$^{13}$C–METHYL FORMATE: OBSERVATIONS OF A SAMPLE OF HIGH-MASS STAR-FORMING REGIONS INCLUDING ORION–KL AND SPECTROSCOPIC CHARACTERIZATION

CÉCILE FAVRE$^1$, MIGUEL CARVAJAL$^2$, DAVID FIELD$^3$, JES K. JØRGENSEN$^4,5$, SUZANNE E. BISCHOP$^4,5$, NATHALIE BROUILLE$^6,7$, DIDIER DESPOIS$^6,7$, ALAIN BAUDRY$^6,7$, ISABELLE KLEINER$^8$, EDWIN A. BERGIN$^1$, NATHAN R. CROCKETT$^1$, JUSTIN L. NEILL$^1$, LAURENT MARGULES$^9$, THÉRÈSE R. HUET$^9$, AND JEAN DEMAISON$^9$

1 Department of Astronomy, University of Michigan, 500 Church Street, Ann Arbor, MI 48109, USA; cfavre@umich.edu
2 Dpto. Física Aplicada, Unidad Asociada CSIC, Facultad de Ciencias Experimentales, Universidad de Huelva, E-21071 Huelva, Spain; miguel.carvalj@dfa.uhu.es
3 Department of Physics and Astronomy, University of Aarhus, Ny Munkegade 120, DK-8000 Aarhus C, Denmark
4 Centre for Star and Planet Formation, Niels Bohr Institute, University of Copenhagen, Juliane Maries Vej 30, DK-2100 Copenhagen Ø, Denmark
5 Natural History Museum of Denmark, University of Copenhagen, Øster Voldgade 5-7, DK-1350 Copenhagen K, Denmark
6 Univ. Bordeaux, LAB, UMR 5804, F-33270, Floirac, France
7 CNRS, LAB, UMR 5804, F-33270, Floirac, France
8 Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS, UMR 7583, Université de Paris-Est et Paris Diderot, 61, Av. du Général de Gaulle, F-94010 Créteil Cedex, France
9 Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, Université Lille I, F-59655 Villeneuve d’Ascq Cedex, France

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ABSTRACT

We have surveyed a sample of massive star-forming regions located over a range of distances from the Galactic center for methyl formate, HCOOCH$_3$, and its isotopologues H$_2^{13}$COCOCH$_3$ and HCOO$^{13}$CH$_3$. The observations were carried out with the APEX telescope in the frequency range 283.4–287.4 GHz. Based on the APEX observations, we report tentative detections of the $^{13}$C-methyl formate isotopologue HCOO$^{13}$CH$_3$ toward the following four massive star-forming regions: Sgr B2(N-LMH), NGC 6334 IRS 1, W51 e2, and G19.61-0.23. In addition, we have used the 1 mm ALMA science verification observations of Orion–KL and confirm the detection of the $^{13}$C-methyl formate species in Orion–KL and image its spatial distribution. Our analysis shows that the $^{12}$C/$^{13}$C isootope ratio in methyl formate toward the Orion–KL Compact Ridge and Hot Core-SW components (68.4 ± 10.1 and 71.4 ± 7.8, respectively) are, for both the $^{13}$C-methyl formate isotopologues, commensurate with the average $^{12}$C/$^{13}$C ratio of CO derived toward Orion–KL. Likewise, regarding the other sources, our results are consistent with the $^{12}$C/$^{13}$C in CO. We also report the spectroscopic characterization, which includes a complete partition function, of the complex H$_3^{13}$COCOCH$_3$ and HCOO$^{13}$CH$_3$ species. New spectroscopic data for both isotopomers H$_3^{13}$COCOCH$_3$ and HCOO$^{13}$CH$_3$, presented in this study, have made it possible to measure this fundamentally important isotopic ratio in a large organic molecule for the first time.

Key words: astrochemistry – ISM: abundances – line: identification – methods: data analysis – methods: laboratory: molecular – techniques: spectroscopic

Online-only material: color figures, machine-readable table

1. INTRODUCTION

Determination of elemental isotopic ratios is valuable for understanding the chemical evolution of interstellar material. In this light, carbon monoxide $^{12}$C/$^{13}$C can be an important tracer of the process of isotopic fractionation. Numerous measurements of the $^{12}$C/$^{13}$C ratios toward Galactic sources have been carried out using simple molecules such as CO, CN, and H$_2$CO (Langer & Penzias 1990, 1993; Wilson & Rood 1994; Wouterloot & Brand 1996; Milam et al. 2005). These studies have shown that the $^{12}$C/$^{13}$C ratio becomes larger with increasing distance from the Galactic Center. More specifically, Wilson (1999) gives a mean $^{12}$C/$^{13}$C ratio of 69 ± 6 in the local interstellar medium (ISM), 53 ± 4 at 4 kpc (the molecular ring) and of about 20 toward the Galactic center, showing a strong gradient that can be given for CO by (Milam et al. 2005):

$$^{12}\text{C}/^{13}\text{C} = 5.41(1.07)D_{\text{GC}} + 19.03(7.90)$$

with $D_{\text{GC}}$ the distance from the Galactic center in kiloparsecs. Furthermore, Milam et al. (2005) have shown that the $^{12}$C/$^{13}$C gradient for the CO, CN, and H$_2$CO molecular species can be defined by:

$$^{12}\text{C}/^{13}\text{C} = 6.21(1.00)D_{\text{GC}} + 18.71(7.37),$$

with $D_{\text{GC}}$ the distance from the Galactic center in kiloparsecs. This makes these carbon isotopologue species valuable indicators of Galactic chemical evolution: although they are formed through different chemical pathways and present different chemical histories, they do not show significantly different $^{12}$C/$^{13}$C ratios.

Until now, the $^{12}$C/$^{13}$C ratio has been measured predominantly in simple species that form mostly via reactions in the gas phase. In contrast, complex molecules are believed to form, for the most part, on grain surfaces, although gas phase formation cannot be ruled out (e.g., Herbst & van Dishoeck 2009; Charnley & Rodgers 2005). In this case, for complex species, the isotopic ratios might betray evidence of the grain surface formation as the ratio would differ from pure gas phase formation since gas phase processes, such as selective photodissociation and fractionation in low-temperature ion–molecule reactions, would impact the $^{12}$C/$^{13}$C ratio which is then implanted in...
larger species (Charnley et al. 2004; Wirstöm et al. 2011). Indeed, Wirstöm et al. (2011) have shown that the isotopic $^{12}\text{C}/^{13}\text{C}$ ratio in methanol ($\text{CH}_3\text{OH}$) can be used to distinguish a gas-phase origin from an ice grain mantle one. Methanol is believed to be formed on dust grains from hydrogenation of CO (e.g., Cuppen et al. 2009). If this is the case, the measured $^{12}\text{C}/^{13}\text{C}$ ratios in CO and CH$_2$OH should be similar. Otherwise, the isotopic $^{12}\text{C}/^{13}\text{C}$ ratio in methanol should be higher than the one in CO due to fractionation of species that rely on the atomic “carbon isotope pool” for formation (see Wirstöm et al. 2011; Langer et al. 1984).

In that light, we extend the $^{12}\text{C}/^{13}\text{C}$ investigation to interstellar methyl formate (HCOOCH$_3$, hereafter MF or $^{12}\text{C}$-MF), which is among the most abundant complex molecules detected in massive star-forming regions (e.g., Liu et al. 2001; Remijan et al. 2004; Bisschop et al. 2007; Demyk et al. 2008; Shiao et al. 2010; Favre et al. 2011; Friedel & Snyder 2008; Friedel & Widicus Weaver 2012). Also, the detection of both $^{13}\text{C}$-MF isotopologues, H$^{13}$COOH$_3$ (hereafter, $^{13}\text{C}$-MF) and HCOOH$_3$CH$_3$ (hereafter, $^{13}\text{C}_2$-MF), have been reported toward Orion–KL by Carvajal et al. (2009) based on IRAM 30 m antenna observations. More specifically, we suggest that the $^{12}\text{C}/^{13}\text{C}$ ratio in methyl formate could also be used as an indicator of its formation origin. This since methyl formate may be efficiently formed close to the surface of icy grain mantles during the hot core warm up phase via reactions involving mobile radical species such as CH$_2$O and HCO, which are produced by cosmic-ray induced photodissociation of methanol ices and ultimately owe their origin to hydrogenation of CO (e.g., Bennett & Kaiser 2007; Horn et al. 2004; Neill et al. 2011; Garrod & Herbst 2006; Garrod et al. 2008; Herbst & van Dishoeck 2009). In this instance, and in agreement with Wirstöm et al. (2011), if the $^{12}\text{C}/^{13}\text{C}$ ratios in methyl formate, methanol, and CO are similar, that would likely suggest a formation on grain surfaces.

In this paper, we investigate the carbon isotopic ratio for methyl formate isotopologues and therefore address the issue of whether the $^{12}\text{C}/^{13}\text{C}$ ratio is the same for both small and large molecules. Our analysis is based on recent spectroscopic and laboratory measurements of both the common isotopologue and the $^{13}\text{C}$ isotopologues (see Carvajal et al. 2007, 2009, 2010; Ilyushin et al. 2009; Kleiner 2010; Margules et al. 2010; Haykal et al. 2014, and this study). We would particularly like to stress that in order to derive a $^{12}\text{C}/^{13}\text{C}$ ratio with accuracy and to significantly reduce uncertainties, homogeneous observational data are a necessity. In Section 2, we present the ALMA Science Verification observations of Orion–KL along with the APEX observations of our massive star-forming regions sample. Spectroscopic characterization of the $^{13}\text{C}$-methyl formate molecules is presented in Section 3. Data modeling, results, and analysis are presented and discussed in Sections 4, 5, and 6, with conclusions set out in Section 7.

