Shape and Width of IR Absorption Lines of Ammonia Expanded in a Supersonic Jet

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Abstract. Line-width and -shape of absorption lines of the v_2 vibration of ammonia were measured for a series of transitions starting from vibrational groundstate levels with a different rotational energy. An increase in linewidth was found for larger rotational energies of the initial states. This effect has been attributed to the spatial rotational non-equilibrium in the supersonic jet expansion.

For expansions of NH_3 seeded in He and Ar a very pronounced dip in the absorption profile has been observed, due to the formation of clusters.

In the last decade the supersonic free jet technique has become an important tool in spectroscopy. A substantial rotational and vibrational cooling and a high optical density characterize the free jet expansion. Jets have been used in laser-induced fluorescence [1–3], molecular beam resonance [4,5], pulsed Fourier-transform microwave spectroscopy [6,7], Raman scattering [8] and more recently, in high-resolution IR absorption studies [9–11]. Several studies have been devoted to the characterization of the supersonic free jet [12–21]. In most of these works the effect of the source conditions (stagnation pressure p_0, nozzle diameter D and source temperature T_0) on the expansion was investigated.

Usually the evolution of the expansion is characterized by the behaviour of local parameters, such as the density ϱ, rotational temperature T_{rot}, vibrational temperature T_{vib}, translational temperature T_{trans}, as function of the distance from the nozzle, X. The definition of rotational and vibrational temperatures assumes that the population of rotational and vibrational levels can be approximately described by a Boltzmann distribution. Many experiments up to now showed that this assumption is valid for the rotational

distribution, although some exceptions were found [22,24]. The definition of a vibrational temperature for expansions of poly-atomic molecules in a jet does not seem to be justified, since vibrational non-equilibrium has been observed in several cases [25–26].

The most interesting part of a free jet expansion is the region very close to the nozzle, where the relaxation processes occur. In a distance of a few nozzle diameters collisional energy transfer carries away rotational and vibrational energy and sometimes clusters are formed. Especially spectroscopic methods can increase our insight in these very important processes. Recently Barth and Huisken [27] combined the CARS technique with a more conventional mass spectrometer to study NH_3 expansions. In the present work line-width and -shape of absorption lines of the v_2 vibration of NH_3 were investigated for various source conditions and for different laser-nozzle distances. Our scope was to obtain qualitative information about the dependence of the rotational temperature on the distance from the jet-axis. For all experimental conditions, the central piece of the jet (i.e., on-axis) was found to be rotationally colder than the outer regions. This result is partly in disagreement with calculations of Gaveau et al. [15,28], but agrees with work of Murphy and Miller [29].

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The second part of this contribution deals with the presence of dips in the absorption lines of a free jet expansion. These dips have been attributed to cluster formation on the jet-axis [13], but a systematic investigation of this phenomenon has never been performed. Taking the work of Barth and Huisken [27] as a starting point, we demonstrated that cluster formation is indeed responsable for very pronounced dips in the NH_3 absorption lines.

1. Experimental Conditions

The experimental apparatus has been described in detail before [25] and will be discussed only briefly. A diode-laser spectrometer (Laser Analytics model SP 5000) with diodes supplied by the same firm was used in combination with a pulsed molecular jet (Lasertechnics LPV). The pressure in the vacuum chamber was kept at 4×10^{-6} mbar without beam and increased to 1.3×10^{-4} mbar, under typical operating conditions. The pulsed source, with a nozzle opening of 300 µm diameter, could be moved up and down with respect to the laser radiation, allowing a variation in the laser nozzle distance from 1 up to 20 mm. The absorption of the molecular jet was enhanced by a multipass set-up, which directed the laser beam about 20 times through the expansion in a plane perpendicular to the propagation of the jet (Fig. 1). The laser radiation, using the multiple reflection set-up, was illuminating a section of 1 mm height and about 7 mm width under the nozzle.

