

Protostellar and Cometary Detections of Organohalogens

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Organohalogens, a class of molecules that contain at least one halogen atom bonded to carbon, are abundant on Earth where they are mainly produced through industrial and biological processes [1]. Consequently, they have been proposed as biomarkers in the search for life on exoplanets [2]. Simple halogen hydrides have been detected in interstellar sources and in comets, but the presence and possible incorporation of more complex halogen-containing molecules such as organohalogens into planet-forming regions is uncertain [3, 4]. Here we report the first interstellar detection of two isotopologues of the organohalogen CH_3Cl and put some constraints on CH_3F in the gas surrounding the low-mass protostar IRAS 16293-2422, using the Atacama Large Millimeter/submillimeter Array (ALMA). We also find CH_3Cl in the coma of comet 67P/Churyumov-Gerasimenko (67P/C-G) using the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) instrument. The detections reveal an efficient pre-planetary formation pathway of organohalogens. Cometary impacts may deliver these species to young planets and should thus be included as a potential abiotical production source when interpreting future organohalogen detections in atmospheres of rocky planets.

Organohalogens are well known for their use in industry, and for their detrimental effect

on the ozone layer [1]. Some organohalogens are also produced naturally [5], through different geological and biological processes. Because of their relationship to biology and industry on Earth, organohalogens have been proposed as biomarkers on other planets [2, 6, 7]. Methyl chloride (CH_3Cl), the most abundant organohalogen in the Earth's atmosphere, has both natural and synthetic production pathways. Its total production rate approaches 3 megatonnes per year, with the majority originating from biological processes [8]. Recent observations of Cl-bearing organic molecules, including methyl chloride, on Mars by the rover Curiosity, has challenged a straightforward connection between organohalides and biology; one proposed source of Cl-bearing organic molecules on Mars is meteoritic impacts [9, 10]. This naturally raises the question of whether circumstellar and interstellar environments can produce organohalogens abiotically, and in which amount.

Our understanding of interstellar and protostellar halogen chemistry is limited. The only halogen-bearing species observed in interstellar environments to date are di- and tri-atomic molecules: HCl , HCl^+ , H_2Cl^+ , HF , and CF^+ [3, 4, 11, 12, 13]. Current astrochemical models can account for these small molecules, but do not include larger halogen-bearing species such as organohalogens. It is therefore not known how this simple halogen chemistry and organic chemistry couple under interstellar conditions. In this work, we have searched for the simplest organohalogens, CH_3Cl and CH_3F in two sources with previous detections of HCl and a wealth of organic molecules: the envelope of a low-mass protostar IRAS 16293-2422 (see [14] for HCl and [15, 16, 17] amongst others for detections of organic species), and the coma of comet 67P/Churyumov-Gerasimenko (67P/C-G) (see Dhooghe et al., in press for halogen detections and [18] for an inventory of organic

molecules).

IRAS 16293-2422 (hereafter IRAS 16293) is a low-mass protostellar binary system in the ρ Ophiuchi star-forming region at a distance of 120 pc [19]. The masses of the individual protostars suggest that the two components of the binary, IRAS 16293A and IRAS 16293B, will eventually evolve into two Solar-like T Tauri stars, each surrounded by a planet-forming disk [20]. IRAS 16293 is most well known for its rich inventory of organic molecules, which are distributed on scales of 10s to 100s of AU around the two sources [e.g. 15, 16, 17]. The detection of HCl in its envelope [14], together with its rich organic chemistry, makes IRAS 16293 an ideal target to search for methyl chloride and related organohalogenes. We use data from the PILS (Protostellar Interferometric Line Survey) program [21], an ALMA unbiased survey of IRAS 16293-2422 covering a wide frequency window between 329 and 363 GHz with a spatial resolution of ~ 60 AU, a spectral resolution high enough to distinguish individual rotational lines of CH_3Cl , as well as its fluorinated homologue CH_3F .

We combine our search for organohalogenes in IRAS 16293 with an analogous search in the coma of Jupiter-family comet 67P/C-G. Comets are believed to preserve the chemical composition of the solar nebula, and potentially the Sun's birth cloud as well. By comparing abundances of organohalogenes in comet 67P/C-G with the nascent solar nebula analog IRAS 16293, we can assess whether such an inheritance is likely in the case of organohalogenes. We focus on 67P/C-G because its volatile inventory is known with unprecedented detail and sensitivity for a comet, thanks to the *Rosetta* mission (Dhooghe et al., in press, [18]). In this letter we make use of results

from ROSINA and its Double Focus Mass Spectrometer (DFMS), whose very high mass resolution and sensitivity [22] enables detections of minor constituents, including organohalogens if present.

