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Letter to the Editor

Methanol: The second most abundant ice species towards the high-mass protostars RAFGL7009S and W 33A*

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Abstract. We present ground-based L-band spectra of the high-mass protostars RAFGL7009S and W 33A. Absorption bands at 3.54, 3.84 and 3.94 μm arise in both lines of sight. We attribute these bands to the methanol ν_3 CH_3 symmetric stretch and combination modes. The CH_3OH abundance relative to water ice is about 30% for RAFGL7009S and 5-22% for W 33A, making CH_3OH the most abundant solid state molecule after H_2O toward these two sources. The profiles of the absorption features toward these objects are very similar, showing that the methanol is located in similar ice environments. Detailed spectral comparison with laboratory data implies that the methanol is not mixed uniformly with the water ice. The similarities in the spectra of these two protostars are discussed within the context of chemical differences along other lines of sight. Methanol appears to be more efficiently produced on grain mantles in the vicinity of high-mass protostars than in other locations.

Key words: ISM: abundances – ISM: dust, extinction – ISM: H II regions – ISM: individual objects: – infrared: ISM: continuum – infrared: ISM: lines and bands

1. Introduction

The composition of grain mantles in dark clouds is of prime importance because it reveals the physical-chemistry of grain surfaces and its possible influence on gas phase chemistry. Thanks to ISO observations, the presence of grain species such as H_2O, CO, CO_2 and CH_4 is being determined along numerous lines of sight (see 1996 A&A Vol. 315, No. 2). However, at infrared wavelengths accessible from the ground the ISO spectroscopic sensitivity on point sources is not as good as those of ground based telescopes whose collecting surfaces are much larger.

Among the species in the solid form observed from the ground, methanol (CH_3OH) is an important one to constrain. Methanol can be observed in the infrared via many transitions such as the 3.54 μm ν_3 stretching mode, 3.84-3.94 μm combination modes, 6.85 μm CH_3 deformation modes, 8.9 μm CH_3 rock and 9.7 μm CO stretching mode. The features at 3.54 μm and 3.84-3.94 μm have been detected previously from the ground towards several sources (Grim et al. 1991; Geballe 1991; Allamandola et al. 1992, Brooke et al. 1996; Schutte et al. 1996a). The 6.85 μm band falls in a region where CH_3 deformation modes appear in many molecules (Tielens et al. 1984). The contribution of methanol at this wavelength was assessed by Schutte et al. (1996b) as $\sim$ 25% in NGC 7538/IRS9. The only detection of the 8.9 and 9.7 μm modes was made from the ground by Skinner et al. (1992) towards GL2136, after subtraction of the strong silicate absorption. To date methanol only has been detected towards high-mass protostars. Towards field stars or low mass protostars in the Taurus dense cloud the nondetection of the 3.54 μm band gives upper limits of about 2 to 7% for the methanol content relative to H_2O (Chiar et al. 1996), possibly pointing to a systematic difference with the high-mass stellar environments. The specific location of methanol in various dense cloud regions could shed light on its formation mechanism.

2. Observations and results

Spectra of RAFGL7009S and W 33A were obtained on UT 1998 July 5 at the United Kingdom Infrared Telescope (UKIRT) on Mauna Kea using the facility grating spectrometer CGS4 and its 40 line/mm grating. The grating was set to provide coverage from 3.42 to 4.04 μm (2475-2920 cm^{-1}). The spectrometer's 0.6 arcsec wide entrance slit (oriented east-west) was used, yielding a resolving power of $\sim$1500. Measurements were made in the standard stare/nod mode, with the source or calibration star positioned alternatively at two locations along the slit. The spectrum was sampled every 1/3 resolution element by successively repositioning the detector array along the dispersion direction. Total integration times were 576 seconds for each source and 192 seconds for each calibration star, HR6378 (for W 33A) and HR 6493 (for RAFGL7009S).

