THE c2d SPITZER SPECTROSCOPIC SURVEY OF ICES AROUND LOW-MASS YOUNG STELLAR OBJECTS. IV. NH₃ AND CH₃OH

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ABSTRACT

NH₃ and CH₃OH are key molecules in astrochemical networks leading to the formation of more complex N- and O-bearing molecules, such as CH₂CN and CH₃OCH₂. Despite a number of recent studies, little is known about their abundances in the solid state. This is particularly the case for low-mass protostars, for which only the launch of the Spitzer Space Telescope has permitted high-sensitivity observations of the ices around these objects. In this work, we investigate the ~8–10 μm region in the Spitzer IRS (InfraRed Spectrograph) spectra of 41 low-mass young stellar objects (YSOs). These data are part of a survey of interstellar ices in a sample of low-mass YSOs studied in earlier papers in this series. We used both an empirical and a local continuum method to correct for the contribution from the 10 μm silicate absorption in the recorded spectra. In addition, we conducted a systematic laboratory study of NH₃- and CH₃OH-containing ices to help interpret the astronomical spectra. We clearly detect a feature at ~9 μm in 24 low-mass YSOs. Within the uncertainty in continuum determination, we identify this feature with the NH₃ ν₂ umbrella mode and derive abundances with respect to water between ~2% and 15%. Simultaneously, we also revisited the case of CH₃OH ice by studying the ν₄ C–O stretch mode of this molecule at ~9.7 μm in 16 objects, yielding abundances consistent with those derived by Boogert et al. based on a simultaneous analysis of the ν₃ and ν₄ mode data. Our study indicates that NH₃ is present primarily in H₂O-rich ices, but that in some cases, such ices are insufficient to explain the observed narrow FWHM. The laboratory data point to CH₃OH being in an almost pure methanol ice, or mixed mainly with CO or CO₂, consistent with its formation through hydrogenation on grains. Finally, we use our derived NH₃ abundances in combination with previously published abundances of other solid N-bearing species to find that up to 10%–20% of nitrogen is locked up in known ices.

Key words: astrochemistry – infrared: ISM – ISM: abundances – ISM: molecules – stars: formation

Online-only material: color figures

1. INTRODUCTION

Ammonia and methanol are among the most ubiquitous and abundant (after H₂ and CO) molecules in space. Gaseous NH₃ and CH₃OH are found in a variety of environments such as infrared dark clouds, dense gas surrounding ultra-compact H II regions, massive hot cores, hot corinos, and comets. Solid CH₃OH has been observed in the ices surrounding massive young stellar objects (YSOs; e.g., Schutte et al. 1991; Dartois et al. 1999; Gibb et al. 2004) and more recently toward low-mass protostars (Pontoppidan et al. 2003). The presence of solid NH₃ has been claimed toward massive YSOs only (Lacy et al. 1998; Dartois et al. 2002; Gibb et al. 2004; Gürtler et al. 2002), with the exception of a possible detection in the low-mass object IRAS 05445+3242 (Gürtler et al. 2002). However, these detections are still controversial and ambiguous (Taban et al. 2003). Both molecules are key participants in gas–grain chemical networks resulting in the formation of more complex N- and O-bearing molecules, such as CH₂CN and CH₃OCH₂ (e.g., Rodgers & Charnley 2001). Moreover, UV processing of NH₃- and CH₃OH-containing ices has been proposed as a way to produce amino acids and other complex organic molecules (e.g., Muñoz Caro & Schutte 2003; Bernstein et al. 2002; Öberg et al. 2009). In addition, the amount of NH₃ in the ices has a direct impact on the content of ions such as NH₄⁺ and OCN⁻, which form reactive intermediates in solid-state chemical networks. A better knowledge of the NH₃ and CH₃OH content in interstellar ices will thus help to constrain chemical models and to gain a better understanding of the formation of more complex, prebiotic, molecules.

During the pre-stellar phase, NH₃ is known to freeze out on grains (if the core remains starless long enough; Lee et al. 2004). Moreover, CH₃OH is known to have gas-phase abundances with respect to H₂ in hot cores/corinos that are much larger than in cold dense clouds: ~(1 – 10) × 10⁻⁶ versus < 10⁻⁷, with the former values most likely representing evaporated ices in warm regions (e.g., Genzel et al. 1982; Blake et al. 1987; Federman et al. 1990). Together, these findings suggest that the ices are...
Table 1
Selected Near- and Mid-infrared Features of NH₃ and CH₃OH

| Mode                             | λ (µm) | ν (cm⁻¹) | Problem                                                                 |
|----------------------------------|--------|----------|------------------------------------------------------------------------|
| NH₃ features                      |        |          |                                                                        |
| v₁ N-H stretch                   | 2.96   | 3375     | Blended with H₂O (O-H stretch, 3.05 µm/3275 cm⁻¹)                      |
| v₂ H-N-H bend                    | 6.16   | 1624     | Blended with H₂O (H-O-H bend, 5.99 µm/1670 cm⁻¹), HCOOH               |
| v₂ umbrella                      | 9.00   | 1110     | Blended with silicate                                                  |
| CH₃OH features                   |        |          |                                                                        |
| v₂ C-H stretch                   | 3.53   | 2827     | ...                                                                    |
| v₀ & v₁-CH₃ deformation          | 6.85   | 1460     | Blended (e.g., with NH₄⁺)                                             |
| v₁ CH₃ rock                      | 8.87   | 1128     | Weak, blended with silicate                                           |
| v₄ C-O stretch                   | 9.75   | 1026     | Blended with silicate                                                 |
| Torsion                          | 14.39  | 695      | Blended with the H₂O libration mode                                   |

Notes. The bold lines indicate the features studied here. The nomenclature for the NH₃ and CH₃OH vibrational modes is adopted from Herzberg (1945).

In principle, the molecular environment also provides information on the formation pathway of the molecule. For example, NH₃ ice is expected to form simultaneously with H₂O and CH₄ in the early, low-density molecular cloud phase from hydrogenation of N atoms (e.g., Tielens & Hagen 1982). In contrast, solid CH₃OH is thought to result primarily from hydrogenation of solid CO, a process which has been confirmed in several laboratory experiments to be rapid at low temperatures (e.g., Watanabe & Kouchi 2002; Hidaka et al. 2004; Fuchs et al. 2009). A separate, water-poor layer of CO ice is often found on top of the water-ice rich layer in low-mass star-forming regions due to the “catastrophic” freeze-out of gas-phase CO at high densities (Pontoppidan et al. 2003; Pontoppidan 2006). Hydrogenation of this CO layer should lead to a nearly pure CH₃OH ice layer (e.g., Cuppen et al. 2009), which will have a different spectroscopic signature from that of CH₃OH embedded in a water-rich matrix. The latter signature would be expected if CH₃OH ice were formed by hydrogenation of CO in a water-rich environment or by photoprocessing of H₂O:CO ice mixtures, another proposed route (e.g., Moore & Hudson 1998).

Here, we present Spitzer spectra between 5 and 35 µm of ices surrounding 41 low-mass protostars, focusing on the ∼8–10 µm region that contains the v₂ umbrella and v₄ C-O stretch modes of NH₃ and CH₃OH, respectively. This work is the fourth paper in a series of ice studies (Boogert et al. 2008, hereafter Paper I; Pontoppidan et al. 2008; Öberg et al. 2008) carried out in the context of the Spitzer Legacy Program “From Molecular Cores to Planet-Forming Disks” (“c2d”; Evans et al. 2003). In Section 2, we carry out the analysis of the Spitzer data in the 8–10 µm range. In Section 3, we present the laboratory data specifically obtained to help interpret the data that are discussed in Section 4. Finally, we conclude in Section 5 with a short discussion of the joint astronomy-laboratory work (including the overall continuum determination).

2. ASTRONOMICAL OBSERVATIONS AND ANALYSIS

The source sample consists of 41 low-mass YSOs that were selected based on the presence of ice absorption features. The entire sample spans a wide range of spectral indices α = −0.25 to +2.70, with α defined as d log(Fₜ) / d log(λ), where d indicates the derivative and Fₜ represents all the photometric fluxes available between λ = 2.17 µm (Two Micron All Sky Survey (2MASS) Kₜ band) and λ = 24 µm (Spitzer/MIPS band). In the infrared broadband classification scheme, 35 out of 41 objects fall in the embedded Class 0/I category (α > 0.3). The remaining six objects are flat-spectrum-type
objects ($-0.3 < \alpha < 0.3$; Greene et al. 1994). Spitzer/IRS spectra (5–35 $\mu$m) were obtained as part of the c2d Legacy program (PIDs 172 and 179), as well as a dedicated open time program (PID 20604), and several previously published guaranteed time observation (GTO) spectra (Watson et al. 2004). We refer the reader to Table 1 and Section 3 of Paper I for the source coordinates and a description of the data reduction process (including overall continuum determination).

