

WATER–AMMONIUM ICES AND THE ELUSIVE 6.85 μm BAND

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ABSTRACT

The 6.85 μm band observed in the spectra of young stellar objects has been analyzed recently and the most usually accepted assignment to the ν_4 bending mode of NH_4^+ is still under debate. We present here a laboratory study of frozen solutions of NH_4^+Cl^- in water in an astrophysical range of concentrations and temperatures. The samples are prepared by hyper-quenching of liquid droplets on a cold substrate. The ν_4 band of NH_4^+ , which is very strong in the pure crystal and in the liquid solution at ambient temperature, becomes almost blurred in IR spectra of the frozen solution. The effect of the chlorine anion is expected to be of little relevance in this study. The experimental results are supported by theoretical calculations, which predict a broad range of weak ν_4 features for amorphous samples containing different ammonium environments. The present results indicate that the ammonium ion surrounded by water molecules only cannot suffice to explain this spectral feature. This paper contributes with new evidence to the discussion on the assignment of the 6.85 μm band.

Key words: infrared; general – line: identification – methods: laboratory

1. INTRODUCTION

The observations made with the *Spitzer Space Telescope* on young stellar objects (YSOs) have prompted a renewed interest on the IR spectra of ices in the long wavelength range. In particular, a very recent study of the 5–8 μm region (Boogert et al. 2008) deals with a number of band components and proposes up to eight different carriers for their interpretation. These include, besides solid water, CH_3OH , CH_4 , NH_3 , HCOOH , H_2CO , and the possible ions HCOO^- and NH_4^+ . Even more recently, Zasowski et al. (2009) published a study based on *Spitzer* observations of the Taurus–Auriga dark cloud star-forming region, more specifically on 12 Class I and four Class II protostars in 6 μm and 15.2 μm . Although these publications deal with a number of different astrophysical problems, in both of them the well-known 6.8 μm spectral feature, discovered 30 years ago (Puetter et al. 1979) but still controversial, is analyzed in detail. This band is detected in all sources of the low-mass YSOs surveyed by Boogert et al., and also in those reported by Zasowski et al., although with varying depth and profile along different lines of sight. The most generally accepted carriers for this feature are CH_3OH and NH_4^+ (e.g., Boogert & Ehrenfreund 2004; Schutte & Khanna 2003), although there is no complete agreement in the literature. Methanol, if present, must be confirmed by other strong modes in the mid- and near-IR spectrum. NH_4^+ , in turn, requires the presence of a counter-ion, being OCN^- and HCOO^- usually proposed, the latter also presenting an absorption at 6.3 μm . Boogert et al. (2008) suggest NH_4^+ as the dominant carrier for these absorptions. However, the temperature of the ice mixture containing the ion has to be about 200 K in order to match the frequency position of a possible component of this band, and they argue that such high temperature is hard to explain in many of the sources where it is observed. From a very detailed study, Zasowski et al. (2009) conclude that a combination of equal contributions from NH_4^+ and from CH_3OH in a water-dominated matrix, with varying amounts of nearly pure CH_3OH , affords the closest reproduction of the strength and profile of the 6.8 μm feature in the YSOs that they investigate, although the authors admit that even those combinations are inadequate to explain the feature fully, and it

may be even impossible to describe all the observed spectral characteristics by a single set of components. To this, it should perhaps be added that whereas in astrophysical ices in general all the neutral species mentioned above are firmly accepted, the presence of ionic components still raises some doubts, because of insufficient agreement with laboratory spectra (Boogert et al. 2008).

