



Universiteit  
Leiden  
The Netherlands

## The infrared band strengths of CH<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> in laboratory simulations of astrophysical ice mixtures

Kerkhof, O.; Schutte, W.A.; Ehrenfreund, P.

### Citation

Kerkhof, O., Schutte, W. A., & Ehrenfreund, P. (1999). The infrared band strengths of CH<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> in laboratory simulations of astrophysical ice mixtures. *Astronomy And Astrophysics*, 346, 990-994. Retrieved from <https://hdl.handle.net/1887/7296>

Version: Not Applicable (or Unknown)

License: [Leiden University Non-exclusive license](#)

Downloaded from: <https://hdl.handle.net/1887/7296>

**Note:** To cite this publication please use the final published version (if applicable).

# The infrared band strengths of CH<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> in laboratory simulations of astrophysical ice mixtures

O. Kerkhof, W.A. Schutte, and P. Ehrenfreund

Raymond and Beverly Sackler Laboratory for Astrophysics at Leiden Observatory, P.O. Box 9513, 2300 RA Leiden, The Netherlands

Received 16 March 1999 / Accepted 20 April 1999

**Abstract.** Results from groundbased observations and the Infrared Space Observatory (ISO) indicate that CH<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> 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<sub>3</sub>OH and CH<sub>4</sub> 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<sub>3</sub> does show a significant decrease when diluted in H<sub>2</sub>O ice. For this reason the original estimates of the abundance of NH<sub>3</sub> 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<sub>3</sub>OH and NH<sub>3</sub> 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<sub>4</sub> column densities relative to H<sub>2</sub>O 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<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> in astrophysically relevant ice mix-

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 ( $A/A_{\text{pure}}$ ) 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<sub>2</sub>O(liquid), triply distilled; CO<sub>2</sub>(gas), Praxair, 99.996%; NH<sub>3</sub>(gas), Praxair, 99.9995%; CH<sub>4</sub>(gas), Praxair, 99.9995%; CH<sub>3</sub>OH(liquid), Janssen Chimica 99.9%. The deposition rate and sample thickness growth rate were  $\sim 10^{15}$  molec cm<sup>-2</sup> s<sup>-1</sup> and  $\sim 1$   $\mu$ m hr<sup>-1</sup>, respectively. The deposition time was  $\sim 10$  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:

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

where  $F_i$  is the desired flow rate of species  $i$  in molecules·cm<sup>-2</sup>·s<sup>-1</sup>,  $\Delta P$  the measured pressure increase in the system in torr and  $m_i$  the relative molecular mass of species

Send offprint requests to: W.A. Schutte (schutte@strw.leidenuniv.nl)

$i$  (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 sublimates 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:

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

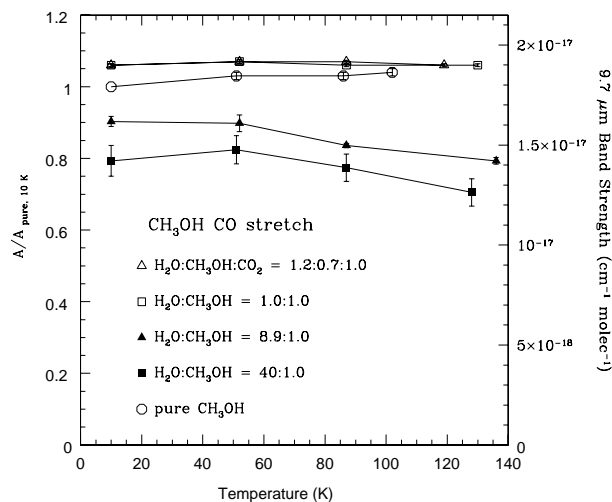
Using the band strengths for pure ices (d'Hendecourt & Allamandola 1986, Hudgins et al. 1993, Boogert et al. 1997) the band strength in the mixed ice is obtained. The exact mixing ratio is determined by measuring the column densities of the species, where the column density of the subject gas is calculated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