2. OBSERVATIONS AND DATA REDUCTION

2.1. ALMA Science Verification Observations

Orion–KL was observed with 16 antennas (each 12 m in diameter) on 2012 January 20 as part of the ALMA Science Verification (hereafter, ALMA-SV) program. The observations cover the frequency range 213.7 GHz to 246.6 GHz in band 6. The phase-tracking center was $\alpha_{2000} = 05^\text{h}35^\text{m}14^\text{s}, \delta_{2000} = -05^\circ22'35''00$. The observational data consist of 20 spectral windows, each with 488 kHz channel spacing resulting in 3840 channels across 1.875 GHz effective bandwidth.

We used the public release calibrated data that are available through the ALMA Science Verification Portal. Data reduction and continuum subtraction were performed using the Common Astronomy Software Applications (CASA) software. More specifically, the continuum emission was estimated by a zeroth order fit to the line-free channels within each spectral window (hereafter spw) and subtracted. Finally, the spectral line data cleaning was performed using the Clark (1980) method and a pixel size of $0.4$. Also, a Briggs weighting with a robustness parameter of 0.0 was applied giving a good trade-off between natural and uniform weighting (Briggs 1995). The resulting synthesized beam sizes are:

1. $1.6' \times 1.1'$ (P.A. of about $-176^\circ$–$4^\circ$) for the spw 0, 1, 4, 5, 8, 9, 12, 13, 16 and 17;
2. $1.7' \times 1.2'$ (P.A. of about $-1^\circ$–$11^\circ$) for the spw 2, 3, 6, 7, 10, 11, 14, 15, 18 and 19.

2.2. APEX Observations

2.2.1. Source Sample

Our survey is composed of a sample of seven high-mass star-forming regions that are listed in Table 1 together with their respective coordinates, LSR velocities, and distances from the Sun as well as from the Galactic center. The seven sources were primarily selected using the following criteria: (1) the previous detection of the main HCOOCH$_3$ isotopologue, based on single-dish and/or interferometric observations (e.g., Liu et al. 2001; Remijan et al. 2004; Bisschop et al. 2007; Demyk et al. 2008; Friedel & Snyder 2008; Shiao et al. 2010; Favre et al. 2011; Belloche et al. 2009; Widicus Weaver & Friedel 2012; Fontani et al. 2007; Olmi et al. 2003; Beuther et al. 2007, 2009; Kalenskii & Johansson 2010; Requena-Torres et al. 2006; Hollis et al. 2000; Meieringer et al. 1997), with a derived column density in the range $10^{16}$–$10^{17}$ cm$^{-2}$ depending on the source and the assumed source size, and (2) covering a wide range in distance from the Galactic center, here from 0.1 kpc to 8.9 kpc (see Table 1).

2.2.2. Observations

The observations were performed with the APEX telescope on Llano de Chajnantor, Northern Chile, between 2012 March and August (see Table 1). The Swedish Heterodyne Facility Instrument (SHeFi) APEX-2 receiver, which operates with an IF range of 4–8 GHz, was used in single sideband mode in connection with the eXtended bandwidth Fast Fourier Transform Spectrometer (XFFTS) backend with a bandwidth of 8.24 GHz over the entire band. Also, the XFFTS backend covers 2.5 GHz bandwidth instantaneously with a spectral resolution of about 0.08 MHz (corresponding to 0.08 km s$^{-1}$). However, noting that line widths of the target lines are estimated to be between 4 and 8 km s$^{-1}$ based on earlier methyl formate observations referred to above, the spectra were smoothed to a spectral resolution of 1.5 km s$^{-1}$. Further, in this paper, the spectra are reported in...
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Table 1
Summary of the APEX Telescope

| Source         | Observed Date | α2000 | δ2000 | VLSR | Distance from the Sun | Distance from the GC |
|----------------|---------------|-------|-------|------|-----------------------|----------------------|
| Sgr B2(N-LMH)  | 2012 Apr 2, 3 | 17:47:19.9 | −28:22:19.5 | 64.0 | 7.1 | 0.1^a |
| G24.78+0.08    | 2012 Apr 2    | 18:36:12.6 | −07:12:11.0 | 110.0 | 7.7 | 3.7^b |
| G29.96-0.02    | 2012 Apr 1    | 18:46:04.0 | −02:59:21.5 | 98.8 | 6.0 | 4.6^c |
| G19.61-0.23    | 2012 Mar 28   | 18:27:38.1 | −11:56:39.0 | 40.0 | 3.5 | 4.8^d |
| NGC 6334 IRS 1 | 2012 Mar 28   | 17:20:53.0 | −35:47:02.0 | 8.0  | 1.7 | 6.8^e |
| W51 e2         | 2012 Apr 2    | 19:23:43.9 | +14:30:34.8 | 55.3 | 5.41 | 8.3^f |
| Orion–KL       | 2012 Apr 1    | 05:35:14.2 | −05:22:36.0 | 8.0  | 0.4 | 8.9^g |

Notes.

^a Milam et al. (2005).
^b Beltrán et al. (2011).
^c Pratap et al. (1999).
^d Remijan et al. (2004).
^e Kraemer et al. (1998).
^f Sato et al. (2010).
^g Remijan et al. (2003).

Table 2
Reference Position for Position Switching Mode

| Source          | OFF Position  |
|-----------------|---------------|
| Orion–KL        | EQ[7071−0000, 0000] |
| NGC 6334 IRS 1  | EQ[−752′.2, 342′'] |
| Sgr B2(N-LMH)   | EQ[−750′.0, 0000] |
| G24.78+0.08     | EQ[707′.1, −947′] |

Note. The coordinates are given in the equatorial (EQ) system.

These contaminants have been identified from the detailed model of molecular emission toward Orion–KL which matched the TMB scale.

3. SPECTRAL CHARACTERIZATION FOR THE 13C-METHYL FORMATE ISOTOPOLOGUES

The interstellar identifications of 13C1-MF, 13C2-MF were carried out from their spectral predictions in the frequency range of the facilities. The spectroscopic characterization of 13C1-MF isotopologues is based on the Hamiltonian parameters of the 13C2-MF isotopologue provided by Carvajal et al. (2009) and of the 13C1-MF isotopologue from Carvajal et al. (2010). The dipole moments used in the intensity calculation were given by Margulés et al. (2010).

The spectroscopic characterization of 13C-MF isotopologues was carried out starting with millimeter- and submillimeter-wave recordings in the laboratory and followed by their spectral analysis and the assignments of lines through an established fitting procedure. The effective Hamiltonian used for the global spectroscopic analysis of both isotopologues is based on the so-called Rho-Axis Method (RAM; Herbst et al. 1984; Hougen et al. 1994; Kleiner 2010) applicable for molecules with a CH3 rotor. The BELGI version of the RAM code used in this study is available online. Further details regarding its application are available.
The ground torsional state \( \nu_t \) on the CDMS database \(^{16}\) (Müller et al. 2001, 2005) and at \(^{17}\) www.splatalogue.net.\(^{15}\) The Astrophysical Journal Supplement Series for MF and \(^{13}\)C-MF treat both of the torsional substates—those concerned, on the partition function. This was computed under the same level of approximation for all the molecular species under study. Table 3 shows the values of the partition function used for \(^{12}\)COOCH\(_3\). These values were computed on the basis of the new calculations in this manuscript to more fully account for the effect of vibrationally excited levels. In the JPL catalog entry, only contributions of the \( \nu_t = 0 \) and \( \nu_t = 1 \) first excited torsional state have been recently processed (Haykal et al. 2014). A more extensive set of experimental data (\( \sim 7500 \) transition lines) of the ground and first excited states of \(^{13}\)C\(_1\)-MF has been used in the fit of the RAM Hamiltonian. The complete set of available experimental data (see Willaert et al. 2006; Carvajal et al. 2009; Maeda et al. 2008a, 2008b) was compiled in Carvajal et al. (2010).

### 3.1. Partition Functions

To calculate the observed intensities of the spectral lines, the populations of each level must be estimated using an accurate partition function in order to provide reliable estimates of the temperatures and column densities of the different regions in the ISM. With this goal in mind, a convergence study for the partition functions of \(^{13}\)C-isotopologues, which ensures that high enough energy levels have been included for a particular temperature, has been carried out in this work. The partition function calculations are described in the Appendix A. Table 3 summarizes the rotational–torsional–vibrational partition function values that are used here for \(^{13}\)C\(_1\)-MF and \(^{13}\)C\(_2\)-MF.

### 4. DATA ANALYSIS

#### 4.1. Database and MF, \(^{13}\)C-MF Frequencies

We used the measured and predicted transitions coming from both the table of Ilyushin et al. (2009) and the JPL database (Pickett et al. 1992, 1998) for the MF line assignments, as in Favre et al. (2011). Regarding the methyl formate isotopologue \(^{13}\)C\(_1\)-MF and \(^{13}\)C\(_2\)-MF line assignments, our present analysis is based on this study (see Section 3) and on the spectroscopic characterization performed by Carvajal et al. (2007, 2009, 2010). Likewise, the measured and predicted transitions of the species \(^{12}\)C\(_1\)-MF species (Carvajal et al. 2010) are now available on the CDMS database (Müller et al. 2001, 2005) and at Splatalogue (Remijan et al. 2007). Current spectroscopic data for MF and \(^{13}\)C-MF treat both of the torsional substates—those with A symmetries and those E symmetries—simultaneously.

