compared to the two cyclic structures with twofold-coordinated molecules only, originates in the first appearance of threefold-coordinated molecules. The blue shift further increases when going from the pentamer to the hexamer and the heptamer, caused by the occurrence of more threefold-coordinated and the first fourfold-coordinated molecules (see Table II of paper I). From the nonamer onward, the shift does not increase anymore.

Except for the dodecamer ($n = 12$), the larger clusters up to $n = 18$ exhibit, due to the lack of symmetry, an increasing number of spectral lines. The dodecamer itself was shown in paper I to be a nice D_{6h} -symmetry cage, with three additional orthogonal C_2 axes and as many orthogonal symmetry planes. For each molecule, two of the N-H bonds are engaged in the cohesion of the cage, pointing to the lone pairs

of the two nearest ammonia molecules, while the third N-H bond is free, pointing outward. The ammonia molecules are consequently fourfold coordinated in the dodecamer. The two different environments of the N-H bonds are responsible for the existence of two distinct lines in the spectrum of the $(\text{NH}_3)_{12}$ cage. Obviously, the more blue shifted line at 1206.1 cm^{-1} is due to the connected N-H bonds, while the less blue shifted one at 1096.4 cm^{-1} is responsible for the free bond.

Going to the largest considered cluster, two groups of lines gradually build up. The less blue shifted one seems to converge to the solid state frequency (1063 cm^{-1}), as can be seen by a comparison with the uppermost panel, in which the experimental spectrum of Bromberg *et al.*¹⁸ is depicted.

As experimental counterpart of the calculated spectra for the clusters up to the pentamer, the IR photodissociation spectra of Huisken and Pertsch⁸ are plotted in Fig. 2. Fitted with Lorentzian line shape functions, the experimental spectra reveal three absorption peaks for the dimer (972.5 , 981.3 , and 1003.4 cm^{-1}), two for the trimer (1006.1 and 1016.3 cm^{-1}), two for the tetramer (1036.4 and 1044.7 cm^{-1}), and, finally, two peaks for the pentamer, 999.6 and 1044.8 cm^{-1} , with the latter peak being much broader than all the others.

Even though the overall structure of the experimental spectra is well reproduced by the calculated stick spectra, the agreement with the peaks assigned by Huisken and Pertsch⁸ is only semiquantitative, since, in order to bring the calculated spectra in agreement with the experimental ones, overall red shifts had to be applied to the calculated data (indicated in the upper left corner of each panel). Although we calculate according to Eq. (3) only the frequency shift, the anharmonicity of the intramolecular force field directly enters the formula by the coupling to the derivative of the intermolecular potential with respect to the normal coordinate. Since the available intramolecular force field of Morino