As mentioned previously, spectral signatures in the $\sim$8–10 $\mu$m region are dominated by the Si–O stretching mode of silicates. The overall shape as well as the substructure of the silicate feature depends on grain size, mineralogy, level of crystallinity. These effects are degenerate and so these different factors cannot be easily separated. For example, large grains and the presence of SiC both produce a shoulder at 11.2 $\mu$m (e.g., Min et al. 2007). Therefore, trying to fit the 10 $\mu$m silicate feature by determining the composition and size of the grains is a complex process. For this reason, we use two alternative methods to model the silicate profile and extract the NH$_3$ (and CH$_3$OH) feature(s) from the underlying silicate absorption.

2.1. Local Continuum

The first method uses a local continuum to fit the shape of the silicate absorption. For this, we fit a fourth-order polynomial over the wavelength ranges 8.25–8.75, 9.23–9.37, and 9.98–10.4 $\mu$m, avoiding the positions where NH$_3$ and CH$_3$OH absorb around 9 and 9.7 $\mu$m. These fits are shown as thick blue/black lines in Figure 1. After subtraction of the local continuum from the observations, we fit a Gaussian to the remaining NH$_3$ and/or CH$_3$OH feature, when present, as shown in Figure 2. The results of the Gaussian fits are listed in Table A1 of Appendix A.

2.2. Template

The second method assumes that the 8–10 $\mu$m continuum can be represented by a template silicate absorption feature, selected among the observed sources. A comparison of the results obtained using a template to those obtained using a simple local continuum provides an estimate of the influence of the continuum choice on the shape and depth of the NH$_3$ and CH$_3$OH features. The templates were chosen using an empirical method. Upon examination of the 10 $\mu$m feature of the entire sample, the sources could be separated into three general categories, depending on the shape of the wing of the silicate absorption between ~8 and 8.7 $\mu$m (which we will refer to as the 8 $\mu$m wing): (1) sources with a straight 8 $\mu$m wing (Figure 3(a)), (2) sources with a curved 8 $\mu$m wing (Figure 3(b)), and (3) sources with a rising 8 $\mu$m wing ("emission" sources, Figure 3(c)).

Note that, since radiative transfer in the 8–10 $\mu$m region can be complicated by the presence of silicate emission, we only consider sources that are the least affected by emission, that is those falling in one of the first two categories. Nevertheless, non-rising silicate profiles might still suffer from the presence of emission. To try and estimate the impact of this potential effect, we used two silicate emission sources from Kessler-Silacci et al. (2006) and subtracted these emission profiles from our absorption profiles, assuming that the emission represented 10% to 50% of the observed absorption. After removal of a local continuum, we determined the integrated optical depths of the NH$_3$ and CH$_3$OH features in the spectra corrected for emission and compared these to the integrated optical depths of the uncorrected spectra. We find that the difference can be up to a factor of 2 and therefore identify this possible presence of underlying emission as the largest source of uncertainty in our abundance determinations.

For each of the straight and curved 8 $\mu$m wings, two sources (in order to test for template-dependent effects) were selected as possible templates for the silicate feature. The selection criteria were: (1) a silicate feature as deep as possible to minimize the effects of silicate emission and (2) little NH$_3$ and CH$_3$OH signal, as estimated after subtraction of a local continuum. Additionally, we added to this list the GCS3 spectrum observed by Kemper et al. (2004) toward the Galactic Center. The spectra of these templates in the 8–10 $\mu$m region are displayed in Figure 4.

For all the other sources in our sample, the best template was determined by scaling the possible templates to the observed optical depth at different wavelengths (8.75, 9.30, 9.37, 9.70, 9.98 $\mu$m) and finding the combination (template + scaling point) that gave the least residuals over the same wavelength ranges used to estimate the local continuum (8.25–8.75, 9.23–9.37, 9.98–10.4 $\mu$m). The result of this process is displayed for each source in the top part of Figure 1, where the best template is shown by a red/grey line. The bottom panels of Figure 1 show sources for which no reasonable template could be found, as well as emission sources, in which case only the local continuum is overlaid. As in the case of the local continuum method, the spectra obtained after subtraction of the templates are shown in Figure 2. Taken together, NH$_3$ features are detected in 24 out of 41 sources.

The top panel of Figure 2 shows that the CH$_3$OH feature is not affected by the continuum choice, whereas the width of the NH$_3$ band is somewhat sensitive to this choice, especially if there is no CH$_3$OH absorption, in which case the local continuum yields a wider NH$_3$ profile. For both continua, there is a clear feature around 9 $\mu$m, which we attribute to NH$_3$, with the characteristics and limitations given and discussed in the following sections.

2.3. NH$_3$ Ice Column Densities and Abundances

Gaussian fits were performed to the NH$_3$ and/or CH$_3$OH features when present, and derived parameters for NH$_3$ are listed in Table A1 (Appendix A). Table 2 gives the column densities derived for NH$_3$ for each of the two methods employed to determine the continuum, using a band strength of 1.3 × 10$^{-17}$ cm molecule$^{-1}$ for the NH$_3$ $\nu_2$ umbrella mode appropriate for a water-rich ice (d’Hendecourt & Allamandola 1986; Kerkhof et al. 1999). The two methods generally agree to within a factor of 2 or better. A similar factor of $\lesssim 2$ overall uncertainty is estimated for those sources for which only the local continuum has been used.

The position of the NH$_3$ $\nu_2$ umbrella mode is very close to that of the $\nu_2$–CH$_3$ rock mode of CH$_3$OH. As illustrated by our laboratory data (see Section 3), sources with an absorption depth at ~9.7 $\mu$m (C–O stretch mode of CH$_3$OH) at least twice as large as the absorption depth at ~9 $\mu$m (blend of CH$_3$–rock mode of CH$_3$OH and NH$_3$ umbrella mode) have a significant contribution to the 9 $\mu$m integrated optical depth from the CH$_3$–rock mode of CH$_3$OH. In these cases (sources followed by an asterisk in Table 2 and in Table A1 of Appendix A), we performed the following correction: we scaled an H$_2$O:CH$_3$OH = 9:1 laboratory spectrum to the observed optical depth of the C–O stretch mode of CH$_3$OH, determined the integrated optical depth of the CH$_3$–rock mode of CH$_3$OH in that scaled spectrum, and subtracted it from the total observed optical depth at 9 $\mu$m. This correction is justified by the fact that the H$_2$O:CH$_3$OH:NH$_3$ = 10:4:1 spectrum, a typical interstellar abundance mixture,
Figure 1. Top: local continuum (thick blue/black lines) and template (red/grey lines) fits to all sources for which a template could be found; see Section 2.2 for details. Bottom: local continuum fits to emission sources or sources for which no reasonable template could be found.
(A color version of this figure is available in the online journal.)

is well reproduced around 8–10 μm by a combination of H$_2$O:CH$_3$OH = 9:1 and H$_2$O:NH$_3$ = 9:1 (see Section 3).

The inferred NH$_3$ ice abundances range from $\lesssim$1% to 15% with respect to H$_2$O ice, excluding the abnormally high value of EC 82. When considering all values (except that of EC 82) determined with the local continuum method, this relative abundance is centered on 5.3% with a standard deviation of 2.0%. If we use values determined with the template method whenever available, we find a mean of 7.0% ± 3.2%. Either way, within the errors, this is similar to what was obtained
by Öberg et al. (2008) for CH$_4$ (4.7% ± 1.6%), another ice component that should form via hydrogenation. For six out of the eight sources where both NH$_3$ and CH$_4$ are detected, the NH$_3$-to-CH$_4$ abundance ratio is slightly larger than 1 (∼1.2). Based on elemental abundance ratios, one would expect NH$_3$/CH$_4$ smaller than 1, but since two thirds of the carbon is in refractory grains and some fraction of the gaseous CO locked up in CO at the ice formation threshold, NH$_3$-to-CH$_4$ ratios larger than 1 are consistent with both NH$_3$ and CH$_4$ being formed by hydrogenation of N and C, respectively. Further comparison between these and other ice species will be addressed in an upcoming paper (K. I. Öberg et al. 2010, in preparation).

Regarding CH$_3$OH, we only report values for the Gaussian parameters and derived column densities in Appendix A (see
Figure 3. Examples illustrating the three shapes of the 8 μm wing shown by the thick gray line: (a) straight, (b) curved, and (c) rising.

Figure 4. Silicate features of the sources used as templates for a straight 8 μm wing (left), curved 8 μm wing (middle), and GCS3 (right). The bottom panels of each plot are the residuals after removal of the local continuum shown in gray in the top panels. The optical depth scale is kept fixed for comparison. These sources are selected to have no or at most weak NH3 and CH3OH absorptions.

Table A.2), to show that the numbers we obtain in this independent study are consistent with those reported in Paper I. Our recommended abundances are those from Paper I, based on the combined 9.75 and 3.53 μm analysis. The inferred CH3OH abundances range from <1% to >25% with respect to H2O ice, indicating significant CH3OH/NH3 abundance variations from source to source. Such relative abundance variations can already be clearly seen from the changing relative depths of the 9.0 and 9.7 μm features (see also Paper I). Thus, NH3 and CH3OH ices are likely formed through different formation pathways and/or in different ice environments.