We unambiguously detect both ^{35}Cl and ^{37}Cl isotopologues of CH_3Cl toward IRAS 16293B. The spectra in the top and middle panels of Fig. 1 show the clear identification of the $J'_K - J''_K = 13_K - 12_K$ rotational progression of $\text{CH}_3^{35}\text{Cl}$ and $\text{CH}_3^{37}\text{Cl}$, with all the transitions attributed up to $K=4$ in a spectrum extracted one beam ($0.5''$) away from source B (position *ii* in figure 2). This off-source position has been identified as an optimal location for most molecular identification in IRAS 16293, since it contains strong and narrow lines that are relatively unaffected by continuum absorption. The observed transitions have an upper energy level between 116 and 386 K for $\text{CH}_3^{35}\text{Cl}$ and between 114 and 384 K for $\text{CH}_3^{37}\text{Cl}$. The hyperfine splitting induced by the nuclear spin of $3/2$ for both chlorine isotopes is partially resolved for $K \geq 4$. Based on the fitting of synthetic spectra, which assumes that the gas is in local thermal equilibrium (LTE, see Methods sections), the $\text{CH}_3^{35}\text{Cl}$ excitation temperature is 102 ± 3 K, and the column density is $(4.6 \pm 0.7) \times 10^{14} \text{ cm}^{-2}$ in a $0.5''$ beam, where the main source of uncertainty is the absolute calibration (Table 1). The reported error does not take into account possible error introduced by adopting an LTE framework. The excitation temperature is at the lower end of the range of temperatures obtained for some other organic molecules through the PILS dataset [23]. The $\text{CH}_3^{37}\text{Cl}$ column density is constrained to be $(2.2 \pm 0.4) \times 10^{14} \text{ cm}^{-2}$ using the excitation temperature and FWHM derived from the stronger $\text{CH}_3^{35}\text{Cl}$ lines. This yields a $^{35}\text{Cl}/^{37}\text{Cl}$ ratio of 2.1 ± 0.4 , which is consistent with the previously reported $^{35}\text{Cl}/^{37}\text{Cl}$ ratio of 2.1 derived for HCl in the envelope of IRAS 16293 encompassing both source A and B [14]. CH_3F is not securely detected (bottom panel of Fig. 1) through its $J'' - J' = 7-6$

rotational progression. Due to the high number of overlapping rotational lines from other species, only an upper limit on the column density of $4.6 \times 10^{13} \text{ cm}^{-2}$ can be derived, assuming the same excitation temperature and line width as those derived for $\text{CH}_3^{35}\text{Cl}$.

In addition to the spectra displayed in Fig. 1, spectra of the three molecules are extracted at two more source positions: half a beam, and two beams away from IRAS 16293B (positions *i* and *iii* in Fig. 2). The excitation temperature, column density and upper limits for the CH_3Cl isotopologues and CH_3F are reported in Table 1 for all three locations. The column density ratios of the organohalogens over methanol, the most widespread organic molecule found in protostars and key parent to many interstellar organic species, are also reported in Table 1. The ratios are $\sim 7 \times 10^{-5}$ for CH_3Cl (combining the two isotopologues) and below $< 2 \times 10^{-6}$ for CH_3F , using methanol column densities reported for the corresponding locations (Jørgensen et al., in prep and [21]), and assuming that the emission is uniform over the beam (*i.e.* beam filling factor of unity). We also identified $\text{CH}_3^{35}\text{Cl}$ 0.3'' away from IRAS 16293A, and the inferred column density ratio with respect to methanol is consistent with what is extracted from the spectra toward source B where the lines are better resolved.

