Organic chemistry in the dark clouds L1448 and L183. A Unique grain mantle composition.

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ABSTRACT

We present high sensitivity observations of the complex organic molecules (COMs) CH\(_3\)OH, C\(_2\)H\(_5\)OH, HCOOCH\(_3\), HCOOH and H\(_2\)CO and of SiO toward the quiescent dark cloud L183 and the molecular outflow L1448–mm. We have not detected C\(_2\)H\(_5\)OH, HCOOCH\(_3\) and SiO in L183 and in the quiescent gas of L1448–mm. The abundances of CH\(_3\)OH, H\(_2\)CO and SiO are enhanced by factors 4–20 in the shock precursor component, and those of CH\(_3\)OH and SiO by 3 and 4 orders of magnitude in the shocked gas, without substantial changes (< factor of 2) in the abundances of C\(_2\)H\(_5\)OH and HCOOCH\(_3\) relative to that of CH\(_3\)OH. The large enhancements of SiO and CH\(_3\)OH can be explained by the shock ejection of an important fraction of the grain mantle material into gas phase. Our upper limits to the C\(_2\)H\(_5\)OH/CH\(_3\)OH and HCOOCH\(_3\)/CH\(_3\)OH ratios are consistent with the rather constant ratios measured in hot cores and Galactic center clouds. However, the upper limits to the HCOOCH\(_3\)/CH\(_3\)OH and the HCOOH/CH\(_3\)OH ratios are at least one order of magnitude smaller than those found in “hot corinos” surrounding low mass protostars. We speculate that the observed abundances of COMs in different objects are consistent with a sort of “universal” grain mantle composition which is locally changed by the processes of low mass star formation.

Subject headings: astrochemistry — molecular data — ISM: molecules — techniques: spectroscopic — ISM: individual(L1448, L183)

1. Introduction

Large abundances of complex organic molecules (COMs) like CH\(_3\)OH, C\(_2\)H\(_5\)OH, HCOOCH\(_3\), HCOOH and H\(_2\)CO, have been observed in the interstellar medium (ISM) mostly associated with grain chemistry \cite{Charnley95, Horn04} in hot cores associated with massive star formation regions \cite{Ikeda01}. 

in hot cores associated with low mass star formation (the so called "hot corinos"; Bottinelli et al. 2006, and in molecular clouds affected by shocks in the Galactic center (GC) region (Martín-Pintado et al. 1999; Requena-Torres et al. 2006). The comparison between the abundances of COMs in those sources has shown that the chemistry of COMs in the GC clouds and in hot cores are very similar suggesting that evaporation/sputtering of a "universal" grain mantle composition are responsible for the gas phase abundances of complex molecules in these objects. However, in hot corinos the COMs show different relative abundances (Bottinelli et al. 2006) than those found in hot cores and GC clouds, suggesting that either the grain mantle composition in dark clouds is different than in hot cores and in the GC, or star formation processes locally change the gas phase abundances of COMs in dark clouds (Garrod & Herbst 2006).

In dark clouds without signs of star formation, the abundances of COMs in gas phase should not be influenced by the evaporation/ejection of complex molecules from the dust grains, and their abundances should reflect the gas phase chemistry (Irvine et al. 1987; Hasegawa & Herbst 1993a,b). Moreover, observations of solid phase molecules in dark clouds have shown the existence of COMs like HCOOH on the grains mantles (Knez et al. 2005). Dark clouds with very young outflows should show the abundances of the COMs just ejected from the grain mantles by shocks. Therefore dark clouds offer a unique possibility to study the formation of COMs in the ISM.