As we aim to derive accurate isotopic ratios, we should be confident with the intensity calculation of the molecular species at different temperatures. Therefore, the isotope ratio accuracy will depend, on one hand, on the spectroscopic determination of transition frequencies, assignments, and line strengths and, on the other hand, on the partition function approximation considered. Accurate spectroscopic characterizations of the main isotopologue was carried out previously (Ilyushin et al. 2009) using the RAM method, while for the \(^{13}\)C-MF isotopologues, we used the same values for the electric dipole moments as for the \(^{12}\)C-MF species (see Section 3.1). This assumption would not affect the line strengths by more than \( \sim 1\% \). Hence, the accurate derivation of the abundance ratio between different isotopologues will rely, as far as the spectroscopic data are concerned, on the partition function. This was computed under the same level of approximation for all the molecular species under study.

### Table 3

| \( T \) (K) | \(^{13}\)C\(_1\)-MF | \(^{13}\)C\(_2\)-MF | \(^{12}\)C-MF |
|---|---|---|---|
| 300.0 | 252230.47 | 255988.58 | 249172.44 |
| 225.0 | 105303.23 | 106847.86 | 104015.96 |
| 150.0 | 36879.42 | 37442.27 | 36433.43 |
| 75.0 | 9003.31 | 9162.12 | 8946.06 |
| 37.50 | 2920.56 | 2971.20 | 2885.30 |
| 18.75 | 1027.71 | 1054.22 | 1015.31 |
| 9.375 | 364.76 | 370.95 | 360.33 |

Note. \(^{a}\) The nuclear spin degeneracy was not considered in these calculations (see Appendix A).

\(^{15}\) http://spec.jpl.nasa.gov/home.html

\(^{16}\) http://www.astro.uni-koeln.de/cdms

\(^{17}\) www.splatalogue.net
et al. 2014). This allows us to make reliable line identifications and determine where potential line blends may exist. Further details regarding the XCLASS modeling of the Herschel/HIFI Orion–KL spectral scan, along with fit parameters, can be found in Crockett et al. (2014).

In the present analysis, we assumed that the $^{13}$C$_{1}$-MF and $^{13}$C$_{2}$-MF species emit within the same source size, at the same rotational temperature and velocity, and with the same line width as the methyl formate molecule. The only adjustable parameter is the molecular column density. To initialize the model of the ALMA-SV observations of Orion–KL, we used as input parameters (source size, rotational temperature, column density, $v_{\text{LSR}}$, and $\Delta v_{\text{LSR}}$), the values derived from our previous Plateau de Bure Interferometer (PdBI) observations, which were performed with a similar angular resolution ($1.8^\prime\times0.8^\prime$, see Favre et al. 2011). Regarding the APEX observations, we used previously related and reported values derived from single-dish (JCMT, IRAM–30m, Herschel) and/or interferometric observations (BIMA, CARMA) as starting values to initialize the fitting. More specifically, we used the values derived by Bisschop et al. (2007) for G24.78+0.08; by Zernickel et al. (2012) and Bisschop et al. (2007) for NGC 6334I; by Demyk et al. (2008) for W51 e2; by Shiao et al. (2010) for G29.96–0.02; by Belloche et al. (2009) for Sgr B2(N); by Remijan et al. (2004) and Shiao et al. (2010) for G19.61–0.23; and by Tercero et al. (2012), Carvajal et al. (2009), and Crockett et al. (2014) for Orion–KL.

5. RESULTS

In the following section we report the main results for each observing facility.

5.1. ALMA-SV Observations of Orion–KL

5.1.1. Emission Maps

The mean velocity for emission observed toward the Compact Ridge and Hot Core-SW regions is around 7.3 km s$^{-1}$ for all the methyl formate isotopologues. We also observed a second velocity component around 9 km s$^{-1}$ toward the Compact Ridge in HCOOCH$_{3}$ (as reported by Favre et al. 2011). This velocity component is not observed in $^{13}$C-MF. Figure 1 shows maps of the MF, $^{13}$C$_{1}$-MF, and $^{13}$C$_{2}$-MF emission in the 7.2 km s$^{-1}$ channel measured at 234124 MHz, 220341 MHz, and 216671 MHz, respectively. The HCOOCH$_{3}$ emission distribution shows an extended V-shaped molecular emission that links radio source I to the BN object as previously observed in methyl formate by Favre et al. (2011) and Friedel & Snyder (2008). Likewise, as reported by Favre et al. (2011), the main molecular peaks are located toward the Compact Ridge and the Hot Core-SW (respectively labeled MF1 and MF2 in Figure 1, for more details see Favre et al. 2011). Also from the optically thick HCOOCH$_{3}$ lines, we note that another cold component ($T \sim 40–50$ K) is observed arising from the vicinity of the source IRC7. However, we did not analyze this component in the present study. Finally, the $^{13}$C-MF isotopologues are mainly detected toward the Compact Ridge and the Hot Core-SW (5$\sigma$ detection level; see Figure 1).

5.1.2. Spectra

Numerous transitions of $^{12}$C-MF and $^{13}$C-MF with $J_{\text{up}} > 10$ D$^{2}$ and from upper energy levels of 166 K up to 504 K for the main molecule and $E_{\text{up}}$ of 99 K up to 330 K for the $^{13}$C-MF species, are present in the ALMA data. We have modeled each spectral window individually (see Section 6.1.3). Table 4 provides the number of clearly detected MF and $^{13}$C-MF transitions per spectral window toward both the Compact Ridge and the Hot Core-SW. Table 12 in Appendix B summarizes the line parameters for all detected, blended, or not detected transitions of $^{12}$C-MF, $^{13}$C$_{1}$-MF, and $^{13}$C$_{2}$-MF in all ALMA spectral windows. Furthermore, Figures 5, 6, and 7 in Appendix C show the $^{12}$C-MF, $^{13}$C$_{1}$-MF, and $^{13}$C$_{2}$-MF transitions that are detected and/or partially blended in the ALMA-SV data along with our

### Table 4

| Spw$^{b}$ | Compact Ridge | Hot Core-SW |
|----------|---------------|-------------|
|          | HCOOCH$_{3}$ | H$^{13}$COOCH$_{3}$ | HCOO$^{13}$CH$_{3}$ | HCOOCH$_{3}$ | H$^{13}$COOCH$_{3}$ | HCOO$^{13}$CH$_{3}$ |
| 0        | 1             | 1            | 2            | 1             | ...          | 2            |
| 1        | 3             | ...          | 6            | 3             | ...          | 1            |
| 2        | 19            | 10           | 3            | 19            | 7            | 3            |
| 3        | 5             | 6            | 3            | 5             | 3            | 3            |
| 4        | 11            | 7            | 4            | 10            | 3            | 4            |
| 5        | 20            | 13           | 6            | 19            | 5            | 5            |
| 6        | 5             | 12           | ...          | 5             | 4            | ...          |
| 7        | 6             | 2            | 13           | 4             | ...          | 6            |
| 8        | 11            | 11           | 1            | 8             | 5            | ...          |
| 9        | 10            | 13           | 2            | 9             | 10           | 2            |
| 10       | 4             | 1            | 5            | 4             | 1            | 3            |
| 11       | 20            | 10           | 4            | 20            | 5            | 2            |
| 12       | 1             | ...          | 15           | ...           | 6            | ...          |
| 13       | 2             | 4            | 17           | 2             | 3            | 11           |
| 14       | 3             | 9            | 2            | 3             | 6            | ...          |
| 15       | 6             | 4            | ...          | 6             | 2            | ...          |
| 16       | 15            | 12           | 8            | 15            | 6            | 6            |
| 17       | 23            | 16           | 3            | 21            | 12           | 2            |
| 18       | 2             | 3            | 17           | 2             | 1            | 5            |
| 19       | ...           | 1            | 11           | ...           | 6            | ...          |

Notes.

$^{a}$ The corresponding line frequencies are given in Figures 5–10.

$^{b}$ The ALMA-SV data consist of 20 spectral windows (see Section 2).
HCOOCH$_3$ (12C-MF, 220341 MHz, $E_{upp} = 179$ K, $S_{μ^2} = 35$ D$^2$, top left panel), H$_{13}$COOCH$_3$ (13C-MF, 216671 MHz, $E_{upp} = 152$ K, $S_{μ^2} = 36$ D$^2$, bottom panel) emission channel maps at 7.22 km s$^{-1}$ as observed with ALMA. The first contour and level step are 500 mJy beam$^{-1}$ ($\sim$14σ) and 100 mJy beam$^{-1}$ ($\sim$5σ) for 12C-MF and 13C-MF, respectively. The synthesized beam size is 1$''$.7 x 1$''$.1. The black cross indicates the centered position of the observations. The main HCOOCH$_3$ emission peaks (MF1 to MF5) identified by Favre et al. (2011) are indicated.

(A color version of this figure is available in the online journal.)

Best XCLASS models toward the Compact Ridge. In addition, Figures 8, 9, and 10 in Appendix D show the emission of the same transitions, along with our models, toward the Hot Core-SW. The quality of our models is based on the reduced $\chi^2$, which lies in the range 0.3–2.4, depending on the fit. More specifically, the bulk of the emission is best reproduced for the following.

1. A source size of 3$''$ (in agreement with the ALMA-SV observations) toward both the Compact Ridge and the Hot Core-SW.

