Spectroscopic characterization of N$_2$O aggregates: from clusters to the particulate state

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Abstract

Collisional cooling is used to generate N$_2$O particles with radii ranging from the subnanometer to the submicrometer region. The vibrational dynamics of the aggregates is studied by Fourier transform infrared spectroscopy. In the region of the stretching fundamentals and combination bands, the infrared spectra of the particles exhibit characteristic size-dependent features. For the very small particles, the results obtained from collisional cooling are compared for the first time with corresponding results from supersonic jet expansions. It turns out that with both methods very similar clusters are generated. A pronounced temperature dependence of a combination band maximum in the collisional cooling cell spectra is found. This correlation is exploited to estimate cluster temperatures in supersonic jet spectra.

Keywords: N$_2$O particles; Collisional cooling; Supersonic jet expansion; Fourier transform infrared spectroscopy

1. Introduction

A detailed understanding of the transition from isolated molecules to bulk material requires the characterization of molecular aggregates over a broad size range. The preparation of particles with various sizes, however, is one of the major experimental difficulties in the investigation of particulate matter. To generate large molecular aggregates, either expansion techniques [1–13] or collisional cooling cells [14–23] are typically used. Free supersonic jet expansions are particularly suitable to generate particles in the subnanometer to nanometer region. Aggregates in this size range are often called clusters. The particles formed in collisional cooling cells have much larger sizes, typically tens of nanometers. The gap for particle sizes between a few nanometers and tens of nanometers can be and has been partially bridged by the use of constrained jet expansions [2,13,24–26].

The present investigation demonstrates that this intermediate size gap can be filled in an even more general way by extending the collisional cooling technique down to liquid-helium temperatures [22]. Classical nucleation theory [2] teaches us...
that the final particle size can be controlled in a much wider range by a change in temperature than by a change in concentration. The latter affects the final particle volume more or less linearly, whereas a change in the temperature by a few percent can change the number of condensation nuclei (and thus the inverse volume of the fully grown particles) by orders of magnitude. As model systems, we use weakly bound aggregates of N₂O which are characterized by their Fourier transform infrared spectra. Previous studies in supersonic jet expansions [1,4,11,12] have demonstrated that the infrared spectra of N₂O clusters exhibit prominent size-dependent features in the subnanometer to nanometer region. Section 3.1 for the first time compares such jet spectra with corresponding infrared spectra recorded in a collisional cooling cell near 4 K. In addition, the spectral evolution observed with increasing particle size up to tens of nanometers is discussed. In Section 3.2, mean particle radii are estimated from the size-dependent features in the infrared spectra.

2. Experiment

The N₂O aggregates were generated in a collisional cooling cell. A detailed description of the cell and of the experimental setup is given in Refs. [22,23]. In a collisional cooling cell, the particles are formed by injecting a molecular gas into a cold bath gas. The supersaturation that builds up in this way leads to the particle formation. The size of the particles generated depends on the supersaturation. A higher supersaturation leads to the formation of more condensation nuclei and, for a fixed amount of sample gas, to correspondingly smaller aggregates. In the present experiments, the supersaturation was increased by reducing the bath gas temperature. To cover the maximum temperature range, the cell was cooled with liquid-nitrogen for temperatures down to 78 K and with liquid-helium for temperatures between 78 and 4 K. Helium (Messer, 99.999%) was used as bath gas and mixtures of 1–10% N₂O in He, in Ar or in He/Ar-mixtures at backing pressures between 0.5–2 bar were used [27].

The infrared spectra were recorded with a Bruker IFS 66v/S or a Nicolet Magna-550 Fourier transform spectrometer equipped with a Globar light source, a KBr beam splitter and an InSb or HgCdTe detector. The spectral resolution was set between 0.1 and 1 cm⁻¹. The collisional cooling cell was equipped with White optics. For the present experiments, the optical path length amounted to about 16 m.

3. Results

3.1. Size-dependent particle spectra

In a previous study [23], we have reported how N₂O particles with radii down to several ten nanometers can be generated in a collisional cooling cell at bath gas temperatures around 78 K. The generation of still smaller particles by reducing the amount of the sample gas introduced into the cell, however, was found to be limited at 78 K for two reasons. The total absorbance and correspondingly the signal to noise ratio decreases significantly. In addition, problems with small impurities such as water become more serious. As described in Section 2, another possibility to generate smaller particles is to reduce the temperature of the bath gas in the cooling cell [22,23]. In the following, the suitability of this method to
generate particles with different sizes down to the subnanometer region is demonstrated.