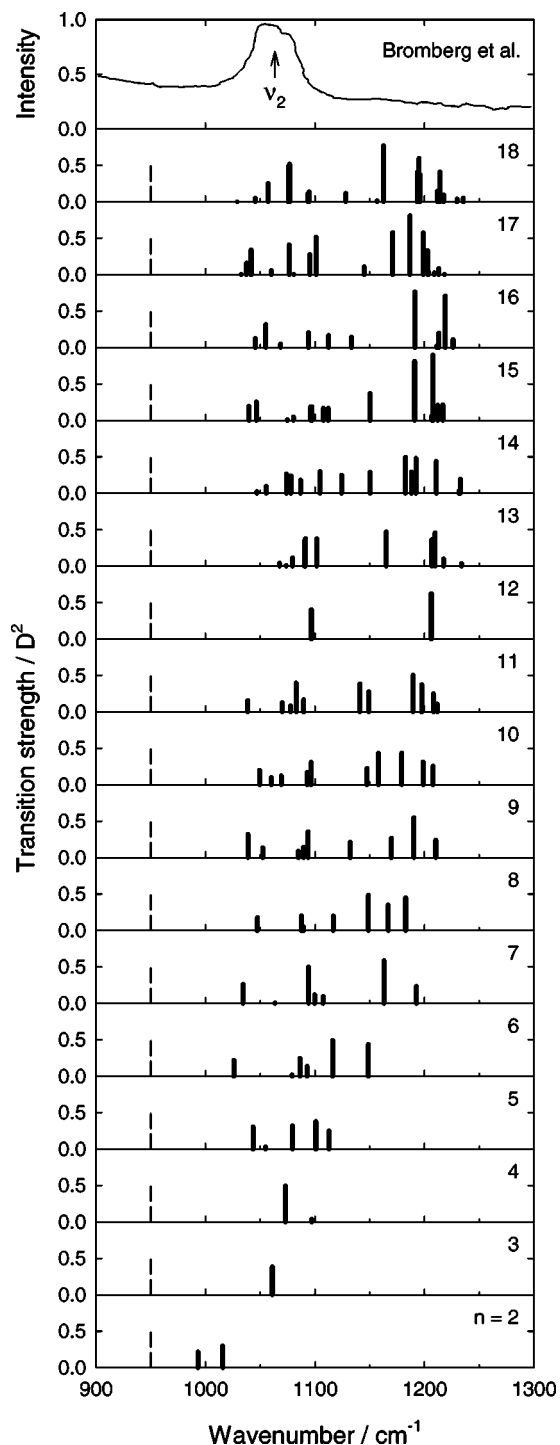


FIG. 1. Calculated IR spectrum for the umbrella mode (ν_2) for the ammonia clusters from $n=2$ –18 in D^2 . For comparison the spectrum of the solid is shown.

*et al.*¹⁵ already overestimates the monomer frequency for the ν_2 mode by 53 cm^{-1} , it is plausible that this is probably the reason for the too large shift.

Now let us discuss in detail the calculated structure of the spectra in Fig. 2 which is, in contrast to the absolute shift, in very good agreement with the experiment. For the dimer, the first peak is split, in agreement with Ref. 6. This is due to the inversion tunneling of the energetically lower components in the excited state, which is not accounted for in our

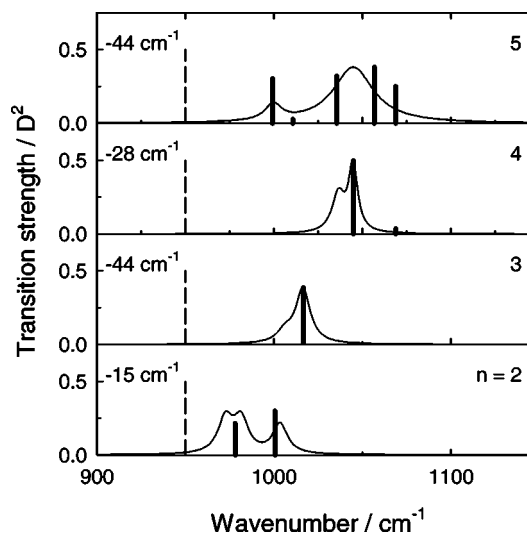


FIG. 2. A comparison of calculated (sticks) and measured (solid lines Ref. 8) spectra for ammonia dimers to pentamers for the umbrella mode. The sticks give absolute intensities in D^2 , but are shifted by the amount indicated to match the experimental data.

calculation.^{19,20} In the energetically higher component this splitting is buried under the interchange splitting and not resolved anymore.

For the trimer and tetramer essentially one peak is calculated, shifted to larger frequencies, as compared to the dimer. The measurements exhibit the same trends with an additional, smaller red shifted side band in both cases. The origin of this band has been explained in Ref. 8. Since in the photodissociation experiment of Huisken and Pertsch two photons are necessary to dissociate these complexes (in agreement with our results in paper I) and a double resonance experiment revealed that the second photon has a slightly red shifted resonance,⁷ the red shifted shoulders appear as a consequence of two overlapping bands with different frequencies and widths.²¹

For the pentamer the calculation explains all the experimental details. The cluster has a smaller incremental binding energy than the trimer and tetramer, so that one photon is sufficient for the dissociation. The spectrum consists of a very broad and a small peak. The reason is not the nonrigidity of the molecular motions but the nonequivalent position of all five molecules caused by the asymmetric structure. The large peak consists of three lines close to the tetramer frequency, caused by the two three-coordinated double donor single acceptor (DDA) molecules with the largest shift and one DA molecule (see Fig. 1 in paper I). The smaller peak originates from the two DAA molecules, from which one has a diminishing intensity.