From astronomical observations of CH<sub>3</sub>OH (Skinner et al. 1992, Dartois et al. 1999), NH<sub>3</sub> (Lacy et al. 1998) and CH<sub>4</sub> (Boogert et al. 1996, Boogert et al. 1997) it appeared that CH<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> are embedded in ices dominated by polar molecules. Observations indicate that these ices may either be H<sub>2</sub>O dominated, or containing CH<sub>3</sub>OH and CO<sub>2</sub> in similar proportions (Ehrenfreund et al. 1998, Gerakines et al. 1999). Therefore we investigated polar ice mixtures in the laboratory with a ratio: H<sub>2</sub>O/candidate  $\sim 10$  (candidate = CH<sub>3</sub>OH, NH<sub>3</sub> or CH<sub>4</sub>), approximately corresponding to the observed astronomical abundance. To further investigate the effect of dilution we also used a H<sub>2</sub>O/candidate  $\sim 40$  mixture. Alternatively we used H<sub>2</sub>O/CH<sub>3</sub>OH/CO<sub>2</sub>/candidate  $\sim 1/1/1/x$  mixtures where the abundance  $x$  was chosen to correspond to the observed CO<sub>2</sub>/candidate ratios. For NH<sub>3</sub> this ratio is  $\sim 1.5$  and for CH<sub>4</sub>  $\sim 5$ – $10$  (see Table 1).

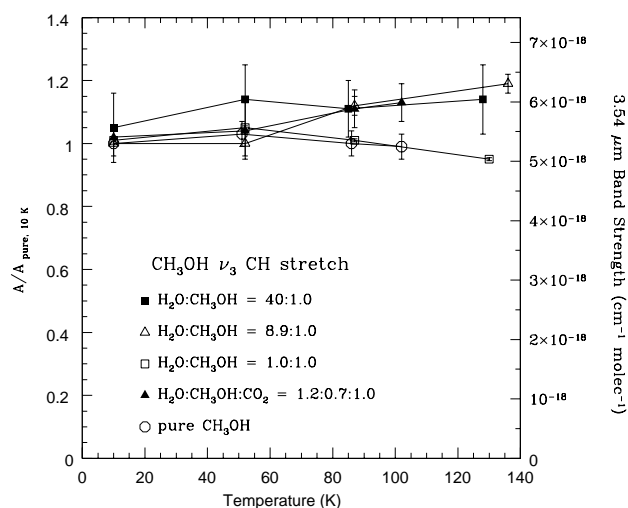
### 3. Results

#### 3.1. CH<sub>3</sub>OH mixtures

The band strengths of the CO stretch in CH<sub>3</sub>OH at 1026 cm<sup>-1</sup> (9.7  $\mu$ m) are shown in Fig. 1, for pure CH<sub>3</sub>OH and mixtures with H<sub>2</sub>O and CO<sub>2</sub>. 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 H<sub>2</sub>O libration mode at 760 cm<sup>-1</sup> (13.2  $\mu$ m) could be subtracted using a baseline of order 2 or 3. The band strength of the 9.7  $\mu$ m band is slightly reduced by 20% for the strongly diluted ice (filled squares) after initial deposition at 10 K. The ice mixture with H<sub>2</sub>O and CH<sub>3</sub>OH in equal abundance (open squares) shows a minor increase in band strength of  $\sim 6\%$ . Subsequent addition of CO<sub>2</sub> in equal abundance to this ice mixture causes no additional changes in measured band strengths (open triangles). Warm-up



