The infrared band strengths of CH_3OH, NH_3 and CH_4 in laboratory simulations of astrophysical ice mixtures

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Abstract. Results from groundbased observations and the Infrared Space Observatory (ISO) indicate that CH_3OH, NH_3 and CH_4 are important constituents of interstellar ice mantles. In order to accurately calculate the column densities of these molecules, it is important to have good measurements of their infrared band strength in astrophysical ice analogs. Band strength measurements of CH_3OH and CH_4 are presented showing that they depend only weakly on the composition of the ice matrix and the temperature. On the other hand, the umbrella mode of NH_3 does show a significant decrease when diluted in H_2O ice. For this reason the original estimates of the abundance of NH_3 in interstellar ice need to be revised upward by 30%.

Key words: methods: laboratory – ISM: abundances – ISM: dust, extinction – ISM: molecules – infrared: ISM: lines and bands

1. Introduction

In cold dense clouds atomic and molecular species accrete efficiently on grains. Additional surface chemistry leads to the formation of new species. As a result, astrophysical ices consist of complex mixtures of molecules. The abundances of the various molecules in the ice mantles provide important clues to the chemical processes in dense interstellar clouds, and therefore it is important to accurately measure the band strengths of their infrared features. With the help of laboratory spectroscopy many ice species as well as their specific properties have been identified in astronomical spectra (Whittet 1993, Schutte 1999, d'Hendecourt et al. 1999).

Groundbased observations showed that CH_3OH and NH_3 can be abundant in the line of sight of some massive protostars (Grim et al. 1991, Allamandola et al. 1992, Skinner et al. 1992, Schutte et al. 1996, Lacy et al. 1998, Dartois et al. 1999). Ground based and ISO-Short Wavelength Spectrometer (ISO-SWS) observations showed solid CH_4 column densities relative to H_2O of 0.4–3.9% toward high mass protostellar objects (Lacy et al. 1991, Boogert et al. 1996, d'Hendecourt et al. 1996).

In this paper we report measurements of the band strengths of CH_3OH, NH_3 and CH_4 in astrophysically relevant ice mix-

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tures. Previous measurements have employed pre-mixed gases for preparation of the ice mixtures. Band strengths were subsequently calculated under the assumption that the composition of the ice equals the composition of the gas mixture as obtained by partial pressure measurements. However, several problems arise in this procedure, which can lead to large measurement errors (Gerakines et al. 1995, henceforth G95). As described by G95 we have produced ice mixtures using simultaneous depositions of pure gases through separate deposition tubes. We then have the ability to measure the ratio of the band strengths of molecules in a multicomponent ice to those in pure ice (A/A_{pure}) by keeping the column density in each case (pure and mixed) the same.

2. Experimental

For an extensive description of the setup, the reader is referred to G95. The compounds we used to produce laboratory ice mixtures and their purities are as follows: H_2O(liquid), triply distilled; CO_2(gas), Praxair, 99.996%; NH_3(gas), Praxair, 99.9995%; CH_4(gas), Praxair, 99.9995%; CH_3OH(liquid), Janssen Chimica 99.9%. The deposition rate and sample thickness growth rate were $\sim 10^{15}$ molec cm^{-2} s^{-1} and ~ 1 μm hr^{-1}, respectively. The deposition time was ~ 10 minutes. Under these conditions the pressure drop in the bulb after one deposition is negligible.

The experimental procedures applied for measuring the infrared band strengths for a molecule in a binary or multicomponent ice are described in detail by G95. Here we give a short summary. Two gas bulbs, one containing the gas for which the infrared band strengths are to be measured (henceforth the "subject" gas) and one containing the gas(es) in which this species is to be diluted (henceforth the "dilutant"), are connected to the entries of two deposition tubes. Before cooling the substrate, the gas-flows are set by adjusting the variable leak valves to the desired flow. This is done by monitoring the pressure increase in the system and calculating the flow through:

$$F_i \propto \frac{\Delta P}{\sqrt{m_i}}, \qquad (1)$$

where F_i is the desired flow rate of species i in molecules·cm^{-2}·s^{-1}, ΔP the measured pressure increase in the system in torr and m_i the relative molecular mass of species

i (Schutte et al. 1993). The constant of proportionality is obtained by determining the deposited amount of species i from the infrared spectrum of the pure ice (e.g. Hudgins et al. 1993).