B. The symmetric and asymmetric N–H stretch modes

The results for the symmetric and asymmetric N–H stretch modes are presented in Figs. 3 and 4. For the clusters up to the pentamer, essentially the same analysis applies to the ν_1 symmetric stretch as for the ν_2 symmetric bend, merely with blue shifts replaced by red shifts. Moreover, the spectra show the same shifting patterns.

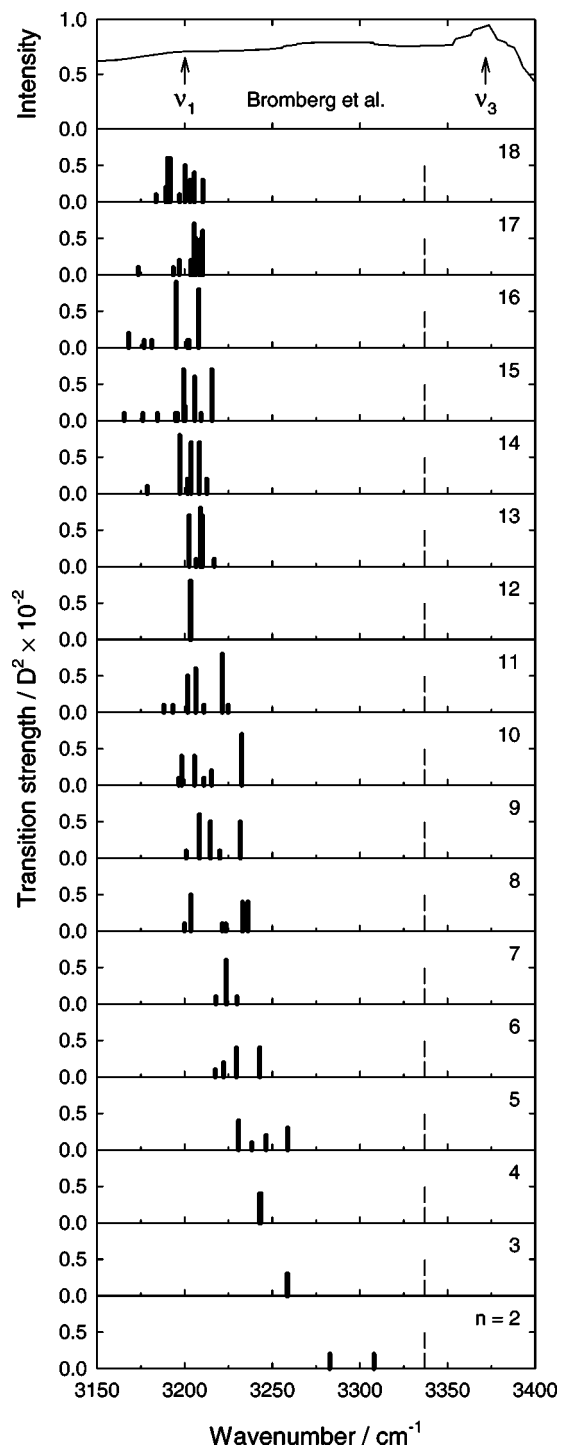


FIG. 3. The calculated IR spectrum for the symmetric N–H stretch mode (ν_1) for the ammonia clusters from $n=2$ –18 in D^2 . For a comparison the spectrum of the solid is shown.

The dimer spectrum (see Fig. 3) features two lines, at 3282.8 and 3308.0 cm^{-1} , the first one mainly due to the donor and the second one mostly due to the acceptor molecule. The spectra of the highly symmetric planar trimer and the nearly planar tetramer, with all molecular bonds in equivalent positions, are again very simple, being composed of a single doubly degenerate line. With an increasing cluster size, the number of calculated spectral lines increases correspondingly.

