Organic Matter in Space
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Observational constraints on the formation of interstellar methanol

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Abstract. The processes by which methanol, one of the most abundant interstellar organics, is formed in the interstellar medium are not yet accurately known. Pure gas-phase chemistry models fail to reproduce observed abundances by orders of magnitude, pointing to formation on grains and subsequent desorption.
Observations of methanol and its isotopologue $^{13}CH_3OH$ in several sources have been used to trace the origin, and thus the formation routes of methanol on interstellar grains, by means of isotope labelling a posteriori.

Keywords. Astrochemistry, ISM: molecules, ISM: abundances, radio lines: ISM, submillimeter

1. Introduction

Methanol is one of the most abundant interstellar organic molecules (typically 10^{-7} in hot cores and 10^{-9} in dark clouds, relative to H_2). It is observationally very important, being a sensitive probe of both density and temperature in a wide range of interstellar environments, as well as a "chemical clock" for the embedded phase of massive star formation.

Recent storage ring measurements have shown that the previously generally accepted gas-phase production of methanol by dissociative recombination of $CH_3OH_2^+$ cannot be efficient enough to explain the high observed abundances of this molecule (Geppert *et al.* 2006, Garrod *et al.* 2006). Instead, formation on grain surfaces, with subsequent desorption, is now viewed as its most plausible origin, but there are several such alternatives. The first one is repetitive hydrogenation of carbon monoxide, frozen out on grain surfaces, which experimentally has been shown to form methanol (Nagaoka *et al.* 2005). Another is the formation of methanol from electron-irradiated mixed H_2O/CH_4 ice, demonstrated in a recent laboratory study (Wada *et al.* 2006), where the carbon comes from either CH_3 or CH_2 and H_2O is consumed in the process.

2. Method

Because of ^{13}C fractionation into CO at low gas-phase temperatures (e.g. Langer *et al.* 1984), the production of methanol through hydrogenation of CO on grains would result in methanol showing a $^{12}C/^{13}C$ ratio similar to that of cold CO, and considerably lower than in molecules formed by gas-phase ion-neutral chemistry. The $^{12}C/^{13}C$ ratio can therefore serve as an indicator of the generation pathway of interstellar methanol - isotope labelling a posteriori.

Table 1. Summary of observations, results and comparisons to ice data.

Source	Telescope	$\frac{^{12}CH_3OH_{gas}}{^{13}CH_3OH_{gas}}$	$\frac{^{12}CO_{2,\ ice}}{^{13}CO_{2,\ ice}}$	$\frac{^{12}CH_3OH_{gas}}{H_2O_{gas}}$	$\frac{^{12}CH_3OH_{ice}}{H_2O_{ice}}$
GL 989 (NGC 2264)	OSO, Apex	58±8	131±21[a]	–	–
NGC 7538 IRS9	OSO	75±12	80±11[b]	–	–
S140 IRS1	OSO	128±63	111±11[a]	–	–
Orion KL	Odin	57±14	33±9[a,c]	0.07[d], 4.3[e]	0.1

[a] Gibb *et al.* (2004); [b] Boogert *et al.* (2000); [c] IRc2; [d,e] Hot Core & Compact ridge resp. (Persson *et al.* 2007)

Since solid CO_2 emerges from solid CO through addition of atomic oxygen, the $[\frac{^{12}CO_2}{^{13}CO_2}]_{ice}$ ratio may be used as an indirect measure of the $^{12}CO/^{13}CO$ ratio in interstellar ices. In order to determine the gas-phase methanol $^{12}C/^{13}C$ ratio, the Onsala 20 m telescope has been used to observe $J = 2 - 1$ $^{12}CH_3OH$ and $^{13}CH_3OH$ lines around 96.7 and 94.4 GHz respectively; the APEX-2A receiver has been employed to observe $J = 7 - 6$ lines around 338 and 330 GHz; and >70 $^{12}CH_3OH$ and >20 $^{13}CH_3OH$ lines in the ranges 486–492 and 541–577 GHz have been observed with the Odin satellite. Our source sample was chosen to mainly include objects with ISO ice-observations of CO_2 and $^{13}CO_2$, allowing comparisons of gas and ice ratios.

3. Results & Discussion

So far, $^{13}CH_3OH$ have been detected in four out of eight observed sources (Table 1). Those observed with the Onsala telescope, in which the $CO_{2,ice}$ ratio is known, show optically thin lines arising in cold and extended gas, based on rotation diagram analysis. The $^{12}C/^{13}C$ ratios in this gas are of the order of, or smaller than, the corresponding $CO_{2,ice}$ ratios (Table 1). The absence of ^{13}C depletion as compared to CO_2 ices points to a methanol formation from cold CO, possibly via hydrogenation of CO on grains. In the case of GL989 this formation alternative is further strengthened by the gas-phase $^{12}C^{18}O/^{13}C^{18}O$ ratio of 56±4, observed by Langer & Penzias (1990), which is very close to our observed methanol ratio.

The gas-phase methanol $^{12}C/^{13}C$ ratio in Orion KL as observed by Odin does not exclude formation on cold grain surfaces. In addition, while the hot core component shows a CH_3OH/H_2O gas-phase ratio similar to that in ice, this ratio is 60 times higher in the compact ridge component. This increase is accompanied by a decrease in the water abundance, suggesting that water here is consumed in the formation of methanol in accordance with formation from mixed H_2O/CH_4 ice.

So far, our sample is too limited to unveil which grain-surface reaction path is most important for interstellar methanol, and how this depends on the local environment.

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