To aid in the analysis of astrophysical observations, a number of laboratory experiments also have been performed, in most cases by processing frozen mixtures of gases through UV radiation (e.g., Schutte & Khanna 2003; Demyk et al. 1998; Muñoz Caro et al. 2004), proton bombardment (Moore et al. 2007), thermal treatment, or several of these techniques simultaneously. When NH_3 is in untreated samples, NH_4^+ seems to be formed in photolysis-induced reactions, being characterized by its spectroscopic signatures, namely a strong ν_4 band $\sim 1450\text{ cm}^{-1}$ (6.9 μm), and the features in the 3.3 μm region, $2\nu_4$ (2828 cm^{-1}), the Fermi pair $\nu_3/\nu_2+\nu_4$ ($3126/3060\text{ cm}^{-1}$), and $\nu_1+\nu_5$ (3223 cm^{-1}) (Wagner & Hornig 1950). The former band is particularly interesting, as it is sufficiently detached from any water bands that might obscure its identification. Besides, it is a good candidate for the assignment of the 6.85 μm band observed in the above-mentioned astrophysical measurements.

In the laboratory works cited in the previous paragraph, the NH_4^+ ion is always surrounded by several species in the ice matrix. The presence of different species in the ices and their processing inevitably induce a number of interactions and effects difficult to trace, which could affect the positions and widths of the NH_4^+ IR absorptions. For this reason, it seems convenient to analyze in detail the spectroscopic properties of a simpler system containing water and the ammonium ion, which, as far as we know, has not been studied yet. Although most astrophysical ices have a more complex composition, the existence of, e.g., an $\text{NH}_4^+/\text{H}_2\text{O}$ ice region unmixed with the rest of ice species cannot be disregarded. Moreover, the information obtained for this simple system could shed light on some of the spectroscopic features still under discussion in the astrophysical community. Of course, a counter-ion must also be present in the samples, but this can be chosen so as not to interfere, or

at least to do so to a minimum extent, with the spectroscopic analysis.

To this aim, we have prepared ice samples of water and ammonium chloride of different concentrations, and have studied their spectroscopic properties at the deposition temperature, 14 K, and after warming until most of the water has sublimated. The results have astrophysical implications, as they raise some questions concerning the assignment of the 6.85 μm band to the ammonium ion. To support the experimental results, we have performed theoretical calculations of model systems with water and ammonium chloride and predicted their infrared spectra. A similar trend to that observed when comparing experimental spectra of the pure salt and water mixtures is found in the calculated results.

2. EXPERIMENTAL PART

Ice samples of amorphous solid water (ASW) containing ammonium ions were prepared by hyperquenching of liquid droplets (Tizek et al. 2002) of ammonium chloride solutions on a cold substrate placed inside a vacuum chamber. The main aspects of the experimental setup have been described in detail in previous publications (Gálvez et al. 2008; Maté et al. 2003; Carrasco et al. 2002). Very briefly, our basic equipment consists in a chamber evacuated by a turbomolecular pump where solid samples are prepared by direct deposition on a cold substrate. In the present experiments, a Si plate mounted in a copper block in contact with the cold head of a closed cycle He cryostat (ARS 4HW) was used. The substrate plate can be warmed and its temperature can be controlled with 1 K accuracy between 14 K and 300 K. The background pressure inside the evacuated chamber is $\sim 10^{-8}$ mbar. The chamber is coupled to a Vertex70 Bruker FTIR spectrometer through a purged pathway, which allows spectra to be recorded at all times during the experiments. Transmission spectra of the samples were recorded using a Mercury Cadmium Telluride detector refrigerated with liquid nitrogen.

The liquid solution droplets impinging on the cold substrate were expanded from a room temperature pulsed valve (General Valve, series 9), usually employed for the generation of free jets and molecular beams (Abad et al. 1995). The exit orifice has a 0.5 mm nominal diameter and the distance between the valve exit and the substrate was ~ 15 mm. After deposition of the droplets the valve was removed from the IR beam path by means of a movable feed through. A slight He overpressure behind the liquid solution filling the valve led to an improvement of the performance.