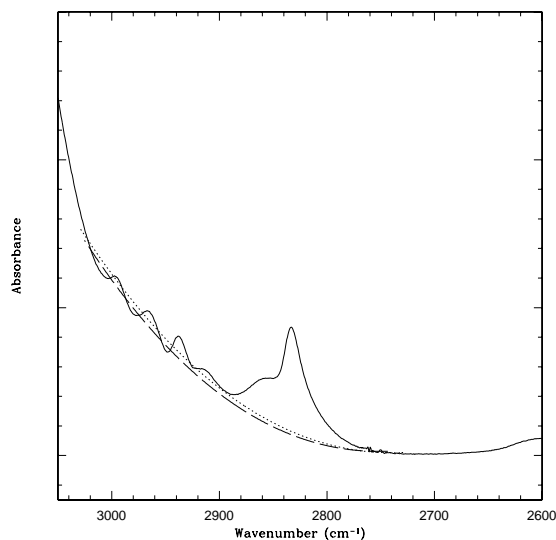
**Fig. 1.** Measured values of the band strength of the CO stretch in CH<sub>3</sub>OH at 1026 cm<sup>-1</sup> (9.7  $\mu$ m) as a function of temperature in various mixtures, ratioed by the band strength of the 9.7  $\mu$ m band in pure CH<sub>3</sub>OH directly after deposition at 10 K.



**Fig. 2.** As Fig. 1, but now for the CH<sub>3</sub>OH  $\nu_3$  CH stretching mode at 2827 cm<sup>-1</sup> (3.5  $\mu$ m).

of the pure ice and the ices with all components in equal proportions leads to a variation  $< 5\%$  in the observed band strength. The H<sub>2</sub>O dominated ice mixtures show a stronger dependence on temperature with the band strength decreasing by  $\sim 12\%$  at higher temperatures.

The  $\nu_3$  CH stretch of CH<sub>3</sub>OH at 2827 cm<sup>-1</sup> (3.54  $\mu$ m) is much weaker but can still be discerned in astronomical spectra. Fig. 2 shows the effect on the 3.5  $\mu$ m band when CH<sub>3</sub>OH is diluted with H<sub>2</sub>O and CO<sub>2</sub>. At 10 K no change with respect to pure CH<sub>3</sub>OH 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 H<sub>2</sub>O and also in the H<sub>2</sub>O-CH<sub>3</sub>OH-CO<sub>2</sub> mixture. The binary mixture with H<sub>2</sub>O and CH<sub>3</sub>OH in equal proportions shows a variation  $< 5\%$  in the band strength and closely follows pure CH<sub>3</sub>OH ice. The relatively large errors (up to 10% for the mixture with the highest H<sub>2</sub>O abundance)



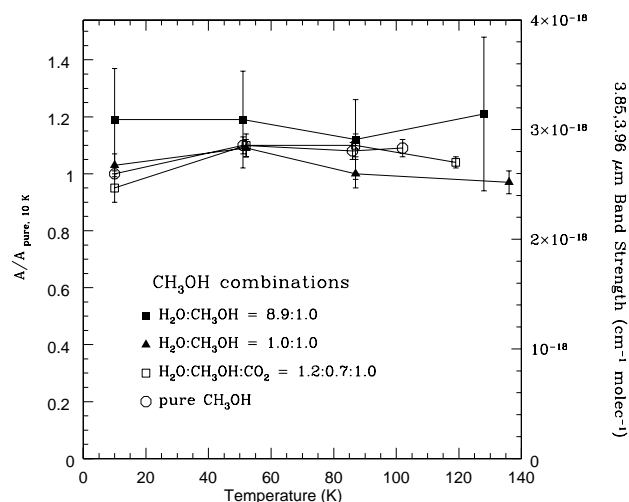
**Fig. 3.** The 2827 cm<sup>-1</sup> (3.5 μm) band of CH<sub>3</sub>OH in a H<sub>2</sub>O:CH<sub>3</sub>OH = 8.9:1 mixture demonstrates the uncertainty involved in producing a baseline fit due to the underlying feature of the H<sub>2</sub>O OH stretch at 3280 cm<sup>-1</sup> (3.0 μm). The dotted and dashed curves are polynomial baseline fits of order 4 and 5 respectively. The figure also shows the ν<sub>9</sub> CH stretches of CH<sub>3</sub>OH centered around 2951 cm<sup>-1</sup>.

demonstrate the uncertainty in producing a baseline fit due to the underlying feature of the OH stretch in H<sub>2</sub>O at 3280 cm<sup>-1</sup> (see Fig. 3).