After setting the flow, the substrate is cooled down to $\sim$10 K, the subject gas and the dilutant are deposited simultaneously, and the infrared spectrum of the mixture is measured. After obtaining spectra for various temperatures, the substrate is heated until the sample sublimes and then recooled. The next step is the deposition of the pure subject gas for the same length of time as the first deposition, resulting in a pure ice containing the same number of subject molecules. Then, the band strength A of an absorption band of the subject molecule embedded in the ice mixture is given by:

$$A(mix) = A(pure) \cdot \frac{\tau_{int}(mix)}{\tau_{int}(pure)}. \qquad (2)$$

Using the band strengths for pure ices (d'Hendecourt & Allamandola 1986, Hudgins et al. 1993, Boogert et al. 1997) the band strength in the mixed ice is obtained. The exact mixing ratio is determined by measuring the column densities of the species, where the column density of the subject gas is calculated from the spectrum of the pure subject gas deposition.

From astronomical observations of CH₃OH (Skinner et al. 1992, Dartois et al. 1999), NH₃ (Lacy et al. 1998) and CH₄ (Boogert et al. 1996, Boogert et al. 1997) it appeared that CH₃OH, NH₃ and CH₄ are embedded in ices dominated by polar molecules. Observations indicate that these ices may either be H₂O dominated, or containing CH₃OH and CO₂ in similar proportions (Ehrenfreund et al. 1998, Gerakines et al. 1999). Therefore we investigated polar ice mixtures in the laboratory with a ratio: H₂O/candidate $\sim$10 (candidate = CH₃OH, NH₃ or CH₄), approximately corresponding to the observed astronomical abundance. To further investigate the effect of dilution we also used a H₂O/candidate $\sim$40 mixture. Alternatively we used H₂O/CH₃OH/CO₂/candidate $\sim$ 1/1/1/x mixtures where the abundance x was chosen to correspond to the observed CO₂/candidate ratios. For NH₃ this ratio is $\sim$1.5 and for CH₄ $\sim$5–10 (see Table 1).

3. Results

3.1. CH₃OH mixtures

The band strengths of the CO stretch in CH₃OH at 1026 cm⁻¹ (9.7 μm) are shown in Fig. 1, for pure CH₃OH and mixtures with H₂O and CO₂. Error bars were estimated from the results obtained by using polynomials for a baseline fit, whereby the order of the polynomial and the continuum regions were varied within reasonable limits. The underlying band of the H₂O libration mode at 760 cm⁻¹ (13.2 μm) could be subtracted using a baseline of order 2 or 3. The band strength of the 9.7 μm band is slightly reduced by 20% for the strongly diluted ice (filled squares) after initial deposition at 10 K. The ice mixture with H₂O and CH₃OH in equal abundance (open squares) shows a minor increase in band strength of $\sim$6%. Subsequent addition of CO₂ in equal abundance to this ice mixture causes no additional changes in measured band strengths (open triangles). Warm-up
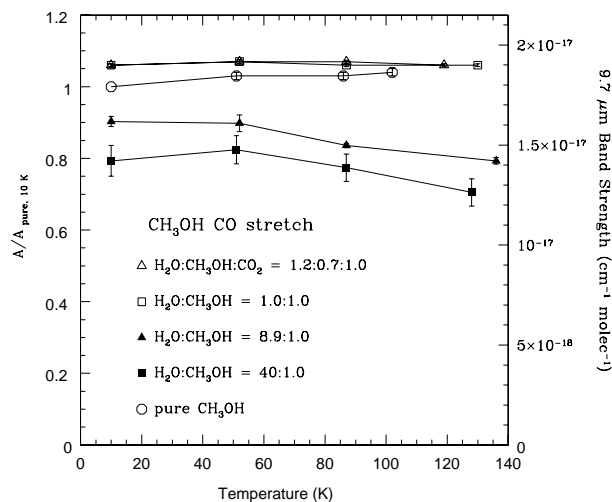

Fig. 1. Measured values of the band strength of the CO stretch in CH₃OH at 1026 cm⁻¹ (9.7 μm) as a function of temperature in various mixtures, ratioed by the band strength of the 9.7 μm band in pure CH₃OH directly after deposition at 10 K.
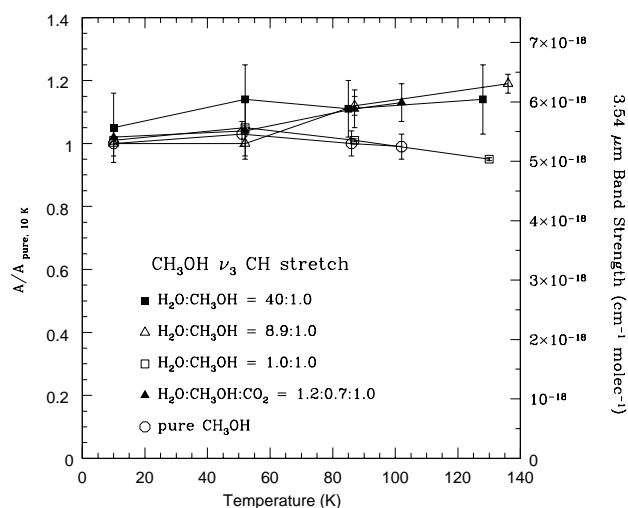