Friberg et al. 1988 have previously observed CH$_3$OH and (CH$_3$)$_2$O in the dark cloud L183, deriving upper limits to their relative abundance in agreements with those obtained by Requena-Torres et al. 2006. In this paper, we present high sensitivity observations of COMs toward the dark clouds L183 and L1448. L183 is a cold quiescent dark cloud without signatures of outflow activity and with a rich oxygen chemistry dominated by gas phase reactions (Pagani et al. 2005). L1448 is a dark cloud which harbors an extremely young outflow, L1448–mm. It has been proposed that the three velocity components observed in this object correspond to the quiescent gas (4.7 km s$^{-1}$), the magnetic precursor of C–shocks (5.2 km s$^{-1}$) and the shocked gas (broad velocity wings; Jiménez-Serra et al. 2004, 2005). The enhancement of the SiO and CH$_3$OH abundances in the shock precursor suggests that these molecules have been recently ejected from grains with little post ejection processing. This provides an unique opportunity to establish the “universality” of the grain mantle composition.

2. Observations and results

The observations of the molecular lines listed in Table 1 toward L183 and two positions in the L1448–mm outflow were carried out with the IRAM 30m radio telescope at Pico Veleta (Spain). The data were obtained in two different sessions in 2005. The half-power beam width of the telescope was ∼24", 17" and 12" for the 3, 2 and 1.3 mm bands. The receivers, equipped with SIS mixers, were tuned to single sideband with image rejections of ≥10 dB. For the observations of L1448–mm we used the frequency and wobbler-switched modes with frequency and position throws of 7.2 MHz and 240", respectively. A spectral resolution of ∼40 kHz corresponding to velocity resolutions of ∼0.14, 0.08, and 0.05 km s$^{-1}$ at the observed frequencies was achieved using autocorrelators. For L183 we used the frequency switched mode and the same setup as for L1448–mm for the 2 and 3 mm lines but with a spectral resolution of 80 kHz at 1.3 mm (velocity resolution of 0.09 km s$^{-1}$). The typical system temperatures were ∼100–650 K. Spectra were calibrated using the standard dual load system. The line intensities are given in units of $T_A^*$. The observed spectra are shown in Figure I. In the left panel we show the line profiles observed toward L183 and, in the central and right panels, the line profiles observed toward L1448 (0,−20) and (−30,+74) respectively. The vertical dashed lines show the quiescent gas in L183 at 2.5 km s$^{-1}$ and the quiescent and the shock precursor components in L1448 (0,−20) at 4.8 and 5.2–5.5 km s$^{-1}$. For the (−30,+74) position in the L1448–mm outflow the the emission is centered at 4.6 km s$^{-1}$ (vertical dashed line in Figure I) and the shock precursor as traced by the narrow SiO emission is overlapped...
with the quiescent gas. Toward L1448 (0,−20), we have also detected high velocity redshifted wings in CH$_3$OH (2mm lines) and SiO which are associated with the shocked gas. The high velocity wings for the 1 mm CH$_3$OH transitions are very uncertain due to poor baselines in the frequency switching observations.

As expected for a shock tracer, the SiO emission is only detected in the shock precursor and the shocked gas of L1448–mm but not in the quiescent gas of L183 and L1448–mm. CH$_3$OH emission has been detected in all sources and in all velocity components. H$_2$CO has been detected in all sources but toward L1448–mm their line profiles are different than the other molecules. Toward the L1448 (0,−20) position, the H$_2$CO emission arises from the quiescent and shock precursor components like for H$_2$S (Jiménez-Serra et al. 2005). Toward the position L1448 (∼30,+74) we also find a broad H$_2$CO profile indicating the presence of shocked gas. HCOOH has been only detected in L183 and the most complex molecules like C$_2$H$_5$OH and HCOOCH$_3$, are not detected toward any of the sources.