Fig. 1a, Fig. 2a and b show a series of N$_2$O particle spectra recorded at bath gas temperatures between 78 and 4.5 K in the region of the $v_1$ (predominantly N–O stretching), the $v_3$ (mostly N–N stretching), and the $v_1 + v_3$ combination band, respectively. For all three bands, a similar evolution with decreasing temperature can be observed. The vibrational bands broaden, mainly toward lower frequencies, and in addition the band structures change. In the case of the $v_1$ and the $v_1 + v_3$ vibration, the bands are partitioned into two main peaks labeled C and S in Figs. 1 and 2b. The occurrence of the S-bands is also found for the $v_1 + 2v_2$, $2v_1$, and the $v_2 + v_3$ bands [28]. For the $v_3$ band shown in Fig. 2a, one cannot distinguish unambiguously between a C- and a S-band. Here, the two bands overlap. The reason lies in the large transition dipole moment of this vibrational tran-
position which causes relatively broad bands through exciton coupling [29–31]. The C-bands, or high-frequency bands, clearly dominate the spectra at high temperatures. At lower temperatures, however, the contribution from the S-bands, or low-frequency bands, becomes increasingly prominent.

Another noteworthy effect is observed most prominently in Fig. 2b. The position of the C-band maximum of the \( v_1 + v_3 \) band shows a systematic shift towards smaller wavenumbers with temperature. This is confirmed by numerous measurements over a wide temperature and concentration range [28]. The corresponding data are summarized in Fig. 3. While no significant concentration or size-dependence could be detected, the temperature dependence is very systematic. This is demonstrated by the full line in Fig. 3. It corresponds to a fit of a polynomial to the experimental data points. The best fit is:
\[ \tilde{\nu}_{v_1+v_3}(T)/\text{cm}^{-1} = 3510.06(45) - 0.012(18)(T/\text{K}) - 2.2(15) \times 10^{-4}(T/\text{K})^2 \]  

(1)

\[ \tilde{\nu}_{v_1+v_3} \] is the position of the combination band maximum and \( T \) is the temperature. The standard deviations are given in parentheses in terms of the last significant digits. This correlation will be exploited below (see also Table 1) to estimate cluster temperatures in supersonic jet spectra. We will not attempt to discuss the exact origin of this thermal effect, which has also been observed in related systems [5].

At this point, it is not clear what causes the observed temperature-dependent changes in the spectra of the \( \text{N}_2\text{O} \) aggregates. As outlined above and already conjectured in our previous study [23], the size of the \( \text{N}_2\text{O} \) particles generated should decrease with decreasing temperature in the collisional cooling cell. With the present systematic investigation, we can now prove this hypothesis and in particular that the observed spectral changes can be traced back mainly to different particle sizes.

### 3.1.1. Investigations with different sample gas concentrations

A first clear hint comes from corresponding investigations with different sample gas concentrations. At a fixed bath gas temperature in the collisional cooling cell, a decrease of the sample gas concentration leads to the formation of smaller particles. We have systematically investigated the infrared spectra recorded for gas mixtures containing between 10–1000 ppm \( \text{N}_2\text{O} \) (Section 2). As an example, Fig. 1a and b shows a comparison between temperature-dependent spectra for a 1000 ppm and for a 100 ppm mixture, respectively. The spectral changes observed for the 1000 ppm mixture between 22 and 4.5 K appear at much higher temperatures for the 100 ppm mixture. The intensity ratio between the \( C \)- and the \( S \)-band observed in Fig. 1a at 22 K is reached in Fig. 1b already at 31 K. Similarly, the intensity ratio between the \( C \)- and the \( S \)-band observed in Fig. 1a at 4.5 is reached in Fig. 1b at about 22 K. At a fixed bath gas temperature, however, we know that the particles formed from the 100 ppm mixture must be smaller than those generated from the 1000 ppm mixture. The 22 K spectrum in Fig. 1b arises from smaller particles than the 22 K spectrum in Fig. 1a. Combining these arguments leads us to the conclusion that the spectral

