Refractive index and density of ammonia ice at different temperatures of deposition

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Abstract

Despite its relevance in astrophysical scenarios, optical properties and density of ammonia have been scarcely studied. This work presents new data on the real part of the refractive index of ammonia at 632.8 nm and density at different temperatures of deposition from 13 K up to its desorption temperature around 110 K. The results show a significant variability for both parameters versus temperature, representing an increase of 50% for density and a 10% for refractive index as temperature increases in the range 13 - 60 K, and at temperatures higher than 60 K a constant value is reached for both parameters. This initial variation and the further plateau reflects structural differences in its form at low and high temperatures that can play an important role in its interaction with other molecules of astrophysical interest.

Keywords:
Ices, Experimental techniques, Satellites surfaces, Trans-neptunian objects, Comets

1. Introduction

Ammonia ice is present in many astrophysical scenarios in Solar System bodies, on satellites as Enceladus (Emery et al., 2005; Verbiscer et al., 2006), Miranda (Bauer et al., 2002), on TNO’s as Charon (Brown & Calvin, 2000; Dumas et al., 2001; Cook et al., 2006, 2007), or Quaoar (Jewitt & Luu, 2004), even in comets (Kawakita & Watanabe, 2002) and references therein). All these works confirm the prediction of Lewis (1972) who proposed ammonia as one of the most abundant molecules incorporated into the outer Solar System bodies, recently Pizzarello & Williams (2012) confirmed the presence of ammonia from carbonaceous carbonites in the Early Solar System. Moreover ammonia modifies water properties, (Kargel, 1992; Lodders, 2003; Marion et al., 2012), even could be important not only for the surfaces but even for inner parts of icy satellites (Leliwa-Kopystynski et al., 2002).

However, scarce studies have been performed on the optical properties of this ice under astrophysical conditions (low pressure and low temperature).

Concerning density (hereafter $\rho$), experimental...
data are even more scarce, since the few reported
data are obtained at around 80 K or around 25
K. The results published so far show higher val-
ues when density is obtained at 80 K. These results
obey the same behaviour than \( n \) i.e.: significantly
lower values of density at low temperatures (20 K)
(Wood & Roux, 1982) respect that obtained around
80 K (Olovsson & Templeton, 1959; Manzhelii &
Tolkachev, 1964; Wood & Roux, 1982).

Differences in both, \( n \) and \( \rho \), at low and high
temperatures invite to infer different structures.
During decades authors agree about an amorphous
structure at low temperatures and a crystalline one
at high temperatures. But no agreement is achieved
about a likely metastable structure that seems to
appear in a different range of temperatures depend-
ing on the authors. To clarify this controversial
question, two different experimental works (Zheng
& Kaiser, 2007; Dawes et al., 2007) has been re-
cently performed and both conclude in their results
the existence of only two different structures: an
amorphous one below around 60 K (hereafter low
temperatures means below 60 K) and a crystalline
one for temperatures higher than 60 K (hereafter
high temperatures means above 60 K).

To help to disentangle the problem of the differ-
ent structures of ammonia (amorphous, metastable
and crystalline phase), it would be relevant finding
additional values of \( n \) and \( \rho \) for different tempera-
tures of those present in the literature.

On the other hand \( n \) and \( \rho \) are relevant by them-
selves for different. If the refractive index of a
species is known, it is possible to calculate the thick-
ness of a deposited film from the number of interfer-
eence fringes obtained with a coherent light beam. In
our experiments we determine \( n \) at 632.8 nm (He-
Ne laser). This data is especially useful because the
He-Ne wavelength is commonly used as a standard
in almost any laboratory. Thickness is needed in
the determination of another very important physi-
cal characteristic as density, which is relevant in
the assessment of many magnitudes of astrophysi-
cal interest as the integrated absorbance strength,
porosity, penetration depth of ions impinging an
ice, etc.