The estimated column densities for all molecules in the different components using the Local Thermodynamic Equilibrium (LTE) approximation and the excitation temperatures ($T_{ex}$) derived from the population diagrams of CH$_3$OH are given in Table 2. We obtained a $T_{ex}$ between 5–10 K as expected for dark clouds with densities of few $10^{3}$cm$^{-3}$ and kinetic temperatures of 10–20 K (Dickens et al. 2000; Curiel et al. 1999). We estimated the H$_2$ column densities from the HCO$^+$, H$_3^{13}$CO$^+$ and HN$^{13}$C mole column densities by assuming a C$^{12}$/C$^{13}$ ratio of 90 and a HCO$^+$/H$_2$ and HNC/H$_2$ abundances of $1\times10^{-8}$ for L1448 (Irving et al. 1987) and a C$^{12}$/C$^{13}$ ratio of 64 and a HCO$^+$/H$_2$ and HNC/H$_2$ abundances of $8\times10^{-9}$ for L183 (Dickens et al. 2000). The H$_2$ column densities and the relative molecular abundances of SiO and CH$_3$OH are shown in Table 2. This table also shows the abundances of C$_2$H$_5$OH, HCOOCH$_3$, HCOOH and H$_2$CO relative to that of CH$_3$OH.

As expected for the quiescent gas in L1448 (0,−20)-q and in L183-q, the SiO abundance is very low, of $<2\times10^{-12}$, suggesting that SiO is depleted into the grains and on the grain mantles (Ziurys et al. 1989; Martín-Pintado et al. 1992). This is in contrast with the abundance of CH$_3$OH and H$_2$CO in the quiescent gas which varies by more than one order and two orders of magnitude, respectively between L1448–mm and L183. For the other COMs we derive similar upper limits to their abundances in the quiescent gas in both sources.

As reported by Jiménez-Serra et al. (2005), we find a moderate increase (by a factor of 3) of the CH$_3$OH abundance and a large increase by a factor of >15 in the SiO abundance in the shock precursor (L1448 (0,−20)-p) with respect to that in the quiescent gas. We also find a large increase by more than one order of magnitude in the H$_2$CO abundance in the shock precursor in both positions of L1448–mm, as expected if this molecule, like SiO and CH$_3$OH, was ejected from the grain mantles. The upper limits to the abundances for the other COMs are similar to those in the quiescent gas suggesting that the abundances of these molecules have not been strongly affected by the ejection from grain mantles.

The abundances of SiO and CH$_3$OH in the shocked gas [see source L1448 (0,−20)-s in Table 2] have been enhanced by nearly 4 orders of magnitude with respect to those of the quiescent gas due to the sputtering of these molecules from the grain mantles. Surprisingly, the H$_2$CO to CH$_3$OH abundance ratio decreases by more than one order of magnitude in the shocked gas as compared with that in the shock precursor component. Our data suggest that the abundance of H$_2$CO in the grain mantles is smaller than that of CH$_3$OH. However, our upper limits to the abundance ratios of C$_2$H$_5$OH, HCOOCH$_3$, and HCOOH to that of CH$_3$OH in the shocked gas are small compared with those measured in “hot corinos”, but consistent with those measured in hot cores and the GC clouds.

3. Discussion

The abundances of SiO and of the COMs that we have derived in dark clouds with different star formation activity show a clear trend. The quiescent gas in L183 and L1448–mm show a very low SiO abundance ($<10^{-12}$) as expected if the molecular complexity in gas phase has not been significantly affected by the ejection of molecules from grain mantles (Martín-Pintado et al. 1992).
Gas phase models should then explain the observed molecular abundance of COMs in the quiescent gas. Chemical models for the formation of COMs in dark clouds (Hasegawa et al. 1992, Hasegawa & Herbst 1993a,b) predict abundances that are consistent with our upper limits for the COMs in the quiescent gas of L1448-mm, except for H$_2$CO, which shows lower abundances than expected from chemical models. Low abundances of H$_2$CO ($\sim 10^{-10}$) are also found in the envelope of the central position in L1448-mm, possibly related with the CO depletion (see Maret et al. 2005). In the case of L183, we find discrepancies by up to one order of magnitude between the predictions and the measured CH$_3$OH, HCOOH and H$_2$CO abundances in the quiescent gas. However, the models of gas-phase chemistry in dark clouds need to be revisited since it has been shown that the formation of CH$_3$OH in gas phase is much less efficient than previously assumed (see e.g. Geppert et al. (2005)). On the other hand, it is very likely that some of the COMs in dark clouds are also formed on grains (Knez et al. 2005).