Spectra were recorded at the beginning of each experiment, at 14 K. The samples were then warmed up to 220 K to induce sublimation of the water. This was achieved after a few minutes, as shown by the disappearance of the water bands in the spectrum. Then we cooled the samples again to 14 K and recorded the spectra, characterized by narrow features from pure NH_4Cl . It should be noted that, after evaporation of the water, all the bands observed in the mid-IR region under study correspond to vibrations of the NH_4^+ molecular ion in the crystal. The intensity of the ν_4 band of NH_4^+ at ~ 1400 cm^{-1} was used to measure the actual concentration in the solid sample, by reference to the standard band strength value by Schutte & Khanna (2003), $A(\nu_4, \text{NH}_4^+) = 4.4 \times 10^{-17}$ $\text{cm}^2 \text{molecule}^{-1}$. Similarly, the water concentration in the ices was estimated by reference to the 3 μm water band intensity value reported by Hudgins et al. (1993) at 10 K, $A(\text{H}_2\text{O}) = 1.7 \times 10^{-16}$ $\text{cm}^2 \text{molecule}^{-1}$. We found that the relative amount of

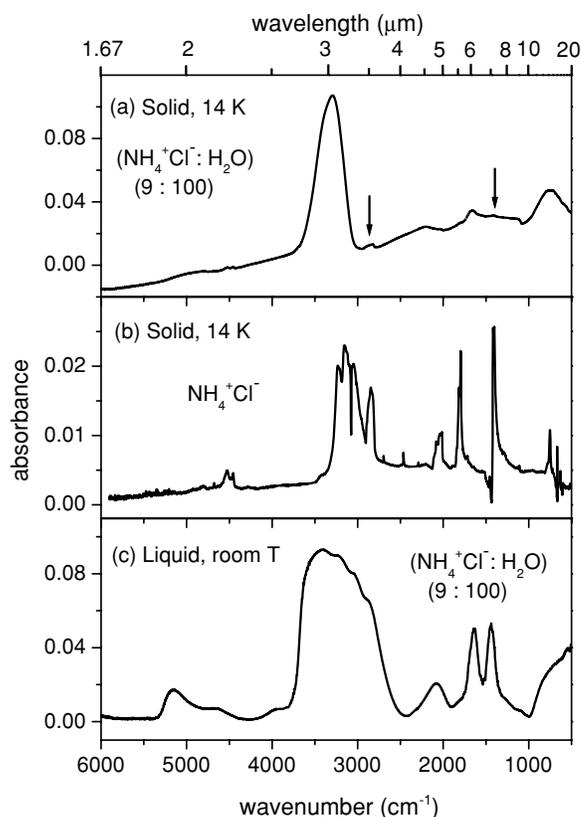


Figure 1. Transmission IR spectra of 9:100 ammonium chloride/water solutions of approximate thickness of 80 nm. (a) Solid deposited at 14 K. The most representative vibrations of NH_4^+ are indicated by arrows; (b) the same sample after warming at 220 K to sublimate all water from the solution, and cooling to 14 K again; (c) liquid solution at ambient temperature.

ammonium in the ice was usually somewhat larger than that of the liquid solution from which it was formed, due probably to the partial evaporation of water in the course of the droplet expansion used to generate the samples.

Two examples of our measurements are collected in Figures 1 and 2, discussed in detail below. In the bottom trace of Figure 1 we include the spectrum of a liquid solution of the same concentration as that of the upper trace.

3. RESULTS

3.1. Experimental Spectra

Panel (a) of Figure 1 reproduces the IR spectrum of a hyper-quenched sample of $\text{NH}_4\text{Cl}:\text{H}_2\text{O}$ of 9:100 concentration at 14 K. The main features of this spectrum correspond to amorphous water. The presence of NH_4^+ is hardly revealed by a wrinkle at ~ 1400 cm^{-1} and a bump at ~ 2825 cm^{-1} , highlighted by arrows, on the low-frequency side of the water bending and stretching modes, respectively. However, when water is evaporated and the sample cooled again, the full spectrum of NH_4^+ is manifest (Figure 1(b)), the assignment of the stronger observed bands being indicated in Table 1. Most of these bands, together with water bands, are seen in the spectrum of the liquid solution of the same concentration as that measured in the solid, at ambient temperature (Figure 1(c)).