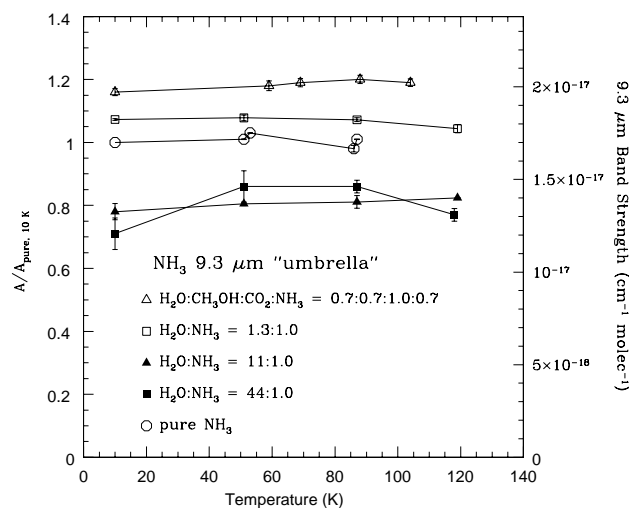
A third band that is used to determine CH<sub>3</sub>OH abundances in space is the CH<sub>3</sub>OH combination mode at 2600,2526 cm<sup>-1</sup> (3.85,3.96 μm). Fig. 4 shows the effect on this band when CH<sub>3</sub>OH is diluted with H<sub>2</sub>O and CO<sub>2</sub>. Only the mixture with H<sub>2</sub>O 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 H<sub>2</sub>O due to the underlying H<sub>2</sub>O combination mode at ~2220 cm<sup>-1</sup> (4.5 μm, Hagen et al. 1981). Compared with the ν<sub>3</sub> CH stretch, the CH<sub>3</sub>OH 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. NH<sub>3</sub> mixtures

The NH<sub>3</sub> “umbrella” mode at 1070 cm<sup>-1</sup> (9.3 μm) is the only band of NH<sub>3</sub> that is not completely blended with H<sub>2</sub>O 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 H<sub>2</sub>O libration mode at 760 cm<sup>-1</sup> (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 H<sub>2</sub>O and NH<sub>3</sub> 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 CH<sub>3</sub>OH combination mode at 2600,2526 cm<sup>-1</sup> (3.85,3.96 μm).



**Fig. 5.** As Fig. 1, but now for the “umbrella” mode of NH<sub>3</sub> at 1070 cm<sup>-1</sup> (9.3 μm).

strength of ~16%. The H<sub>2</sub>O:NH<sub>3</sub>=44:1 ice mixture displays a variation of ~15% during warm-up, whereas the other mixtures display a variation ≲5%.

### 3.3. CH<sub>4</sub> 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 CH<sub>4</sub> in binary and multicomponent mixtures. The band intensity of the CH<sub>4</sub> deformation mode is slightly increased (~5–8%) when the molecule is strongly diluted. When CH<sub>4</sub> is in equal or comparable abundance with the other components of the mixture, the band strength is enhanced by ~21–23%. CH<sub>4</sub> 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<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> 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<sub>4</sub> (Boogert et al. 1997).