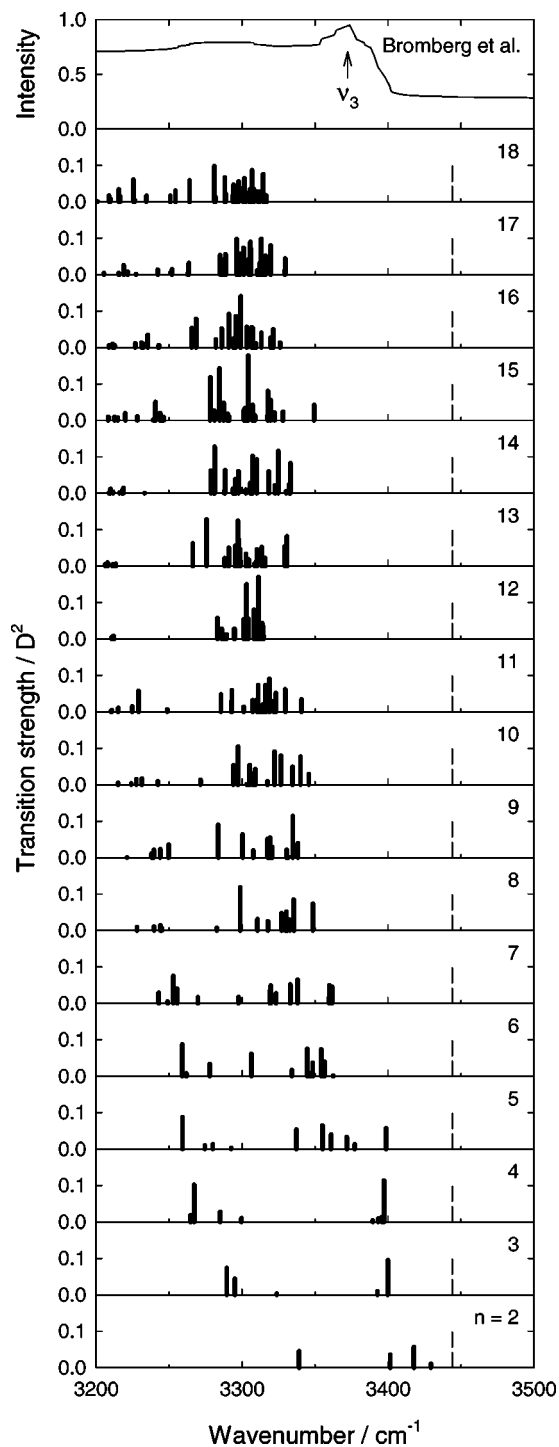


FIG. 4. The calculated IR spectrum for the asymmetric N–H stretch mode (ν_3) for the ammonia clusters from $n=2$ –18 in D^2 . For a comparison the spectrum of the solid is shown.

The dodecamer is again a special case due to its highly symmetrical shape, producing just a single spectral line at 3203.3 cm^{-1} . Another vibration (at 3184.85 cm^{-1}), primarily caused by the free N–H bonds, though permitted, is practically indistinguishable in the plot due to the very low associated transition dipole moment (approximately 30 times lower). The lower dipole moment for this transition as compared to the corresponding one from the spectrum for the ν_2 mode can be explained by the fact that in the case of the ν_1

symmetrical stretch the displacements of the free H atoms take place *along* the bonds, roughly preserving the equilibrium D_{6h} symmetry of the cluster. It is also noteworthy that for the very same reason the transition strengths for the ν_1 mode are, in general, by two orders of magnitude lower than those for the ν_2 mode. A nice feature of the spectra for the larger clusters is that the spectral lines seem to aggregate toward the solid state frequency at 3200 cm^{-1} .¹⁸

The complicated motion of the degenerate asymmetric N–H stretch mode leads also to a much more complicated pattern than those observed for the other two modes. The very symmetric trimer and tetramer exhibit at least two very well-separated groups of lines, which can be attributed to the motion of mainly free and mainly bound molecules, respectively. For the larger clusters more and more lines appear in the gap between these two groups. Even for the dodecamer, a bunch of lines is obtained, its spread being, however, the smallest of all investigated clusters. The shift of the larger ones does not change anymore, but overestimates the shift for the solid. Whether this is caused by the different structure of the clusters or appears as a consequence of the incorrect intramolecular force field cannot be decided without the direct comparison with measurements.

In conclusion we note that, in spite of some deficiencies in predicting the correct absolute shifts, the calculated spectra are in very good agreement with the experimental result that are available for the umbrella mode of small clusters. This gives us some confidence that also the predictions for the larger clusters are quite reliable.

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