A two-channel Boxcar integrator (PAR model 162) was synchronized to the pulsed source. The absorption by the molecules in the jet was detected differentially; channel A of the Boxcar registrated the laser power 500 µs before the jet pulse, channel B coincided with the central part of the pulse (see also Fig. 2). Both
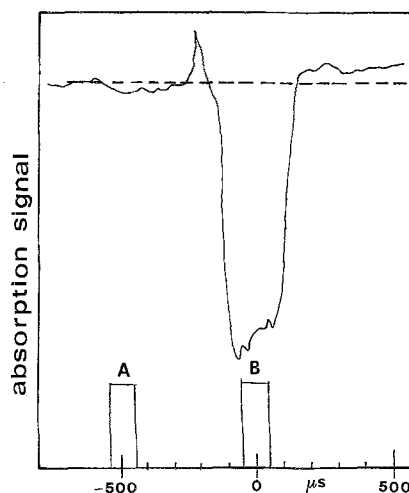
Fig. 2. The positions of the two Boxcar gates A and B with respect to the absorption signal are shown. We observed that for our pulsed valve, the plunger sometimes rebounds after closing the nozzle, and produces a second pulse. In order to avoid registration of this second pulse the zero-signal recorded in channel A, is timed before the jet-pulse

Boxcar gates had 100 µs gates. The absorption by the jet (measured as the difference of channels A and B) was typically between 10 and 30% of the laser power.

In order to measure the laser frequency jitter and the effects of static background gas absorption, we increased the pressure in the vacuum chamber for the jet expansion, by introducing ammonia through a needle valve in the system. The absorption was measured for some transitions, which are also present in the jet spectra. For a background pressure of 1.3×10^{-4} mbar the strongest absorption observed was about 1%. The linewidth was 95 ± 5 MHz, which implies a laser frequency jitter of 30–50 MHz, assuming a Doppler width of 86 MHz.
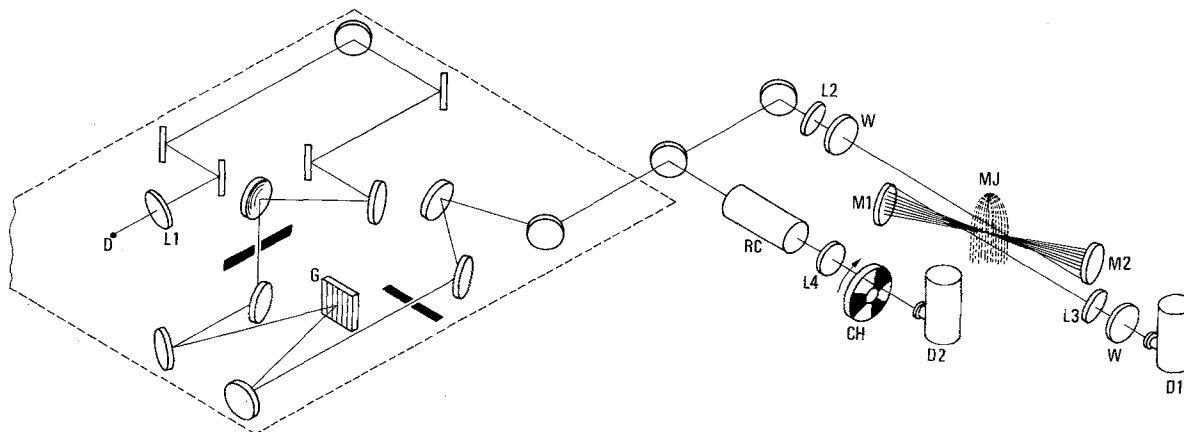
Fig. 1. Experimental set-up. (D: diode, G: grating, W: window, D1, D2: HgCdTe detectors, L1–L4: lenses, RC: reference-cell, CH: mechanical chopper, MJ: molecular jet, M1 and M2 are the mirrors of the multipass system)

