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*Letter to the Editor*

# The detection of ethanol in W51M

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## SUMMARY

We have searched for 3 rotational transitions of ethanol, $CH_3CH_2OH$, toward W51M and Orion-KL, detecting it in the former source. Our analysis indicates that, in W51M, the ethanol emission arises in a warm gas probably similar to that detected previously in methanol and dimethyl ether. The abundances of all 3 molecules are much higher than predicted by gas phase chemistry and we suggest a novel mechanism for the formation of such complex species in grain surface reactions. This mechanism appears able to account for, in a qualitative manner, the overabundance of dimethyl ether compared to ethanol in Orion-KL and suggests that branched chain hydrocarbon molecules might be abundant in hot dense regions.

*Key words:* Atomic and molecular processes - Interstellar molecules - Millimeter lines.

## 1. INTRODUCTION

Ethanol, $CH_3CH_2OH$, was first detected in the interstellar medium by Zuckerman et al. (1975) toward Sgr B2 which has remained, until now, the only interstellar source known to contain ethanol. This molecule is of interest chemically not only because of its complexity and extent of hydrogenation - most interstellar molecules are highly unsaturated - but also because its isomer dimethyl ether, $CH_3OCH_3$, has been detected in a small number of interstellar clouds. Toward Sgr B2, the observations indicate an abundance ratio of 1:1 but in Orion dimethyl ether is apparently more than 40 times more abundant than ethanol (Irvine et al. 1987).

During a recent search for CCl in interstellar clouds, Millar et al. (1987) tentatively identified a line at a frequency of 103.7 Ghz in Orion-KL and W51M as the $9_{18}$-$8_{27}$ transition of ethanol. To confirm this idenification we have made observations of the two sources at frequencies close to 104.6 Ghz in order to detect the $5_{15}$-$4_{04}$ and $7_{07}$-$6_{16}$ transitions. In this Letter, we confirm the presence of ethanol in W51M but not in Orion, compare its abundance in W51M to that of dimethyl ether (Johansson et al. 1984) and present some arguments concerning the formation of these complex molecules.

## 2. OBSERVATIONS AND RESULTS

The first observations leading to a tentative identification of $CH_3CH_2OH$ were performed in May 1985 while line searches to verify this identification were done in April 1987, all with the Onsala 20m telescope. The main

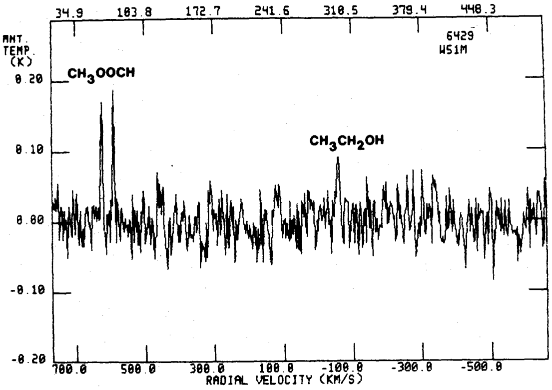

Figure 1: The spectrum of W51M near 103.7 GHz. In addition to the $9_{18}$-$8_{27}$ line of ethanol, the $8_{26}$-$7_{25}$ A and E lines of methyl formate are detected.

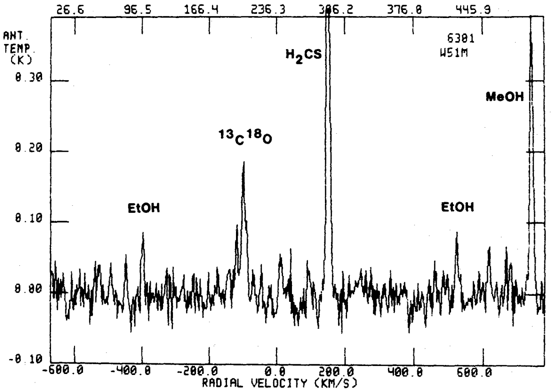

Figure 2: The spectrum of W51M near 104.6 GHz. 'EtOH' marks the $5_{14}$-$4_{04}$ and $7_{07}$-$6_{16}$ lines of ethanol, while 'MeOH' refers to the $10_4$-$11_3$ A$^+$ line of methanol. Other detections include the 1-0 line of $^{13}C^{18}O$ and the $3_{12}$-$2_{11}$ line of $H_2CS$.

beam efficiency, measured through the radome, of the telescope is 0.37 and the HPBW is ~ 37". The SSB-tuned SiS-mixer gave a total system temperature of ~ 200 K (SSB) at 104 Ghz. The observing procedures were the same as described by Millar et al. (1987).

