Precursors of complex organic molecules: NH_3 and CH_3OH in the ices surrounding low-mass protostars

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Abstract. NH_3 and CH_3OH are key molecules in the chemical networks leading to the formation of complex N- and O-bearing organic molecules. However, despite a number of recent studies, there is still a lot to learn about their abundances in the solid state and how they relate to those of other N/O-bearing organic molecules or to NH_3 and CH_3OH abundances in the gas phase. This is particularly true in the case of low-mass young stellar objects (YSOs), for which only the recent advent of the *Spitzer* Space Telescope has allowed high sensitivity observations of the ices in their enveloppes. We present a combined study of *Spitzer* data (obtained within the Legacy program "From Molecular Cores to Planet-Forming Disks", *c2d*) and laboratory spectra, leading to the detections of NH_3 and CH_3OH in the ices of low-mass protostars. We investigate correlations with other ice features and conclude with prospects on further studies linking these two precursors of complex organic molecules with their gas-phase products.

Keywords. Line: identification, ISM: molecules, ISM: abundances, infrared: stars, stars: formation, astrochemistry

1. Introduction

NH_3 and CH_3OH are among the most ubiquitous and abundant molecules. They are found in the gas-phase in a variety of environments such as infrared dark clouds, ultra-compact H II regions, massive hot cores, hot corinos, and comets. Solid NH_3 and CH_3OH have also been observed in the ices of massive YSOs (e.g. Schutte *et al.* 1991, Lacy *et al.* 1998, Dartois *et al.* 2002) and more recently of low-mass protostars (for CH_3OH, Pontoppidan *et al.* 2003). These two molecules are also key species in gas-grain chemical networks since they are the reactants leading to the formation of complex N- and O-bearing organic molecules, such as CH_3CN and CH_3OCH_3 (e.g. Rodgers & Charnley 2001). Moreover, UV processing of solid NH_3- and CH_3OH-containing ices could produce amino-acids, (e.g. Muñoz Caro & Schutte 2003). Finally, the presence and amount of NH_3 in ices also has an impact on constraining the content of ions such as NH_4^+ and OCN^-,
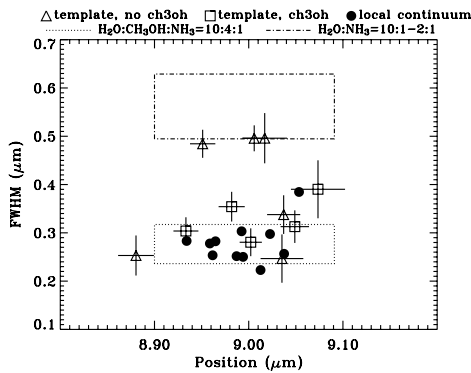
Figure 1. FWHM vs position for the NH_3 feature. Filled circles represent the values obtained with the local continuum method for subtracting the silicate absorption. Triangles and squares show the values obtained with the template method for CH_3OH-poor and CH_3OH-rich sources, respectively. The dash–dot and dotted lines indicate the range of values measured in the laboratory spectra of $H_2O:NH_3$ and $H_2O:CH_3OH:NH_3 = 10:4:1$ mixtures, respectively.

which are important species in solid-state chemical networks since they react more easily. Thus, a better knowledge of the NH_3 and CH_3OH content of interstellar ices, especially in enveloppes surrounding low-mass protostars, would help to constrain chemical models, and gain a better understanding of the formation of (pre-)biotic molecules in young solar analogs.

Both these species have been noted to have gas-phase abundances in hot cores/ corinos much larger than in cold dense clouds. This indicates that ices are an important reservoir of NH_3 and CH_3OH and that prominent features should be seen in the absorption spectra towards high- and low-mass protostars. Unfortunately, NH_3 and CH_3OH features are often blended with deep water and/or silicate absorptions, making the identifications and column density measurements difficult. Despite the blend with the so-called 10-μm silicate feature, the umbrella mode of NH_3 at $\sim$9 μm and the C–O stretch of CH_3OH at $\sim$9.7 μm appear as the most promising features to determine or better constrain the abundances of these two molecules. This kind of study has only become possible for low-mass (hence low-luminosity) protostars with the recent advent of *Spitzer* whose sensitivity enabled the observations of these objects. We present here a combined space and laboratory study of solid NH_3 and CH_3OH in the $\sim$ 8–10 μm region.

2. Observations and laboratory work

Astronomical data. The source sample consists of 41 low-mass protostars, out of which 35 fall in the embedded Class 0/I category, the remaining 6 objects being flat-type objects. We refer the reader to Boogert *et al.* (2008) for a complete description of the sample, data reduction process, and SED continuum determination.