2. Results

2.1. Temporal Behaviour of Absorption Signal

In the present work a pulsed source has been used instead of a continuous one, in order to avoid the high back ground pressures, which have been encountered in other experiments [13, 21]. Using 500 μs pulses with a repetition rate of 40 Hz, and a stagnation pressure of 1 bar, an average background pressure of 4×10^{-5} mbar was measured. During the operation of the pulsed valve the density of the background gas is varying in time and in space. The *average* pressure has been measured by a ionization gauge mounted at a distance of about 20 cm from the jet. For a static ammonia pressure of 4×10^{-5} mbar in the vacuum system (with the pulsed valve switched off) the absorption was less than 0.5%, which can be neglected with respect to the 10–30% absorption of the jet. The temporal behaviour of our source has been measured by a fast ionization gauge, mounted about 5 cm down stream of the nozzle. A nearly square pulse, slightly rounded at head and tail, could be produced for pulse durations from 100 μs up to 1 ms. In first approximation one expects an absorption signal, which is proportional to the molecular density, with a very similar shape. Experimental [14] and theoretical [30] studies, however, demonstrated that head and tail of a jet-pulse are not comparable with an expansion produced by a continuous source. When the source opens, the first molecules coming out form a kind of boundary layer, a barrel shock, which separates the real jet from the background gas, and when the source closes, the boundary layer closes in from behind. The molecules in this boundary layer have an almost random velocity, and are therefore "hot" in comparison to those of the cold jet.

Measurements were performed for expansions of pure NH_3, and NH_3 seeded in Ar and He, with stagnation pressures between 1 and 5 bar, while the laser frequency was fixed at the $aQ(1, 1)$ and $aQ(2, 2)$ transitions. A nearly square pulse, slightly rounded at the edges, was observed for the pure ammonia jet; the seeded expansions showed strong absorption at head and tail and a weaker central plateau in between. The duration of both head and tail of the pulse was 40 μs, in agreement with the results of [14] for the expansion of He by a pulsed source. The intensity of the absorption signal of the central part of the pulse diminished for increasing stagnation pressure. These observations can be explained by the formation of clusters, which reduces the density of free ammonia molecules, and therefore the absorption signal. The $aQ(1, 1)$ and $aQ(2, 2)$ transitions start from levels with the lowest rotational energy. The population of these levels is high for the cold central part of the pulse and lower for
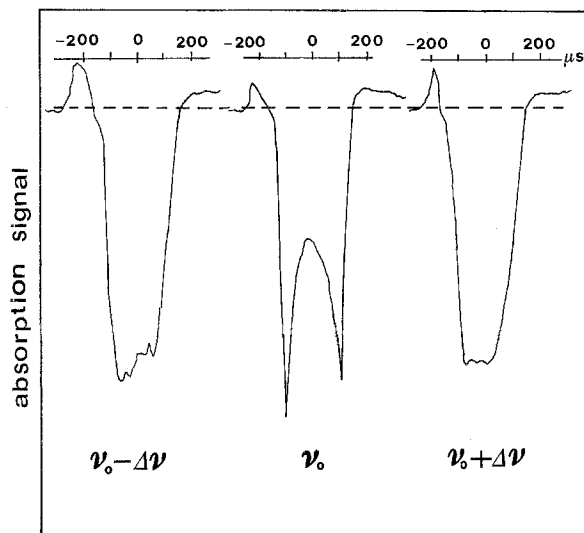

Fig. 3. The temporal behaviour of absorption signals at different laser frequencies. Experimental conditions: 5% NH_3 in He, stagnation pressure is 3 bar. Laser-nozzle distance 5 mm. v_0 corresponds with the $aQ(1, 1)$ transition at 931.628 cm^{-1} Δv is a detuning of the laser of about 35 MHz with respect to v_0

the hotter head and tail. This effect is apparently dominant for the pure ammonia jets, whereas the cluster formation dominates the seeded expansions.