2. A rotation temperature of 80 K toward the Compact Ridge and of 128 K toward the Hot Core-SW.

3. A $v_{LSR}$ of 7.3 km s$^{-1}$ for both components.

4. A line width of 1.2 km s$^{-1}$ toward the Compact Ridge and of 2.4 km s$^{-1}$ toward the Hot Core-SW.

Only the column density differs within the different spectral windows between the spatial components associated with Orion–KL and between the isotopologues. The $^{12}$C-MF models include the observed second velocity component well reproduced for a $v_{LSR}$ of 9.1 km s$^{-1}$, a source size of 3$''$, a rotation temperature of 120 K, and a column density of $7 \times 10^{16}$ cm$^{-2}$.

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$^{19}$ The optically thick lines, although some of them are shown in Appendices C and D, are excluded from our model due to an optical depth problem.
Figure 2. Isotopic ratio distribution of the methyl formate isotopologues within each ALMA spectral window as derived toward the Orion–KL Compact Ridge (top panel) and Hot Core-SW (bottom panel). Top sub-panels: isotopic ratio distribution for the $^{12}$C/$^{13}$C ratio. Middle sub-panels: isotopic ratio distribution for the $^{12}$C/$^{13}$C$_2$ ratio. Bottom sub-panels: isotopic ratio distribution for the $^{12}$C/$^{13}$C ratio, assuming the two $^{13}$C-MF isotopologues have similar abundances. The derived average isotopic ratio is indicated in each sub-panel.

(A color version of this figure is available in the online journal.)
Figure 3. Spectra centered at 285.450 GHz as observed with the APEX telescope for all the sources. The name of each observed source is indicated on each plot. The spectral resolution is smoothed to 1.5 km s$^{-1}$. Line assignment is shown in the Orion–KL spectrum (bottom panel) in red for the detected methyl formate $^{12}$C-MF and $^{13}$C-MF transitions and in gray for the other molecules (based on the Herschel/HIFI spectral fit to Orion–KL for the latter; see Crockett et al. 2014).

(A color version of this figure is available in the online journal.)

5.1.3. Isotopic $^{12}$C/$^{13}$C Ratio

Figure 2 shows the distribution of the $^{12}$C/$^{13}$C$_{1}$-MF, $^{12}$C/$^{13}$C$_{2}$-MF, and $^{12}$C/$^{13}$C-MF isotopic ratios we derived within each ALMA spectral window toward both the Compact Ridge and the Hot Core-SW. The average $^{12}$C/$^{13}$C$_{1}$ and $^{12}$C/$^{13}$C$_{2}$ ratios are $67.5 \pm 10.1$ and $69.3 \pm 10.3$ in the direction of the Compact Ridge and $73.0 \pm 7.1$ and $71.7 \pm 9.2$ in the direction of the Hot Core-SW. If we assume the ratio to be the same for both isotopologues, meaning there is no significant difference, we derive an average $^{12}$C/$^{13}$C isotopic ratio in methyl formate of $68.4 \pm 10.1$ and of $71.4 \pm 7.8$ toward the Compact Ridge and the Hot Core-SW, respectively.

20 An outlier at $^{12}$C/$^{13}$C $\sim 100$ is seen toward the Compact Ridge in each distribution. It results from the MF measurement performed in the spw #16. The outlier likely does not impact the derived isotopic ratio since we either include or exclude the value because the derived ratio remains the same within the uncertainties.

5.2. APEX Observations of all the Sources

Figure 3 shows the spectra observed with the APEX telescope toward our sample of seven sources (see Table 1). Lines that have been identified through the Herschel/HIFI
spectral fit are indicated in the Orion–KL spectrum (see bottom panel on Figure 3). The molecular richness of the observed sources is clearly seen. Also, the different spectra illustrate the problem of the spectral confusion for the weaker emissive lines.

5.2.1. Main Isotope: HCOOCH$_3$

Table 5 lists the detected or partially blended methyl formate transitions, with $S\mu^2 \geq 2.5$ D$^2$ and $E_{up}$ up to 304 K as observed with APEX toward the different sources. Note that for some partially blended lines, the emission arising from the contaminant has been identified through the Herschel template spectra in which emission from 35 molecules has been modeled assuming LTE (Crockett et al. 2014). The following procedure was used: (1) superposing the Herschel resulting model on the APEX observations and identifying the potential contaminant(s), and (2) adjusting the observational parameters (e.g., velocity, typical line width) to the model and checking the coherence over the full spectrum. The adopted parameters (source size, rotational temperature, column density, velocity, and line width) that were used to model the APEX observations are given in Table 6 for each source. The quality of our models is based on the reduced $\chi^2$, which lies in the range 0.23–4.75. In addition, Figure 4 shows the observed methyl formate spectrum of the transition at 285973.267 MHz (23$_{8,15}$–22$_{8,14}$,E) along with our models for each source.

The main observational results for the methyl formate molecule are briefly summarized below for the individual sources.

**Orion–KL.** We detected 16 HCOOCH$_3$ lines and observed 15 transitions that are partially blended with $S\mu^2 \geq 4$ D$^2$ (see Table 5). The LSR velocity is 7.7 km s$^{-1}$ and the derived column density is $9.7 \times 10^{16}$ cm$^{-2}$.

**W51 e2.** We detected 11 HCOOCH$_3$ lines and observed 6 transitions that are partially blended. Fourteen transitions (with $S\mu^2 \leq 12$ D$^2$) are too faint to be detected (which is commensurate with our model of the source). The spectra display a $v_{LSR}$ of 55.6 km s$^{-1}$ and we derived a column density of $9.0 \times 10^{16}$ cm$^{-2}$.

**G19.61-0.23.** We detected 10 HCOOCH$_3$ lines and observed 7 transitions that are partially blended while 14 transitions were too faint to be detected. The $v_{LSR}$ is 39.7 km s$^{-1}$ and the derived column density is $7.0 \times 10^{16}$ cm$^{-2}$.

**NGC 6334 IRS 1.** We detected 11 HCOOCH$_3$ lines and observed 6 transitions that are partially blended with 14 transitions that were too faint to be detected. Spectra exhibit a $v_{LSR}$ of $-8$ km s$^{-1}$ and we derived a column density of $6.0 \times 10^{15}$ cm$^{-2}$.

**Sgr B2(N).** We detected 7 HCOOCH$_3$ lines and observed 9 transitions that are partially blended while 14 transitions were too faint to be detected. The $v_{LSR}$ is around 63.7 km s$^{-1}$ and we derived a column density of $3.0 \times 10^{17}$ cm$^{-2}$.

**G29.96-0.02.** We detected 10 HCOOCH$_3$ lines and observed 7 transitions that are partially blended. Fourteen transitions were too faint to be detected. Spectra display a $v_{LSR}$ of 97.8 km s$^{-1}$ and we derived a column density of $3.0 \times 10^{17}$ cm$^{-2}$.

**G24.78+0.08.** We detected 10 HCOOCH$_3$ lines and observed 7 transitions that are partially blended while 14 transitions were too faint to be detected. The $v_{LSR}$ is 111 km s$^{-1}$ and we derived a column density of $6.0 \times 10^{15}$ cm$^{-2}$.

**G29.96-0.02.** We detected 10 HCOOCH$_3$ lines and observed 7 transitions that are partially blended. Fourteen transitions were too faint to be detected. Spectra display a $v_{LSR}$ of 97.8 km s$^{-1}$ and we derived a column density of $3.0 \times 10^{17}$ cm$^{-2}$.
Table 5
Transitions of $^{12}$C and $^{13}$C-Methyl Formate Observed with the APEX Telescope

| Frequency (MHz) | Transition | $E_{up}$ (K) | $S_{up}$ (D²) | Note\a |
|----------------|------------|--------------|---------------|--------|
| 283734.887     | 23$^{13}$C→22$^{13}$C       | 243.2        | 45.4          | D      |
| 283746.738     | 23$^{13}$C→22$^{13}$C       | 243.2        | 45.4          | C      |
| 283760.086     | 23$^{13}$C→22$^{13}$C       | 243.2        | 45.4          | D      |
| 284398.680     | 13$^{13}$C→12$^{13}$C       | 70.4         | 2.5           | D      |
| 284410.529     | 13$^{13}$C→12$^{13}$C       | 70.4         | 2.7           | D      |
| 284810.313     | 23$^{13}$C→22$^{13}$C       | 180.8        | 55.8          | D      |
| 284826.396     | 23$^{13}$C→22$^{13}$C       | 180.8        | 55.8          | D      |
| 284855.531     | 27$^{16}$→27$^{16}$          | 303.7        | 7.6           | D      |
| 284866.320b    | 27$^{16}$→27$^{16}$          | 303.7        | 6.1           | D      |
| 284920.240     | 23$^{13}$C→22$^{13}$C       | 217.0        | 49.8          | D      |
| 284937.218     | 23$^{13}$C→22$^{13}$C       | 217.0        | 49.9          | D      |
| 284942.751     | 23$^{13}$C→22$^{13}$C       | 217.0        | 49.9          | D      |
| 284945.147     | 23$^{13}$C→22$^{13}$C       | 219.9        | 49.8          | D      |
| 285016.270     | 23$^{13}$C→22$^{13}$C       | 173.3        | 6.3           | D      |
| 285016.977     | 23$^{13}$C→22$^{13}$C       | 173.3        | 6.3           | D      |
| 285351.819     | 24$^{13}$C→23$^{13}$C       | 187.0        | 6.8           | D      |
| 285370.140     | 24$^{13}$C→23$^{13}$C       | 187.0        | 6.8           | D      |
| 285515.739     | 22$^{13}$C→21$^{13}$C       | 169.4        | 53.7          | D      |
| 285542.584     | 22$^{13}$C→21$^{13}$C       | 169.4        | 53.7          | D      |
| 285924.822     | 23$^{13}$C→22$^{13}$C       | 205.9        | 51.8          | D      |
| 285940.794     | 23$^{13}$C→22$^{13}$C       | 205.9        | 49.9          | D      |
| 285973.267     | 23$^{13}$C→22$^{13}$C       | 206.0        | 49.9          | D      |
| 286012.485     | 23$^{13}$C→22$^{13}$C       | 205.9        | 51.8          | D      |
| 286467.129b    | 25$^{13}$C→24$^{13}$C       | 272.2        | 5.5           | D      |
| 286984.997     | 16$^{13}$C→15$^{13}$C       | 62.8         | 3.2           | D      |
| 286994.417     | 16$^{13}$C→15$^{13}$C       | 62.8         | 3.2           | D      |
| 287038.552     | 16$^{13}$C→15$^{13}$C       | 62.8         | 3.2           | D      |
| 287094.976     | 24$^{13}$C→22$^{13}$C       | 257.4        | 6.3           | D      |
| 287101.120     | 24$^{13}$C→22$^{13}$C       | 257.4        | 6.3           | D      |
| 287146.630     | 23$^{13}$C→22$^{13}$C       | 196.4        | 53.4          | D      |
|                | H$^{13}$COOH\b\c       |              |               |        |
| 283853.856     | 23$^{13}$C→22$^{13}$C       | 204.3        | 52.9          | D      |
| 286035.726     | 23$^{13}$C→22$^{13}$C       | 195.0        | 56.7          | D      |
|                | HCOO$^{13}$CH\b\c      |              |               |        |
| 284729.511b    | 27$^{13}$C→26$^{13}$C       | 194.2        | 71.1          | D      |
| 284729.537b    | 27$^{13}$C→26$^{13}$C       | 194.2        | 71.1          | D      |
| 284730.102b    | 27$^{13}$C→26$^{13}$C       | 194.2        | 71.1          | D      |
| 284730.127b    | 27$^{13}$C→26$^{13}$C       | 194.2        | 71.1          | D      |