Fig. 2. As Fig. 1, but now for the CH₃OH ν_3 CH stretching mode at 2827 cm⁻¹ (3.5 μm).

of the pure ice and the ices with all components in equal proportions leads to a variation $<$5% in the observed band strength. The H₂O dominated ice mixtures show a stronger dependence on temperature with the band strength decreasing by $\sim$12% at higher temperatures.

The ν_3 CH stretch of CH₃OH at 2827 cm⁻¹ (3.54 μm) is much weaker but can still be discerned in astronomical spectra. Fig. 2 shows the effect on the 3.5 μm band when CH₃OH is diluted with H₂O and CO₂. At 10 K no change with respect to pure CH₃OH is observed. Annealing the ice mixtures leads to an increase of the band strength of 10–20% in the ice mixtures with an overabundance of H₂O and also in the H₂O-CH₃OH-CO₂ mixture. The binary mixture with H₂O and CH₃OH in equal proportions shows a variation $<$5% in the band strength and closely follows pure CH₃OH ice. The relatively large errors (up to 10% for the mixture with the highest H₂O abundance)
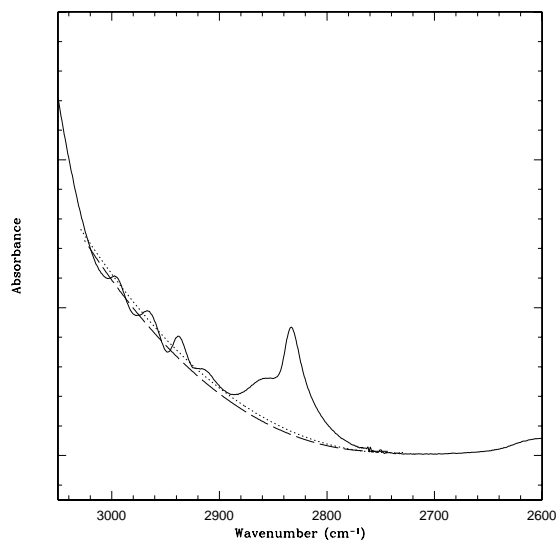
Fig. 3. The 2827 cm⁻¹ (3.5 μm) band of CH₃OH in a H₂O:CH₃OH = 8.9:1 mixture demonstrates the uncertainty involved in producing a baseline fit due to the underlying feature of the H₂O OH stretch at 3280 cm⁻¹ (3.0 μm). The dotted and dashed curves are polynomial baseline fits of order 4 and 5 respectively. The figure also shows the ν₉ CH stretches of CH₃OH centered around 2951 cm⁻¹.

demonstrate the uncertainty in producing a baseline fit due to the underlying feature of the OH stretch in H₂O at 3280 cm⁻¹ (see Fig. 3).

A third band that is used to determine CH₃OH abundances in space is the CH₃OH combination mode at 2600,2526 cm⁻¹ (3.85,3.96 μm). Fig. 4 shows the effect on this band when CH₃OH is diluted with H₂O and CO₂. Only the mixture with H₂O in overabundance (filled squares) shows an increase of the band intensity (∼20%). The temperature effect is small (<10%) in all displayed mixtures. The estimated errorbars are very large (up to ∼20%) in the mixture with an overabundance of H₂O due to the underlying H₂O combination mode at ∼2220 cm⁻¹ (4.5 μm, Hagen et al. 1981). Compared with the ν₃ CH stretch, the CH₃OH combinations are two times weaker and in addition show a more flat and broad profile, thus enhancing the problems in producing a proper baseline fit.