3. LABORATORY WORK AND ANALYSIS

The band profiles presented in Figure 2 contain information on the ice environment in which NH3 and CH3OH are located, and thus their formation and processing history. To extract this information, a systematic laboratory study of the NH3 and CH3OH features in a variety of ices has been carried out. Specifically, three features between 8 and 10 μm have been analyzed:

1. the NH3 ν2 umbrella mode, at ~9.35 μm or 1070 cm⁻¹ in pure NH3 ice, and with band strength A_pure = 1.7 × 10⁻¹⁷ cm molecule⁻¹ (d’Hendecourt & Allamandola 1986),
2. the CH3OH ν4 C–O stretching mode, at ~9.74 μm or 1027 cm⁻¹ in pure CH3OH ice, and with A_pure = 1.8 × 10⁻¹⁷ cm molecule⁻¹ (d’Hendecourt & Allamandola 1986),
3. the CH3OH ν7–CH3 rocking mode, at ~8.87 μm or 1128 cm⁻¹ in pure CH3OH ice, and with A_pure = 1.8 × 10⁻¹⁸ cm molecule⁻¹ (Hudgins et al. 1993).

It should be noted that, as mentioned in the above list, the quoted positions are for pure ices only and therefore slightly deviate from the astronomical values given in Table 1.

This laboratory study targeted pure, binary, and tertiary interstellar ice analogs consisting of different mixtures of H2O, NH3, CH3OH, CO, and CO2, the major ice components. All measurements were performed under high vacuum conditions.
Table 2
NH3 Column Densitiesa and Abundances with Respect to H2O Iceb

| Source          | NH3, local | % H2Oc | NH3, template | % H2Oc | Template | Scaling Point | μm       |
|-----------------|------------|--------|---------------|--------|----------|---------------|----------|
| IRAS 03235+3004 | 6.83 (0.98) | 4.71 (1.00) | 8.94 (1.03) | 6.17 (1.20) | IRAS 12553 | 9.30           |
| L1455 IRS3      | 0.57 (0.23) | 6.21 (3.51) | 1.41 (0.27) | 15.37 (6.86) | GCS3      | 9.37           |
| IRAS 03254+3050 | 2.44 (0.39) | 6.66 (1.37) | 4.58 (0.49) | 12.52 (2.10) | IRAS 12553 | 10.40          |
| B1-b            | ~7.3       | ~4.2   | ~9.8          | ~5.6   | IRAS 12553 | 9.70           |
| IRAS 04108+2803 | 1.23 (0.24) | 4.29 (1.03) | 2.07 (0.39) | 7.21 (1.69) | IRAS 23238 | 9.70           |
| HH 300          | 0.90 (0.22) | 3.46 (0.90) | 2.23 (0.37) | 8.60 (1.65) | DG Tau B | 9.70           |
| IRAS 08242–5050 | 4.77 (0.46) | 6.13 (0.85) | 4.41 (0.54) | 5.66 (0.89) | IRAS 12553 | 9.70           |
| IRAS 15398–3359 | 8.73 (1.18) | 5.90 (1.77) | 13.80 (1.35) | 9.33 (2.65) | IRAS 12553 | 9.70           |
| B59 YSO5        | 4.92 (0.72) | 3.53 (0.88) | 6.37 (0.99) | 4.57 (1.17) | IRS7 A    | 9.70           |
| 2MASS17112317–272431 | 13.10 (1.06) | 6.70 (0.54) | 20.60 (2.76) | 10.58 (1.42) | IRAS 23238 | 9.70           |
| SVS 4-5         | ~2.4       | ~4.3   | ~5.8          | ~10.3  | GCS3      | 8.75           |
| R CrA IRS 5     | 0.91 (0.23) | 2.54 (0.67) | 1.49 (0.31) | 4.15 (0.92) | IRAS 12553 | 9.70           |
| RNO 15          | 0.80 (0.21) | 11.58 (3.18) | ...          | ...    | ...      | ...            |
| IRAS 03271+3013 | 4.90 (0.88) | 6.37 (1.86) | ...          | ...    | ...      | ...            |
| B1-a            | 3.46 (0.69) | 3.33 (0.98) | ...          | ...    | ...      | ...            |
| L1489 IRS       | 2.31 (0.30) | 5.42 (0.96) | ...          | ...    | ...      | ...            |
| IRAS 13546–3941 | 0.94 (0.16) | 4.56 (0.87) | ...          | ...    | ...      | ...            |
| RNO 91          | 2.03 (0.30) | 4.78 (0.81) | ...          | ...    | ...      | ...            |
| IRAS 17081–2721 | 0.86 (0.16) | 6.54 (1.39) | ...          | ...    | ...      | ...            |
| EC 74           | 1.00 (0.29) | 9.35 (3.13) | ...          | ...    | ...      | ...            |
| EC 82           | 1.22 (0.14) | 31.31 (6.65) | ...          | ...    | ...      | ...            |
| EC 90           | 0.67 (0.20) | 3.94 (1.24) | ...          | ...    | ...      | ...            |
| EC 92           | ~0.5       | ~3.0    | ...          | ...    | ...      | ...            |
| CrA IRS7 B      | ~3.0       | ~2.8    | ...          | ...    | ...      | ...            |
| L1014 IRS       | 3.72 (0.91) | 5.20 (1.43) | ...          | ...    | ...      | ...            |
| CK4             | 0.84 (0.13) | 5.37 (0.86) | ...          | ...    | ...      | ...            |

3σ upper limits

| Source          | NH3, local | % H2Oc | NH3, template | % H2Oc | Template | Scaling Point | μm       |
|-----------------|------------|--------|---------------|--------|----------|---------------|----------|
| LDN 1448 IRS1   | 0.20       | 4.15   | ...           | ...    | ...      | ...            |
| IRAS 03245+3002 | 17.28      | 4.40   | ...           | ...    | ...      | ...            |
| L1455 SMM1      | 15.10      | 8.29   | ...           | ...    | ...      | ...            |
| IRAS 03301+3111 | 0.24       | 5.93   | ...           | ...    | ...      | ...            |
| B1-c            | 11.93      | 4.04   | ...           | ...    | ...      | ...            |
| IRAS 03439+3233 | 0.31       | 3.10   | ...           | ...    | ...      | ...            |
| IRAS 03435+3242 | 0.47       | 2.09   | ...           | ...    | ...      | ...            |
| DG Tau B        | 0.47       | 2.05   | ...           | ...    | ...      | ...            |
| IRAS 12553-7651 | 0.61       | 2.04   | ...           | ...    | ...      | ...            |
| Elias 29        | 0.28       | 0.93   | ...           | ...    | ...      | ...            |
| CBRR 2422.8–342 | 0.52       | 1.23   | ...           | ...    | ...      | ...            |
| HH 100 IRS      | 0.46       | 1.89   | ...           | ...    | ...      | ...            |
| CrA IRS7 A      | 0.97       | 0.89   | ...           | ...    | ...      | ...            |
| CrA IRS32       | 5.44       | 10.35  | ...           | ...    | ...      | ...            |
| IRAS 23238+7401 | 1.60       | 1.24   | ...           | ...    | ...      | ...            |

Notes. Sources in bold were used as templates. Uncertainties quoted in parentheses are statistical errors from the Gaussian fits while absolute errors are up to a factor of 2. Sources with τν7 μm > 2 × τν0 μm, for which an estimated contribution from the CH3-rock mode of CH3OH was subtracted (see the text for details).

a Derived using a bandstrength of 1.3 × 10−17 cm molecule−1.

b Using the H2O ice column densities listed in Paper I.

c Values are likely upper limits (see Section 4.2 for details).

(~10−7 mbar) using an experimental approach described in Gerakines et al. (1995), Bouwman et al. (2007), and Oberg et al. (2007). The ice spectra were recorded in transmission using a Fourier transform infrared spectrometer covering 25–2.5 μm (400–4000 cm−1) with 1 cm−1 resolution and by sampling relatively thick ices, typically several thousands Langmuirs thick. These ices were grown at a speed of ~1016 molecules cm−2 s−1 on a temperature-controlled CsI window.

A typical reduced spectrum for an ice mixture containing H2O:CH3OH:NH3 = 10:4:1 at 15 K is shown in Figure 5. Since band profiles and strengths change with ice composition and also with temperature, the three fundamentals mentioned above were investigated as a function of temperature ranging from 15 to 140 K with regular temperature steps for a number of binary and tertiary mixtures (listed in Appendix B). An IDL routine was used to determine the location of the band maximum, FWHM, and integrated absorbance of the individual absorption bands. For the asymmetric NH3 ν3 umbrella mode, the band position has been determined by the maximum absorbance and for the symmetric profiles the spectral parameters have been measured.

12 One Langmuir corresponds to a pressure of 10−6 torr for 1 s and measures the exposure of a surface to adsorption of gases. One Langmuir is equivalent to about 1015 molecules cm−2.
The resulting absolute frequency uncertainty is of the order determined from Gaussian fits of baseline subtracted spectra. This spectrum can be approximated as the sum (solid green/dark gray line) of H$_2$O:CH$_3$OH = 9:1 (solid red/light gray line) and H$_2$O:NH$_3$ = 9:1 (dash-dotted blue/gray line). The bottom plot is the difference between the two, showing that the feature at 9 $\mu$m (blend of NH$_3$ and CH$_3$OH CH$_3$-rock modes) is well reproduced by the sum of the two individual signatures. This figure also illustrates the fact that the positions of the features in mixed ices differ from that in pure ices (see the list at the beginning of this section).