In the case of experiments of irradiation, the pen-
etration depths depends directly on density and
determine whether an experiment is a thin (ions
passing the film) or thick (ions stopped in the film)
film experiment, by determining the stopping power
with specialized programs as Ziegler’s SRIM pro-
gram (Ziegler et al. (1985)).

Density is also important in the analysis of many
results: observational, experimental and theoreti-
cal. The integrated absorbance value \( A \) (cm
molecule\(^{-1}\)), can be used to estimate column densi-
ties of ice constituents from the absorption spectra
of the ices (Hudgins et al., 1993). Integrated ab-
sorbance is defined as:

\[
A = \frac{1}{\tau} \int_{\nu_{1}}^{\nu_{2}} \tau_{\nu} d\nu
\]

where \( C \) is the concentration of the absorbers,
often expressed as molecule \( \text{cm}^{-3} \) (or \( \text{mol} \text{ l}^{-1} \)), \( l \) is
the path-length of the beam through the material, \( \nu \)
is the frequency in \( \text{cm}^{-1} \), \( \tau_{\nu} = \ln(I_{0}/I) \) is the ratio
of the incident to the transmitted beam, with the
integration performed over the band. \( C \) is obtained
as follows:

\[
C = \frac{\rho N_{A}}{M_{\rho}}
\]

where \( \rho \) is the density of the ice in g \( \text{cm}^{-3} \), \( N_{A} \)
is the Avogadro constant in molecule \( \text{mol}^{-1} \) and \( M_{\rho} \)
is the molecular mass in g \( \text{mol}^{-1} \). d’Hendecourt
& Allamandola (1986) assumed that, for the cal-
culation of \( A \), the largest uncertainties arises from
evaluating \( C \) (concentration of absorbers), as the
densities of ices are not accurately known. They
assumed the densities to be constant (1 g \( \text{cm}^{-3} \)).
This assumption was also made by many other au-
tors, among them is used by Hudgins et al. (1993)
in their exhaustive work to determine optical con-
stants and integrated absorbance for mid- and far-
infrared spectroscopy of ices.

Density is even relevant by itself in the physical
chemistry of ices. The course of chemical differen-
tiation depends very much on the relative densities
of important phases and whether they tend to sink
or float (Kargel, 1991). This author presents densi-
ties of representative cryovolcanic liquids and solids
versus temperature. Knowing the density at tem-
peratures relevant for astrophysical scenarios helps
to understand part of their surface dynamics.

We present in this work new results on the real
part of refractive index at 632.8 nm and bulk den-
sity of NH\(_{3}\) at different temperatures (ranging from
10 to 100 K). These results can be used to bet-
ter reproduce irradiation, integrated absorbances
and buoyancy of ices at different temperatures and
could help to better understand the structure of
ammonia. In this article, a review of the exper-
imental setup and procedures is described in the
next section. In section 3 the experimental results
are showed and discussed, and finally in section 4
the conclusions are exposed.
2. Experimental

The experimental apparatus and the procedure to obtain the refractive index and density is briefly summarized here. A more detailed explanation in some aspects is presented in Satorre et al. (2008). A simple schematic of the apparatus is shown in Figure 1.

![Figure 1: Experimental setup](image)

We have measured refractive index and density of NH\textsubscript{3} ice under high vacuum conditions (base pressure < 10\textsuperscript{−7} mbar) and temperature ranging from 13 to 100 K.

Sample holder (quartz crystal microbalance, hereafter QCMB) temperature is operated by the Intelligent Temperature Controller ITC 503S (Oxford Instruments). It uses the feedback of a silicon diode sensor (Scientific Instruments) located just beside the quartz, that allows the temperature to vary between 10.0 and 300.0 ± 0.5 K, by means a resistive heater.

Refractive index has been obtained by double laser interferometry at 632.8 nm. This technique has been widely used in the literature as for example in the work of Tempelmeyer and Mills (1968).