### Table 1

<table>
<thead>
<tr>
<th>Jet measurement</th>
<th>( T_{\text{cluster}}/\text{K} ) (Eq. (1))</th>
<th>( T_{\text{rot}}/\text{K} ) (see Ref. [27])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas mixture</td>
<td>( \tilde{\nu}_{v_1+v_3}/\text{cm}^{-1} ) (Eq. (1))</td>
<td>( T_{\text{rot}}/\text{K} )</td>
</tr>
<tr>
<td>50% N(_2\text{O})/He</td>
<td>3505.3</td>
<td>125(7)</td>
</tr>
<tr>
<td>40% N(_2\text{O})/He</td>
<td>3505.4</td>
<td>123(7)</td>
</tr>
<tr>
<td>30% N(_2\text{O})/He</td>
<td>3505.6</td>
<td>120(7)</td>
</tr>
<tr>
<td>20% N(_2\text{O})/He</td>
<td>3505.8</td>
<td>117(7)</td>
</tr>
<tr>
<td>10% N(_2\text{O})/He</td>
<td>3506.6</td>
<td>103(8)</td>
</tr>
<tr>
<td>7.5% N(_2\text{O})/He</td>
<td>3507.2</td>
<td>92(9)</td>
</tr>
<tr>
<td>5% N(_2\text{O})/He</td>
<td>3508.6</td>
<td>60(12)</td>
</tr>
<tr>
<td>4% N(_2\text{O})/He</td>
<td>3509.4</td>
<td>35(18)</td>
</tr>
<tr>
<td>3% N(_2\text{O})/Ar</td>
<td>3509.1</td>
<td>45(15)</td>
</tr>
</tbody>
</table>

**First column:** Sample gas mixture used for the jet measurement. **Second column:** Position of the \( v_1+v_3 \) band maximum in the jet spectra. **Third column:** Estimated cluster temperature \( T_{\text{cluster}} \) according to Eq. (1) (see also Fig. 3). An accuracy of the band position of ±0.4 cm\(^{-1} \) leads to the uncertainties of the temperature given in parentheses. **Fourth column:** Rotational temperature of residual gas phase in the jet expansion \( T_{\text{rot}} \) from Ref. [27].

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Fig. 3. Positions of the C-band maxima (\( \tilde{\nu}_{v_1+v_3} \)) of the \( v_1+v_3 \) band as a function of the bath gas temperature in the collisional cooling cell. The sample gas concentrations for the experimental data points are specified in the figure and in Section 2. The full line represents the fit with Eq. (1).
changes observed between 22 and 4.5 K in Fig. 1a (or between 31 and 22 K in Fig. 1b) arise indeed from a decrease in the size of the particles investigated. A decrease in the bath gas temperature apparently leads to a decrease in the particle size. We note at this point that the same behavior as documented here for the $v_1$ band is observed for all other vibrational bands investigated.

3.1.2. Comparison with spectra from free jet expansions

The above observations imply that the smallest particles should be formed at the lowest bath gas temperatures and for sample gas concentrations as small as possible. In the example shown here, this holds for the spectra recorded below 22 K in Fig. 1b. The general trend of an increase and finally a dominance of the S-band is clearly followed here. The same behavior has been reported earlier for the spectra of N$_2$O clusters generated in supersonic jet expansions [1,4,12].

The spectra recorded in the jet at moderate sample gas concentrations (or moderate backing pressures) agree with the spectra recorded in the collisional cooling cell at 4.5 K in Fig. 1b. These spectra are clearly dominated by the S-bands. At higher sample gas concentrations (or higher backing pressures), the jet spectra also show the characteristic C-band blue-shifted relative to the S-band in agreement with the spectra from collisional cooling. A comparison for this case between the two methods is shown in Figs. 4 and 5 for the $v_3$ band, the $v_1$ band, and the corresponding combination band $v_1 + v_3$ (from top to bottom). The jet spectra [12,27] are depicted in the upper traces of each panel. The lower traces contain the spectra measured in the collisional cooling cell. The sharp features in the jet spectra arise from residual gas phase and not from the particles. This effect is due to the higher temperature in the jet compared with the cooling cell as discussed below. Fig. 4 compares the 4.5 K 1000 ppm spectra of Fig. 1a, Fig. 2a and b with a jet spectrum recorded for a sample consisting of 2% N$_2$O in Ar. The agreement between the two methods is astonishingly good. Both, the coarse band structures and the overall band widths are well reproduced.

Above all, the intensity ratio between the C- and S-bands agree nicely. The same holds for the comparison between the 11 K 1000 ppm spectrum measured in the collisional cooling cell and the 10% N$_2$O/He spectrum recorded in the jet. The corresponding spectra in the region of the $v_3$, the $v_1$, and the $v_1 + v_3$ band are depicted in Fig. 5. These spectra show significantly less prominent S-bands than those depicted in Fig. 4. Detailed simulations have demonstrated previously [1,12] that the jet spectra in Fig. 4 arise from smaller particles than the jet spectra depicted in Fig. 5. Thus, from the above comparison we conclude...
that the same has to be true for the collisional cooling spectra of Figs. 4 and 5. This again confirms that smaller particles are generated at lower cell temperatures. According to the simulations already mentioned [1,12], the S-bands arise from absorption of the molecules in the surface layer. In contrast, the C-bands have been found to be dominated by absorptions in the particle core. Consequently, the S-bands are more prominent in the spectra of the smaller particles. At a microscopic level, the partition in C- and S-bands can be understood by the surface or core character of the normal modes [12].