Up to this point the laser frequency was kept at resonance with the two mentioned transitions, probing the molecules on-axis, i.e. with nearly zero Doppler shift. In Fig. 3 three absorption pulses are shown, measured for three different laser frequencies $v_0 - \Delta v$, v_0, and $v_0 + \Delta v$ (v_0 is on resonance, Δv is a detuning of the laser of about 35 MHz), for an expansion of 5% NH_3 in He, stagnation pressure 3 bar. The two pulses for $v_0 \pm \Delta v$ do not exhibit the particular head and tail spikes, which are characteristic for the resonant frequency v_0. This can be explained when one considers that cluster formation occurs mainly on-axis.

2.2. Width of Absorption Lines in a Jet

The line-width for absorption by a gas in thermal equilibrium is determined by pressure broadening and Doppler broadening. The Doppler width, caused by the randomly oriented velocity of the molecules, can be expressed as

$$\Gamma_{\text{Doppler}} = 7.16 \times 10^{-7} v_0 (T/M)^{1/2}, \tag{1}$$

where T is the temperature of the gas and M the molecular weight in a.m.u.

In a supersonic expansion the velocity is not randomly oriented, but directed away from the nozzle. Molecules which have a velocity component $v_{\parallel}$

(anti)parallel to the propagation of the laser beam, absorb at a slightly (Doppler) shifted frequency $v_0 \pm \Delta v_{Doppler}$. This Doppler shift $\Delta v_{Doppler}$ is given by

$$\Delta v_{Doppler} = v_0 v_{\parallel}/c. \tag{2}$$

As a consequence the absorption lineshape in a supersonic jet expansion is mainly determined by the divergency of the jet in the section probed by the laser. When the laser crosses the jet perpendicularly, the molecules on the jet-axis have no velocity component parallel to the laser, and absorb at a non-Doppler shifted frequency. A Doppler shift which is proportional to the distance from the axis, is introduced however for molecules which are not on the jet axis. The number density in the jet has its maximum on the axis, corresponding to a maximum in the absorption line for zero Doppler shift. The maximum Doppler shift occurs for molecules which have almost reached the barrel shock which separates the jet from the background gas. The absorption profile therefore has a broad maximum and falls off very rapidly at the maximum Doppler shift. This behaviour was confirmed by the line-shape observed in our experiments.

If the interaction between molecules and laser photons occurs at laser-nozzle distances X, which are much larger than the nozzle diameter D (typically $X/D > 10$) two assumptions are valid. First of all the molecules do not collide anymore, which implies that the so-called pressure broadening disappears. Secondly, the direction of the molecules is correlated with their position in the expansion, in such a way that molecules further away from the beam axis have a larger velocity component perpendicular to this axis.

In general, for a gas in thermal equilibrium at room temperature, the Doppler width depends only on the mass M of the molecule ($\Gamma_{Doppler} \lesssim 50$ MHz for $M \geq 50$ at 1000 cm^{-1}) and is smaller than the line width in a jet (typically ≥ 70 MHz), which is mainly determined by geometrical factors. For jet expansions of ammonia the observed line widths always exceeded the Doppler width at room-temperature [9,13,21].

2.3. Spatial Dependence of the Rotational Temperature

If the rotational temperature depends only on the nozzle-laser distance X, but is constant in every plane perpendicular to the jet axis (note that in our experiment the laser radiation probes the molecules in such a plane) one expects that line-width and line-shape do not change for different ro-vibrational transitions, neglecting back ground gas absorption and cluster formation. A variation of rotational temperature in the plane probed by the laser induces differences in

rotational population along the laser path, which gives rise to different line widths, depending on the rotational level involved.

