

# Precursors of complex organic molecules: NH<sub>3</sub> and CH<sub>3</sub>OH in the ices surrounding low-mass protostars

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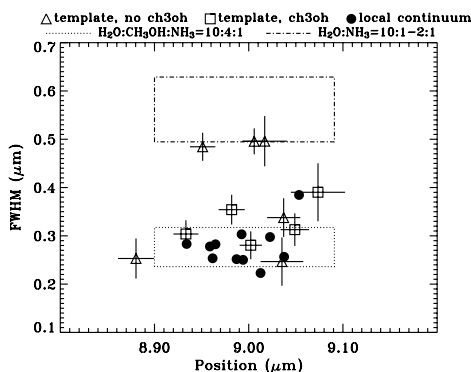
**Abstract.** NH<sub>3</sub> and CH<sub>3</sub>OH are key molecules in the chemical networks leading to the formation of complex N- and O-bearing organic molecules. However, despite a number of recent studies, there is still a lot to learn about their abundances in the solid state and how they relate to those of other N/O-bearing organic molecules or to NH<sub>3</sub> and CH<sub>3</sub>OH 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 envelopes. 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<sub>3</sub> and CH<sub>3</sub>OH 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

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## 1. Introduction

NH<sub>3</sub> and CH<sub>3</sub>OH 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<sub>3</sub> and CH<sub>3</sub>OH 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<sub>3</sub>OH, 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<sub>3</sub>CN and CH<sub>3</sub>OCH<sub>3</sub> (e.g. Rodgers & Charnley 2001). Moreover, UV processing of solid NH<sub>3</sub>- and CH<sub>3</sub>OH-containing ices could produce amino-acids, (e.g. Muñoz Caro & Schutte 2003). Finally, the presence and amount of NH<sub>3</sub> in ices also has an impact on constraining the content of ions such as NH<sub>4</sub><sup>+</sup> and OCN<sup>-</sup>,



**Figure 1.** FWHM vs position for the NH<sub>3</sub> 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<sub>3</sub>OH-poor and CH<sub>3</sub>OH-rich sources, respectively. The dash-dot and dotted lines indicate the range of values measured in the laboratory spectra of H<sub>2</sub>O:NH<sub>3</sub> and H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub> = 10:4:1 mixtures, respectively.

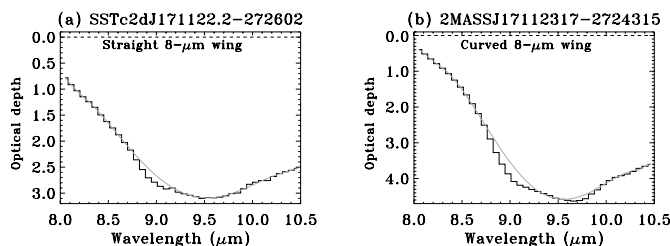
which are important species in solid-state chemical networks since they react more easily. Thus, a better knowledge of the NH<sub>3</sub> and CH<sub>3</sub>OH content of interstellar ices, especially in envelopes surrounding low-mass protostars, would help to constrain chemical models, and gain a better 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<sub>3</sub> and CH<sub>3</sub>OH and that prominent features should be seen in the absorption spectra towards high- and low-mass protostars. Unfortunately, NH<sub>3</sub> and CH<sub>3</sub>OH 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- $\mu$ m silicate feature, the umbrella mode of NH<sub>3</sub> at  $\sim$ 9  $\mu$ m and the C–O stretch of CH<sub>3</sub>OH at  $\sim$ 9.7  $\mu$ m 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<sub>3</sub> and CH<sub>3</sub>OH in the  $\sim$  8–10  $\mu$ m 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<sub>3</sub> umbrella mode at  $\sim$ 9.0  $\mu$ m (1110 cm<sup>-1</sup>) and the CH<sub>3</sub>OH CO-stretch mode at  $\sim$ 9.7  $\mu$ m (1027 cm<sup>-1</sup>) in circumstellar ice analogs. Using a Fourier Transform InfraRed (FTIR) spectrometer, we obtained transmission spectra for 12 binary and tertiary mixtures of H<sub>2</sub>O, CH<sub>3</sub>OH and/or NH<sub>3</sub> 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- $\mu\text{m}$  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<sub>2</sub>O:NH<sub>3</sub> mixtures, the NH<sub>3</sub> umbrella mode is located around 8.9–9.0  $\mu\text{m}$  (1110–1128  $\text{cm}^{-1}$ ) and has FWHM between 0.5 and 0.6  $\mu\text{m}$ .
- in H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub> mixtures, the same values are found for the position and FWHM of the NH<sub>3</sub> umbrella mode, except that the FWHM in the strong CH<sub>3</sub>OH mixture (H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub> = 10:4:1) is reduced to 0.24–0.32  $\mu\text{m}$ .
- in both H<sub>2</sub>O:CH<sub>3</sub>OH and H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub> mixtures, the CH<sub>3</sub>OH CO-stretch mode is located at 9.7–9.8  $\mu\text{m}$  (1020–1028  $\text{cm}^{-1}$ ) and has FWHM 0.2–0.27  $\mu\text{m}$ .