Figure 2 illustrates the spatial extent of the CH_3Cl emission around IRAS 16293B. The brightest line, $\text{CH}_3^{35}\text{Cl}$ 13_0-12_0 , is clearly spatially resolved (line integrated intensity shown in the left column, middle panel), and is detected almost out to the edge of the dust continuum emission, 1'' or 120 AU away from the source center (left column upper panel). Similar to other lines of other species, $\text{CH}_3^{35}\text{Cl}$ 13_0-12_0 is under-luminous toward the continuum peak of the B source

due to continuum absorption [21, 24]. Compared to CH_3OCHO , an archetypical complex organic molecule found around protostars, CH_3Cl is somewhat more extended but the difference is too small to be conclusive. The CH_3OCHO spatial extent for lines with similar upper level energies is shown in the bottom left panel of Figure 2 through the imaging of one of its line integrated intensity and the relative spectral line strengths for both species extracted at the three positions *i*, *ii*, and *iii* away from source B is displayed in the right panel of Figure 2.

The origin of the detected CH_3Cl is not known and difficult to constrain without major theoretical and experimental efforts since astrochemical networks do not include its formation, or that of any other organohalogen beyond CH_2Cl^+ . Amongst the potential formation routes, we suggest that there are at least two that are consistent with the observed CH_3Cl excitation temperature of about 100 K and its extended spatial emission: 1) ion-molecule gas-phase chemistry with CH_4Cl^+ as an intermediate and 2) formation on grains through successive hydrogenation and halogenation of carbon followed by sublimation. Details on these pathways are available in the supplementary information appendix.

CH_3Cl is also detected in the coma of the 67P/C-G comet as shown in Fig. 3 by the mass spectrometer response centered on mass 49.99 u/e, corresponding to the presence $\text{CH}_3^{35}\text{Cl}$. $\text{CH}_3^{37}\text{Cl}$ and CH_3F are below the detection limit. While there are possible abundance variations in the coma along the comet orbit, a relative abundance of $\text{CH}_3\text{Cl}/\text{HCl} = (4 \pm 2) \times 10^{-3}$ can be obtained by fitting six spectra similar to the one presented in Fig. 3 centered at mass 49.99 u/e ($\text{CH}_3^{35}\text{Cl}$) and mass 35.98 u/e (H^{35}Cl), obtained in May 2015 where the HCl signal in the coma

was at its highest. Adopting the HCl/H₂O ratio of $(0.02-3) \times 10^{-4}$ (Dhooghe et al., in press) and a CH₃OH/H₂O ratio of $(3.1 - 5.5) \times 10^{-3}$ [18], we estimate the bulk ratio of CH₃Cl over CH₃OH to be $(0.007 - 6) \times 10^{-4}$. This is consistent with the value derived for the protostar IRAS 16293, and therefore with a scenario where comets in our Solar System and in extra-solar systems generally contain interstellar organohalogens.

The non-detection of CH₃³⁷Cl in the coma of comet 67P/C-G is consistent with a ³⁵Cl/³⁷Cl ratio of 3.1, the average value in the Solar System. The ³⁵Cl/³⁷Cl ratio of 2.1 ± 0.2 obtained in the vicinity of IRAS 16293B using CH₃Cl is lower but agrees well with that measured using HCl in the gas around IRAS 16293[14]. The origin of this lower isotopic ratio in IRAS 16293 compared to the Solar System has so far been explained by explosive nucleosynthesis, where massive star nucleosynthesis is disrupted by a nearby explosive event such as a supernova explosion [14]. While a chemical origin for fractionation cannot be excluded, the nucleosynthesis process alone can explain the difference in ³⁵Cl/³⁷Cl between IRAS 16293 and the Solar System.

Based on the cometary methyl chloride abundance, we can estimate how much methyl chloride could have been delivered to the young Earth, and may currently be delivered to nascent exoplanets, assuming that 67P/C-G is representative for comets and exo-comets alike. For this calculation, we assume the maximum ratio of 1.2×10^{-6} of CH₃Cl with respect to H₂O derived for 67P/C-G, and recent estimates of the maximum peak influx of impactors onto the young Earth during the late heavy bombardment of 10^{-6} Earth masses Myr⁻¹ during a 80 Myrs period [25]. We further assume that 20% of the impactors have a cometary origin, and that 40% of the comet

nucleus is water ice. Under these conditions, we estimate that up to 600 tonnes per year of CH_3Cl could have been delivered to the young Earth, with an accumulated maximum of 50 gigatonnes.