These spectra provide grounds for discussion. In the first place, why are NH_4^+ bands so much weaker in the solid than in the liquid phase? Vibrations in the amorphous solid cannot be expected to cancel by symmetry reasons, as they sometimes do

Table 1
Mid-IR Spectrum of NH_4Cl

Assignment	This Work (cm^{-1})	This Work (μm)	W & H ^a (cm^{-1})	W & H ^a (μm)
$2\nu_6$?	752 (m)	13.29		
ν_4	1403, 1418 (vs)	7.128, 7.052	1403 (10)	7.128
$\nu_4 + \nu_5$	1795, 1817 (s)	5.571, 5.504	1794, 1817 (4)	5.580, 5.503
$\nu_2 + \nu_5$	2014–2082 (m)	4.965, 4.803	2005–2010 (2)	4.988–4.975
$2\nu_4$	2846 (s)	3.514	2828 (8)	3.536
$\nu_2 + \nu_4$	3055 (vs)	3.273	3050 (42)	3.279
ν_3	3156 (vs)	3.168	3089 (5), 3126 (41)	3.237, 3.199
$\nu_1 + \nu_5, 2\nu_4 + \nu_6$	3225 (vs)	3.101	3223 (6)	3.103
$\nu_1 + \nu_4$?	4456 (w)	2.244		
$\nu_3 + \nu_4$?	4524 (w)	2.210		

Notes.

Assignment of the mid-IR spectrum observed in this work with tentative identifications for some overtone or combination bands (with qualitative intensity in parentheses; w: weak, m: medium, s: strong, vs: very strong).

^a Measured values of Wagner & Hornig (1950), including estimated intensities in parentheses.

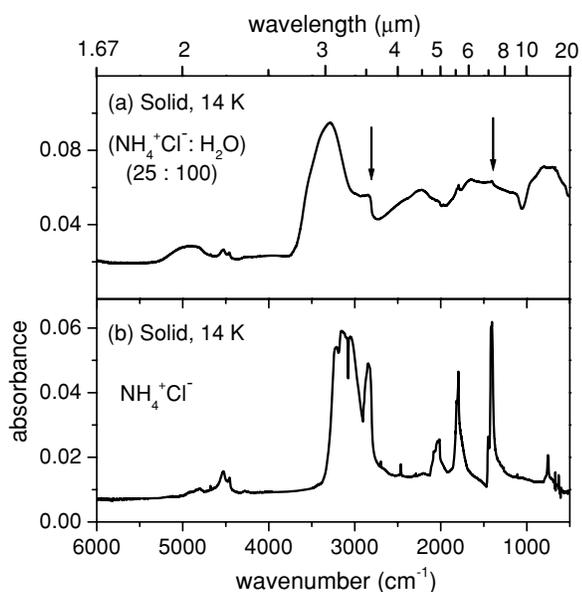


Figure 2. Transmission IR spectra of 25:100 ammonium chloride/water solutions of approximate thickness of 60 nm. (a) Solid deposited at 14 K; as in Figure 1 the most representative vibrations of NH_4^+ are indicated by arrows; (b) the same sample after warming at 220 K to sublimate all water from the solution, and cooling to 14 K again.

in ordered crystal structures. In contrast, a possible explanation would be that because of a very disordered environment, the IR bands are largely broadened and become almost melted in the baseline.

The second question has more direct astrophysical implications. As proved in our experiments, in samples containing only water and NH_4^+ , the ν_4 band of the ion is so weak that it could possibly pass undetected in noisier spectra from observational missions. This contrasts with the strong feature observed at $6.85 \mu\text{m}$ by *Spitzer* for many objects (Boogert et al. 2008), whose assignment to NH_4^+ has been proposed. Either the presence of other species in the ices induces a large intensity enhancement of this vibration, or else this band must be attributed to other molecules, NH_4^+ being in that case only one component of a possible mixture.

Figure 2 displays spectra of a similar experiment performed on a more concentrated sample, with 25% $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$, a concentration higher than plausible for astrophysical objects.