### 3. Analysis: estimating the silicate contribution

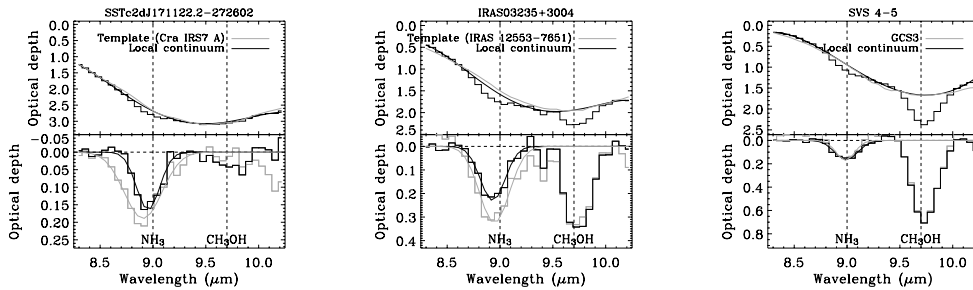
*Local continuum.* The first approach was to derive a local continuum by fitting a fourth-order polynomial to the wavelength regions 8.25–8.75, 9.23–9.37, and 9.98–10.4  $\mu\text{m}$ . The position of the NH<sub>3</sub> and the position and FWHM of CH<sub>3</sub>OH features derived with this method agree with the values obtained from the laboratory spectra. However, the FWHM of the NH<sub>3</sub> feature is around 0.3  $\mu\text{m}$  (regardless of the relative amounts of NH<sub>3</sub> and CH<sub>3</sub>OH – see filled circles in Figure 1); for CH<sub>3</sub>OH-rich sources, this narrow width is consistent with that seen in the laboratory data of the H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub>=10:4:1 mixture (dotted line in Figure 1), but there is a disagreement in the case of CH<sub>3</sub>OH-poor sources since the FWHM of NH<sub>3</sub> in H<sub>2</sub>O:NH<sub>3</sub> 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<sub>3</sub> and CH<sub>3</sub>OH, but another way is needed to determine the possible influence of the 10- $\mu\text{m}$  silicate absorption. This was investigated using an empirical method. Upon examination of the 10- $\mu\text{m}$  feature of the entire sample, the sources could be separated into two broad categories: sources with a “straight” profile between 8 and 8.5  $\mu\text{m}$  (hereafter the 8- $\mu\text{m}$  wing), and sources with a “curved” 8- $\mu\text{m}$  wing (see Figure 2). In each category, a source with little NH<sub>3</sub> and CH<sub>3</sub>OH (hence with an almost pure silicate absorption at 10  $\mu\text{m}$ ) was selected as template for the silicate feature, scaled to the optical depth at 9.7  $\mu\text{m}$  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- $\mu\text{m}$  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<sub>3</sub> at 9  $\mu\text{m}$  and CH<sub>3</sub>OH at 9.7  $\mu\text{m}$  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- $\mu\text{m}$  silicate absorption: comparison between the local continuum (black lines) and template method (gray lines). The left and middle panels show local sources with a straight and curved 8- $\mu\text{m}$  wing respectively, and the right panel displays SVS 4-5, the only sources for which the best template is the GCS3 spectrum.

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

As can be seen from Figure 3, the relative amounts of  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  vary greatly from source to source. No correlation was found between the  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  abundances, but upon investigation of possible correlations with other ice components, we found one between  $\text{NH}_3$  and  $\text{CH}_4$ , as measured by Öberg *et al.* (2008). Since all three species are expected to form via hydrogenation of C, N and CO (for  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$ , 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  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$  and  $\text{CH}_4$  (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<sup>-</sup>. We didn't see any other product apart from the OCN<sup>-</sup>.

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).