The SiO abundance in the shock precursor component toward the L1448 ($0,-20$) position (5.2 km s$^{-1}$) increases by more than one order of magnitude due to the ejection of SiO or Si from the grain mantles produced by the sudden acceleration of ions relative to neutrals as the C-shocks propagate through the quiescent molecular cloud (Jiménez-Serra et al. 2004, 2005). The H$_2$CO abundance in this component is also enhanced by more than a factor 10. A smaller enhancement by only a factor of $\sim 3$ is observed in CH$_3$OH. The upper limits to the abundance of HCOOH, C$_2$H$_5$OH and HCOOCH$_3$ in the shock precursor indicate that these molecules are not ejected from the grain mantles in the first stages of the shock interaction. A moderate increase of the CH$_3$OH abundance is also observed for the mixture of quiescent and precursor gas in L1448 ($-30,+74$) together with a large enhancement of the SiO and H$_2$CO abundances and no enhancement for the other COMs.

The trend observed in the abundance of some molecules in the shock precursor is even more dramatic in the post shocked gas in the L1448-mm outflow. While the SiO and the CH$_3$OH abundances increase by 4 and 3 orders of magnitude respectively in the shocked gas, the abundance ratio of the other COMs (including H$_2$CO) relative to that of CH$_3$OH remains similar to those observed in the quiescent gas.

For comparison with our results, Table 2 also shows the ratio between the abundance of COMs to that of CH$_3$OH for all kinds of objects where these molecules have been detected: hot cores, “hot corinos” and molecular clouds in the GC. The abundance ratios C$_2$H$_5$OH/CH$_3$OH and HCOOCH$_3$/CH$_3$OH in the GC and in hot cores suggest a similar grain mantle composition in these two type of objects. In fact, Charnley & Rodgers (2005) have proposed paths to form large molecules on the grain mantles which will lead to a sort of universal grain mantle composition.

Our upper limits to the relative abundance of C$_2$H$_5$OH and HCOOCH$_3$ to that of CH$_3$OH in the quiescent and the shocked gas are consistent with those measured in hot cores and the CG clouds and therefore, compatible with similar grain mantle composition in all objects. However, the large COMs abundance ratios measured in hot corinos exceed by more than one order of magnitude those of the shocked gas in L1448-mm. Unless a dramatic change in the grain mantle composition between different clouds exists, this suggests that the large enhancement of the COMs in gas phase is restricted to the surrounding material affected by the process of low mass star formation.

Garrod & Herbst (2006) have recently proposed that the protostellar switch-on phase could lead to a very effective grain-surface and gas formation of COMs due to the warm up of the circumstellar gas and dust. Although the models are not able to reproduce the large HCOOCH$_3$/CH$_3$OH ratio found in hot corinos they indicate local changes associated with star formation. The large abundance of COMs observed in the GC cannot be however explained by this model, since star formation does not play any role over large scales, and the grain surface reactions are not very effective due to relatively low temperatures for the bulk of grains (<15 K, Rodríguez-Fernández et al. 2004).

In summary, the low abundance ratios of COMs that we find in the two dark clouds, support the scenario proposed by Maret et al. (2003) where
the abundances are locally enhanced in the circumstellar material. But the bulk of the quiescent material could have the same grain mantle composition as observed in the GC clouds and in the hot cores, suggesting a sort of “universal” grain mantle composition as proposed by [Requena-Torres et al. (2006)](#). High sensitivity and resolution measurements of the COMs abundances towards the exciting source of the L1448–mm outflow will help to clarify if the high abundances of some of the COMs observed in hot corinos are a local effect associated with low mass star formation.