The NH_4^+ spectrum after sublimation of water (Figure 2(b)) is now about three times more intense than the corresponding one in Figure 1, as expected from the sample composition. Although the NH_4^+ features are now more evident in the spectrum of the frozen solution (see arrows in Figure 2(a)) than in the more diluted experience (panel (a) of Figure 1), the complicated appearance of this spectrum indicates that the region near $6.85 \mu\text{m}$ is not a favorable choice to deduce the presence of NH_4^+ in the sample. In fact, the band at $\sim 3.4 \mu\text{m}$ (2825 cm^{-1}) might be a better choice for that particular purpose.

Similar hyper-quenching experiments with the deposition substrate kept at higher temperatures, up to 120 K, also have been conducted on solutions of the same concentration obtaining comparable results. Within this temperature range, accessible in some astrophysical objects, the spectral characteristics of these ices are therefore invariable.

The influence of the counter-anion should also be considered. Since in this case the anion is monoatomic, its only effect on the spectrum should be to induce shifts in NH_4^+ vibrations, due to the weak Coulomb bonding between Cl^- and the closest hydrogens of the cation, but no further vibrational bands are expected in this mid-IR region. Therefore, the presence of this anion is not expected to interfere with the conclusions of this investigation.

3.2. Theoretical Calculations

To get further insight into the mechanisms responsible for the observed disappearance or attenuation of the $\text{NH}_4^+ \nu_4$ band, we performed a series of density functional calculations (DFTs) on model systems representing the NH_4^+Cl^- species trapped in ice. The calculations were performed with the SIESTA 2.0 package (Soler et al. 2002; Ordejón et al. 1996), using the BLYP functional for the treatment of the exchange and correlation energy (Becke 1988; Lee et al. 1988; Miehlich et al. 1989), a double-zeta-polarized basis set to expand the wave functions of the valence electrons, and Troullier–Martins pseudopotentials to represent the core electrons, which were tested in previous works (Martín-Llorente et al. 2006). The initial system consisted of a unit cell containing eight water molecules arranged as in the ice Ih structure, with the hydrogen atoms located as in Buch et al. (1998), model number 4. We calculated the IR absorption spectrum of this system using the method described in Fernández-Torre et al. (2005a). The models used to represent the NH_4^+Cl^- trapped in ice were constructed by substituting