3.2. NH₃ mixtures

The NH₃ "umbrella" mode at 1070 cm⁻¹ (9.3 μm) is the only band of NH₃ that is not completely blended with H₂O bands. The "umbrella" is therefore used to determine astronomical abundances of this molecule. We used second and higher order polynomials to correct the baseline for the broad H₂O libration mode at 760 cm⁻¹ (13.2 μm). The measurements that are displayed in Fig. 5 contain errors between 1–7%. The band strength of the 9.3 μm band is reduced by 30% for the strongly diluted ice (filled squares) after initial deposition at 10 K. The ice mixture with H₂O and NH₃ in equal abundance (open squares) shows a small increase in band strength of ∼7%. The multicomponent mixture (open triangles) shows the largest increase in band
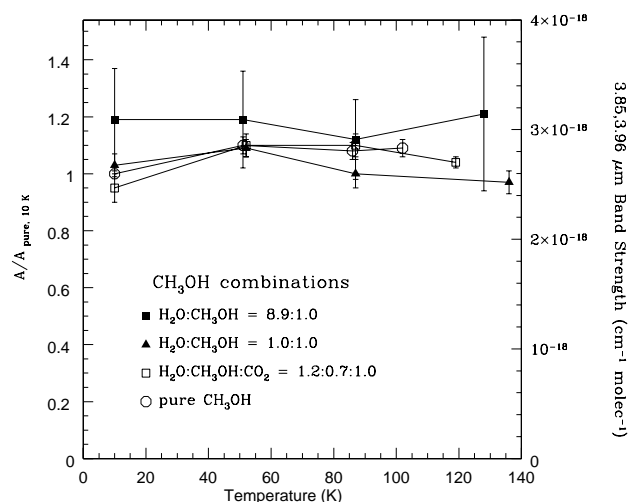

Fig. 4. As Fig. 1, but now for the CH₃OH combination mode at 2600,2526 cm⁻¹ (3.85,3.96 μm).

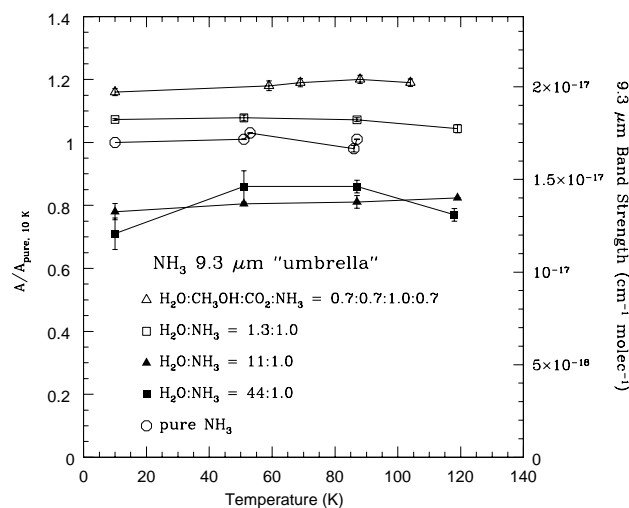**Fig. 5.** As Fig. 1, but now for the "umbrella" mode of NH₃ at 1070 cm⁻¹ (9.3 μm).

strength of ∼16%. The H₂O:NH₃=44:1 ice mixture displays a variation of ∼15% during warm-up, whereas the other mixtures display a variation ≲5%.

3.3. CH₄ mixtures

Table 1 lists the absorption band strengths of the above displayed mixtures at 10 K. Also listed are the band strengths of the deformation mode of CH₄ in binary and multicomponent mixtures. The band intensity of the CH₄ deformation mode is slightly increased (∼5–8%) when the molecule is strongly diluted. When CH₄ is in equal or comparable abundance with the other components of the mixture, the band strength is enhanced by ∼21–23%. CH₄ is highly volatile and the sublimation of the pure ice starts well below 50 K. No temperature dependence was measured for this molecule.

Table 1. Band strengths for solid CH_3OH, NH_3 and CH_4 in various ice mixtures dominated by polar molecules. Band strength values for the pure species were taken from d'Hendecourt (1986), except for pure CH_4 (Boogert et al. 1997).