The QCMB is used to calculate the mass of ice accreted per unit area (in g cm\textsuperscript{−2}). This value is obtained from the QCMB variation in frequency by using the Sauerbrey equation: \( \Delta f = -S \cdot \Delta m \). In this equation \( \Delta f \) is variation in frequency, \( \Delta m \) represents the mass accreted onto the balance and \( S \) is a specific constant for every QCMB. From the value obtained with the QCMB signal and the thickness, density is obtained.

During deposition, gas flows from the prechamber to the deposit vacuum chamber controlled by a needle valve (Leybold D50968). To form the ice film, a constant rate of deposition is used (around 1 \( \mu \)m h\textsuperscript{−1}), maintaining almost constant the aperture of the valve. NH\textsubscript{3} enters the deposition chamber and deposit on the coldest parts growing a film onto the QCMB. The pressure of ammonia and contaminants composition during film growth is checked through the Quadrupole mass spectrometer (QMS) (AccuQuad RGA 100 with a resolution of ∼ 0.5 amu). Some experiments, at different temperatures, are repeated to check its reproducibility and all the results are within the error bars. Ammonia used is Praxair 99.999.

<table>
<thead>
<tr>
<th>T. (K)</th>
<th>Density (g cm\textsuperscript{−3})</th>
<th>Refractive index</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \rho \pm 5% )</td>
<td>Lit.</td>
<td>( n \pm 2.5% )</td>
</tr>
<tr>
<td>13</td>
<td>0.67</td>
<td>1.38</td>
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</tr>
<tr>
<td>20</td>
<td>0.72</td>
<td>0.76\textsuperscript{a}</td>
<td>1.40</td>
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<td></td>
<td></td>
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<td>1.42\textsuperscript{b}</td>
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<tr>
<td>25</td>
<td></td>
<td>1.44\textsuperscript{c}</td>
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<td>40</td>
<td>0.80</td>
<td>1.45</td>
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<td>60</td>
<td>0.89</td>
<td>1.49</td>
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<tr>
<td>75</td>
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<td>1.48\textsuperscript{c}</td>
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<tr>
<td>77</td>
<td>0.861\textsuperscript{d}</td>
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<td>80</td>
<td>0.87</td>
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<td>81</td>
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<td>0.90</td>
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<td>1.50\textsuperscript{e}</td>
</tr>
<tr>
<td>100</td>
<td>0.85</td>
<td>1.48</td>
<td>1.48\textsuperscript{c}</td>
</tr>
</tbody>
</table>

References
\textsuperscript{a}: Wood and Roux(1982)
\textsuperscript{b}: Pipes et al.(1978)
\textsuperscript{c}: Dawes et al.(2007)
\textsuperscript{d}: Olovsson and Templeton(1959)
\textsuperscript{e}: Romanescu et al.(2010)
\textsuperscript{f}: Manzhelii and Tolkachev(1964)
3. Results and discussion

The motivation of our work is to provide new data for \( n \) and \( \rho \) at temperatures at which they are no previously obtained. These data are useful because from previous results is clear that ammonia ice structure depends on the temperature of deposition. In this section we discuss the validity of our results comparing with experimental data obtained with both, the same and other experimental techniques.

Density and refractive index obtained at different temperatures in our set of experiments (ranging 13 to 100 K), has been collected and presented in Table 1 together with other values taken from the literature, in order to compare them. Additionally, all the data for \( n \) and \( \rho \) have been plotted in Figure 2 and 3 respectively. The errors considered in these graphs are 2.5 % for \( n \) and 5 % for \( \rho \). Errors in the temperature are not marked since they are within the symbol size.

Our experimental data show two different behaviours, below and above 60 K. Below it (left side in Figures 2 and 3), \( n \) and \( \rho \) vary with temperature as \( n = (1.35 + 0.00231 \, T) \) and \( \rho = (0.628 + 0.00462 \, T) \) g cm\(^{-3}\), with \( n \) growing from 1.38 to 1.48 and \( \rho \) increasing from 0.67 to 0.87. In both cases a plateau is reached for temperatures higher than 60 K (right side in Figures 2 and 3), being \( \rho_{\text{plateau}} = 1.48 \pm 0.05 \), and \( n_{\text{plateau}} = 0.67 \pm 0.02 \) g cm\(^{-3}\). If we substitute, in the straight fits, the plateau values of \( n \) and \( \rho \) versus temperature is reached, we obtain a temperature for transition of 58 ± 5 K. These results suggest a progressive increase of structural order for ammonia molecules below 60 K and a stable structure above it.