Notes.
\a D: detected; TD: tentative detection; PB: partial blend; ND and ND*: not detected (too faint emission). Also, ND$^*$ indicates the $^{13}$C$_1$– and $^{13}$C$_2$–HCOOCH$_3$ transitions that are emitting with an intensity less than or equal to three times the noise level which we used to constrain our model. The symbol “\*” indicates that part of the spectrum has been removed (see Section 2.2.2).
b These two transitions are predicted, i.e., not measured.
c Pile-up of these four lines. Also the frequencies presented in this table are only computed (i.e., not measured) because experimental data for these transitions are not yet available.

5.2.2. H$^{13}$COOCH$_3$

The $^{13}$C$_1$-MF lines all appear to be blended or just at or below the confusion limit level. We note that some transitions overlap with lines from strongly emissive molecules such as ethyl cyanide (whose presence is known through the Herschel template spectra to Orion–KL; Crockett et al. 2014), which might hide faint emission. We therefore do not detect the $^{13}$C$_1$–methyl formate toward any of the observed sources, excluding Orion–KL and that only in the supplementary ALMA data.

5.2.3. HCOO$^{13}$CH$_3$

We report the detection of one transition of $^{13}$C$_2$-MF toward Orion–KL, W51 e2, NGC 6334 IRS 1, and (tentatively) G19.61-0.23 and Sgr B2(N) (see Figure 4 and Table 5). More specifically, the spectral feature that we assigned the observed spectrum of the HCOO$^{13}$CH$_3$ transition emitting at $284729$–$284730$ MHz, with a line strength of $71$ D$^2$ and an upper energy level of $194$ K (Table 5). Figure 4 exhibits the observed spectrum of the HCOO$^{13}$CH$_3$ transition emitting at $284730$ MHz along with our XCLASS for each source (reduced...
χ² of about 0.23–0.69). We infer that it is difficult to attribute this spectral feature to another molecule on the basis that:

1. The line rest frequencies of these four lines are predicted with an uncertainty of 0.012 MHz (which corresponds to 0.012 km s⁻¹).
2. Several ¹³C₂–methyl formate transitions with similar Sμ² and Eμ are detected in the ALMA-SV data of Orion–KL (see Section 5.1.). Furthermore, their excitation level in Orion–KL is consistent with the emission level of this line (and non-detection of other lines) in the APEX data.
3. This is the strongest line in the APEX band and the two next highest Sμ² lines (at 67 and 61 D²) are respectively blended and at the level of the confusion limit.

We note that, given the sensitivity limit in all the sources except Orion–KL (because of the ALMA-data), we cannot claim a definitive detection of this molecule in the APEX observations.

### 5.2.4. Isotopic ¹²C/¹³C Ratio

Since we do not have definitive detections of the ¹³C-MF, Table 7 lists the lower limits of the isotopic ¹²C/¹³C ratio that are estimated assuming that the two ¹³C-MF isotopologues have similar abundances. Please note that the upper limits of the ¹³C-MF column density have been set by adjusting the observational parameters to the model with a resulting fit constrained by a 3σ upper limit. The quality of our models is still based on the reduced χ² calculations.²¹

#### Table 6

| Source                | θₕ (°) | Tᵣₜ (K) | HC3OCH₃ | HCOOC₁³CH₃ | HCOOC₁³CH₃ | ³⁰sL₁ (km s⁻¹) | Δ₁ (km s⁻¹) |
|-----------------------|--------|---------|---------|------------|------------|----------------|-------------|
| Sgr B2(N-LMH)         | 4      | 80      | 3.0 × 10¹⁷ | ≤1.8 × 10¹⁶ | ≤1.8 × 10¹⁶ | 63.7           | 7.0         |
| G24.78+0.08b          | 10     | 121     | 6.0 × 10¹⁵ | ≤3.0 × 10¹⁴ | ≤3.0 × 10¹⁴ | 111.0          | 6.0         |
| G29.96-0.02b          | 10     | 150     | 3.5 × 10¹⁵ | ≤3.0 × 10¹⁴ | ≤3.0 × 10¹⁴ | 97.8           | 5.5         |
| G19.61-0.23a          | 3.3    | 230     | 7.0 × 10¹⁶ | ≤5.0 × 10¹⁵ | ≤5.0 × 10¹⁵ | 39.7           | 4.5         |
| NGC 6334 IRS 1c       | 3      | 115     | 4.5 × 10¹⁷ | ≤2.0 × 10¹⁶ | ≤2.0 × 10¹⁶ | −8.0           | 5.0         |
| W51 e²b               | 7      | 176     | 9.0 × 10¹⁶ | ≤3.0 × 10¹⁵ | ≤3.0 × 10¹⁵ | 55.6           | 8.0         |
| Orion–KLc             | 10     | 100     | 9.7 × 10¹⁶ | ≤1.82 × 10¹⁵| ≤1.82 × 10¹⁵| 7.7            | 3.7         |

Notes.

a Observed sources where HCOOC₁³CH₃ is tentatively detected.

b Observed sources where HCOOC₁³CH₃ is not detected.

c Observed sources where one transition of HCOOC₁³CH₃ is detected.

#### Table 7

| Source                  | ¹²C/¹³C−HCOOC₁³CH₃ as Measured with ALMA and APEX, Respectively |
|-------------------------|---------------------------------------------------------------|
|                         | ¹²C/¹³C for CO CN and H²COa                                    |
|                         | ¹²C/¹³C for CO Onlyb                                           |
|                         | ¹²C/¹³C−HCOOC₁³CH₃c                                            |
| **ALMA observations**   |                                                               |
| Orion−KL—Compact Ridge | 74 ± 16                                                        |
| Orion−KL—Hot Core-SW   | 74 ± 16                                                        |
|                         | 67 ± 17                                                        |
|                         | 68.4 ± 10.1                                                    |
|                         | 71.4 ± 7.8                                                     |
| **APEX observations**   |                                                               |
| Sgr B2(N-LMH)d          | 19 ± 7                                                        |
| G24.78+0.08b            | 42 ± 11                                                       |
| G29.96-0.02b            | 47 ± 12                                                       |
| G19.61-0.23a            | 49 ± 12                                                       |
| NGC 6334 IRS 1f         | 61 ± 14                                                       |
| W51 e²f                | 70 ± 16                                                       |
| Orion−KLf              | 74 ± 16                                                       |
|                         | 67 ± 17                                                        |
|                         | 44 ± 13                                                       |
|                         | 45 ± 13                                                       |
|                         | 57 ± 15                                                       |
|                         | 64 ± 17                                                       |
|                         | 64 ± 17                                                       |
|                         | 64 ± 17                                                       |
|                         | 64 ± 17                                                       |
|                         | 53                                                            |

Notes.

a Based on the following equation for CO, CN, and H²CO, ¹²C/¹³C = 6.21(1.00)D₀₂Ｃ + 18.71(7.37) from Milam et al. (2005) (see Equation (2)).

b Based on the following equation for CO, ¹²C/¹³C = 5.41(1.07)D₀₂Ｃ + 19.03(7.90) from Milam et al. (2005) (see Equation (1)).

c This study, assuming that both ¹³C₂-MF and ¹³C₂-MF isotopologues have similar abundances (i.e., (¹²C−¹³C)/¹²C = (¹²C−¹³C)/¹³C, see Section 5.1 and Figure 2).

d Observed sources where HCOOC₁³CH₃ is tentatively detected.

e Observed sources where HCOOC₁³CH₃ is not detected.