Spectra were extracted from each final flatfielded and coadded spectral image, wavelength calibrated with the assistance of an arc lamp spectrum obtained at the time of the observations,

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and ratioed to produce the flux-calibrated spectra shown in the top portions of each panel of Fig. 1. The wavelength calibration is accurate to better than 0.001 μm (1 cm^{-1}). We assumed L= 2.24 mag, T=9000K for HR6378 and L=3.69 mag, T=7000K for HR6493 and interpolated across the H I 8-5 line near 2673 cm-1, which is in absorption in the calibration stars. We defined the continuum level at the edges of the two spectral regions in Fig. 1. We used the dot-dashed continuum lines shown in Fig. 1 to derive the optical depth spectra for comparison with laboratory data and used the same wavelength interval in defining the “continua” in the laboratory spectra. The exact method of defining the continuum has little effect on the shape of the bands at 3.84 and 3.94 μm as the region is clean on both sides of the absorptions. A similar approach seems justified for the 3.54 μm band as the wing of the strong water ice absorption and the antisymmetric modes of methanol itself below 2900 cm^{-1} ($\sim$3.45 μm) do not allow an accurate determination of the real continuum.

3. Methanol profiles and abundance

The exact positions of the solid methanol bands are very sensitive to the water content of the ice, as can be seen in the laboratory spectra displayed in the lower part of Fig. 1. The interaction between CH_3OH and polar molecules such as H_2O causes a noticeable shift in each band. With less water the bands shift toward longer wavelengths (see traces c,d,e). Furthermore, the short wavelength shoulder on the 3.54 μm feature disappears. The best fits obtained from the laboratory spectra are shown in traces a and a’, superposed on the optical depth spectra of W 33A and RAFGL7009S. The mixtures used for the fits are the same for both objects and imply the presence of two mantle phases, in addition to a third one dominated by water, along the lines of sight. In one phase half of the methanol content is mixed with equal proportions of CO_2 and H_2O, as confirmed by the CO_2 bending mode observations (Ehrenfreund et al. 1998, Dartois et al. 1999). In the other phase the remaining methanol is almost pure. Thus the methanol observed towards W 33A and RAFGL7009S either resides in different locations in these clouds than most of the water ice or is part of a different ice layer on the same grains. This was first suggested by Skinner et al. (1992) for GL2136, using other transitions, and now appears to be a common phenomenon in high mass protostars.

We emphasize that the positions and widths of the methanol features in both objects are identical within the uncertainties due to the baseline correction procedure. For the combination modes this is an especially remarkable result in view of their strong sensitivity to the matrix environment (Allamandola et al. 1992; Fig. 1). The chemical nature of the ice environment in which the methanol is embedded is thus very similar in these two sources.

The column densities of methanol are estimated using the integrated absorption coefficients of the combination modes (Table 1). We use a range of values derived in the study of Hudgins et al. (1993) for the case of pure methanol and the so called “strong mixture” (H_2O:CH_3OH = 2:1), in agreement with the positions of the absorptions in Fig. 1. Our derived column densities towards W 33A are in good agreement with that of Allamandola et al. (1992) taking into account the updated values for the methanol band strengths.

Table 1. Methanol column densities

	$\int \tau(\nu)d\nu$ (cm^{-1})	A* (cm/molec.)	N (molec.cm^{-2})
comb. (3.84,3.94) in RAFGL7009S	10.7	2.8×10^{-18} ^{a} 3.2×10^{-18} ^{b}	3.8×10^{18} 3.3×10^{18}
comb. (3.84,3.94) in W 33A	5.5	2.8×10^{-18} ^{a} 3.2×10^{-18} ^{b}	2.0×10^{18} 1.7×10^{18}

* From Hudgins et al. 1993, ^{a} pure CH_3OH, ^{b} strong mixture.

For W 33A, using column densities of 0.9-4.2 $\times10^{19}$ cm^{-2} for water ice (Tielens & Allamandola 1987, Allamandola et al. 1992), we derive a methanol to water ratio of 0.05-0.22. As the H_2O column estimate is quite uncertain for W 33A, it is instructive to compare the column density of methanol to those of other molecules. From the CO column density of 8.9 $\times10^{17}$ cm^{-2} (Chiar et al. 1998), the ratio of methanol to CO is 1.9-2.2; from the CO_2 column density (Gerakines et al. 1999) the ratio of methanol to CO_2 is 1.2-1.4. Similarly, for RAFGL7009S, using the results of d’Hendecourt et al. (1996) and Dartois et al. (1998) the CH_3OH/H_2O = 0.28-0.32, CH_3OH/CO = 1.8-2.1 and CH_3OH/CO_2 = 1.3-1.5. The derived H_2O column density toward RAFGL7009S assumes that the 6 μm absorption band in this source is due entirely to water ice. Thus the methanol-to-water ratio is a lower limit. We find similar methanol abundances relative to CO and CO_2 in both sources. Clearly, **in these lines of sight, methanol is the second most abundant species after water ice**. This was pointed out previously by Allamandola et al. (1992) for W 33A.