(A color version of this figure is available in the online journal.)

determined from Gaussian fits of baseline subtracted spectra. The resulting absolute frequency uncertainty is of the order of 1 cm$^{-1}$. The measurements are presented in Table B.1 of Appendix B, and are included in the Leiden laboratory database.\textsuperscript{13}

NH$_3$ and CH$_3$OH both have the ability to form hydrogen bonds in water-rich matrices, so it is not surprising that the band profiles change compared with pure ices because of the various molecular interactions (e.g., d’Hendecourt & Allamandola 1986).

In addition to profiles, band strengths can change with environment and with temperature, as discussed for the cases of CO and CO$_2$ in water-rich ices in Kerkhof et al. (1999), Öberg et al. (2007), and Bouwman et al. (2007). Figure 6 shows how the NH$_3$ $v_2$ umbrella mode absorption maximum shifts from 1070 cm$^{-1}$ (9.35 $\mu$m) for pure NH$_3$ ice to 1118 cm$^{-1}$ (8.94 $\mu$m) for an astronomically more realistic H$_2$O:NH$_3$ = 9:1 (hereafter 9:1) mixture, for which the FWHM and integrated band strength also change significantly. For example, the band strength is lowered in the 9:1 mixture to 70% of its initial value in pure NH$_3$ ice. This is in good agreement with previous experiments performed by Kerkhof et al. (1999). The spectral appearance also depends on temperature; for the 9:1 mixture a temperature increase from 15 to 120 K results in a redshift of the peak position from 1118 to 1112 cm$^{-1}$ (8.94–8.99 $\mu$m) and the FWHM decreases from 62 to 52 cm$^{-1}$ (0.50–0.42 $\mu$m) (see Figure 7). The NH$_3$ band strength, on the other hand, does not show any temperature dependence.

If NH$_3$ is in a water-poor environment with CO and/or CO$_2$, the $v_2$ peak position shifts to the red compared with pure NH$_3$, to as much as 1062 cm$^{-1}$ (9.41 $\mu$m). The FWHM is not much affected whereas the band strength is lowered by 20%. Because of the intrinsically large difference in band maximum position between NH$_3$ in a water-poor and water-rich environment, the astronomical observations can distinguish between these two scenarios.

Methanol-containing ices have been studied in a similar way (see Figure 8). The weakly absorbing $v_7$–CH$_3$ rocking mode at $\sim$1125 cm$^{-1}$ (8.89 $\mu$m) is rather insensitive to H$_2$O mixing, but the $v_4$ C–O stretch vibration shifts to the red from 1028 to 1020 cm$^{-1}$ (9.73–9.80 $\mu$m) when changing from a pure CH$_3$OH ice to an H$_2$O:CH$_3$OH = 9:1 mixture. In the latter spectrum, the CH$_3$OH $v_4$ C–O stretch mode needs to be fitted with a double Gaussian. A substructure appears for a temperature of 80 K (right panel of Figure 8) while for even higher temperatures, a clearly double peaked structure becomes visible (as previously seen in, e.g., Figure 2 of Schutte et al. 1991). This splitting hints at different physical sites and has been previously ascribed to type II clathrate formation in the ice (Blake et al. 1991).

When CH$_3$OH is mixed with CO, the band maximum shifts from 1028 to 1034 cm$^{-1}$ (9.73–9.67 $\mu$m) when going from a 9:1 to a 1:9 CH$_3$OH:CO mixture. When 50% or more CO is mixed in, the CH$_3$OH $v_4$ C–O stretch mode starts to show a shoulder and cannot be fitted correctly by a single Gaussian component (see Figure 9). Such a two-component profile would not be recognized, however, at the spectral resolution and signal/noise of our Spitzer data, so for the comparison between laboratory and observational data a single Gaussian is used. Overall, the

\textsuperscript{13} www.strw.leidenuniv.nl/~lab/
shifts of the CH$_3$OH $v_4$ mode between water-rich and CO-rich mixtures are much smaller than in the case of the NH$_3$ $v_2$ mode.

The effect of CH$_3$OH on the 4.7$\mu$m $v_1$ stretch mode of CO has also been investigated. The band maximum shifts from 2139 cm$^{-1}$ (4.68$\mu$m) for the nearly pure 9:1 CO:CH$_3$OH mixture to 2136 and 2135 cm$^{-1}$ for the 1:1 and 1:9 mixtures, respectively. The CO band located at 2136 cm$^{-1}$ is often referred to as CO residing in a polar, mainly H$_2$O ice, environment. Clearly, the polar CH$_3$OH molecules can also contribute to CO absorption at 2136 cm$^{-1}$ when intimately mixed in an astronomical ice.

Binary mixtures of NH$_3$ and CH$_3$OH have been studied as well. The CH$_3$OH modes behave very much as they do in a pure methanol ice, but the NH$_3$ $v_2$ umbrella mode is clearly suppressed. Its integrated absorbance is readily reduced to 70% of the integrated absorbance of pure NH$_3$ in a CH$_3$OH:NH$_3$ = 1:1 mixture and becomes even lower for a 4:1 binary composition. The NH$_3$ band also broadens compared to pure NH$_3$ or H$_2$O:NH$_3$ mixtures and strongly overlaps with the C–O stretching mode of CH$_3$OH, to the level that it becomes difficult to measure.

A qualitative comparison with the astronomical data (see Section 4) indicates that neither pure NH$_3$, CH$_3$OH, nor mixed CH$_3$OH:NH$_3$ or H$_2$O-diluted binary ices can simultaneously explain the different NH$_3$ profiles in the recorded Spitzer spectra. Thus, a series of tertiary mixtures with H$_2$O:CH$_3$OH:NH$_3$ in ratios 10:4:1, 10:1:1, and 10:0.25:1 have been measured, because CH$_3$OH is the next major ice component. These ratios roughly span the range of observed interstellar column density ratios. In Figure 10, the spectra of H$_2$O:CH$_3$OH:NH$_3$ tertiary mixtures are plotted and compared to binary H$_2$O:CH$_3$OH and H$_2$O:NH$_3$ data. The NH$_3$ $v_2$ umbrella mode shifts slightly to the blue in the presence of both H$_2$O and CH$_3$OH, with an absorption maximum at 1125 cm$^{-1}$ (8.90$\mu$m) for the 10:4:1
10. Normalized spectra of the CH$_3$OH $\nu_4$ C–O mode (right panel), and the NH$_3$ $\nu_2$ umbrella mode (left panel) for an H$_2$O:CH$_3$OH:NH$_3$ = 10:0.25:1, an H$_2$O:CH$_3$OH:NH$_3$ = 10:1:1, and an H$_2$O:CH$_3$OH:NH$_3$ = 10:4:1 mixture at a temperature of 15 K. These mixture ratios span the range of observed interstellar column density ratios. Spectra were normalized to better show the changes in band maximum position and FWHM of each feature. Spectra of an H$_2$O:CH$_3$OH = 9:1 and an H$_2$O:NH$_3$ = 1:1 mixture were offset and overlaid in light gray in the right and left panels, respectively. In the case of H$_2$O:CH$_3$OH:NH$_3$ = 10:4:1, the NH$_3$ $\nu_2$ umbrella mode is heavily blended with the CH$_3$OH $\nu_7$–CH$_3$ rocking mode, so that the dark gray line actually shows the Gaussian fit to the underlying NH$_3$ feature, whereas the full 9 $\mu$m feature is shown in black.

(A color version of this figure is available in the online journal.)

H$_2$O:CH$_3$OH:NH$_3$ mixture (compared to 1118 cm$^{-1}$ (8.94 $\mu$m) in the H$_2$O:NH$_3$ = 9:1 mixture). The peak intensity of the NH$_3$ $\nu_2$ umbrella mode band in this tertiary mixture is small compared with that of the CH$_3$OH $\nu_7$–CH$_3$ rocking mode, but its integrated intensity is a factor of 2 larger because of the larger NH$_3$ width.

The $\nu_4$ C–O stretching vibration profile of CH$_3$OH in the tertiary mixture does not differ much from the binary values for the highest water content. The position of the absorption maximum is also only marginally affected by the temperature. The FWHM decreases from 30 cm$^{-1}$ (0.29 $\mu$m) for the 10:4:1 mixture to 22 cm$^{-1}$ (0.21 $\mu$m) for the 10:0.25:1 mixture.

Besides H$_2$O, other species may also be regarded as potential candidates for changing the spectral appearance of the NH$_3$ and/or CH$_3$OH features. Chemically linked is HCOOH (Bisschop et al. 2007) which unfortunately cannot be deposited in the present setup because of its reactive behavior when mixed with NH$_3$. Tertiary mixtures with CO and CO$_2$, two other important constituents in interstellar ices, have been measured (see Appendix B) but here the differences are small compared with the observed binary water-rich or CO-rich mixtures, and do not offer an alternative explanation.