Molecule	Ice	Mode	Position ( $\mu\text{m}$ )	$A$ ( $\text{cm}\cdot\text{molec}^{-1}$ )	$A/A_{\text{pure}}$
CH <sub>3</sub> OH	H <sub>2</sub> O:CH <sub>3</sub> OH = 40:1	CO stretch	9.75	$1.4\cdot 10^{-17}$	0.79
		$\nu_3$ CH stretch	3.54	$5.6\cdot 10^{-18}$	1.05
	H <sub>2</sub> O:CH <sub>3</sub> OH = 8.9:1	CO stretch	9.75	$1.6\cdot 10^{-17}$	0.90
		$\nu_3$ CH stretch	3.54	$5.3\cdot 10^{-18}$	1.00
	H <sub>2</sub> O:CH <sub>3</sub> OH = 1:1	combination	3.84,3.96	$3.1\cdot 10^{-18}$	1.19
		CO stretch	9.75	$1.9\cdot 10^{-17}$	1.06
		$\nu_3$ CH stretch	3.54	$5.4\cdot 10^{-18}$	1.01
	H <sub>2</sub> O:CH <sub>3</sub> OH:CO <sub>2</sub> = 1.2:0.7:1.0	combination	3.84,3.96	$2.7\cdot 10^{-18}$	1.03
		CO stretch	9.75	$1.9\cdot 10^{-17}$	1.06
		$\nu_3$ CH stretch	3.54	$5.4\cdot 10^{-18}$	1.02
combination		3.84,3.96	$2.5\cdot 10^{-18}$	0.95	
NH <sub>3</sub>	H <sub>2</sub> O:NH <sub>3</sub> = 44:1	“umbrella”	9.35	$1.2\cdot 10^{-17}$	0.71
	H <sub>2</sub> O:NH <sub>3</sub> = 11:1	“umbrella”	9.35	$1.3\cdot 10^{-17}$	0.78
	H <sub>2</sub> O:NH <sub>3</sub> = 1.3:1	“umbrella”	9.35	$1.8\cdot 10^{-17}$	1.07
	H <sub>2</sub> O:CH <sub>3</sub> OH:CO <sub>2</sub> :NH <sub>3</sub> = 0.7:0.7:1.0:0.7	“umbrella”	9.35	$2.2\cdot 10^{-17}$	1.16
CH <sub>4</sub>	H <sub>2</sub> O:CH <sub>4</sub> = 24:1	deformation	7.68,7.71	$7.0\cdot 10^{-18}$	1.05
	H <sub>2</sub> O:CH <sub>4</sub> = 1.03:1	deformation	7.68,7.71	$8.1\cdot 10^{-18}$	1.21
	H <sub>2</sub> O:CH <sub>3</sub> OH:CO <sub>2</sub> :CH <sub>4</sub> = 0.6:0.7:1.0:0.1	deformation	7.68,7.71	$7.2\cdot 10^{-18}$	1.08
	H <sub>2</sub> O:CH <sub>3</sub> OH:CO <sub>2</sub> :CH <sub>4</sub> = 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<sub>3</sub>OH and CH<sub>4</sub> show only limited dependence on the nature of the ice matrix ( $\lesssim 20\%$  relative to pure ices). NH<sub>3</sub> shows somewhat stronger variations up to 30%. These results are reminiscent of earlier data on CO and CO<sub>2</sub> 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<sub>3</sub>OH of  $\sim 17\%$  for the CO stretch in CH<sub>3</sub>OH (H<sub>2</sub>O/CH<sub>3</sub>OH=10) and of  $\sim 24\%$  for the deformation mode of CH<sub>4</sub> (H<sub>2</sub>O/CH<sub>4</sub>=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<sub>3</sub>OH is not homogeneously mixed with the dominant H<sub>2</sub>O ice component, but rather resides in a separate ice phase together with comparable quantities of H<sub>2</sub>O and CO<sub>2</sub> (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<sub>3</sub>OH ice, is very small ( $\leq 10\%$ ), as indicated in Table 1. Astronomical abundance calculations and studies of NH<sub>3</sub> profiles in comparison with laboratory analogs indicate H<sub>2</sub>O/NH<sub>3</sub>  $\sim 10$  toward the high mass protostar NGC7538:IRS9 (Lacy et al.