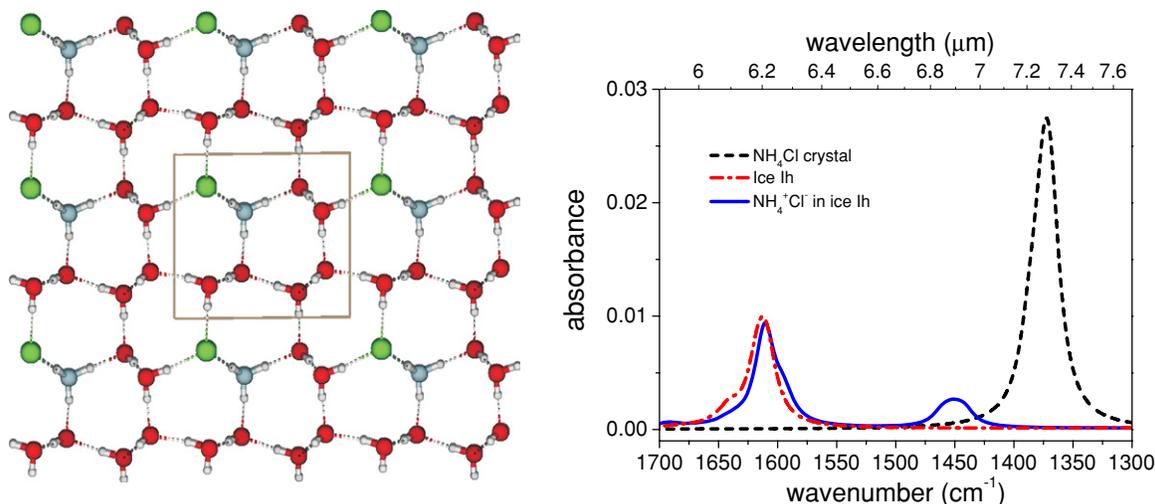


Figure 3. Left panel: calculated lowest energy structure for the NH_4^+Cl^- species trapped in ice. The unit cell is indicated in beige. The chloride ions are colored in green, the oxygens in red, the nitrogens in blue, and the hydrogens in white. The H-bonding network is indicated with dashed lines. Right panel: calculated IR spectra of the NH_4Cl crystal (black dashed line), the ice Ih model (red point-dashed line), and the lowest energy structure for the NH_4^+Cl^- trapped in ice (blue line). The spectra of the ice and the salt have been rescaled to have the same amount of H_2O and NH_4Cl molecules per unit cell as in the model system used to represent the NH_4^+Cl^- trapped in ice.

one H_2O molecule from the water ice unit cell by an NH_4^+ ion, which saturates all four tetrahedral valences of the vacant site, and another water molecule by a Cl^- anion. These substitutions yield a $\text{NH}_4^+/\text{H}_2\text{O}$ mixing ratio of 1:6, not far from that of the laboratory spectra of Figure 2. The number of possible different structures arising from such substitutions is 28. These were taken as initial geometry values and were then fully relaxed to obtain their corresponding IR spectra. The left-hand panel of Figure 3 depicts the configuration of the minimum energy structure, which presents a H-bonding network very similar to that of ice Ih. The right-hand panel of this figure displays the 1700–1300 cm^{-1} region of the IR spectrum of this structure, together with spectra of both ice Ih and solid NH_4Cl . The latter was calculated for the antiferro-ordered crystal structure (Seek et al. 1998). This is the spectral region under discussion in this Letter, featuring the bending vibrations of both NH_4^+ and H_2O , the latter appearing at $\sim 1610 \text{ cm}^{-1}$. The “scissors” mode of NH_4^+ is calculated at the higher frequency edge of this water band, at $\sim 1690 \text{ cm}^{-1}$, but is not visible in the spectra because its infrared activity is close to zero. On the other hand, the peaks at $\sim 1370 \text{ cm}^{-1}$ and $\sim 1450 \text{ cm}^{-1}$ correspond to the ν_4 vibration of NH_4^+ inside the solid salt and the ice matrix, respectively. The large frequency shift and the important decrease of IR activity in going from the first environment to the second is by far the most striking effect observed when comparing the calculated IR spectra.

From the results of our calculations, we can extract two reasons underlying the apparent disappearance or attenuation of the $\text{NH}_4^+ \nu_4$ band when the ion is trapped in ice. First, as we just mentioned, the IR activity of this mode is predicted to be much smaller in ice than in the crystal of NH_4Cl . Such intensity decrease can be traced back to the Born charges (Gonze & Lee 1997) of the H atoms in the different environments. In the solid salt, the Born charges along the bending mode directions are much larger than those in the ice matrix, resulting in a much larger IR absorption of the solid for this particular mode. This is a purely electronic structure effect which is known to be related to the more ionic or covalent character of the bond in which the atoms are involved (Fernández-Torre et al. 2005a; Pruneda & Artacho 2005). A second reason for the attenuation of the NH_4^+

ν_4 band is the coexistence of several different local structures for the ammonium ion trapped in ice. In our calculations, besides the lowest energy structure considered in Figure 3, we have found other low-energy configurations which, in principle, could be reached by the thermal energy of the initial liquid solution, and could consequently be “frozen” after the quenching at 14 K. Their ammonium bending bands are qualitatively similar to that of the lowest energy structure displayed in Figure 3, but they are somewhat more spread, and for each structure the exact location of this band differs by tens of cm^{-1} . If inside the ice we have local configurations similar to those predicted in this work, the average IR band for the NH_4^+ bending will be consequently broadened and weakened. More details about the results of our calculations will be presented elsewhere. Here we just wanted to stress the fact that the calculated results are in good agreement with the spectra obtained in our laboratory and can provide an explanation for this effect at the molecular level.