4. COMPARISON BETWEEN ASTRONOMICAL AND LABORATORY DATA

4.1. 8–10 $\mu$m Range

The FWHM and band positions of the NH$_3$ and CH$_3$OH features measured in the laboratory and astronomical spectra are shown in Figures 11 (for NH$_3$) and 12 (for CH$_3$OH). For the YSOs, the values obtained after removal of the silicate absorption (see Section 2) using the local continuum method are indicated by filled squares, whereas those obtained from the template method are plotted with open squares. Note that the presence of significant amounts of CH$_3$OH may artificially lower the inferred NH$_3$ $\nu_2$ width in CH$_3$OH rich sources (indicated with * in Table 2) because of the contribution of the narrower $\nu_7$–CH$_3$ rock mode.
Regardless of the method used to subtract the continuum, or the type of source (CH$_3$OH-rich/poor), we find that the observational band positions and FWHM of the $\nu_2$ NH$_3$ umbrella mode absorptions vary, within the errors, between 8.9 and 9.1 $\mu$m and between $\sim$0.2 and 0.5 $\mu$m, respectively. These position and width are not well simultaneously reproduced by any of the investigated mixtures. Regarding the positions, those measured in water-rich ice mixtures are the closest, whereas the positions in pure NH$_3$ or CO/CO$_2$ rich ices are too far away to be representative of the astronomical positions. The derived Spitzer FWHM values range between 0.23 and 0.32 $\mu$m (except for B1-b: 0.39 $\mu$m), when using the local continuum method, not depending on whether the target is CH$_3$OH-rich or -poor. For the template method, CH$_3$OH-rich sources generally tend to have a narrower inferred FWHM, 0.3–0.5 $\mu$m, contrary to what would be expected if the NH$_3$ mode is contaminated by the CH$_3$-rock feature. In any case, most of these widths are still narrower than the laboratory FWHM values. To investigate further the effect of the continuum on the positions and widths of the bands, we performed the following alternative analysis to check whether a continuum could be found that would yield NH$_3$ and CH$_3$OH features with parameters within the laboratory measurements. To do that, we fitted the data between 8.25 and 10.4 $\mu$m with a function that is the sum of a fourth-order polynomial and two Gaussians; positions and widths of the Gaussians were constrained with limits taken from the laboratory data of binary water mixtures (8.9–8.95 $\mu$m for the NH$_3$ position, 0.42–0.52 $\mu$m for its width; 9.67–9.77 $\mu$m for the CH$_3$OH position, 0.2–0.3 $\mu$m for its width). As illustrated in Figure 13, we found that the continuum derived in this way is different from those determined via the other two methods. This result supports the fact that the difference between astronomical and laboratory data could be attributed to the uncertainty in the continuum determination.

Taking the above considerations into account, Figures 11 and 12 suggest that the template method for subtraction of the
Figure 14. Comparison of astronomical data (VLT or Keck measurements at short wavelengths, IRS Spitzer observations elsewhere) and laboratory spectra in selected wavelength ranges: 2.0–4.5 μm (left panels), 5.2–7.5 μm (middle panels), and 8.2–10.2 μm (right panels, silicate absorption subtracted via the template method). Error bars are indicated in the bottom right corner. Overlaid in red/light gray and green/medium gray are laboratory spectra corresponding to H2O:CH3OH:NH3 = 10:4:1 and H2O:NH3 = 9:1, respectively, scaled to the 9 μm NH3 umbrella mode, and smoothed to the Spitzer resolution in the ~5–10 μm range. The dark blue/dark gray line represents the pure water laboratory spectrum scaled to the water column density taken in Paper I. The dotted purple/absorption features in the broad line wings where they blend

Table 3

| Source          | \( \frac{\tau_{\mathrm{H}_2\mathrm{O},3.0}}{\tau_{3.0}} \) | \( \frac{\tau_{\mathrm{max},3.0}}{\tau_{3.0}} \) | \( \frac{\int_{1562}^{1785} \tau_{\mathrm{H}_2\mathrm{O}}}{\int_{1562}^{1785} \tau} \) | \( \frac{\int_{1562}^{1785} \tau_{\mathrm{NH}_3}}{\int_{1562}^{1785} \tau} \) | \( \frac{\tau_{\mathrm{NH}_3,6.16}}{\tau_{C2}} \) |
|-----------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| IRAS 03235+3004 | ...                                           | ...                                           | 0.50                                          | 0.24                                          | 0.02                                          | 0.61                                          |
| IRAS 03254+3050 | 0.73                                          | 1.30                                          | 0.56                                          | 0.92                                          | 0.12                                          | 1.72                                          |
| IRAS 04108+2803 | 0.70                                          | 0.67                                          | 0.58                                          | 0.53                                          | 0.06                                          | 0.49                                          |
| HH 300          | 0.70                                          | 0.57                                          | 0.50                                          | 0.39                                          | 0.05                                          | 0.45                                          |
| IRAS 08242-5050 | 0.76                                          | 0.72                                          | 0.50                                          | 0.45                                          | 0.06                                          | 0.46                                          |
| IRAS 08242-5050 | 0.76                                          | 0.56                                          | 0.50                                          | 0.35                                          | 0.05                                          | 0.36                                          |
| 2MASS J17112317-272431 | ...                                         | ...                                           | 0.69                                          | 0.53                                          | 0.05                                          | 4.23                                          |
| SVS 4-5         | 0.91                                          | 0.94                                          | 0.42                                          | 0.29                                          | 0.00                                          | 0.08                                          |
| R CrA IRS 5     | 0.85                                          | 0.42                                          | 0.63                                          | 0.29                                          | 0.03                                          | 0.21                                          |

Sources with no associated template

| Source          | \( \frac{\tau_{\mathrm{H}_2\mathrm{O},3.0}}{\tau_{3.0}} \) | \( \frac{\tau_{\mathrm{max},3.0}}{\tau_{3.0}} \) | \( \frac{\int_{1562}^{1785} \tau_{\mathrm{H}_2\mathrm{O}}}{\int_{1562}^{1785} \tau} \) | \( \frac{\int_{1562}^{1785} \tau_{\mathrm{NH}_3}}{\int_{1562}^{1785} \tau} \) | \( \frac{\tau_{\mathrm{NH}_3,6.16}}{\tau_{C2}} \) |
|-----------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| RNO 15          | 0.80                                          | 1.97                                          | 0.53                                          | 1.23                                          | 0.16                                          | 0.45                                          |
| IRAS 03271+3013 | ...                                           | ...                                           | 0.36                                          | 0.44                                          | 0.05                                          | 0.60                                          |
| B1-a            | ...                                           | 0.67                                          | 0.43                                          | 0.03                                          | 0.57                                          |
| L1489 IRS       | 0.78                                          | 0.88                                          | 0.60                                          | 0.56                                          | 0.04                                          | 0.83                                          |
| RNO 91          | 0.94                                          | 0.94                                          | 0.53                                          | 0.45                                          | 0.04                                          | 0.53                                          |
| IRAS 17081-2721 | 0.65                                          | 0.95                                          | 0.62                                          | 0.75                                          | 0.05                                          | 1.64                                          |
| EC 74           | 0.95                                          | 2.34                                          | 0.57                                          | 1.18                                          | 0.09                                          | 0.76                                          |
| EC 92           | 0.90                                          | 0.35                                          | 0.38                                          | 0.10                                          | 0.00                                          | 0.01                                          |
| CrA IRS 7 B     | ...                                           | ...                                           | 0.81                                          | 0.19                                          | 0.00                                          | 0.08                                          |
| L1014 IRS       | ...                                           | ...                                           | 0.62                                          | 0.55                                          | 0.06                                          | 0.34                                          |

Notes. Dots indicate that the ratio was not calculated due to the high noise in the 3 μm spectrum. Parameters are: \( \int \tau_{\mathrm{H}_2\mathrm{O},3.0} \) = integrated optical depth of pure water at 3 μm, determined from the column density of Paper I and a band strength of 2.0 × 10^{-16} cm^{-1}, \( \tau_{3.0} \). \( \int \tau_{\mathrm{max},3.0} \) = integrated optical depth over the entire 3 μm region for, respectively, the considered source and the corresponding laboratory mixture (selected from the NH3 feature at 9 μm). \( \frac{\int_{1562}^{1785} \tau_{\mathrm{H}_2\mathrm{O}}}{\int_{1562}^{1785} \tau} \) = integrated optical depth of, respectively, pure water, source spectrum, and laboratory mixture, between 1562 and 1785 cm^{-1} (5.6–6.4 μm). \( \frac{\int_{1562}^{1785} \tau_{\mathrm{NH}_3}}{\int_{1562}^{1785} \tau} \) = integrated and peak optical depth of the 6.16 μm feature of ammonia obtained after subtraction of a pure water spectrum scaled to the optical depth at 3 μm of the laboratory mixture. \( \frac{\tau_{\mathrm{NH}_3,6.16}}{\tau_{C2}} \) = peak optical depth of the C2 component from Paper I.

10 μm silicate absorption is more consistent with the laboratory measurements, but both methods probably miss some weak NH3 absorption features in the broad line wings where they blend with the continuum at the signal-to-noise ratio of the data. If so, the too small line widths inferred from the data (most probably due to the uncertainty in the continuum determination) would
mean that we have underestimated NH₃ abundances by a up to a factor of 2.