²¹ The reduced χ² roughly gives a measure of how the model fits the data over the bandpass.
6. DISCUSSION

6.1. Measurement Caveats

The analysis above relies on some assumptions. In the following section, we discuss whether they could modify the interpretation of our derived $^{12}\text{C}/^{13}\text{C}$ ratio.

6.1.1. LTE and Radiative Pumping Effects

It is important to note that the above analysis hinges upon the assumption that methyl formate is in LTE, which applies at high densities in hot cores. We assumed that LTE is a reasonable approximation given that the model fit to the Herschel observations of methyl formate in Orion–KL contained over a thousand emissive transitions that are closely fit using an LTE model (Crockett et al. 2014). A strong IR radiation field could affect the LTE analysis. Among the observed sources, Orion–KL and Sgr B2(N) have the strongest IR radiation field. Therefore, radiative pumping effects, if present, would be the strongest toward those sources. The Herschel observations and analysis of Orion–KL and Sgr B2(N) (Crockett et al. 2014; Neill et al. 2014) have shown that 1) pumping is not needed to fit the lines as LTE closely matches the observed emission and 2) there was evidence for radiative pumping in emission lines of other molecules, in particular methanol, but not for methyl formate.

6.1.2. Contamination from Strong Absorption Lines in Sgr B2(N)

Contamination from strong absorption lines in Sgr B2(N) may also affect methyl formate emission. There are two potential levels of contamination that could be an issue. First is absorption of methyl formate which lies in the foreground envelope. However, all the transitions that we have detected in this study cover fairly high energy levels that are not populated in the envelope (e.g., Neill et al. 2014). Another issue would be contamination from other species with ground state transitions that have similar frequencies; we see no evidence for this in our data.

6.1.3. Scattering on the Isotopic Ratio of the Methyl Formate Isotopologues within each ALMA Spectral Window

Another possible caveat of our $^{12}\text{C}/^{13}\text{C}$ ratio estimate is the individual modeling of each sub-band of the ALMA-SV observations of Orion–KL. In our exploration of the ALMA-SV data, we found that a large source of uncertainty is a roughly 10% difference in calibration between sub-bands; that is, some sub-bands have a slightly different calibration than other sub-bands. We infer that this is due to some structure (which could be a slope, a curvature, or a frequency dependence) in the calibration that affects the band pass and results in this slight measurement uncertainty that exists within a given sub-band.

Based upon this and due to the fact that different sub-bands have a different number of lines (see Table 4), we have chosen to fit the $^{12}\text{C}/^{13}\text{C}$ ratio in each sub-band individually and to use the relative errors in the fit from those bands to set the absolute uncertainty to our measurement. Nevertheless, it is important to note that a single set of parameters (not shown here) also fit all the data and give rise, within the uncertainties, to a similar isotopic abundance ratio.

6.2. Comparison of the Derived Column Densities with Previous Studies

In this section, we relate our results to previous studies performed toward our source sample. Our models are not unique and some differences with previously reported results can appear. This is in part due to the different (and more accurate) $^{12}\text{C}$-MF partition functions used here (see discussion in Section 4.1). Also, we note that for all the observed sources, the observed $\nu_{\text{LSR}}$ and $\Delta \nu_{\text{LSR}}$ are consistent with those in the literature. Orion–KL. From the ALMA-SV observations of Orion–KL, we derived a methyl formate column density over all the spectral windows of $5-8.5 \times 10^{17}$ cm$^{-2}$ toward the Compact Ridge and of $3.3-4.3 \times 10^{17}$ cm$^{-2}$ toward the Hot Core–SW. These results are higher by a factor of 2–5 with our reported values obtained from observations using the Plateau de Bure Interferometer and performed with a similar synthesized beam (1'8 × 0'8, see Favre et al. 2011). This discrepancy can be explained by the fact that in this study we used a different partition function which, as discussed in Section 4.1, results in a higher inferred $^{12}$C-MF abundance compared with the $^{12}$C-MF abundance derived using the JPL catalog partition function used by Favre et al. (2011). The spatial and the velocity distribution are in agreement with previous observations (Favre et al. 2011; Friedel & Snyder 2008). We refer to Favre et al. (2011) for a detailed comparison with previous related interferometric and single-dish studies performed by Friedel & Snyder (2008), Beuther et al. (2005), Liu et al. (2002), Remijan et al. (2003), Hollis et al. (2003), Blake et al. (1996, 1987), Schilke et al. (1997), and Ziurys & McGregor (1993).

For the Orion–KL observations carried out with the APEX telescope, the bulk of the HCOOCH$_3$ emission is well reproduced by a single component model with a rotational temperature of 100 K, a source size of 10'', and a column density of $9.6 \times 10^{16}$ cm$^{-2}$. Our derived APEX rotational temperature and column density agree with the Herschel/HIFI observations (Crockett et al. 2014) as well as with Favre et al. (2011) in which the authors do not separate the two HCOOCH$_3$ velocity components ($T_{\text{rot}}$ of 101 K, $N_{\text{HCOOCH3}} = 1.5 \times 10^{17}$ cm$^{-2}$).

Regarding the H$_{13}$COOCH$_3$ and HCOO$_{13}$CH$_3$ species, their detection toward Orion–KL has previously been reported by Carvajal et al. (2009) based on IRAM 30 m observations. The authors used a source size of 15'', a column density of $7 \times 10^{14}$ cm$^{-2}$, and a rotational temperature of 110 K to reproduce the emission arising from the Compact Ridge component associated with Orion–KL. The $^{13}$C$_2$-MF column density, derived from the APEX observations, lies in the range 7–9.8 × 10$^{15}$ cm$^{-2}$ and differs from the one derived by Carvajal et al. (2009). This is likely due to the fact that we use a different partition function (see above) along with different assumptions with regard to the beam filling factor (source size of 3'' and a T$_{\text{mb}}$ of 80 K for our best models). W51 e2. From the APEX observations, we derived a slightly lower (factor 1.8) of methyl formate column density in comparison to the measured column density reported by Demyk et al. (2008).

G19.61-0.23. Using CARMA observations (2'' resolution), Shiao et al. (2010) have reported a derived column density of $(9 \pm 2) \times 10^{16}$ cm$^{-2}$ given a rotation temperature of 161 K. Likewise, using BIMA observations, Remijan et al. (2004) derived from a source average of 2'8 and a column density in methyl formate of $3.4 \times 10^{17}$ cm$^{-2}$ given a temperature of 230 K. In our analysis, we have adopted the HCOOCH$_3$ rotation temperature derived by Remijan et al. (2004) rather than the one reported by Shiao et al. (2010). This choice is based upon the fact that Shiao et al. (2010) used a temperature derived from ethyl cyanide observations whereas Remijan et al. (2004) used
a rotation temperature based on methyl formate observations. Our best fit results in a methyl formate column density of \(7 \times 10^{18}\) cm\(^{-2}\) is commensurate with the value derived from the CARMA observations. Regarding the BIMA observations, the difference between the derived column densities is likely due to beam dilution.

G29.96-0.02. Using 2″ resolution CARMA observations, Shiao et al. (2010) have reported a derived column density of \((4 \pm 1) \times 10^{16}\) cm\(^{-2}\) which is in agreement with our results (see Table 6), taking into account the different assumptions about the source size with respect to beam.

G24.78+0.08. The HCOOCH\(_3\) column density derived from the APEX observations (see Table 6) differs from the one derived by Bisschop et al. (2007) likely due to different assumptions with regard to the beam filling factor.

NGC 6334 IRS 1. The deviation from values reported by Bisschop et al. (2007) is also likely due to different assumptions with regard to the beam filling factor. Nonetheless, our value of \(4.5 \times 10^{17}\) cm\(^{-2}\) is consistent with the value reported by Zernickel et al. (2012) \((N = 7 \times 10^{17}\) cm\(^{-2}\) for a 3″ source size) from Herschel/HIFI observations of this region.

Sgr B2(N). Using IRAM 30m observations of Sgr B2(N), Belloche et al. (2009) modeled methyl formate emission using two velocity components associated with two sources separated by only 5″ (based on PdBI and ATCA observations; see Belloche et al. 2008). These components differ by about 9 km s\(^{-1}\). Our best model includes only the component emitting at the systemic velocity of the source (i.e., 63.7 km s\(^{-1}\)) and our derived parameters are in agreement with the study performed by Belloche et al. (2009).

6.3. Isotopologue Detection and Sensitivity

Our analysis points out the need for high sensitivity to detect isotopologues of complex molecules. Indeed, due to lack of sensitivity in our APEX observations, only one \(^{13}\)C\(_2\)-MF line (pile-up of four \(^{13}\)C\(_2\) transitions with \(S/N^2\) of 71 D\(^{-2}\)) is detected and, most of the \(^{13}\)C\(_1\)-MF transitions emit below and/or at the confusion limit level. In contrast, both \(^{13}\)C-MF isotopologues are detected in observations performed with higher sensitivity (e.g., Carvajal et al. 2009, and this study for the supplementary ALMA data.).

6.4. The \(^{13}\)C Budget in the Galaxy

From Equation (1) for CO and Equation (2) for CO, CN, and H\(_2\)CO (Milam et al. 2005), we have calculated the \(^{12}\)C/\(^{13}\)C ratio in CO for each of the sources observed with the APEX telescope and for ALMA-SV observations of Orion–KL. These values are given in Table 7. Our study shows that the derived lower limits for the APEX \(^{12}\)C/\(^{13}\)C–methyl formate ratios are consistent within the uncertainties with the \(^{12}\)C/\(^{13}\)C ratio in CO for each source. The same conclusion applies for the isotopic ratios derived toward the Orion–KL Hot Core-SW and compact ridge positions (ALMA-SV data).