The survival of these organohalogens upon impact depends on the comet size, impact speed and angle, as well as the thermal decomposition parameters of CH_3Cl . Similar to most organic molecules, we expect that the survival rate of the original CH_3Cl brought by comets will be negligible for mid-size, high speed vertical impactors [26, 27], which can induce temperatures up to 15,000 K. By contrast, slower impacts at grazing angles and impacts from larger comets that can provide shielding of the comet nucleus should increase the likelihood of survival. Reformation of CH_3Cl from decomposed parent species through shock chemistry may also be significant. Further studies of impact chemistry and physics is needed to assess the net delivery. The subsequent accumulation of CH_3Cl in the planet atmosphere depends on the atmosphere composition, the UV irradiance (CH_3Cl absorbs at wavelengths shorter than 203 nm), as well as geochemistry and presence of oceans. Dedicated studies are required to evaluate the balance between CH_3Cl sources, i.e. cometary delivery, formation upon impact or outgassing from the planet interior, versus sinks such as atmospheric reaction with OH radicals, adsorption on rocks and solvation in oceans. In this context, the current protostellar and cometary detections of organohalogens represent a new reservoir of halogens and a new potential source of this family of molecules for exoplanets, especially young ones that are heavily impacted. This has consequences for the proposed use of CH_3Cl detection in the atmospheres of exoplanets as a biosignature [2] since a substantial percentage of this species found in rocky planet atmospheres could have actually been inherited from abiotic formation pathways prior to or during planet formation.

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Data Availability The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request. This paper makes use of the ALMA dataset ADS/JAO.ALMA#2013.1.00278.S.

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Author contributions E.C.F. initiated the project, identified, and analyzed the newly detected species in the protostar spectra. E.C.F. and K.I.O. wrote the manuscript together. The PI of the PILS survey J.K.J., together with H.C., and M.H.D.W. generated the datacubes from the ALMA observations and assisted with the column density determinations. H.S.P.M. computed the CH₃F line catalog and assisted with the CH₃Cl spectroscopy interpretations. R.T.G contributed the text on the formation pathways to organohalogenes under ISM conditions. The PI of the ROSINA program K.A., together with M.R. reduced the DFMS data, identified, and provided the CH₃Cl abundance ratios. J.K.J., H.S.P.M., and E.F.vD. provided extensive input on the text. All the authors contributed to discussions of the results and commented on the manuscript.

Figure Captions and Tables

Figure 1

Methyl halides transitions in a spectrum extracted around protostar IRAS 16293B. CH₃³⁵Cl and CH₃³⁷Cl are identified through their $J'_K - J''_K = 13_K - 12_K$ with $K=0$ to 4 in a spectrum around IRAS 16293B (black solid lines) extracted 0.5'' away from source B in a 0.5'' beam (position *ii* in figure 2). The spectral regime of CH₃F $J'_K - J''_K = 7_K - 6_K$ with K up to 3 is also shown,

though identification is not secured. Synthetic spectra with an excitation temperature of ~ 100 K used to derived column densities for each species are overplotted in red. Some other molecular lines are also identified, but most transitions cannot be unambiguously attributed.

Figure 2

CH₃³⁵Cl spatial emission compared to that of CH₃OCHO around protostar IRAS 16293B.

Top left panel: IRAS 16293-2422 band 7 continuum; middle left panel: CH₃³⁵Cl 13₀-12₀ integrated line intensity around source B (upper level energy 116 K); bottom left panel: CH₃OCHO 17_{6,11}-16_{5,12} A in $v=0$ integrated line intensity around source B (upper level energy 115 K); the black contours represent the 3, 5, 7, 10, 15, 20, and 30-sigma detections levels; the size of the observing beam is plotted in the lower left corners; right panel: spectra extracted at position *i*, *ii*, and *iii* labelled in middle left panel overplotted with synthetic spectra of CH₃³⁵Cl and CH₃OCHO (excitation temperature of 120 K) in purple and green respectively. The upper energy level values of the three CH₃³⁵Cl lines range from 116 to 147 K while those of CH₃OCHO $v=0$ are equal to 115 K and CH₃OCHO $v=1$ is equal to 477 K.

Figure 3

Mass spectrum of the coma of comet 67P/C-G for molecular fragments around mass-over-charge equal to 50 u/e. The co-located gaussian in dashed-line centered at 49.99 u/e is due to the presence of CH₃³⁵Cl. The solid line is the sum of the six double co-located Gaussians in dashed lines, which were used to fit the six peaks centered on the molecular fragments. Integration time is 20 s per spectrum and the error bars represent the 1-sigma counting statistics.