The observational band positions and FWHM of the CH₃OH features derived with either the local continuum or the template method are clustered around 9.7–9.75 μm, with the exception of R CrA IRS 5 at 9.66 μm. Similarly the FWHM of the CH₃OH features are all very similar between ~0.22 and 0.32 μm, except for R CrA IRS 5 with 0.39 μm. These values agree (with a few exceptions) with the values obtained from the laboratory spectra. Note that the observed positions of the NH₃ features from the total integrated optical depth at 9 μm, for which the contribution from the CH₃OH CH₃-rock mode is significant. Since the latter and the NH₃ umbrella mode are difficult to disentangle, a single fit was performed (the reported parameters) and the integrated optical depth of the ammonia feature was then obtained from the integrated optical depth at 9 μm by subtracting the estimated contribution of the CH₃OH CH₃-rock mode (see Section 2.2).

We then determined the contributions from the NH₃ features of a 3.47 μm absorption band which could be related to the formation of an ammonia hydrate in the ice mantles: they found that if this band were mostly due to this hydrate, then ammonia abundances would be at most 5% with respect to water. Considering the fact that our derived abundances are larger than 10% in some sources, it is necessary to investigate the effect of such a high abundance on the ammonia features in other spectral ranges. For this, depending on the NH₃-to-CH₃OH abundance ratio observed in the Spitzer spectra, we scale one of the following laboratory spectra to the 9 μm feature of the mixed ice spectrum: H₂O:NH₃ = 9:1, H₂O:NH₃ = 10:1, H₂O:CH₃OH:NH₃ = 10:4:1. Figure 14 illustrates the comparison between the Spitzer and scaled laboratory spectra for the relevant wavelength ranges for a couple of sources, while Figures C.1(a) and (b) (see Appendix C) show the comparison for all sources where NH₃ was tentatively detected.

For further comparison, we also overplotted in Figures 14 and C.1, the following spectra: (1) the pure H₂O ice spectrum derived from the H₂O column density quoted in Paper I (deep blue) and (2) for sources with 3 μm data, the pure H₂O spectrum scaled to the optical depth of the 3 μm feature of the mixed ice laboratory spectrum (purple-dotted). The difference between this scaled pure water spectrum and the mixed ice spectrum gives an indication of the contribution of ammonia features around 3.47 and 6.1 μm.

We then determined the contributions from the NH₃ features to the integrated optical depths of the 3 and 6 μm bands and to the optical depth of component C2, a feature at 6.0–6.4 μm arising from a blend of several species, including NH₃, H₂O, CO₂, HCOO⁻ (see Paper I for more details). These contributions are reported in Table 3.
Table A.2
Parameters of Gaussian Fits to the CH$_3$OH C–O Stretch Mode (After Subtraction of the Continuum with the Local and/or Template Method) and CH$_3$OH Column Densities (or 3$\sigma$ Upper Limits)

| Source          | Local Continuum |         |         |         |         |         |         |         |         |         |         |         |         |         |         | Paper I |
|-----------------|-----------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|                 | $\lambda$ (\mum) | FWHM (\mum) | $\tau_{\text{peak}}$ | $X$ (\% H$_2$O) | $\lambda$ (\mum) | FWHM (\mum) | $\tau_{\text{peak}}$ | $X$ (\% H$_2$O) | $X$ (\% H$_2$O) |
| IRAS 03235+3004 | 9.74 ± 0.02     | 0.26 ± 0.03 | 0.35 ± 0.04 | 4.40 ± 1.04 | 9.74 ± 0.02 | 0.25 ± 0.04 | 0.31 ± 0.04 | 3.84 ± 0.99 | 4.20 ± 1.20 |
| L1455 IRS3      | 9.78 ± 0.01     | 0.14 ± 0.03 | 0.03 ± 0.01 | 3.67 ± 1.80 | 9.78 ± 0.02 | 0.26 ± 0.04 | 0.04 ± 0.01 | 7.17 ± 3.46 | <12.5 |
| IRAS 03254+3050 | ...             | ...       | <5.4      | ...       | ...       | ...       | <5.4      | ...       | <4.6    |
| B1-b            | 9.71 ± 0.01     | 0.30 ± 0.03 | 1.19 ± 0.11 | 14.15 ± 3.16 | 9.71 ± 0.01 | 0.28 ± 0.03 | 1.21 ± 0.11 | 13.75 ± 3.12 | 11.20 ± 0.70 |
| IRAS 04108+2803 | ...             | ...       | ...       | <2.7      | 9.75 ± 0.00 | 0.06 ± 0.04 | 0.04 ± 0.03 | 0.58 ± 0.62 | <3.5 |
| HH 300          | ...             | ...       | <4.7      | <1.2      | ...       | ...       | <1.2      | <1.3     |
| IRAS 08242-5050 | 9.70 ± 0.01     | 0.27 ± 0.03 | 0.25 ± 0.02 | 6.12 ± 1.01 | 9.70 ± 0.01 | 0.29 ± 0.03 | 0.24 ± 0.02 | 6.39 ± 1.09 | 5.50 ± 0.30 |
| IRAS 15398-3359 | 9.73 ± 0.01     | 0.28 ± 0.03 | 0.77 ± 0.06 | 10.26 ± 3.02 | 9.73 ± 0.01 | 0.30 ± 0.03 | 0.75 ± 0.06 | 10.69 ± 3.14 | 10.30 ± 0.80 |
| B59 YSO5        | ...             | ...       | ...       | ...       | ...       | ...       | ...       | ...       | ...       |
| 2MASSI1711237-272431 | 9.75 ± 0.02 | 0.23 ± 0.04 | 0.13 ± 0.02 | 1.03 ± 0.22 | ...       | ...       | ...       | ...       | <2.0    |
| SVS 4-5         | 9.74 ± 0.01     | 0.28 ± 0.03 | 0.77 ± 0.06 | 26.38 ± 6.17 | 9.74 ± 0.01 | 0.31 ± 0.02 | 0.83 ± 0.06 | 31.50 ± 7.12 | 25.20 ± 3.50 |
| R CrA IRS 5     | 9.66 ± 0.01     | 0.39 ± 0.03 | 0.07 ± 0.00 | 5.68 ± 0.60 | 9.66 ± 0.02 | 0.39 ± 0.04 | 0.07 ± 0.00 | 5.51 ± 0.72 | 6.60 ± 1.60 |
| RNO 15          | 9.65 ± 0.03     | 0.44 ± 0.07 | 0.02 ± 0.00 | 11.13 ± 2.16 | ...       | ...       | ...       | ...       | <5.0    |
| IRAS 03271+3013 | ...             | ...       | <4.3      | ...       | ...       | ...       | <4.6      | <5.6     |
| B1-a            | ...             | ...       | <2.4      | ...       | ...       | ...       | ...       | <1.9     |
| L1489 IRS       | 9.78 ± 0.02     | 0.10 ± 0.03 | 0.03 ± 0.01 | 0.44 ± 0.22 | ...       | ...       | ...       | ...       | 4.90 ± 1.50 |
| IRAS 13546-3941 | ...             | <2.0      | ...       | ...       | ...       | <2.0      | ...       | <3.9     |
| RNO 91          | 9.77 ± 0.01     | 0.11 ± 0.03 | 0.03 ± 0.01 | 0.87 ± 0.32 | ...       | ...       | ...       | <5.6     |
| IRAS 17081-2721 | ...             | <6.6      | ...       | ...       | ...       | <6.6      | ...       | 3.30 ± 0.80 |
| EC 74           | ...             | <13.5     | ...       | ...       | ...       | <13.5     | ...       | <9.3     |
| EC 82           | ...             | <24.6     | ...       | ...       | ...       | <24.6     | ...       | <14.2    |
| EC 90           | 9.70 ± 0.01     | 0.32 ± 0.03 | 0.05 ± 0.00 | 6.91 ± 0.99 | ...       | ...       | ...       | ...       | 6.80 ± 1.60 |
| EC 92           | 9.73 ± 0.01     | 0.30 ± 0.02 | 0.09 ± 0.01 | 11.16 ± 1.46 | ...       | ...       | ...       | ...       | 11.70 ± 3.50 |
| CK4             | ...             | ...       | ...       | ...       | ...       | ...       | ...       | ...       | ...       |
| CyA IRS 7B      | 9.70 ± 0.01     | 0.33 ± 0.02 | 0.36 ± 0.02 | 7.74 ± 1.56 | ...       | ...       | ...       | ...       | 6.80 ± 0.30 |
| L1014 IRS       | 9.69 ± 0.03     | 0.38 ± 0.08 | 0.10 ± 0.01 | 3.61 ± 0.99 | ...       | ...       | ...       | ...       | 3.10 ± 0.80 |