Figures 1 and 2 show the spectra obtained toward W51M in which the identification of ethanol is secure. In Orion-KL, however, a verification was not achieved (see Table I). We note that Turner and Bally (1987) and Ziurys (1987,1988) find lines at $CH_3CH_2OH$ frequencies in their high sensitivity spectra towards Orion-KL. Our joint data set may point at an identification of ethanol in this source but at a low abundance level compared to that in W51M (see Table II).

Table I presents our observational results toward W51M and Orion-KL. A rotation diagram for $CH_3CH_2OH$ in W51M cannot be fit with a single $T_{rot}$ since the high energy $9_{18}$-$8_{27}$ line is strong relative to the two lower energy lines and perhaps indicates that the $9_{18}$-$8_{27}$ line arises in a different region. Using only our results for the $9_{18}$-$8_{27}$ line and with $T_{rot}$ in the range 50-200 K, we find $N(CH_3CH_2OH) = (0.9\text{-}4.0)\ 10^{15}\ cm^{-2}$ assuming that the emission is optically thin. Similarly, we calculate $N(CH_3OCH_3) = (1.6\text{-}2.6)\ 10^{15}\ cm^{-2}$ in W51M. A comparision of $V_{LSR}$ and $\Delta v$ given in Table I with the data for the high excitation ($E_1$ = 112.6 K) $15_{2,13}$ - $15_{1,14}$ line of dimethyl ether (Johansson et al. 1984) indicates that ethanol and dimethyl ether exist in the same region, presumably a hot molecular core.

## 3. DISCUSSION

If ethanol and dimethyl ether are coexistant in W51M we derive an abundance ratio of [dimethyl ether]/[ethanol] ~ 2 - 0.7 depending on the value assumed for $T_{rot}$. This ratio is more similar to that derived for Sgr B2 than that for Orion. Recent observations (Goldsmith et al. 1987, Vogel et al. 1987) have shown that the Sgr B2 molecular cloud has an extremely complex morphology and contains a number of hot cores and outflows. The abundance ratio of 1:1 estimated for Sgr B2 (Cummins et al. 1986; beam size ~ 2 arcmin) may therefore be an artefact of of poor spatial resolution and positional offsets rather than a true reflection of the actual abundance ratio. This point can be addressed through high spatial resolution observations of Sgr B2.

It is of interest to compare the ethanol and dimethyl ether abundances in W51M with that of methanol for which Johansson et al. (1984) and Menten et al. (1986) derive $T_{rot}$ ~ 100 K and $N(CH_3OH) \sim 2\ 10^{16}\ cm^{-2}$ averaged over a 40" beam. For $T_{rot}$ = 100 K we derive beam-averaged ratios:

$$\frac{[CH_3OH]}{[CH_3CH_2OH]} \sim \frac{[CH_3OH]}{[CH_3OCH_3]} \sim 10.$$

In Orion the relative abundances are $[CH_3OH]:[CH_3OCH_3]:[CH_3CH_2OH] \sim 200:10:<1$ (Johansson et al. 1984). The fractional abundances of these molecules with respect to molecular hydrogen are difficult to estimate accurately without specific knowledge of the source size. Menten et al. (1986) have argued that the thermal emission of $CH_3OH$ in W51M arises from a source of size ~ 10 arcsec and have derived a fractional abundance $x(CH_3OH) \sim 10^{-7}$. If the ethanol and dimethyl ether emissions emanate from this same region, then $x(CH_3CH_2OH)$ and $x(CH_3OCH_3) \sim 10^{-8}$. Table II compares these abundances with the results of a model calculation by Herbst and Leung (1986). This model incorporates purely gas-phase processes but does not address the formation of molecules in hot dense gas. In their scheme complex molecule formation is based on radiative association reactions which normally have a steep inverse dependence on temperature so that the fractional abundances in Table II are realistic upper limits for what one can expect from gas-phase schemes in hot dense gas. Herbst and Leung (1986) considered the following radiative association reactions in the synthesis of ethanol and dimethyl ether:

$H_3O^+ + C_2H_4 \longrightarrow CH_3CH_2OH_2^+ + h\nu$
$C_2H_5^+ + H_2O \longrightarrow CH_3CH_2OH_2^+ + h\nu$
$H_3CO^+ + CH_4 \longrightarrow CH_3OCH_4^+ + h\nu$
and $CH_3^+ + CH_3OH \longrightarrow CH_3OCH_4^+ + h\nu$.