Figs. 4 and 5 nicely show that at least in a certain size range nearly identical clusters can be generated with two very different techniques. Above all, the comparison of the jet spectra with the collisional cooling spectra clearly demonstrates that with the collisional cooling technique the particle size can be varied in a wide range via the bath gas temperature. Collisional cooling is a comparatively simple method. In contrast to free jet methods, a wide size range can be covered here using the same experimental equipment. This is a prerequisite for systematic investigations of size-dependent effects in particulate systems.

3.1.3. Other effects

Although the overall agreement between the results obtained from collisional cooling and from jet expansions is very good, there remain several differences to be discussed. As already mentioned, the sharp features in the jet spectra arise from residual gas phase monomers. They are due to the higher temperature in the jet compared with the cooling cell. The jet temperature is more difficult to obtain due to the lack of thermal equilibrium in the jet. One indirect source is the rotational temperature of the monomers [27] in the expansion, which may however differ from the cluster temperature. An independent estimate is based on the empirical correlation between the \(\nu_1 + \nu_3\) cluster band maximum and the collisional cooling cell temperature shown in Fig. 3. Both estimates are tabulated in Table 1 for a selection of jet spectra. Within statistical and systematic errors, the two estimates are seen to agree quite nicely. For the jet spectra shown in Fig. 4, we thus estimate a cluster temperature of about 50 K. For those shown in Fig. 5, a temperature of 100 K is found to be realistic. This is consistent with the higher fraction of gas phase in Fig. 5 compared with Fig. 4 and the results given in Ref. [12]. Above all, these values illustrate the huge difference in the temperature between the two generation methods. In Fig. 4, a temperature of 50 K in the jet has to be compared with a temperature of 4.5 K in the cooling cell. The temperatures of 100 and 11 K, respectively, determined for the spectra in Fig. 5 indicate an even larger difference, which is immediately evident from the large shift in the C-band maximum of the \(\nu_1 + \nu_3\) band.

Not surprisingly, the temperature is also responsible for further small differences between the jet
spectra and the collisional cooling spectra. The first difference concerns the slightly more prominent band structure in the jet spectra. It is most obvious in the case of the $v_3$ band. We interpret the loss of structural details in the collisional cooling spectra as a hint to a more pronounced amorphous character of the particles formed in the cooling cell compared with those formed in the jet. In the latter case, the heat of condensation and evaporative mechanisms may slow down the intrinsically high cooling rate. Indeed, the particles have been found to be crystal-like [8,12]. This interpretation is consistent with the observations of Ovchinnikov and Wight [32] that the spectra of thin layers with more amorphous character show broader and less structured bands than the spectra of crystalline layers.

3.2. Estimation of the particle size

The size-dependence of the C- and S-bands allows us to estimate the particle sizes from the experimental infrared spectra. The determination of the particle sizes is based on the following assumptions: (1) Molecules in the interior of the particles absorb exclusively in the region of the C-band. Molecules in the surface layer only contribute to the S-bands. While shown to be somewhat oversimplified [12], this assumption is adequate for the present purpose. (2) The particles are spheres with a total radius $r$ and with a surface layer of thickness $r_s = 0.566$ nm. The thickness of the surface layer corresponds to the length of the cubic unit cell of crystalline N$_2$O [33]. In addition, we assume a constant density of the molecules throughout the whole particle. (3) Only a mean particle radius is determined. The existence of a size distribution is neglected. (4) The molecular oscillator strength is assumed to be independent on the position. Based on these assumptions, the mean particle radius $r$ can be determined from the ratio of the integrated absorbance $A_S$ of the S-band and the integrated absorbance $A_C$ of the C-band according to the following equation.

$$\frac{A_S}{A_S + A_C} = 1 - \left(\frac{r - r_s}{r}\right)^3$$

The values for $A_S$ and $A_C$ are determined from the experimental infrared spectra by a simple profile analysis of the absorption bands. This is illustrated by the dashed and dotted lines in Fig. 6. For the profile analysis different Gaussian curves were adjusted. For the spectra of the $v_1$ band recorded above 50 K, we used two Gaussian curves for the C-bands and one Gaussian curve for the S-bands. At lower temperatures and for the $v_1 + v_3$ transition, each band is represented by a single Gaussian curve. A more general method for particle size characterization based on monolayer coating has been used in Ref. [21].