Notes. This table shows that CH$_3$OH column densities obtained in this paper are consistent with those in Paper I, which are our recommended values. Uncertainties are statistical errors from the Gaussian fits.
| Ice Mixture | Molecule | Peak Position | FWHM | Intensity |
|-------------|----------|---------------|------|----------|
| 1           | CH₃OH    | 1070          | 9.341| 66       | 0.577    |
| 1           | CH₃OH    | 1076          | 9.291| 70       | 0.605    |
| 1           | CH₃OH    | 1100          | 9.091| 77       | 0.637    |
| 1           | CH₃OH    | 1118          | 8.947| 62       | 0.496    |
| 1           | CH₃OH    | 1124          | 8.897| 53       | 0.420    |
| 1           | CH₃OH    | 1094          | 9.144| 75       | 0.627    |
| 1           | CH₃OH    | 1122          | 8.916| 57       | 0.453    |
| 1           | CH₃OH    | 1098          | 9.108| 82       | 0.681    |
| 1           | CH₃OH    | 1062          | 9.414| 66       | 0.586    |
| 1           | CH₃OH    | 1129          | 8.856| 108a     | 0.849    |
| 1           | CH₃OH    | 1029          | 9.722| 30       | 0.283    |
| 1           | CH₃OH    | 1128          | 9.707| 35       | 0.275    |
| 1           | CH₃OH    | 2823          | 3.543| 28       | 0.035    |
| 1           | CH₃OH    | 1111          | 8.994| 115a     | 0.934    |
| 1           | CH₃OH    | 1029          | 9.720| 29       | 0.274    |
| 1           | CH₃OH    | 1132          | 8.833| 35       | 0.273    |
| 1           | CH₃OH    | 2820          | 3.546| 26       | 0.033    |
| 1           | CH₃OH    | 1086          | 9.209| 137      | 1.166    |
| 1           | CH₃OH    | 1029          | 9.716| 26       | 0.246    |
| 1           | CH₃OH    | 1135          | 8.813| 44       | 0.342    |
| 1           | CH₃OH    | 2817          | 3.550| 26       | 0.033    |
| 1           | CH₃OH    | 1080          | 9.258| 118      | 1.015    |
| 1           | CH₃OH    | 1030          | 9.711| 22       | 0.207    |
| 1           | CH₃OH    | 1128          | 8.865| 35a      | 0.275    |
| 1           | CH₃OH    | 2813          | 3.555| 27       | 0.034    |
| 1           | CH₃OH    | 1078          | 9.278| 98       | 0.845    |
| 1           | CH₃OH    | 1030          | 9.707| 16       | 0.151    |
| 1           | CH₃OH    | 1125          | 8.888| 32a      | 0.253    |
| 1           | CH₃OH    | 2824          | 3.541| 26       | 0.033    |
| 1           | CH₃OH    | 1119          | 8.937| 59       | 0.472    |
| 1           | CH₃OH    | 1017          | 9.833| 22       | 0.213    |
| 1           | CH₃OH    | 2829          | 3.534| 30a      | 0.037    |
| 1           | CH₃OH    | 1123          | 8.903| 61       | 0.484    |
| 1           | CH₃OH    | 1022          | 9.784| 24       | 0.230    |
| 1           | CH₃OH    | 2830          | 3.533| 15       | 0.019    |
| 1           | CH₃OH    | 1130          | 8.848| 62       | 0.489    |
| 1           | CH₃OH    | 1023          | 9.777| 30       | 0.288    |
| 1           | CH₃OH    | 1124          | 8.896| 23       | 0.183    |
| 1           | CH₃OH    | 2830          | 3.534| 14       | 0.017    |
| 1           | CH₃OH    | 1028          | 9.729| 28       | 0.265    |
| 1           | CH₃OH    | 1125          | 8.888| 34       | 0.269    |
| 1           | CH₃OH    | 2828          | 3.536| 33       | 0.041    |
| 1           | CH₃OH    | 1025          | 9.755| 33       | 0.314    |
| 1           | CH₃OH    | 1124          | 8.897| 40       | 0.317    |
| 1           | CH₃OH    | 2828          | 3.536| 23       | 0.029    |
| 1           | CH₃OH    | 1020          | 9.801| 23       | 0.221    |
| 1           | CH₃OH    | 1126          | 8.883| 13       | 0.103    |
| 1           | CH₃OH    | 2828          | 3.536| 23       | 0.029    |
| 1           | CH₃OH    | 1034          | 9.675| 25       | 0.229    |
| 1           | CH₃OH    | 1119          | 8.938| 30       | 0.242    |
Figures 14, C.1, and Table 3 show that (1) the scaled laboratory spectra generally do not overestimate the observed absorption features, and (2) for most sources, the presence of NH$_3$ at the level we determine from the 9 mm feature does not explain by itself the depth of the C2 component and of the red wing of the 3 mm band. Hence, our inferred NH$_3$ abundances up to 15% from the 9.7 mm data are not in conflict with the lack of other NH$_3$ features. The only exceptions are two sources (RNO 15 and EC 74), for which the scaled mixed ice spectrum exceeds the data in the 3 mm range. In the case of RNO 15, the NH$_3$ abundance could have been overestimated due to the contribution of the CH$_3$OH CH$_3$-rock feature at ~9 mm. For EC 74, this overestimate and the presence of emission weaken the identification of the NH$_3$ signature. In both cases, the quoted NH$_3$ abundances should be considered as upper limits.

Overall, our reported NH$_3$ abundances are up to a factor of 3 larger than the upper limits derived by Dartois & d’Hendecourt (2001). First, let us recall that the conclusions in their study and in ours are drawn from the analysis of different samples. Second, Dartois & d’Hendecourt made an assumption that does not apply to our sample: they considered a grain size distribution including also scattering from larger grains, producing an enhanced 3 mm wing, whereas the results presented here can be taken as representative of NH$_3$ absorption from small grains. It is beyond the scope of this paper to investigate the effects of grain size distribution and scattering in as much detail as was done in Dartois & d’Hendecourt (2001).

4.3. Nitrogen Ice Inventory

The confirmation of the presence of relatively large amounts of solid NH$_3$, up to 15%, in interstellar ices solves a longstanding problem. Indeed, the detection of solid NH$_3$ has remained elusive and/or controversial, despite a number of clues suggesting its presence:

1. High cosmic abundance of atomic nitrogen: $N_{N}/N_{H} = 7.76 \times 10^{-5}$ (Savage & Sembach 1996), only a factor of a few below those of oxygen and carbon. Here, $N_{H}$ indicates the total number of hydrogen nuclei, $N_{H} = N(H) + 2N(H_2)$.
2. High abundances of gaseous NH$_3$ of $N_{NH_3}/N_{H} \sim 10^{-6}$ to $10^{-5}$ in the Orion-KL nebula (Barrett et al. 1977; Genzel et al. 1982) and in other hot cores such as G9.62+0.19, G29.96−0.02, G31.41+0.31 (Cesaroni et al. 1994), and G10.47+0.03 (Cesaroni et al. 1994; Osorio et al. 2009).
3. Identification of substantial amounts of OCN$^-$ (e.g., van Broekhuizen et al. 2004, 2005) and NH$_2^+$ in ices (e.g., Schute & Khanna 2003; Boogert et al. 2008); considering that these ions form via reactions involving NH$_3$, the non-detection of solid NH$_3$ would be puzzling.

Our results can be used to draw up a possible nitrogen budget. Assuming $N_{H_2O}/N_{H} \sim 5 \times 10^{-5}$ (Pontoppidan et al. 2004; Boogert et al. 2004), and average abundances with respect to H$_2$O of 5.5% for NH$_3$ (see Section 2.3), 7% for NH$_2^+$ (from Table 3 of Paper I), and 0.6% for OCN$^-$ (van Broekhuizen et al. 2005), the NH$_3$, NH$_2^+$ and OCN$^-$ abundances with respect to total H are 2.8, 3.5, and 0.3 \times 10^{-6}, respectively. This corresponds to, respectively, 3.4%, 4.4%, and 0.4% of the atomic nitrogen cosmic abundance so that, in total, about 10% of the cosmically available nitrogen would be locked up in ices, leaving solid and gaseous N$_2$, N, and HCN as other substantial nitrogen carriers. The main uncertainty in this determination is the adopted H$_2$O ice abundance with respect to total H; in several sources this may well be a factor of 2 larger, leading to about 20% of the nitrogen accounted for in ices.

5. CONCLUSION

We have analyzed in detail the 8–10 mm range of the spectra of 41 low-mass YSOs obtained with Spitzer and presented in Paper I. The sources are categorized into three types: straight, curved, and rising 8 mm silicate wings, and for each category template sources with little or no absorption from ices around 9–10 mm have been determined. This has led to two ways of subtracting the contribution from the 10 mm silicate absorption: first, by determining a local continuum and second, by scaling the templates to the optical depth at 9.7 mm. The two methods give consistent band positions of the NH$_3$ features, but the resulting widths can be up to a factor of 2 larger using the template continuum method. Taking into account the uncertainty in continuum determination, NH$_3$ ice is most likely detected in 24 of the 41 sources with abundances of ~2% to 15% with respect to H$_2$O, with an average abundance of 5.5\% \pm 2.0%. These abundances have estimated uncertainties up to a factor of 2 and are not inconsistent with other features in the 3 and 6 mm ranges. CH$_3$OH is often detected as well, but the NH$_3$/CH$_3$OH abundance ratio changes strongly from source to source. Our inferred CH$_3$OH column densities are consistent with the values derived in Paper I.