Molecule	Ice	Mode	Position (μm)	A (cm·molec^{-1})	A/A_{pure}
CH_3OH	$H_2O:CH_3OH = 40:1$	CO stretch	9.75	$1.4 \cdot 10^{-17}$	0.79
		ν_3 CH stretch	3.54	$5.6 \cdot 10^{-18}$	1.05
	$H_2O:CH_3OH = 8.9:1$	CO stretch	9.75	$1.6 \cdot 10^{-17}$	0.90
		ν_3 CH stretch	3.54	$5.3 \cdot 10^{-18}$	1.00
		combination	3.84,3.96	$3.1 \cdot 10^{-18}$	1.19
	$H_2O:CH_3OH = 1:1$	CO stretch	9.75	$1.9 \cdot 10^{-17}$	1.06
		ν_3 CH stretch	3.54	$5.4 \cdot 10^{-18}$	1.01
		combination	3.84,3.96	$2.7 \cdot 10^{-18}$	1.03
	$H_2O:CH_3OH:CO_2 = 1.2:0.7:1.0$	CO stretch	9.75	$1.9 \cdot 10^{-17}$	1.06
		ν_3 CH stretch	3.54	$5.4 \cdot 10^{-18}$	1.02
		combination	3.84,3.96	$2.5 \cdot 10^{-18}$	0.95
NH_3	$H_2O:NH_3 = 44:1$	"umbrella"	9.35	$1.2 \cdot 10^{-17}$	0.71
	$H_2O:NH_3 = 11:1$	"umbrella"	9.35	$1.3 \cdot 10^{-17}$	0.78
	$H_2O:NH_3 = 1.3:1$	"umbrella"	9.35	$1.8 \cdot 10^{-17}$	1.07
	$H_2O:CH_3OH:CO_2:NH_3 = 0.7:0.7:1.0:0.7$	"umbrella"	9.35	$2.2 \cdot 10^{-17}$	1.16
CH_4	$H_2O:CH_4 = 24:1$	deformation	7.68,7.71	$7.0 \cdot 10^{-18}$	1.05
	$H_2O:CH_4 = 1.03:1$	deformation	7.68,7.71	$8.1 \cdot 10^{-18}$	1.21
	$H_2O:CH_3OH:CO_2:CH_4 = 0.6:0.7:1.0:0.1$	deformation	7.68,7.71	$7.2 \cdot 10^{-18}$	1.08
	$H_2O:CH_3OH:CO_2:CH_4 = 0.4:0.6:1.0:0.2$	deformation	7.68,7.71	$9.6 \cdot 10^{-18}$	1.23

4. Discussion

4.1. Comparison with previous studies

Our results show that the band strengths of the infrared features of CH_3OH and CH_4 show only limited dependence on the nature of the ice matrix ($\lesssim 20\%$ relative to pure ices). NH_3 shows somewhat stronger variations up to 30%. These results are reminiscent of earlier data on CO and CO_2 in astrophysically relevant ices, which likewise showed only limited variability in the band strengths (G95). Our results differ slightly from those of Hudgins et al. (1993) who found variations relative to pure CH_3OH of $\sim$17% for the CO stretch in CH_3OH ($H_2O/CH_3OH=10$) and of $\sim$24% for the deformation mode of CH_4 ($H_2O/CH_4=20$). We found variations of only 10% and 5%, respectively, in the same mixtures (see Table 1). However, the accuracy limit of 30% given by Hudgins et al. (1993) indicates that our measurements are in reasonable agreement with previous data.

4.2. Astrophysical implications

Observations indicate that interstellar solid CH_3OH is not homogeneously mixed with the dominant H_2O ice component, but rather resides in a separate ice phase together with comparable quantities of H_2O and CO_2 (Skinner et al. 1992, Ehrenfreund et al. 1998, Gerakines et al. 1999, Boogert et al. 1999). For such mixtures the corrections to the previously published column densities, which were based on the band strength of pure CH_3OH ice, is very small ($\leq$10%), as indicated in Table 1. Astronomical abundance calculations and studies of NH_3 profiles in comparison with laboratory analogs indicate $H_2O/NH_3 \sim 10$ toward the high mass protostar NGC7538:IRS9 (Lacy et al.

1998). The band strength of the NH_3 "umbrella" in such H_2O dominated ice mixtures becomes 1.3 times smaller than in pure ice, independent of the ice temperature. Therefore the abundance of NH_3 should be 30% larger than originally estimated by Lacy et al. 1998, i.e. we find $NH_3/H_2O \sim 0.13$ toward NGC7538:IRS9. Abundance measurements of H_2O and CH_4 toward some sources indicate H_2O/CH_4 abundance ratios between 25–250 (Boogert et al. 1996, d'Hendecourt et al. 1996). However, comparison of ISO-SWS observations with laboratory data show that laboratory mixtures with $H_2O/CH_4=2$–16 produce the best fits (Boogert et al. 1996). This indicates inhomogeneous mixing of H_2O and CH_4. Good fits were also obtained by adding CH_3OH to mixtures with a higher H_2O/CH_4 abundance ratio. Our study shows that the band strength of CH_4 in mixtures with a moderate H_2O abundance ($H_2O/CH_4=1$–2) becomes 1.2 times smaller than in pure ice (see Table 1). In H_2O dominated mixtures ($H_2O/CH_4=6$–24) the band strength measurements for pure CH_4 may be used. The presented results on improved band strength measurements of CH_3OH, NH_3 and CH_4 allow to accurately calculate abundances of these interstellar ice species and provide therefore an important tool for the current analysis and interpretation of ISO satellite data.

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