4. The 2878 cm^{-1} band

In Fig. 1 an additional band appears on the short wavelength side of the 3.54 μm feature, centered near 2878 cm^{-1}. An assignment to the ν_4 mode of solid formaldehyde could be considered (Schutte et al. 1996a). However, the ν_1 mode of formaldehyde at 2820 cm^{-1}, which would produce a long wavelength shoulder on the 3.54 μm band (see Fig. 1, trace b), was not detected. The 2878 cm^{-1} band has been attributed by Allamandola et al. (1992) to a C-H stretch in tertiary carbon atoms (diamond-like) and alternatively attributed by Brooke et al. (1996) to C-H bonds in a volatile material. If instead we assume that this band is due to the ν_4 mode of formaldehyde in W 33A, then we are unable to provide a reasonable fit (shape and optical depth) to the four bands simultaneously (see Fig. 1 trace b). Furthermore, the methanol column density deduced from the combination modes is compatible with the 3.54 μm band being entirely due to CH_3OH. The two strongest modes of formaldehyde fall at 5.8 (ν_2) and 6.69 μm (ν_3), a spectral region covered by ISO. For W 33A, the attribution of the 2878 cm^{-1} band to formaldehyde would lead to optical depths of about 0.45 and 0.25 in the ν_2 and ν_3 modes respectively (Schutte et al. 1996a), incompatible with ISO observations. In RAFGL7009S, we have already re-