Targeted laboratory experiments have been carried out to characterize the NH$_3$ and CH$_3$OH profiles (position, FWHM,
Figure C.1. (a) Comparison between astronomical and laboratory data for sources whose silicate absorption feature was fitted with a template. For a given source (displayed in either the left or the right column of the figure), the middle and right panels show 5.2–7.5 and 8.2–10.2 μm regions from IRS Spitzer spectra overlaid with laboratory spectra, scaled to the 9 μm NH3 umbrella mode, and smoothed to the Spitzer resolution. Error bars for the Spitzer spectra are indicated in the bottom right corner. The dark blue/dark gray line represents the pure water laboratory spectrum scaled to the water column density taken in Paper I. Other colors, or linestyles for the gray-scale version, are representative of laboratory spectra and are indicated at the bottom of the figure. When available (see Boogert et al. 2008), Very Large Telescope (VLT) or Keck data (2.0–4.5 μm, left panel) are also plotted. In this case, we overplotted (dotted purple/light gray line) a pure water spectrum scaled to the 3 μm water feature of the mixed ice spectrum. Whenever present, a dashed line in the right panel of a given source represents an H2O:CH3OH = 9:1 laboratory spectrum scaled to the 9.7 μm CH3OH CO-stretch mode; this gives an indication of the contribution of the 9 μm CH3OH CH3-rock mode to the total 9 μm feature. The laboratory spectra are recorded at 15 K unless indicated differently. (b) Same as (a) but for sources with no associated template, i.e., with the 10 μm silicate feature subtracted via the local continuum method.

(A color version of this figure is available in the online journal.)
integrated absorbance). Comparison with the observational data shows reasonable agreement (within ~1%) for the position of the NH$_3$ feature in H$_2$O-rich ices, but the observed widths are systematically smaller than the laboratory ones for nearly all sources. The silicate template continuum method gives widths that come closest to the laboratory values. This difference in width (i.e., widths derived from astronomical spectra smaller than those in the laboratory spectra) suggests that the NH$_3$ abundances determined here may be on the low side.

The CH$_3$OH profile is most consistent with a significant fraction of the CH$_3$OH being in a relatively pure or CO-rich phase, consistent with its formation by the hydrogenation of CO ice. In contrast, the most likely formation route of NH$_3$ ice remains hydrogenation of atomic N together with water ice formation in a relatively low-density molecular phase. Finally, the nitrogen budget indicates that up to 10% to 20% of nitrogen is locked up in known ices.

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See Table B.1.

APPENDIX C
COMPARISON BETWEEN ASTRONOMICAL AND LABORATORY DATA FOR ALL SOURCES
See Figure C.1.

REFERENCES
Barrett, A. H., Ho, P. T. P., & Myers, P. C. 1977, ApJ, 211, L39
Bernstein, M. P., Dworkin, J. P., Sandford, S. A., Cooper, G. W., & Allamandola, L. J. 2002, Nature, 416, 401
Bisschop, S. E., Fuchs, G. W., Boogert, A. C. A., van Dishoeck, E. F., & Linnartz, H. 2007, A&A, 470, 749
Blake, D., Allamandola, L., Sandford, S., Hudgins, D., & Freund, F. 1991, Science, 254, 548
Blake, G. A., Sutton, E. C., Masson, C. R., & Phillips, T. G. 1987, ApJ, 315, 621
Boogert, A. C. A., et al. 2004, ApJS, 154, 359
Boogert, A. C. A., et al. 2008, ApJ, 678, 985 (Paper I)
Bouwman, J., Ludwig, Awad, Z., A-Berg, K. I., Fuchs, G. W., van Dishoeck, E. F., & Linnartz, H. 2007, A&A, 476, 995
Cesaroni, R., Churchwell, E., Hofner, P., Walmsley, C. M., & Kurtz, S. 1994, A&A, 288, 903
Cuppen, H. M., van Dishoeck, E. F., Hofst, E., & Tielens, A. G. G. M. 2009, A&A, 508, 275
Dartois, E., & d'Hendecourt, L. 2001, A&A, 365, 144
Dartois, E., d'Hendecourt, L., Thi, W., Pontoppidan, K. M., & van Dishoeck, E. F. 2002, A&A, 394, 1057
Dartois, E., Schutte, W., Geballe, T. R., Demyk, K., Ehrenfreund, P., & d'Hendecourt, L. 1999, A&A, 342, L32
d'Hendecourt, L. B., & Allamandola, L. J. 1986, A&AS, 64, 453
Evans, N. J., II., et al. 2003, PASP, 115, 1124
Fedorman, S. R., Huntress, T. W., Jr., & Prasad, S. S. 1990, ApJ, 354, 504
Fuchs, G. W., Cuppen, H. M., Ioppolo, S., Romanzin, C., Bisschop, S. E., Anderson, S., van Dishoeck, E. F., & Linnartz, H. 2009, A&A, 505, 629
Garrod, R. T., Ho, P. T. P., Bieging, J., & Downes, D. 1982, ApJ, 259, L103
Gerakines, P. A., Schutte, W. A., Greenberg, J. M., & van Dishoeck, E. F. 1995, A&A, 296, 810
Gibb, E. L., Whitsett, D. C. B., Boogert, A. C. A., & Tielens, A. G. G. M. 2004, ApJS, 151, 35
Greene, T. P., Wilking, B. A., Andre, P., Young, E. T., & Lada, C. J. 1994, ApJ, 434, 614
Güttler, J., Klaas, U., Henning, T., Abraham, P., Lemke, D., Schreyer, K., & Lehmann, K. 2002, A&A, 390, 1075
Herbst, G. 1945, Molecular Spectra and Molecular Structure V ol. 2: Infrared and Raman Spectra Of Polyatomic Molecules (New York: Van Nostrand-Reinhold)
Hira, H., Watanabe, N., Shiraki, T., Nagaoaka, A., & Kouchi, A. 2004, ApJ, 614, 1124
Houck, J. R., et al. 2004, ApJS, 154, 18
Hudgins, D. M., Sandford, S. A., Allamandola, L. J., & Tielens, A. G. G. M. 1993, ApJS, 86, 713
Kemper, F., Vriend, W. J., & Tielens, A. G. G. M. 2004, ApJ, 609, 826
Kerkhof, O., Schutte, W. A., & Ehrenfreund, P. 1999, A&A, 346, 990
Kessler-Silacci, J., et al. 2006, ApJ, 639, 275
Lacy, J. H., Faraji, H., Sandford, S. A., & Allamandola, L. J. 1998, ApJ, 501, L105
Lee, J., Bergin, E. A., & Evans, N. J. II, 2004, ApJ, 617, 360
Min, M., Waters, L. B. F. M., de Koter, A., Hovenier, J. W., Keller, L. P., & Markwick-Kemper, F. 2007, A&A, 462, 667
Moore, M. H., & Hudson, R. L. 1998, Icarus, 135, 518
Muñoz Caro, G. M., & Schutte, W. A. 2003, A&A, 412, 121
Öberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., Blake, G. A., Evans, N. J., Lahuis, F., & van Dishoeck, E. F. 2008, ApJ, 678, 1032 (Paper III)
Öberg, K. I., Bottinelli, S., & van Dishoeck, E. F. 2009, A&A, 494, L13
Öberg, K. I., Fraser, H. J., Boogert, A. C. A., Bisschop, S. E., Fuchs, G. W., van Dishoeck, E. F., & Linnartz, H. 2007, A&A, 462, 1187
Oosorio, M., Anglada, G., Lizano, S., & D'Alessio, P. 2009, ApJ, 694, 29
Pontoppidan, K. M. 2006, A&A, 453, L47
Pontoppidan, K. M., Dartois, E., van Dishoeck, E. F., Thi, W.-F., & d'Hendecourt, L. 2003, A&A, 404, L17
Pontoppidan, K. M., van Dishoeck, E. F., & Dartois, E. 2004, A&A, 426, 925
Pontoppidan, K. M., et al. 2008, ApJ, 678, 1005 (Paper II)
Rodgers, S. D., & Charnley, S. B. 2001, ApJ, 546, 324
Savage, B. D., & Sembach, K. R. 1996, AR&AA, 34, 279
Schutte, W. A., & Khanna, R. K. 2003, A&A, 399, L79
Schutte, W. A., Tielens, A. G. G., & Sandford, S. A. 1991, ApJ, 382, 523
Skinner, C. J., Tielens, A. G. G. M., Barlow, M. J., & Justtanont, K. 1992, ApJ, 399, L79
Taban, I. M., Schutte, W. A., Pontoppidan, K. M., & van Dishoeck, E. F. 2003, A&A, 399, 169
Tielens, A. G. G. M., & Hagen, W. 1982, A&A, 114, 245
van Broekhuizen, F. A., Keane, J. V., & Schutte, W. A. 2004, A&A, 415, 425
van Broekhuizen, F. A., Pontoppidan, K. M., Fraser, H. J., & van Dishoeck, E. F. 2008, A&A, 441, 249
Watanabe, N., & Kouchi, A. 2002, ApJ, 571, L173
Watson, D. M., et al. 2004, ApJS, 154, 391