6.5. Implications

Numerous measurements of the \(^{12}\)C/\(^{13}\)C isotopic ratio have been performed through several molecular tracers, such as CO and OCS, toward Orion–KL. For example, from OCS and H\(_2\)CS isotopologue observations Tercero et al. (2005) have reported an average ratio of 45 ± 20. Using methanol observations, Persson et al. (2007) have found a \(^{12}\)C/\(^{13}\)C isotopic ratio 57 ± 14. Savage et al. (2002) derived a ratio of 43 ± 7 in CN. From \(^{13}\)CO observations, Snell et al. (1984) have reported an average \(^{12}\)CO/\(^{13}\)CO isotopic ratio of 74 ± 9 in the high-velocity outflow of Orion–KL. Likewise, from infrared measurements performed with the Kitt Peak Mayall 4m telescope, Scoville et al. (1983) obtained a \(^{12}\)CO/\(^{13}\)CO isotopic ratio of 96 ± 5. Using C\(_{18}\)O observations, Langer & Penzias (1990) and Langer & Penzias (1993) derived ratios of 63 ± 6 and 74 ± 9 according to the observed position. These findings suggest that the gas in Orion–KL does not seem to be heavily fractionated since the \(^{12}\)C/\(^{13}\)C ratio in most simple species is almost the same. Our results are consistent with this finding since:

1. For each of the \(^{13}\)C-MF isotopologues, the derived isotopic ratios (68.4 ± 10.1 toward the Compact Ridge and of 71.4 ± 7.8 toward the Hot Core-SW; see Figure 2) are consistent with each other.
2. These results are consistent within the error bars with the values derived for CH\(_3\)OH and for CO by Persson et al. (2007), Snell et al. (1984) and Scoville et al. (1983) toward Orion–KL.

Therefore, the present observations do not support methyl formate formation in the gas-phase from \(^{12}\)C/\(^{13}\)C fractionated gas. In addition, regarding methyl formate gas-phase formation mechanisms, Horn et al. (2004) have shown that there are no very efficient gas-phase pathways to form methyl formate, meaning that there are no efficient primary pathways to form the \(^{13}\)C-MF isotopologues either. One possibility that could lead to gas-phase formation of the \(^{13}\)C-MF isotopologues would be a “secondary” fractionation process involving the \(^{12}\)C–methyl formate itself and \(^{13}\)C\(_1\) (E. Herbst 2014, private communication). Such reactions, however, are unlikely to occur since high barriers are expected. This would also argue against the possibility of methyl formate gas-phase formation from \(^{12}\)C/\(^{13}\)C fractionated gas. This finding combined with the hypothesis of Wirstrom et al. (2011) strongly suggests that grain surface reactions are likely the main pathways to form methyl formate (\(^{12}\)C and \(^{13}\)C).

7. CONCLUSIONS

We have investigated the \(^{12}\)C/\(^{13}\)C isotopic ratio in methyl formate toward a sample of massive star-forming regions located over a range of distances from the Galactic center, through observations performed with the APEX telescope. In addition, we have measured the \(^{12}\)C/\(^{13}\)C-methyl formate ratio toward Orion–KL using the ALMA-SV observations. Also, we reported new spectroscopic measurements of the H\(^{13}\)COOCH\(_3\) and HCOO\(^{13}\)CH\(_3\) species. Our study is based on this laboratory spectral characterization and points out the importance of these data in deriving accurate partition functions and therefore abundances of methyl formate. Our analysis also points out that to accurately derive a reliable abundance ratio between different species, it is necessary to use a homogeneous observational database.

We have performed LTE modeling of the observational data. A multitude of \(^{13}\)C\(_1\)-MF and \(^{12}\)C\(_2\)-MF transitions have been detected in the ALMA-SV observations carried out toward Orion–KL, (1) confirming the previous detection of the \(^{13}\)C-MF isotopologues reported by Carvajal et al. (2009) and, (2) imaging their spatial distribution for the first time. Assuming that the two \(^{13}\)C-MF isotopologues have similar abundances, we reported a \(^{12}\)C/\(^{13}\)C isotopic ratio in methyl formate of
68.4 ± 10.1 and 71.4 ± 7.8 toward the Compact Ridge and Hot Core-SW components, respectively. A salient result is that those measurements are consistent with the 12C/13C ratio measured in CO and in CH3OH. Our findings suggest that grain surface chemistry very likely prevails in the formation of methyl formate main and 13C isotopologues.

Regarding the APEX observations, we have reported a tentative detection (>3σ level) of the 12C2-MF isotopologue toward the following four massive star-forming regions: Sgr B2(N-LMH), NGC 6334 IRS 1, W51 e2, and G19.61-0.23. The derived lower limits for the 12C/13C-methyl formate ratio are consistent with the 12C/13C ratio measured in CO showing an increasing ratio with distance from the Galactic center. A larger source sample and further observations with high sensitivity are essential to confirm this trend.

In addition, we used the Herschel/HIFI spectral tools, which are available to the community (Crockett et al. 2014), to make reliable line identifications and to appreciate where potential line blends may exist. The current work illustrates how to conclude the legacy of Herschel with other telescopes such as ALMA.

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Notes.

a The nuclear spin degeneracy was not considered in these calculations.

b The rotational partition function obtained as a direct sum of energy levels up to J = 79 is used in the final result.

A.1. Rotational Partition Function

The rotational partition function $Q_{\text{rot}}$ was obtained using Equation (9) of Groner et al. (2007):

$$Q_{\text{rot}} = \sum_{J,K_a,K_c} (2J + 1) e^{-\frac{E_{J}^{\text{rot}}}{k_{B}T}}, \quad (A2)$$

where $E_{J}^{\text{rot}}$ are the rotational energies, that is, those for the rotational states only in the A-symmetry ground torsional state. The RAM model (Herbst et al. 1984; Hougen et al. 1994; Kleiner 2010) was used to predict the torsional–rotational states as explained before. Also, the torsional–rotational states ($v_t = 0$ and A-symmetry) up to $J = 79$ were included in Equation (A2), which is enough for the convergence study mentioned above.

A comparison was done with the symmetric top approximation for the rotational partition function of Herzberg (1991). For sufficiently high temperatures (or small rotational constants):

$$Q_{\text{rot}}^{\text{app}} \approx \sqrt{\frac{\pi}{A^{\text{PAM}} B^{\text{PAM}} C^{\text{PAM}}}} \frac{1}{h} \left(\frac{k_{B}T}{\hbar} \right)^{\frac{3}{2}}, \quad (A3)$$

where the rotational constants refer to the principal axis system, not to the Rho-Axis System. Therefore, an appropriate transformation was performed from the rotational parameters given in Carvajal et al. (2009, 2010).

The rotational partition function computed as a direct sum (Equation (A2)) is in general, for both 13C-MF isotopologues, slightly larger than the one for the approximated partition function (Equation (A3)), as shown in Table 8. For this reason, we used here the rotational partition function as a direct summation instead of using the approximated partition function.
up to a maximum quantum number $v$ (Equation (A3)). In Table 8 it can be seen that the differences between $Q_{\text{rot}}$ and $Q_{\text{rot}}^{\text{approx}}$ can be around 1% for $T = 9.375$ K, decreasing for higher temperatures to the error range estimated by Herzberg (1991).

A.2. Torsional Partition Function

The torsional contribution $Q_{\text{tor}}$ to the partition function was obtained through the following formula:

$$Q_{\text{tor}}^{\text{max}} = \sum_{v_t=0}^{v_{\text{max}}} \left( e^{-\frac{E^{\text{(tor)}}(v_t, A)}{k_B T}} + e^{-\frac{E^{\text{(tor)}}(v_t, E)}{k_B T}} \right),$$

(A4)

where $E^{\text{(tor)}}(v_t, A)$ and $E^{\text{(tor)}}(v_t, E)$ are the energies of the torsional states with a quantum number $v_t$ for the $A$ ($A_1$ or $A_2$) and $E$ symmetries, respectively, referring to the $v_t = 0$ ground torsional state, i.e., $E^{\text{(tor)}}(v_t = 0, A) = 0$ cm$^{-1}$. Different approximations can be carried out depending on the maximum value $v_{\text{max}}$ considered in the equation. The torsional energies used in Equation (A4) are the following:

1. Torsional energies from $v_t = 0$ to $v_t = 2$ computed from the Hamiltonian parameters of the RAM model. The torsional energies of $^{13}$C$_1$-MF are computed with the parameters of Carvajal et al. (2010) and those of $^{13}$C$_2$-MF are computed with the parameters of Carvajal et al. (2009). These torsional energies are expected to be very reliable for the $^{13}$C$_1$-MF.

2. Torsional energies from $v_t = 3$ to $v_t = 4$ of the main species of methyl formate given by Senent et al. (2005) and considered as a good approximation for both $^{13}$C-MF isotopologues.

3. Torsional energies from $v_t = 5$ to $v_t = 6$ were roughly estimated in the present work, where $E^{\text{(tor)}}(v_t = m, A) = m \times E^{\text{(rot)}}(v_t = 1, A)$ and $E^{\text{(tor)}}(v_t = m, E) = m \times E^{\text{(rot)}}(v_t = 1, E)$ and $m$ will take values of 5 or 6. This is only an estimate to understand the contribution of these torsional levels to the torsional partition function whose contribution is of 3% for $T = 300$ K, 1.2% for $T = 225$ K, 0.2% for 150 K, etc., see Tables 9 and 10.