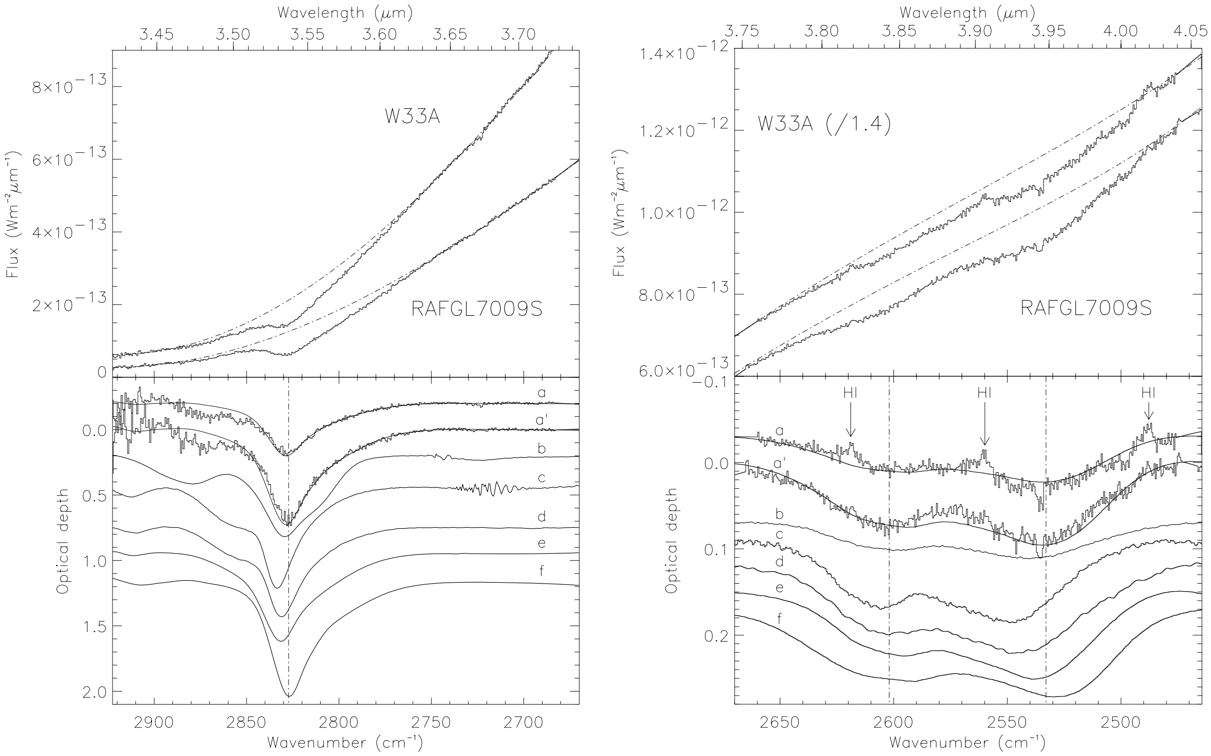

Fig. 1. *Upper half:* Spectra of the sources W 33A and RAFGL7009S obtained at UKIRT. The adopted continuum is shown by dot-dashed lines. *Lower half:* Optical depth spectra for each source (a and a'), together with the spectra of a number of laboratory ice mixtures; (b) H_2O:H_2CO:CH_3OH 3.7:3.1:2 (Schutte et al. 1996a), (c) H_2O:CH_3OH 10:1, (d) H_2O:CH_3OH 2:1, (e) H_2O:CH_3OH:CO_2 1:1:1 (Ehrenfreund et al. 1998), (f) pure CH_3OH. The best fits, both corresponding to 0.5×(e)+0.5×(f), are superimposed on the observed spectra.

ported a low abundance of formaldehyde of $\leq 3\%$ (Ehrenfreund et al. 1997). We thus conclude that formaldehyde cannot be the carrier of this band.

5. Other lines of sight

Table 2 summarizes the methanol-to-water ratios observed towards numerous lines of sight. The upper part of the table contains low mass stars or field stars where no detection of methanol is currently reported. The upper limits derived show that the methanol-to-water ratio cannot exceed $\sim$6%. The lower half of the table gathers the observations of high mass protostars. The higher abundances suggest that methanol production is favored in the circumstellar regions of massive protostars.

6. Origin of the methanol

The result that CH_3OH is more abundant towards high mass protostars than towards field stars and low mass stars indicates that low temperature CO hydrogenation on grain surfaces is not the dominant mechanism for methanol formation. Indeed, models applying this mechanism (Charnley et al. 1997; Tielens & Whittet 1997) predict a $\sim$50% methanol abundance by number in the icy mantles under typical dense cloud conditions ($n_H \leq 10^4 cm^{-3}$), in clear contradiction to the observations of the Taurus cloud sources (Table 2; Chiar et al. 1996). The low efficiency of forming CH_3OH is supported by laboratory experiments by Hiraoka et al. (1998), which show that CH_4 rather than CH_3OH is the end product of low temperature grain surface chemistry of H atoms with CO ice. Based on these experiments we might expect that CH_4 will be more abundant than methanol by almost one order of magnitude. However, there may be a selection effect due to grain temperatures excursions. Such variations will decrease the CH_4/CH_3OH ratio due to the much higher volatility of the former species. The presence of atomic oxygen also could inhibit some of the pathways which lead to methane formation. The Hiraoka et al. experiments were performed in a pure reducing environment of atomic H. In such an environnment CH_4 cannot react further. In the interstellar medium the presence of UV irradiation and oxygen atoms could reduce the high methane formation efficiency as they could break C-H bonds and lead to atomic or group substitution. This could then shift the equilibrium towards methanol formation. Further laboratory work is necessary to investigate this possibility. We note that the CO hydrogenation steps pass through intermediate species such as HCO and CH_3O. These species are not detected in RAFGL7009S nor in any other IR source (see A&A 315, special issue). Another intermediate product, H_2CO, has a relatively low abundance in RAFGL7009S ($\leq 3\%$ of H_2O; Ehrenfreund et al. 1997).

In the laboratory, experiments performed with irradiated astrophysically relevant ice mixtures produce small amounts of methanol, of the order of a few percent of the H_2O content as evidenced by the presence of the strong 9.7 μm band (see

Table 2. Observed methanol to water ratios.