Herbst (1987) has revised the rate coefficients of these reactions in the temperature range 10-50 K and has shown that they are smaller than the values adopted by Herbst and Leung (1986). Using these new rate coefficients, Herbst (1987) has recalculated the ethanol and dimethyl ether abundances and finds *maximum* fractional abundances of a few times $10^{-13}$ for both species at 50 K. Although it now appears that several radiative association reactions may proceed via electronic rather than vibrational stabilisation (Herbst and Bates 1988), it is unlikely that the increase would be enough to reconcile theory and observation. There appears to be no possibility that radiative association reactions, such as those outlined above, can account for these complex oxygen-bearing molecules. Blake et al. (1987) have suggested that the reaction

$$CH_3OH_2^+ + CH_3OH \longrightarrow CH_3OCH_4^+ + H_2O$$

will preferentially form dimethyl ether rather than ethanol in regions containing a large methanol abundance. However, this reaction must compete with a radiative association reaction (Bass et al. 1983) and, in addition, the low ionisation levels likely to occur in hot dense clouds (Brown et al. 1988) probably preclude any efficient ion-molecule chemistry *in situ*. We shall therefore discuss the formation of these molecules in terms of a model which incorporates grain surface processes.

Recently Brown et al. (1988) have developed a model of hot molecular cores which describes the chemical abundances of such regions as arising through a number of processes involving the accretion of material onto interstellar dust grains followed by subsequent surface reactions and the release of processed molecular mantles to the gas phase upon heating. They have argued that little gas phase chemistry can occur for a time in excess of $10^4$ yr since, in the hot gas, the ionisation fraction and the abundance of atoms and radicals are small. In this model, abundances in hot regions reflect either (i) material frozen onto grains - with abundances which can be larger than steady-state estimates if, for example, the accretion time-scale is on the order of that taken to reach peak abundances - and (ii) material formed in reactions between reactive species accreted onto the grain surface.

Since both the ethanol and dimethyl ether abundances are observed to be at least an order of magnitude larger than the peak abundances estimated by gas phase chemistry (Table II), it is likely that process (ii) above dominates the formation of these molecules in W51M. A detailed quantitative model of such a process will be difficult to develop due to the uncertain nature of interstellar grains, surface mobilities and so on but we shall describe a qualitative model which may account for the dimethyl ether:ethanol abundance ratios determined for Orion, W51M and Sgr B2.

During the accretion of gas phase species in cold interstellar clouds the abundance of atomic hydrogen is of crucial importance in determining the amount of hydrogenation which can occur on the grain surface. If x(H) > $10^{-3}$ there will always be H-atoms available to saturate, on a short time-scale, accreted atoms such as O, C and N as well as radicals such as CN and $C_2H$. The mantle will be composed primarily of $H_2O$, $CH_4$ and $NH_3$ with trace amounts of species such as HCN and $C_2H_2$. Under such conditions it is unlikely that molecules as complex as ethanol and dimethyl ether could be formed on the grain surface at sufficient rates to lead to the observed gas phase fractional abundances of $10^{-8}$.

In regions in which the H-atom abundance is small, it is possible that there is insufficient atomic hydrogen to saturate fully accreted atoms and radicals and, in this case, surface reactions between atoms and radicals may become important, as pointed out initially by Pickles and Williams (1977).

Let us first consider a region in which the H-atom abundance is intermediate between the two cases outlined above. In this case radicals such as $H_3C-$ may be the most abundant reactive carbon-bearing species on the surface. Because of its structure, $H_3C-$ can only grow in one direction at low temperatures and a molecule such as dimethyl ether, $H_3C - - O - - CH_3$, where dashed lines indicate the creation of a new bond, may form. Ethanol production would be less efficient in this scenario because the reaction of two contigous $H_3C-$ groups will lead to a saturated species, ethane $C_2H_6$. Such a process may be occuring in Orion.

In regions containing a lower abundance of H-atoms then the basic building blocks will be C-, HC- or $H_2C-$ groups. In this case, the availability of at least two free bonds will ensure linear ´backbone´ growth in two directions, and enable branched chain formation, a point to which we return below. For linear growth the possibilities are (writing down the backbone only)

C - - C - - O  and  C - - O - - C.

Over a long time-scale hydrogenation could lead to ethanol and dimethyl ether although it is likely that complete hydrogenation of these of these backbones will be difficult due to the low H-atom abundance and to the variety of unsaturated linear and branched chain molecules which can be envisaged in this case.