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Table 1

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Transition</th>
<th>Frequency</th>
<th>E_u MHz</th>
<th>K</th>
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</thead>
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<td>HCO⁺⁺⁺</td>
<td>1→0</td>
<td>89187.41</td>
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<td>H13CO⁺⁺⁺</td>
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<td></td>
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<tr>
<td>HN13C⁺⁺⁺</td>
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<td>87090.85</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>C₂H₃OH⁺⁺⁺</td>
<td>414→413</td>
<td>90117.61</td>
<td>9.36</td>
<td></td>
</tr>
<tr>
<td>SiO⁻⁻⁻</td>
<td>2→1</td>
<td>86846.96</td>
<td>6.26</td>
<td></td>
</tr>
<tr>
<td>HCOOCH₃⁻⁻⁻</td>
<td>222→221</td>
<td>90158.03</td>
<td>23.53</td>
<td></td>
</tr>
<tr>
<td>H₂CO⁻⁻⁻</td>
<td>222→221</td>
<td>89517.17</td>
<td>13.57</td>
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</tr>
<tr>
<td>CH₃OH⁻⁻⁻</td>
<td>303→202</td>
<td>21822.19</td>
<td>20.97</td>
<td></td>
</tr>
<tr>
<td>CH₃OH⁻⁻⁻</td>
<td>303→203</td>
<td>21822.19</td>
<td>20.97</td>
<td></td>
</tr>
<tr>
<td>CH₃OH⁻⁻⁻</td>
<td>303→204</td>
<td>90145.23</td>
<td>19.52</td>
<td></td>
</tr>
</tbody>
</table>

Note.—Quantum numbers and frequencies of the observed transitions from the Jet Propulsion Laboratory molecular catalog [Pickett et al. 1998]. We observed L183 toward the position α(J2000)=15h54m08s.6, δ(J2000)=−02°52′10″00 and two different offsets, (0, −20) and (−30, +74), in the L1448 cloud relative to L1448-mm position (α(J2000)=03h25m38s, δ(J2000)=30°33′21″05′).
### Table 2