Laboratory data. A laboratory study was carried out to spectroscopically characterize the NH_3 umbrella mode at $\sim$9.0 μm (1110 cm^{-1}) and the CH_3OH CO-stretch mode at $\sim$9.7 μm (1027 cm^{-1}) in circumstellar ice analogs. Using a Fourier Transform InfraRed (FTIR) spectrometer, we obtained transmission spectra for 12 binary and tertiary mixtures of H_2O, CH_3OH and/or NH_3 at different concentrations. The general procedure was to deposit the ice at 15 K, and to warm it up to 140 K, in 10 K steps. The range of concentrations and temperatures yielded a comprehensive dataset that allowed us, on the one hand, to investigate the behavior of the full-width at half-maximum (FWHM) and position of the features as a function of concentration and temperature, and on the other hand, to perform a direct comparison with the above astronomical observations
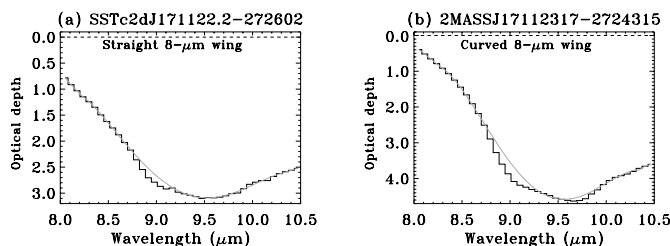
Figure 2. Examples of the two types of profiles for the 8-μm wing of the silicate feature: (a) straight, (b) curved. The gray lines show the local continuum.

in order to determine information on the relative compositions. The main trends in the behaviors are (see dotted and dash-dot lines in Figure 1):

• in H_2O:NH_3 mixtures, the NH_3 umbrella mode is located around 8.9-9.0 μm (1110–1128 cm^{-1}) and has FWHM between 0.5 and 0.6 μm.

• in H_2O:CH_3OH:NH_3 mixtures, the same values are found for the position and FWHM of the NH_3 umbrella mode, except that the FWHM in the strong CH_3OH mixture (H_2O:CH_3OH:NH_3 = 10:4:1) is reduced to 0.24–0.32 μm.

• in both H_2O:CH_3OH and H_2O:CH_3OH:NH_3 mixtures, the CH_3OH CO-stretch mode is located at 9.7–9.8 μm (1020–1028 cm^{-1}) and has FWHM 0.2–0.27 μm.

3. Analysis: estimating the silicate contribution

Local continuum. The first approach was to derive a local continuum by fitting a fourth-order polynomial to the wavelength regions 8.25–8.75, 9.23–9.37, and 9.98–10.4 μm. The position of the NH_3 and the position and FWHM of CH_3OH features derived with this method agree with the values obtained from the laboratory spectra. However, the FWHM of the NH_3 feature is around 0.3 μm (regardless of the relative amounts of NH_3 and CH_3OH – see filled circles in Figure 1); for CH_3OH-rich sources, this narrow width is consistent with that seen in the laboratory data of the H_2O:CH_3OH:NH_3=10:4:1 mixture (dotted line in Figure 1), but there is a disagreement in the case of CH_3OH-poor sources since the FWHM of NH_3 in H_2O:NH_3 mixtures (dash-dot line in Figure 1) is about twice as large.

Template method. The local continuum method is a reliable indicator of the presence of NH_3 and CH_3OH, but another way is needed to determine the possible influence of the 10-μm silicate absorption. This was investigated using an empirical method. Upon examination of the 10-μm feature of the entire sample, the sources could be separated into two broad categories: sources with a "straight" profile between 8 and 8.5 μm (hereafter the 8-μm wing), and sources with a "curved" 8-μm wing (see Figure 2). In each category, a source with little NH_3 and CH_3OH (hence with an almost pure silicate absorption at 10 μm) was selected as template for the silicate feature, scaled to the optical depth at 9.7 μm and subtracted from the other spectra. We also used as an additional template the GCS3 spectrum observed by Kemper *et al.* (2004) towards the Galactic Center.

Figure 3 shows three examples of a comparison between the spectra obtained after subtracting the local continuum (black line) or the template spectrum (light gray line): a straight and curved 8-μm wing (left and middle panel respectively). We also include SVS 4-5, the only source for which the GCS3 spectrum was the best approximation of the silicate feature.