These results complete those published so far and agree with most of them (Figures 2 and 3). Only deviations around 5% are observed for \( n \) at temperatures around 75 K (Figure 2). This particular discrepancy will be discussed in more detail later.

Looking at the literature data, the main conclusion is that around 25 K, values obtained for both \( n \) and \( \rho \) are lower than those obtained at around 80 K or higher. Because the lack of data below 25 K and from 30 up to 80 K it is not possible to establish a relationship between \( n \) and \( \rho \) and the structure of ammonia. Only three constant \( n \) values presented by Romanescu et al. (2010) at 70, 80 and 90 K let us deduce a stable structure.

Refractive index values are usually obtained by double laser interferometry. Dawes et al. (2007) used a technique explained in detail by Westley et al. (1998) based on the interference curves with one laser. Among all these results (including ours), those obtained by Romanescu et al. (2010) by double laser interferometry are probably the most accurate due to their number of experiments for a specific temperature (16 experiments, at 50 K) and because they analyze and subtract the output of the laser signal (using an additional sensor) correcting the artifacts of the device. This procedure presents the advantage that correcting the variation in the laser beam, the interference curves are clarified. Our results, taking into account the error bars,
fully agree with the results of Dawes et al. (2007) at 77 K, and that of Romanescu et al. (2010) at 80, 90 and 100 K (see Figure 2). Dawes et al. (2007) work under UHV conditions and their results at 100 K could be affected because under UHV conditions, depending on the pressure of deposition, two processes could compete in the dynamics of the process, deposition and sublimation.

Pipes et al. (1978) and Wood & Roux (1982) use both almost the same experimental setup. As it is clearly shown in Figure 2, at high temperatures both works obtain lower values than any other authors (including the result obtained in this work) but at 20 K their results are within the error bars of ours. The discrepancy between the results obtained by these authors at high temperatures and all the others, is explained by Romanescu et al. (2010) from the deposition rate in the experiments of Pipes et al. (1978) and Wood & Roux (1982) (in the order of µm min⁻¹).

The explanation of the discrepancy, more evident for crystalline than for amorphous structure, could be that forming any crystalline structure, in the case of ammonia a Face Centered Cubic structure (thereafter FCC, see Figure 4) needs a certain experimental conditions. At higher temperatures than 60 K a crystalline structure is formed if deposition conditions allow it. A new molecule arriving needs a certain time to achieve the appropriate position and orientation. For almost all the experiments performed by many authors with different techniques and different rates of deposition, all of them conclude that no dependence of the rate of deposition is observed, but it seems that this is true up to a certain threshold. If it is exceeded, molecules have no time to reorganize in a crystalline structure, This threshold should be around that rate used by Pipes et al. (1978) and Wood & Roux (1982) as Romanescu et al. (2010) point out as the cause of the discrepancy between their results and those of Pipes et al. (1978), Wood & Roux (1982). If deposition rate finally influences on the result, this effect should be more relevant for the crystalline phase than for amorphous ice, this would explain why at 25 K their data agree with the other ones.

Concerning ρ values, all the results for all the temperatures present in the literature fully agree with our results (see Figure 3), that of Wood & Roux (1982), at 20 and 80 K, using the same experimental technique of us, Manzhelii & Tolkachev (1964) using picnometer, and Olovsson & Templeton (1959) using X-ray diffraction at around 80 K. Romanescu et al. (2010) claim the high accuracy of the experimental technique using picnometers and X-ray diffraction for the ρ values. Our results are within 1% to those last works, and, despite the difficulties of working with the QCMB (mentioned by Romanescu et al. (2010)).