**Derived abundances**

<table>
<thead>
<tr>
<th>Source</th>
<th>$T_{ex}$ (K)</th>
<th>$N(H_2) \times 10^{22}$ cm$^{-2}$</th>
<th>$X_{SiO} \times 10^{-12}$</th>
<th>$X_{CH_3OH} \times 10^{-9}$</th>
<th>$C_2H_5OH \times 10^{-2}$</th>
<th>HCOOCCH$_3$</th>
<th>HCOOH</th>
<th>H$_2$CO</th>
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<tr>
<td>L183-ν</td>
<td>5.7</td>
<td>0.4</td>
<td>≤ 0.4</td>
<td>≤ 0.4</td>
<td>≤ 0.4</td>
<td>≤ 0.4</td>
<td>≤ 0.4</td>
<td>1.3</td>
</tr>
<tr>
<td>L1448 (0,−20)-ν</td>
<td>8.9</td>
<td>1.2</td>
<td>≤ 2</td>
<td>≤ 4</td>
<td>≤ 9</td>
<td>≤ 9</td>
<td>≤ 0.1</td>
<td>≤ 1.3</td>
</tr>
<tr>
<td>L1448 (0,−20)-p</td>
<td>9.8</td>
<td>1.2</td>
<td>2</td>
<td>3</td>
<td>≤ 4</td>
<td>≤ 4</td>
<td>≤ 4</td>
<td>2.4</td>
</tr>
<tr>
<td>L1448 (−30,+74)-q+p</td>
<td>9.3</td>
<td>3.7</td>
<td>12.5</td>
<td>2.2</td>
<td>≤ 1</td>
<td>≤ 1</td>
<td>≤ 1</td>
<td>15.0</td>
</tr>
<tr>
<td>L1448 (0,−20)-s</td>
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<td>3.7</td>
<td>12.5</td>
<td>2.2</td>
<td>≤ 1</td>
<td>≤ 1</td>
<td>≤ 1</td>
<td>15.0</td>
</tr>
<tr>
<td>6–8 km s$^{-1}$</td>
<td>15</td>
<td>$2.1 \times 10^{-3}$</td>
<td>$2.3 \times 10^4$</td>
<td>$1.5 \times 10^3$</td>
<td>≤ 7</td>
<td>≤ 17</td>
<td>≤ 9</td>
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<td>8–10 km s$^{-1}$</td>
<td>15</td>
<td>$7.4 \times 10^{-4}$</td>
<td>$1.4 \times 10^4$</td>
<td>$2.8 \times 10^3$</td>
<td>≤ 11</td>
<td>≤ 25</td>
<td>≤ 13</td>
<td>≤ 0.3</td>
</tr>
<tr>
<td>10–12 km s$^{-1}$</td>
<td>15</td>
<td>$4.8 \times 10^{-4}$</td>
<td>$1.2 \times 10^4$</td>
<td>$2.7 \times 10^3$</td>
<td>≤ 17</td>
<td>≤ 40</td>
<td>≤ 21</td>
<td>≤ 0.4</td>
</tr>
<tr>
<td>12–14 km s$^{-1}$</td>
<td>15</td>
<td>$3.2 \times 10^{-4}$</td>
<td>$1.8 \times 10^4$</td>
<td>$2.6 \times 10^3$</td>
<td>≤ 27</td>
<td>≤ 63</td>
<td>≤ 33</td>
<td>≤ 0.7</td>
</tr>
<tr>
<td>14–16 km s$^{-1}$</td>
<td>15</td>
<td>$2.9 \times 10^{-4}$</td>
<td>$3.2 \times 10^4$</td>
<td>$3.4 \times 10^3$</td>
<td>≤ 45</td>
<td>≤ 76</td>
<td>≤ 55</td>
<td>≤ 0.9</td>
</tr>
<tr>
<td>GC sources$^2$</td>
<td></td>
<td>~3.7</td>
<td>~3.9</td>
<td>~6.9</td>
<td>~6.9</td>
<td>~6.9</td>
<td>~6.9</td>
<td>~1.1</td>
</tr>
<tr>
<td>Hot cores$^3$</td>
<td></td>
<td>~2.5</td>
<td>~6.9</td>
<td>~6.9</td>
<td>~6.9</td>
<td>~6.9</td>
<td>~6.9</td>
<td>~1.1</td>
</tr>
<tr>
<td>Hot cores$^4$</td>
<td></td>
<td>~160</td>
<td>~60</td>
<td>~60</td>
<td>~60</td>
<td>~60</td>
<td>~60</td>
<td>~190</td>
</tr>
</tbody>
</table>

Note.—H$_2$ column density, temperature and the relative abundances of the different COMs to that of H$_2$ and of CH$_3$OH. $^1$ q for quiescent, p for precursor, and s for shocked gas. $^2$ Requena-Torres et al. (2006). $^3$ Bisschop et al. (2006). $^4$ Bottinelli et al. (2006). $^∗$ Assumed by the authors to be related with a cooler gas than the other complex molecules.
Fig. 1.— Line profiles for the different lines observed toward L183 and L1448, the dashed vertical lines show the different velocity components. L183 (left panel) shows one-peaked profiles centered at 2.5 km s\(^{-1}\). The line profiles from the L1448 (0,−20) (central panel) and the L1448 (−30,+74) position (right panel) show velocity components corresponding to the quiescent gas at 4.8 km s\(^{-1}\) and 4.6 km s\(^{-1}\), respectively. The L1448 (0,−20) position also shows the precursor at 5.5 km s\(^{-1}\) and, at higher velocities, the emission associated to the shocked gas for the CH\(_3\)OH (3\(0\)→2\(0\))A+ and (3\(-1\)→2\(-1\))E transitions at 2 mm.