4. Results

Using the template method, we detected NH_3 at 9 μm and CH_3OH at 9.7 μm in 11 and 17 sources respectively, including 6 sources with both features being present. Using band
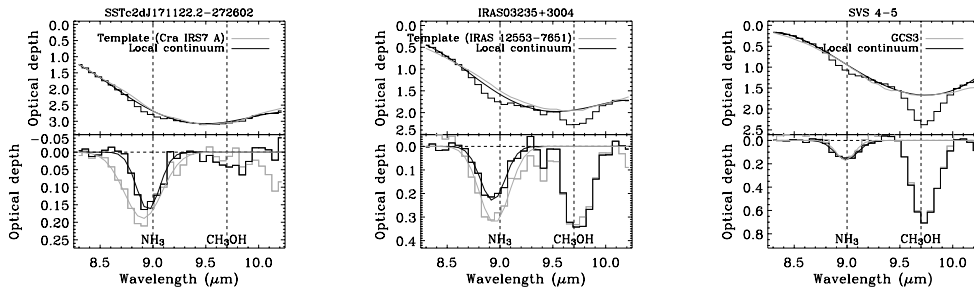
Figure 3. Determination of the contribution of the 10-μm silicate absorption: comparison between the local continuum (black lines) and template method (gray lines). The left and middle panels show sources with a straight and curved 8-μm wing respectively, and the right panel displays SVS 4-5, the only sources for which the best template is the GCS3 spectrum.

strengths of 1.3×10^{-17} and 1.8×10^{-17} cm molecule^{-1} for NH$_3$ and CH$_3$OH, respectively (Kerkhof *et al.* 1999, d'Hendecourt & Allamandola 1986), we derive column densities $N_{\mathrm{NH_3}} = (1.3–19.6) \times 10^{17}$ cm^{-2} and $N_{\mathrm{CH_3OH}} = (0.4\text{-}19.8) \times 10^{17}$ cm^{-2}, corresponding to abundances, with respect to water ice, in the ranges 3–12% and 1–25% for NH$_3$ and CH$_3$OH, respectively.

As can be seen from Figure 3, the relative amounts of NH$_3$ and CH$_3$OH vary greatly from source to source. No correlation was found between the NH$_3$ and CH$_3$OH abundances, but upon investigation of possible correlations with other ice components, we found one between NH$_3$ and CH$_4$, as measured by Öberg *et al.* (2008). Since all three species are expected to form via hydrogenation of C, N and CO (for CH$_4$, NH$_3$ and CH$_3$OH, respectively) on grain surfaces, possible explanations for the (non-)correlations could reside in (*i*) a preferential hydrogenation of atoms over molecules, combined with a time effect, or (*ii*) different C/CO, N/N$_2$ and/or H/H$_2$ ratios towards different line-of-sights. However, further investigation is needed, and in particular, a millimeter search of the possible gas-phase products of evaporated NH$_3$, CH$_3$OH and CH$_4$ (HNC, HNCO, C$_{n=3-5}$H$_2$, CH$_2$CN) is under way, aiming at paving the bridge between grain-mantle components and their offsprings.

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Discussion

KNEZ: Could you comment on the sources that you have both methanol and ammonia, do they have similar abundances?

BOTTINELLI: It actually varies a lot. Sometimes, they seem to have as much ...[searching for relevant slide]... You see, there is already one example [in the spectra I showed] where there is as much ammonia as methanol whereas [in this other source], there is a lot more methanol. It does not seem to be any specific trend.

VAN DISHOECK: So what is the total range in methanol abundances that you find? You go all the way from less than 1% to up to 25%?

BOTTINELLI: It's about the same for ammonia although there are slightly fewer sources with ammonia detection. I need to check those 20% sources; they could be an exception. Usually they are at the 10% range [compared to water].

CECCARELLI: The sources where you detected these ices, do you see any difference between Class 1 and Class 0 sources?

BOTTINELLI: I have tried to plot the ice abundances with respect to water as a function of the alpha which is telling us more or less the Class, but I couldn't see any trend.

VAN DISHOECK: Spitzer can actually observe Class 0 sources, not many but there are a few in the sample that are really in the very deeply embedded phase.

SIVARMAN: We did some experiments with ammonia and methanol in the ice phase and radiate it with 1 keV electrons. The only product that we see is just the OCN^-. We didn't see any other product apart from the OCN^- .

VAN DISHOECK: So this was an ice consisting of?

SIVARMAN: Of ammonia and methanol, 1 to 1.

The Indian delegation (from left to right: D. B. Vaidya, Amit Pathak, C. Muthumariappan, B. Sivaraman).