Our results provide for the first time, enough additional data to show a clear linear increase in n and ρ values from low temperatures up to 60 K and additionally they confirm the presence of a steady state above 60 K. Then all the experimental results point to, at least, two different structures, below and above 60 K.

![Figure 4: Crystal structure for NH₃.](image)

4. Conclusions

In this work the density and refractive index for NH₃ at different temperatures of deposition have been determined.

These values complete a lack of data at different temperatures from 13 up to 100 K. Two different behaviours are obtained, in a first range of temperatures (from 13 to 60 K), both n and ρ increase their values linearly with a rate of 0.00231 K⁻¹ for n and 0.00462 g cm⁻³ K⁻¹ for ρ. Above 58 K a constant value is obtained for both n and ρ (n = 1.48 ± 0.05 and ρ = 0.87 ± 0.02 g cm⁻³), in excellent agreement with the literature (see Figures 2 and 3). Specifically our value for the transition temperature from amorphous to crystalline phase
obtained crossing the plateau with the straight line fits is 58 ± 5 K.

The transition temperature deduced from our procedure is almost the same that obtained by other authors (Dawes et al., 2007; Zheng & Kaiser, 2007).

Despite this agreement, taking into account our experimental error is not possible to discard a metastable structure that has been a controversial point during a long time. This metastable structure was initially proposed by Staats & Morgan (1959) from the work of Reding & Horning (1951), whose results have been reproduced by many authors as revised Ferraro et al. (1980). This structure has also been found by Moore and Hudson (1994) but they called the range at which this features appear as “transition phase”. In order to elucidate the appearance or not of a metastable structure, more recent works of Dawes et al. (2007) and Zheng & Kaiser (2007) have been designed with the aim of clarifying whether this metastable phase of ammonia exists and, if is the case, the range of temperatures in which it is present. Dawes et al. (2007) divide the dependence of the structure in two ranges: below and above 65 K where the transition occurs from amorphous to crystalline FCC. This study is based on the variation of the IR and Visible-UV spectrum of ammonia deposited at 25 K and comparing it with the spectra obtained at different temperatures during warming up. Additionally, they obtain spectra for NH$_3$ deposited directly at higher temperatures and compare them with those deposited at low temperatures and subsequently warmed up.

The study of Zheng & Kaiser (2007) points out the same behaviour but establishing the transition point at slightly lower temperature: 58 K. Despite these authors studied the sample only with the IR, their higher resolution experiment respect Dawes et al. (2007), consents them to show a fine structure of the spectra appearing at 58 K that indicates structural changes associated to the crystalline form.

Zheng & Kaiser (2007) performed additional experiments using mixtures of ammonia with water ice, because water is the most important contaminant in high vacuum systems and because its high reactivity with ammonia in the prechamber. They found that when ammonia is mixed with 1 % of water, the transition temperature changes from 58 to 65 K. These results show that the presence of water ice even as a contaminant, could vary the transition temperature from amorphous to crystalline.

Ice of carbon dioxide presents also a similar variation in temperature for $n$ and $\rho$, but presenting and increase with temperature higher than in the case of NH$_3$ (Satorre et al., 2008). This lower variability in the case of ammonia could be associated to the H-bonds present in this molecule.

Our work is relevant because ammonia is abundant in many astrophysical scenarios. In those, some additional aspects must be taken into consideration: i) The buoyancy of mixtures when ammonia is present in a mixture liquid-solid context, will be greater than expected from their previous used value as its density could decrease down to 20 % (as temperature decreases) from the usually assumed value of 1 g cm$^{-3}$. ii) Irradiation dose (Moore et al., 2007) must be revised for experiments where NH$_3$ is involved since penetration depth is affected by density of the film irradiated, therefore from our results ammonia could present values of penetration higher than expected. iii) Abundance calculated for the NH$_3$ (Hudgins et al., 1993) in the scenarios where is present in solid state must also be revised considering our values for calculation purposes.

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