Source	A_V	N_{CH_3OH}[a] (cm^{-2})	N_{H_2O}[b] (cm^{-2})	N_{CH_3OH}/N_{H_2O}(%)
Elias 3	8^{d}	$\leq 0.56(17)^{c}$	$0.9(18)^{c}$	≤ 6
Elias 13	10^{d}	$\leq 0.24(17)^{c}$	$1.2(18)^{c}$	≤ 2
Elias 15	13^{d}	$\leq 0.84(17)^{c}$	$1.7(18)^{c}$	≤ 5
Elias 16	21^{d}	$\leq 0.72(17)^{c}$	$1.4(18)^{c}$	≤ 5
Tamura 8	18^{d}	$\leq 1.92(17)^{c}$	$2.4(18)^{c}$	≤ 8
HL Tau	10^{k}	$\leq 0.72(17)^{c}$	$1.0(18)^{c}$	≤ 7
Elias 18	19^{d}	$\leq 0.80(17)^{c}$	$1.3(18)^{c}$	≤ 6
HH100		$\leq 2.40(17)^{f}$	$3.9(18)^{f}$	≤ 6.2
Mon R2/IRS3	81^{i}	$\leq 0.9(17)^{g}$	$2.0(18)^{g}$	≤ 4.5
S255/IRS1	97^{i}	$\leq 2.4(17)^{i}$	$2.5(18)^{g}$	≤ 9.6
BN	62^{i}	$\leq 0.8(17)^{i}$	$3.1(18)^{g}$	≤ 2.6
S140/IRS1	75^{i}	$\leq 0.6(17)^{i}$	$2.2(18)^{j}$	≤ 2.7
NGC7538/IRS1	120^{i}	$\leq 0.8(17)^{i}$	$2.2(18)^{j}$	≤ 3.6
AFGL2136	96^{l}	$3.9(17)^{e}$	$4.5(18)^{e}$	8.7
AFGL961 E	40^{i}	$\leq 2.0(17)^{i}$	$4.2(18)^{g}$	≤ 4.8
Mon/IRS2		$\leq 1.6(17)^{i}$	$4.4(18)^{g}$	≤ 3.6
NGC7538/IRS9	84^{i}	$4.85(17)^{h}$	$7.0(18)^{h}$	7
W3/IRS5	144^{i}	$\leq 1.6(17)^{i}$	$5.9(18)^{g}$	≤ 2.7
RAFGL7009S	≥ 75	3.55(18)	1.2(19)	30
W 33A	148	1.85(18)	$0.9\text{-}4.2(19)^{h}$	22-5

[a] methanol column densities were rescaled with A=7.5(-18) cm/molec. for the 3.54 μm mode. For GL2136, we used the 8.7 and 9.7 μm modes (Skinner et al. 1992). For W 33A and RAFGL7009S we take the mean value determined in this paper using the combination modes; [b] derived from the 3 μm band except for W 33A (Allamandola et al. 1992, 3 and 6 μm band) and RAFGL7009S (6 μm band); [c] Chiar et al. 1996; [d] Whittet et al. 1988; [e] Skinner et al. 1992; [f] Graham et al. 1998; [g] Smith et al. 1989; [h] Allamandola et al. 1992; [i] estimated from Brooke et al. data (1996), using $\Delta\nu \sim 30\,cm^{-1}$ for the 3.54 μm transition and $\tau(9.7\mu m)$ for A_V; [j] Willner et al. 1982; [k] Van de Bult et al. 1985; [l] using $A_V = \tau(9.7\mu m) \times 18.9$ (Roche and Aitken, 1984) and $\tau(9.7\mu m)$ given in Willner et al. 1982.

d'Hendecourt et al. 1996). The amounts produced are a factor of 5 to 10 below what is found in ice mantles in the lines of sight toward RAFGL7009S and W 33A, but could account for the methanol detected towards NGC7538/IRS9 and are consistent with the upper limits towards the other sources.

We cannot exclude a gas phase origin for methanol. Under general gas phase conditions, only very small amounts of CH_3OH are predicted in models using ion-molecule reactions (Turner 1998) because complex molecules are not efficiently produced. We can then firmly reject a "classical" gas phase production. Perhaps methanol could be produced under extreme conditions prevalent near high-mass protostars, such as stellar outflows and shocked circumstellar regions. The methanol could subsequently accrete on the grains, explaining the low gas phase abundance of methanol presently observed. This possibility is for the moment entirely speculative, as pointed out by Bergin et al. (1998). Furthermore, the high deuterium content in methanol observed towards hot cores seems inconsistent with its formation in these extreme conditions as deuterium fractionation only proceeds efficiently under low temperature conditions (Walmsley 1989).

7. Conclusion

High methanol abundances in grain mantles have been observed toward the molecular clouds surrounding RAFGL7009S and W 33A. Most of the methanol appears to be segregated from the more abundant water-ice in these clouds. Our present insight into the chemical and physical conditions near high mass protostars does not allow us to identify with confidence a plausible mechanism for producing the high methanol relative abundances, especially toward RAFGL7009S. This poses a challenge to our understanding of the chemistry of star forming regions and calls for further theoretical, laboratory, and astronomical studies.

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