1998). The band strength of the NH<sub>3</sub> “umbrella” in such H<sub>2</sub>O dominated ice mixtures becomes 1.3 times smaller than in pure ice, independent of the ice temperature. Therefore the abundance of NH<sub>3</sub> should be 30% larger than originally estimated by Lacy et al. 1998, i.e. we find NH<sub>3</sub>/H<sub>2</sub>O  $\sim 0.13$  toward NGC7538:IRS9. Abundance measurements of H<sub>2</sub>O and CH<sub>4</sub> toward some sources indicate H<sub>2</sub>O/CH<sub>4</sub> 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<sub>2</sub>O/CH<sub>4</sub>=2–16 produce the best fits (Boogert et al. 1996). This indicates inhomogeneous mixing of H<sub>2</sub>O and CH<sub>4</sub>. Good fits were also obtained by adding CH<sub>3</sub>OH to mixtures with a higher H<sub>2</sub>O/CH<sub>4</sub> abundance ratio. Our study shows that the band strength of CH<sub>4</sub> in mixtures with a moderate H<sub>2</sub>O abundance (H<sub>2</sub>O/CH<sub>4</sub>=1–2) becomes 1.2 times smaller than in pure ice (see Table 1). In H<sub>2</sub>O dominated mixtures (H<sub>2</sub>O/CH<sub>4</sub>=6–24) the band strength measurements for pure CH<sub>4</sub> may be used. The presented results on improved band strength measurements of CH<sub>3</sub>OH, NH<sub>3</sub> and CH<sub>4</sub> 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.

## References

- Allamandola L., Sandford S.A., Tielens A.G.G.M., 1992, ApJ 399, 134  
 Boogert A.C.A., Schutte W.A., Tielens A.G.G.M., et al., 1996, A&A 315, L377  
 Boogert A.C.A., Schutte W.A., Helmich F.P., et al., 1997, A&A 317, 929  
 Boogert A.C.A., Gerakines P.A., Ehrenfreund P., et al., 1999, A&A, in preparation

- Dartois E., Schutte W.A., Geballe T., et al., 1999, *A&A* 342, L32
- d'Hendecourt L.B., Allamandola L.J., 1986, *A&A* 64, 453
- d'Hendecourt L., Jourdain de Muizon M., Dartois E., et al., 1996, *A&A* 315, L365
- d'Hendecourt L., Jourdain de Muizon M., Dartois E., et al., 1999, *Proceedings of the Conference: The Universe as seen by ISO. Paris, France, (ESA SP-427)*
- Ehrenfreund P., Dartois E., Demyk K., d'Hendecourt L.B., 1998, *A&A* 339, L17
- Gerakines P.A., Schutte W.A., Greenberg J.M., van Dishoeck E.F., 1995, *A&A* 296, 810 (G95)
- Gerakines P.A., Whittet D.C.B., Ehrenfreund P., et al., 1999, submitted to *ApJ*
- Grim R.J.A., Baas F., Geballe T.R., Greenberg J.M., Schutte W.A., 1991, *A&A* 243, 473
- Hagen W., Tielens A.G.G.M., Greenberg J.M., 1981, *Chem. Phys.* 56, 367
- Hudgins D.M., Sandford S.A., Allamandola L., Tielens A.G.G.M., 1993, *ApJS* 86, 713
- Lacy J.H., Carr J.S., Evans II N.J., et al., 1991, *ApJ* 376, 556
- Lacy J.H., Faraji H., Sandford S.A., Allamandola L.J., 1998, *ApJ* 501, L105
- Schutte W.A., Allamandola L., Sandford S.A., 1993, *Icarus* 104, 118
- Schutte W.A., Tielens A.G.G.M., Whittet D.C.B., et al., 1996, *A&A* 315, L333
- Schutte W.A., 1999, *Ices in the interstellar medium*. In: Ehrenfreund P., et al. (eds.) *Laboratory Astrophysics and Space Research*. Kluwer Academic Publishers, p. 69
- Skinner C.J., Tielens A.G.G.M., Barlow M.J., Justtanont K., 1992, *ApJ* 399, L79
- Whittet D.C.B., 1993, *Observations of molecular ices*. In: Millar T.J., Williams D.A. (eds.) *Dust and Chemistry in Astronomy*. IOP, Bristol, p. 1