In order to reduce cluster formation and to obtain a reasonable population of many rotational states, pure ammonia was expanded at a stagnation pressure of 1 bar. Line-width (FWHM) and rotational ground-state energies of a series of Q-branch lines are listed in Table 1. This piece of the Q-branch could be covered by one single laser mode, for which we can assume that the laser frequency fluctuation is constant for the whole mode. A significant increase in line-width is observed for transitions with higher rotational energies. A rotational temperature of 80–90 K could be calculated from the relative intensities of the observed absorption signals. The $aQ(7,5)$ transition, however was much stronger than expected from a Boltzmann distribution at 90 K and showed a small dip at the center frequency. Note that the line-width of the $aQ(1,1)$ line is smaller than the Doppler width at room-temperature. It is also important to notice that the observed broadening for high (J, K) transitions can not be caused by back ground gas absorption, since the Doppler width at room-temperature is always less than the observed linewidths. The general trend of increasing line-width for rotational states with a higher energy, was also observed for other stagnation pressures and for different distances X from the nozzle ($X/D = 3$ to 30). Our explanation for these observations is that the rotational temperature is lower on the beam axis and increases with the distance from the axis. If the rotational temperature has a minimum on axis, the population of high lying rotational levels will be lower on axis than close to the barrel shock. In a very extreme case, for the $(7,5)$ level with almost 500 cm^{-1} rotational energy the very small hole at the center

Table 1. The line width of 7 absorption lines, having different ground state energies $E(J,K)$, all observed within the same laser mode is reported. The values reported in the column Δv_{meas} have been obtained by taking the average of at least ten measurements. Assuming a laser frequency instability of 40 MHz a corrected line-width Δv_{cor} has been calculated. The experimental conditions were: 1 bar of NH_3, the nozzle laser distance was 5 mm

(J,K)	Frequency	$E(J,K)$	Δv_{meas}	Δv_{cor}
	[cm^{-1}]		[MHz]	
$aQ(1,1)$	931.628	16	94(3)	84(3)
$aQ(2,2)$	931.333	45	97(3)	88(3)
$aQ(2,1)$	932.136	56	108(4)	100(4)
$aQ(3,2)$	932.094	104	114(6)	107(6)
$aQ(4,3)$	931.774	165	111(6)	104(6)
$aQ(5,4)$	931.178	239	124(6)	117(6)
$aQ(7,5)$	932.011	464	131(6)	125(6)

frequency indicates that the number density for this particular state is smaller on axis than slightly off axis.

It is interesting to compare our experimental results to calculations of Gaveau et al. [15] for expansions of CO in He. They simulated the line-shape of absorption lines for a rotational temperature which decreases for larger distances from the jet-axis. In recent experiments [28] this hypothesis is confirmed for distances rather close to the nozzle $(X/D < 10)$; for $X/D > 10$, however, their results are similar to ours. Our results are also in agreement with those of Murphy and Miller [29], who measured the rotational temperature for different distances from the jet-axis in a H_2 expansion.

A tentative explanation for a lower rotational temperature on the jet-axis is that molecules which are on the jet-axis where the number density is highest undergo more collisions than molecules further away from the axis. Since the rotational relaxation is proportional to the number of collisions one expects colder molecules on axis than off axis.

It is well known that NH_3 clusters are easily formed in a supersonic expansion. Recently Barth and Huisken [27] employed the CARS technique in the 3 µm range to investigate NH_3 beams. They observed spectral features due to ammonia complexes for expansions of 5% NH_3 in He, Ne, and Ar. These cluster features were practically absent in expansions of pure ammonia; in the seeded beams their intensity increased drastically for larger distances from the nozzle and for larger stagnation pressures. In the same work a mass spectrometer was used to analyze the composition of the pulsed beams. In pure NH_3 beams the monomer was found to be the most abundant species; in the seeded beams however, only a very small fraction of the ammonia molecules was *not* involved in molecular complexes.