As the torsional mode is very anharmonic, we cannot use the harmonic approximation for the torsional partition function. From our results (Tables 9 and 10), when computing the torsional partition function, the harmonic approximation could be assumed only for temperatures $T < 100$ K. Above $T = 100$ K, the anharmonicity has the natural effect of increasing the estimated torsional partition function. This effect can be around 5% at 300 K.

In Tables 9 and 10, the torsional partition function at different approximations is shown for $^{13}$C$_1$-MF and $^{13}$C$_2$-MF isotopologues respectively. It can be noted that for $T = 300$ K the convergence is reached to within 1% when the torsional states above $v_t = 6$ are included. For temperatures $T < 200$ K, the contribution of the torsional states above $v_t = 4$ is insignificant. In fact, at temperatures close to 100 K and below, convergence is reached (within 0.9% at $T = 100$ K) when only $v_t = 0, 1, 2$ are considered.

A.3. Vibrational Partition Function

In the calculation of the vibrational partition function $Q_{\text{vib}}$, it is expected that for ISM temperatures, only the information of the vibrational frequencies at lower energies ($<300$ cm$^{-1}$) is necessary. In order to check the convergence of the vibrational partition function, the contribution of the remaining vibrational modes has been taken into consideration. For this purpose, the harmonic approximation of the vibrational partition function is considered in general as:

$$Q_{\text{vib}} = \frac{1}{\Pi_{i=1}^{N-7}} \frac{1}{1 - e^{-E_{i}^{\text{vib}}/k_B T}},$$

(A5)

where $N$ is the number of atoms of the molecule, and $E_{i}^{\text{vib}}$ is the vibrational fundamental frequencies of each vibrational mode of the molecule. As the torsion is treated apart, the product in Equation (A5) will only expand to the $3N - 7$ small amplitude vibrational modes. It is important to note that no experimental vibrational frequencies exist for the $^{13}$C-MF species. Therefore, to take into account the vibrational contribution of the partition function, we assumed that the vibrational fundamental frequencies of $^{13}$C$_1$-MF and $^{13}$C$_2$-MF are approximately the same as for the main isotopologue given the large experimental uncertainties (mostly of 6–15 cm$^{-1}$;
Table 11
Vibrational Partition Function for $^{13}$C$_1$-MF and $^{13}$C$_2$-MF

| $T$ (K) | $Q_{\text{vib}}$  |
|---------|------------------|
| 300.0   | 1.70330          |
| 225.0   | 1.32486          |
| 150.0   | 1.09599          |
| 75.0    | 1.00399          |
| 37.50   | 1.00001          |
| 18.75   | 1.00000          |
| 9.375   | 1.00000          |

Chao et al. (1986). In this instance, the experimental vibrational energies for the main isotopologue taken from Chao et al. (1986) are also valid for their other isotopologues. The vibrational partition function computed with Equation (A5) is given in Table 11.

In this work, for the temperature ranges considered, all the small amplitude vibrational fundamentals in Equation (A5) are included. Nevertheless, when the temperatures are around $T = 200$ K, all vibrational fundamentals could be omitted in the vibrational partition function except those of $\nu_{14}$ and $\nu_1$ modes (around 300 cm$^{-1}$). Below $T = 100$ K, inclusively $\nu_{14}$ and $\nu_1$ modes could be neglected.

A.4. Rotational–torsional–vibrational Partition Function

In addition, we have assessed that the partition function separated into functions of each rotational, torsional, and vibrational contribution is a good enough approximation for temperatures at least under 300 K. This assessment was set up after comparing our partition function calculation with that derived from its general expression, Equation (3), for $v_t = 0$ and 1. Finally, Table 3 summarizes the rotational–torsional–vibrational partition function values that are used here for $^{13}$C$_1$-MF and $^{13}$C$_2$-MF.

APPENDIX B
TRANSITIONS OF $^{12}$C AND $^{13}$C-METHYL FORMATE OBSERVED WITH THE ALMA TELESCOPE TOWARD ORION–KL

Table 12 summarizes the line parameters for all detected, blended, or not detected transitions of $^{12}$C-MF, $^{13}$C$_1$-MF and $^{13}$C$_2$-MF in all ALMA spectral windows.

Table 12
Transitions of $^{12}$C and $^{13}$C-Methyl Formate Observed with the ALMA Telescope

| Frequency (MHz) | Transition | $E_{\text{up}}$ (K) | $\mu^2$ (D$^2$) |
|-----------------|------------|----------------------|-----------------|
| HCOOCH$_3$ a    |            |                      |                 |
| 214631.77 *     | $^{17}$S$_{5,12}$--$^{16}$S$_{6,11}$ (E, $v_t=0$) | 108              | 41              |
| 214652.63 *     | $^{17}$S$_{5,12}$--$^{16}$S$_{6,11}$ (A, $v_t=0$) | 108              | 41              |
| 214782.36 *     | $^{18}$S$_{3,16}$--$^{17}$S$_{3,15}$ (E, $v_t=0$) | 106              | 46              |
| 214792.55 *     | $^{18}$S$_{3,16}$--$^{17}$S$_{3,15}$ (A, $v_t=0$) | 106              | 46              |
| 214816.95       | $^{19}$S$_{2,18}$--$^{18}$S$_{2,17}$ (A, $v_t=1$) | 296              | 49              |
| 214942.87       | $^{19}$S$_{1,18}$--$^{18}$S$_{1,17}$ (A, $v_t=1$) | 296              | 49              |
| 215073.92       | $^{19}$S$_{1,18}$--$^{18}$S$_{1,17}$ (E, $v_t=1$) | 296              | 49              |
| 215193.55       | $^{19}$S$_{1,18}$--$^{18}$S$_{1,17}$ (E, $v_t=1$) | 296              | 49              |
| 215579.61       | $^{20}$S$_{2,19}$--$^{19}$S$_{2,18}$ (A, $v_t=1$) | 293              | 46              |
| 215837.59       | $^{20}$S$_{2,19}$--$^{19}$S$_{2,18}$ (A, $v_t=1$) | 299              | 53              |

Notes.

a This table lists the detected, blended, partially blended, and optically thin lines of HCOOCH$_3$. Transitions that are emitting with an intensity less than or equal to three times the noise level which we used to constrain our model are also listed. Transitions with the "*" symbol are transitions we estimate to be optically thick.

(This table is available in its entirety in a machine-readable form in the online journal. A portion is shown here for guidance regarding its form and content.)

APPENDIX C

METHYL FORMATE EMISSION TOWARD THE ORION–KL COMPACT RIDGE AS OBSERVED WITH ALMA

Figures 5, 6, and 7 show the respective spectra of the detected HCOOCH$_3$, H$^{13}$COOCH$_3$, and HCOO$^{13}$CH$_3$ transitions observed with ALMA toward the Orion–KL Compact Ridge during the science verification program, along with our best models achieved using the XCLASS program.

APPENDIX D

METHYL FORMATE EMISSION TOWARD THE ORION–KL HOT CORE-SW AS OBSERVED WITH ALMA

Figures 8, 9, and 10 show the respective spectra of the detected HCOOCH$_3$, H$^{13}$COOCH$_3$, and HCOO$^{13}$CH$_3$ transitions observed with ALMA toward the Orion–KL Hot Core-SW during the science verification program, along with our best models achieved using the XCLASS program.
Figure 5. HCOOCH$_3$ spectra (black) toward the Compact Ridge component associated with Orion–KL and model (red), as observed with ALMA. The intensity scale is in $T_{MB}$ (K). The x-axis scale is about $\pm$9.5 MHz centered on the line rest frequency, which is indicated below each plot.

(A color version of this figure is available in the online journal.)
Figure 5. (Continued)
Figure 6. $^{13}$COOCH$_3$ spectra (black) toward the Compact Ridge component associated with Orion–KL and model (red), as observed with ALMA. The intensity scale is in $T_{MB}$ (K). The x-axis scale is about ±9.5 MHz centered on the line rest frequency, which is indicated below each plot.

(A color version of this figure is available in the online journal.)
Figure 6. (Continued)
Figure 7. HCOO$^{13}$CH$_3$ spectra (black) toward the Compact Ridge component associated with Orion–KL and model (red) as observed with ALMA. The intensity scale is in $T_{MB}$ (K). The x-axis scale is about $\pm$9.5 MHz centered on the line rest frequency, which is indicated below each plot.

(A color version of this figure is available in the online journal.)
Figure 7. (Continued)
Figure 8. HCOOCH₃ spectra (black) toward the Hot Core-SW component associated with Orion–KL and model (red), as observed with ALMA. The intensity scale is in $T_{MB}$ (K). The x-axis scale is about ±9.5 MHz centered on the line rest frequency, which is indicated below each plot.

(A color version of this figure is available in the online journal.)
Figure 8. (Continued)
Figure 8. (Continued)
Figure 9. $^{13}$COOCH$_3$ spectra (black) toward the Hot Core-SW component associated with Orion–KL and model (red), as observed with ALMA. The intensity scale is in $T_{MB}$ (K). The x-axis scale is about $\pm$9.5 MHz centered on the line rest frequency, which is indicated below each plot.

(A color version of this figure is available in the online journal.)
Figure 9. (Continued)
Figure 9. (Continued)
Figure 10. HCOO$^{13}$CH$_3$ spectra (black) toward the Hot Core-SW component associated with Orion–KL and model (red), as observed with ALMA. The intensity scale is in $T_{MB}$ (K). The x-axis scale is about ±9.5 MHz centered on the line rest frequency, which is indicated below each plot.

(A color version of this figure is available in the online journal.)
Figure 10. (Continued)