Table 1: **Best fit parameters and upper limits for methyl halides around protostar IRAS 16293B.** Excitation temperature, column density, and ratio over CH₃OH for the organohalogenes are reported for positions *i* half a beam away, *ii* one beam away, and *iii* two beams away from IRAS 16293B. The column density values are given assuming a beam filling factor of unity and the reported errors are mainly due to the calibration uncertainty of 15%.

| Molecule | position | T_{ex} (K) | N (cm ⁻²) | N / N_{CH_3OH} |
|----------------------------------|------------|------------------|------------------------------|----------------------|
| CH ₃ ³⁵ Cl | <i>i</i> | 103^{+3}_{-3} | $11 \pm 2 \times 10^{14}$ | 1.1×10^{-4} |
| | <i>ii</i> | 102^{+4}_{-3} | $4.6 \pm 0.7 \times 10^{14}$ | 9×10^{-5} |
| | <i>iii</i> | 85^{+15}_{-13} | $3.1 \pm 0.7 \times 10^{13}$ | - |
| CH ₃ ³⁷ Cl | <i>i</i> | - | $4.9 \pm 0.8 \times 10^{14}$ | 5×10^{-5} |
| | <i>ii</i> | - | $2.2 \pm 0.4 \times 10^{14}$ | 4×10^{-5} |
| | <i>iii</i> | - | $< 1 \times 10^{13}$ | - |
| CH ₃ F | <i>i</i> | - | $< 4 \times 10^{13}$ | $< 4 \times 10^{-6}$ |
| | <i>ii</i> | - | $< 2 \times 10^{13}$ | $< 4 \times 10^{-6}$ |
| | <i>iii</i> | - | $< 5 \times 10^{12}$ | - |

Methods

ALMA observations of the binary system IRAS 16293-2422 were taken during Cycle 2 as part of the PILS program and are explained in detail elsewhere [21]. Briefly, the dataset consists of spectral cubes centered at $\alpha_{J2000} = 16^h 32^m 22^s.72$; $\delta_{J2000} = -24^\circ 28' 34''.3$ with a $0.5''$ beam (~ 60 AU), covering 329-363 GHz at a spectral resolution of about 0.244 MHz. The whole frequency range is covered by 72 spectral settings of 468.75 MHz each divided into 1920 spectral channels. Each setting was observed by the 12m array for 13 min and by the Atacama Compact array (ACA) for 26 min on source, resulting in a spectral noise level of about $7\text{-}10$ mJy beam $^{-1}$ channel $^{-1}$. Titan and Ceres were used as flux calibrators, the quasar J1517-2422 was used as bandpass calibrator, and the quasar J1625-2527 was used as phase calibrator. Standard calibration through the ALMA software CASA, including flagging of bad datasets and phase-only self calibration, was performed to the obtained data cubes. The 12m array and ACA data sets were further combined and a continuum subtracted dataset with a circular restoring beam of $0.5''$ over the whole spectral window was produced [21].

Organohalogen rotational lines were searched for in spectra extracted from the data cubes half a beam, one beam, and two beams away from the peak continuum position of IRAS 16293B. The corresponding coordinates used for the extraction from a $0.5''$ beam are for position *i*: $\alpha_{J2000} = 16:32:22.60$, $\delta_{J2000} = -24.28.32.7$, for position *ii*: $\alpha_{J2000} = 16:32:22.58$, $\delta_{J2000} = -24.28.32.8$, and for position *iii*: $\alpha_{J2000} = 16:32:22.54$, $\delta_{J2000} = -24.28.33.0$. The Markov Chain Monte Carlo Ensemble sampler *emcee* was used to fit the synthetic spectra of CH₃³⁵Cl at the three extracted positions with the column density, Gaussian line full width half maximum, and excitation temperature taken

as free parameters. A conservative absolute flux uncertainty of 15% was adapted, as well as an effective rms of $14 \text{ mJy beam}^{-1} \text{ channel}^{-1}$ that takes into account the potential presence of low intensity unresolved lines for position *i* and *ii* around source B. A total of 200 walkers and 1000 steps were used with a burn-in period of 100 and 500 steps, adjusted after experimentation for the three extracted spectra. The obtained column densities were corrected to account for the high continuum optical depth. The FWHM obtained are 1.1, 0.9, and $0.5 \pm 0.1 \text{ km s}^{-1}$ for position *i*, *ii*, and *iii* around IRAS 16293B respectively. The derived temperature and line width were further used as inputs to derive the column density of $\text{CH}_3^{37}\text{Cl}$ and the CH_3F upper limit at the different positions away from source B using the same method described for $\text{CH}_3^{35}\text{Cl}$.