Cluster formation is occurring mainly on the jet-axis, where the collision probability is higher. As a consequence the density of free molecules on axis decreases, which affects the profile of the absorption lines. Mizugai et al. [9] observed a "pillar-shaped form, frequently showing a shallow dip on the top", Veeken and Reuss [13] attributed the "double peak structure" in their ammonia spectra to the presence of clusters. Baldacchini et al. [31, 32] confirmed the same "double peak structure" and line-shape for ammonia and other molecules.

In our measurements for a pure ammonia expansion no holes or dips, due to cluster formation were observed. Using gas mixtures of 5% NH_3 in He or Ar, the rotational temperature dropped to about 15 K and very pronounced holes appeared in the absorption lines. These holes disappeared when the nozzle-laser distance was very small (less than 1 mm) and increased
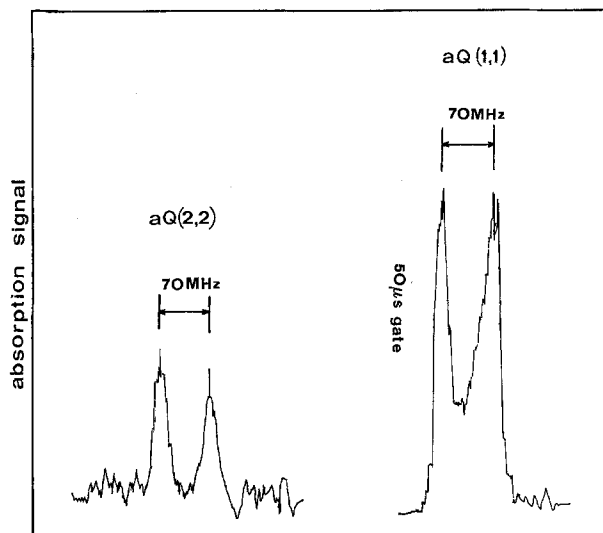

Fig. 4. The absorption signals for the $aQ(1, 1)$ and $aQ(2, 2)$ transitions show very pronounced dips at the center frequency. Experimental conditions: 5% NH_3 in He, stagnation pressure is 5 bar. Laser-nozzle distance 8 mm. Boxcar gates were 50 µs. [Note that in reality the $aQ(2, 2)$ signal is much smaller than the $aQ(1, 1)$ signal]

with larger distances from the nozzle and also for higher stagnation pressures. This behaviour has been observed for the $aQ(1, 1)$, $aQ(2, 2)$, $sQ(1, 1)$, and $sQ(2, 2)$ transitions, other levels are hardly populated for a rotational temperature of 15 K, and is in perfect agreement with the results of Barth and Huisken [27]. As can be seen in Fig. 4, the cluster formation can eliminate almost completely the NH_3 molecules on the jet axis. For an expansion of 5% NH_3 in He, stagnation pressure 5 bar at 8 mm from the nozzle, the dip was so pronounced for the $aQ(2, 2)$ line that at the center frequency the absorption was almost zero. For the $aQ(1, 1)$ this was still 35% of the maximum absorption at a Doppler shift of ± 35 MHz.

Apparently more than 65% of the molecules on axis are involved in molecular complexes which absorb at different frequencies.

3. Conclusions

The expansion of NH_3 in a pulsed jet has been studied by infrared absorption technique. Cluster formation, preferentially on the jet-axis, reduces the on-axis density of the free molecules considerably and causes a very pronounced dip in the ammonia absorption lines. For very mild expansion conditions (stagnation pressure less than 1 bar, pure NH_3) this cluster formation can be greatly reduced, allowing practically clusterfree measurements. Absorption by the back-ground gas could be neglected due to the very low pressure in the vacuum chamber $(4 \times 10^{-5}$ mbar).

It has been demonstrated that the width of the absorption lines increases significantly for transitions with a higher rotational energy. This observation can be explained when one assumes that the rotational temperature increases with the distance from the jet-axis. This assumption seems to be justified if rotational relaxation only depends on the number of collisions of a molecule in the jet expansion.

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