Such a picture offers a ready explanation for the observation that dimethyl ether is much more abundant than ethanol in Orion and may be able to explain the 1:1 ratios in Sgr B2, if this is confirmed by subsequent high angular resolution studies, and W51M. One interesting prediction of this admittedly crude model is that highly unsaturated branched chain molecules are probably best searched for in hot dense regions rather than GMCs. The observations of such molecules would help identify regions in which the H-atom abundance is small enough so that hydrogenation becomes inefficient compared to radical-radical reactions on the grain surface.

## 4. CONCLUSIONS

We have confirmed the presence of ethanol in W51M and shown that the dimethyl ether:ethanol abundance ratio is ~ 1 - 2 with fractional abundances of ~ $10^{-8}$ for these molecules assuming a source size of 10 arcsec and $T_{rot}$ = 100 K. Such large abundances do not seem to be reproducible using gas phase chemistry alone and we suggest a novel method of producing complex molecules through surface reactions on interstellar grains. This model can account qualitatively for the larger abundance of dimethyl ether than ethanol observed in Orion and suggests that large unsaturated branched chain molecules may be present in some hot core regions.

Table I
ETHANOL IN W51M AND ORION-KL

| Freq (MHz) | 104808.6 | 104487.2 | 103702.8 |
|---|---|---|---|
| Transition | $5_{14}-4_{04}$ | $7_{07}-6_{16}$ | $9_{18}-8_{27}$ |
| $E_l$ (K) | 8.4 | 18.3 | 35.2 |
| $S_{ul}$ | 3.2 | 4.2 | 2.3 |
| $T_{mb}$ (mK) | 84(<50)[a] | 87(<50) | 96(84) |
| $\Delta v$ (km $s^{-1}$) | 8 | 8 | 10(14) |
| $V_{LSR}$ (km $s^{-1}$) | 56 | 57 | 58(9) |

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[a] Values in parentheses refer to Orion-KL

Table II
COMPARISION BETWEEN OBSERVED AND
CALCULATED FRACTIONAL ABUNDANCES

| Molecule | Observed[1] Orion | W51M | SgrB2 | Early Time[2] | Steady State[2] |
|---|---|---|---|---|---|
| $CH_3OH$ | 4(-7) | 1(-7) | 2(-7) | 1(-9) | 2(-11) |
| $CH_3CH_2OH$ | <5(-10) | 1(-8) | 3(-9) | 6(-12) | 9(-15) |
| $CH_3OCH_3$ | 2(-8) | 1(-8) | 3(-9) | 6(-11) | 2(-14) |

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[1] Calculated for a 10" source in W51M; [2] n($H_2$) = $10^4$ cm$^{-3}$ T = 50 K, Av = 20 mag., from Herbst and Leung (1986).

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**REFERENCES**

Bass, L.M., Cates, R.D., Jarrold, M.F., Kirchner, N.J. & Bowers, M.T.: 1983, J. Amer. Chem. Soc., **105**, 7024.
Blake, G.A., Sutton, E.C., Masson, C.R. & Phillips, T. G..: 1987, Astrophys. J., **315**, 621.
Brown, P.D., Charnley, S.B. & Millar, T.J.: 1988, MNRAS, **231**, 419.
Goldsmith, P.F., Snell, R.L., Hasegawa, T. & Ukita, N. : 1987, Astrophys. J., **314**, 525.
Herbst, E.: 1987, Astrophys. J., **313**, 867.
Herbst, E. & Bates, D.R.: 1988, Astrophys. J., **329**, 410.
Herbst, E. & Leung, C.M.: 1986, MNRAS, **222**, 689.
Irvine, W.M., Goldsmith, P.F. & Hjalmarson, A.: 1987, in ´Interstellar Processes´, eds. D.J. Hollenbach & H.A. Thronsen, Jr.,(Reidel:Dordrecht), p. 561.
Johansson, L.E.B., Andersson, C., Ellder, J., Friberg, P., Hjalmarson, A., Hoglund, B., Irvine, W.M., Olofsson, H. & Rydbeck, G.: 1984, Astron. Astrophys., **130**, 227.
Menten, K.M., Walmsley, C.M., Henkel, C. & Wilson, T.L. : 1986, Astron. Astrophys., **157**, 318.
Millar, T.J., Ellder, J., Hjalmarson, A. & Olofsson, H.: 1987, Astron. Astrophys., **182**,143.
Pickles, J.B. & Williams, D.A.: 1977, Astrophys. Sp. Sci., **52**, 443.
Turner, B.E. & Bally, J.: 1987, Astrophys. J., **321**, L75.
Ziurys, L.M.: 1987, Astrophys. J., **321**, L81.
Ziurys, L.M.: 1988, Astrophys. J., **324**, 544.
Zuckerman, B. et al.: 1975, Astrophys. J., **196**, L99.