The synthetic spectra for the CH_3Cl isotopologues used above were obtained assuming a Boltzmann distribution with the gas at a local thermal equilibrium (LTE) and using the line frequencies, upper level energies, upper state degeneracies, and line intensities available in the JPL catalogue, based on laboratory line identification of the $J''-J' = 13-12$ transition [1]. For CH_3F , a line catalogue was generated using the molecular constants from the literature [2, and references therein], obtained through line identification in the laboratory from the millimeter to the THz. The program SPCAT [3] was used to translate spectroscopic molecular parameters into Hamiltonian terms and solve the Schrödinger equation to predict line positions and strengths for the CH_3F symmetric rotor. We adopted a spin isomer ratio of unity, which is expected in the explored environments here and fits the data.

Using non-LTE escape probability calculations for CH_3OH , it can be shown that LTE is a reasonable assumption for the immediate environment of IRAS16293-2422 due to the high density

($\gtrsim 3 \times 10^{10} \text{ cm}^{-3}$) [21]. Similar estimates cannot be made for CH_3Cl directly since no collisional rate coefficients with H_2 are available, but for the main transitions the high density should ensure that LTE is a good approximation. The CH_3Cl excitation temperature derived from a single J-ladder should be a good proxy for the gas kinetic temperature; however to obtain a complete view of the rotational population distribution would require additional lines from different J level.

The ROSINA-DFMS spectrum was obtained in May 2015 when the HCl abundance in the coma was maximal. The comet was between 1.7 and 1.5 AU from the Sun and the spacecraft at 130-200 km from the comet center. The high mass resolution of the DFMS allows for the distinction of isotopologues with different elemental composition ($m/\Delta m$ of ~ 9000 at FWHM at mass 28 u/e). Thus the signal centered at 49.99 u/e is univocally a fragment containing a combination of one carbon, one chlorine, and three hydrogens. CH_3Cl being a saturated species, direct fragmentation from heavier molecules only yield CH_3Cl upon secondary reaction after the ionizing stage in the DFMS. Since these reactions are extremely inefficient in low pressure environments, we can securely attribute the 49.99 u/e signal to $\text{CH}_3^{35}\text{Cl}$. An abundance ratio can be derived by performing a least-square fit of the spectra using a linear combination of pre-flight measures of the fragmentation responses for the various species present in the coma [18, 22].

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Supplementary Information

Potential formation pathways of methyl chloride

Methyl chloride may form in the gas-phase from its protonated form, CH_4Cl^+ , followed by dissociative recombination with an electron to yield CH_3Cl (+ H). CH_4Cl^+ may in turn form from radiative association between CH_2Cl^+ and H_2 though the rate of this reaction is currently unknown. The analogous association between CH_3^+ and H_2 is slower than collisional rate ($\sim 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 100 K; e.g. [1]) but yet effective at producing CH_5^+ , due to the large abundance of H_2 . CH_2Cl^+ in astrochemical network is mainly the result of the reaction $\text{CH}_3^+ + \text{HCl}$, where CH_3^+ can form through destruction of CH_3OH by ions such as H_3^+ or He^+ . The observed excitation temperature of methyl chloride is similar to the temperature required for CH_3OH sublimation. Thus, CH_3Cl formation in the gas-phase through a CH_3OH and CH_2Cl^+ mediated chemistry is consistent with the observations presented here.

The excitation temperature and spatial extent of CH_3Cl are also consistent with a formation pathway in or on ice mantles followed by sublimation. In cold interstellar environments, most molecules, except for H_2 , can become frozen onto icy dust grains. There, the successive addition of hydrogen and halogen to a carbon atom could result in efficient methyl halide formation, in

tandem with methane and hydrogenated halogens. Based on experiments on CH₃Cl ice desorption [2], CH₃Cl could sublime at temperatures as low as 70 K under protostellar envelope infall conditions. Taking into account interactions with the water ice matrix, including entrapment, the range of possible sublimation temperatures is 70-150 K, *i.e.* consistent with the observed excitation temperature. A detailed physical and chemical modeling is required to explore whether one or both of the proposed formation pathways is at the origin of the current methyl halide observations.

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