The results obtained from this simple model for the 1000 ppm and the 100 ppm spectra shown in Figs. 1 and 2b are summarized in Table 2 for the $v_1$ band and the $v_1 + v_3$ band. The agreement for the two bands is astonishingly good given the simplicity of the model. While absolute radii may be affected more or less by the model assumptions, temperature trends should be robust. For the spectra recorded at 78 and 80 K (but for different sample gas concentrations), the simple model used here gives only a rough estimate of the particle radius of about 23 and about 12 nm, respectively.
In these two cases, the S-bands are very weak. Thus, the absorptions of residual gas phase monomers and of isotopomers in the region of the S-band lead to comparably high uncertainties in the determination of $A_S$. In addition, a comparison with corresponding results for CO$_2$ particles [19,34] suggests that the assumption of a spherical particle shape becomes worse for larger particles. Deviations from a spherical geometry manifest themselves more prominently in the $v_3$ band (Fig. 2a), due to its stronger transition dipole coupling. Both electrostatic models [28] and exciton coupling patterns [35] point at elongations of the spheres towards cigar-shaped geometries. This can be rationalized, if heat dissipation to the bath gas upon condensation becomes a limiting factor for particle growth. Needle-like or dendritic growth is a well-known consequence of this heat dissipation bottleneck in the liquid phase. For the 78 K spectrum, an upper limit of 50 nm for the particle radius was obtained already earlier from investigations of the scattering contribution in the spectra [23]. This value is obviously consistent with the present result.

For the 4.5 K spectra, our model yields particle radii around 1 nm. If one assumes the same density for these particles as for the crystalline bulk [33], a particle with a radius of 1 nm contains about 90 N$_2$O molecules. This value is again consistent with corresponding values obtained earlier in free jets [1,12].

From these results, we finally conclude that the collisional cooling technique indeed allows to generate N$_2$O particles in the whole size range between the subnanometer and the micrometer region. This property makes it a very promising technique to study size-dependent effects in particulate matter.

### 4. Conclusion

The present investigation demonstrates that the collisional cooling technique is a powerful method to generate particles over the whole size range.

### Table 2
Mean particle radii $r$ derived from the N$_2$O particle spectra shown in Figs. 1 and 2

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Temperature of the bath gas $T$/K</th>
<th>Particle radius $r$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$v_1$ band</td>
</tr>
<tr>
<td>1000 ppm (Fig. 1a, Fig. 2b)</td>
<td>78</td>
<td>21–25$^a$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

|                      |                                   | 10–13$^a$              | _$^b$                  |
|                      | 80                                | 4.9                    | 6–9$^a$                |
| 100 ppm (Fig. 1b)   | 49                                | 2.6                    | 3.1                    |
|                      | 31                                | 1.4                    | 1.5                    |
|                      | 22                                | 1.0                    | 0.9                    |
|                      | 11                                | 0.8                    | <1$^a$                 |

See Section 3.2 for further explanations.

$^a$ The weak S-band or C-band allows only a rough estimate of the radius.

$^b$ The S-band is too weak to determine a radius.
from the subnanometer to the micrometer region. The size of the particles is controlled by the temperature in the collisional cooling cell and the sample gas concentration. Smaller particles are generated at lower cell temperatures and lower sample gas concentrations. In our experiment, the temperature can be varied in a very wide range by cooling the cell with liquid-helium. Optical path lengths up to 20 m enable high absorption sensitivity and consequently low sample gas concentrations.

N2O particles with radii below 10 nm are generated at cell temperatures below 50 K. In this size range, the infrared spectra are mainly determined by characteristic surface effects. The analysis of these effects allow to estimate the particle size. For even smaller aggregates with radii around 1 nm, the collisional cooling technique can be compared with free jet methods. It is found that the two different methods lead to nearly identical results. Small deviations between the infrared spectra recorded with the two methods can be traced back to the large differences in the effective temperature for the two methods.

The present results provide the experimental starting point for a full characterization of particulate N2O. The future analysis of the experimental infrared spectra will require theoretical methods, which cover the whole size range. This surely cannot be achieved by one single method. A useful approach will have to encompass the continuum description used for the bulk, as well as the microscopic description of the small clusters, for example in terms of an exciton model [31].

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