4. DISCUSSION

Our results may be contrasted with those of previous investigations. The laboratory measurements of Schutte & Khanna (2003) consisted in the production of NH_4^+ in photolysed mixtures of $\text{H}_2\text{O}/\text{CO}_2/\text{NH}_3/\text{O}_2$, which also yielded a variety of negative ions. In their processed samples they observed a quite strong band at $\sim 1450 \text{ cm}^{-1}$ ($\sim 6.8 \mu\text{m}$), assigned to ν_4 of NH_4^+ . They detected a strong redshift of this feature with increasing temperature in the range 12–280 K, which matched well the systematic redshift with line-of-sight dust temperature of interstellar observations. They also measured other NH_4^+ bands after water sublimation at 3.12 μm , 3.26 μm , and 3.48 μm , although the correlation of these bands with the ν_4 feature was not positively established. In the photolysis experiment, other species such as HCO_3^- , NO_3^- , and NO_2^- are expected to be formed, some of them with predicted strong IR bands in the 6 μm region (e.g., Fernández-Torre et al. 2005b). The mixture formed induces varying interactions among all the different species in the matrix, which are probably responsible for the increased redshift with temperature (Schutte & Khanna 2003) and also for the large intensity of the ν_4 NH_4^+ feature. The *Spitzer*

observations analyzed by Boogert et al. (2008) and Zasowski et al. (2009) showed this band in a large number of YSOs, but both works concluded that the ν_4 vibration of NH_4^+ alone could not explain the 6.8 μm feature, and that the profile and depth of the observations implied the presence of other species. We have recorded a strong ν_4 band in the spectrum of the pure NH_4^+Cl^- solid salt, which becomes a very broad and almost undetectable feature in the spectra of $\text{NH}_4^+\text{Cl}^-/\text{H}_2\text{O}$ ice mixtures, unchanged with temperature variations of the sample. This leads us to conclude that the ammonium ion in the sole presence of water, with non-interacting counter-ions, cannot explain the observations gathered for the 6.85 μm feature, and that if this band is due to NH_4^+ , then several other species must be present with which different interactions should take place. While this kind of mixed media is expected of many astrophysical observations, the laboratory analysis of simpler systems may be useful for a piecewise interpretation of the complex results.

5. CONCLUSIONS

This work presents a laboratory study of ices of $\text{NH}_4^+\text{Cl}^-/\text{H}_2\text{O}$ in an astrophysical range of concentrations and temperatures. The samples have been prepared by hyper-quenching of liquid droplets on a cold substrate and studied by FTIR spectroscopy. The main conclusions are the following.

1. We have observed that in the water/salt ice the NH_4^+ bands, and in particular the band at 1450 cm^{-1} (6.8 μm), appear much weaker than in the solid salt or liquid solution IR spectra.
2. The effect of the Cl^- anion, which does not contribute to the IR spectra, is expected to be negligible.
3. The experimental work is complemented with theoretical calculations of model ices of water and ammonium chloride that allow predicting the IR spectra. The calculations provide a theoretical interpretation of the results.
4. The weakness of the 6.8 μm band can be explained considering that the ammonium ion in the water matrix is surrounded by a very disordered environment that causes the broadening of the IR absorptions bands. Moreover, the NH_4^+ ion in the water matrix forms covalent bonds that are not present in the salt. Those bonds reduce appreciably the IR activity of the different vibrations.
5. Our results do not discard NH_4^+ as a carrier of the 6.85 μm band observed in astrophysical ices but they provide a new constraint, namely that ammonium ions cannot be surrounded by water molecules only. If NH_4^+ is responsible for that feature, then water cannot be the single other component of the ice in that particular astrophysical object,

and any other components must be in a position that facilitates interactions with the ammonium ion.

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