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On the formation of deuterated methyl formate in hot corinos

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ABSTRACT

Methyl formate, HCOOCH₃, and many of its isotopologues have been detected in astrophysical regions with considerable abundances. However, the recipe for the formation of this molecule and its isotopologues is not yet known. In this work, we attempt to investigate, theoretically, the successful recipe for the formation of interstellar HCOOCH₃ and its deuterated isotopologues. We used the gas–grain chemical model, UCLCHEM, to examine the possible routes of formation of methyl formate on grain surfaces and in the gas-phase in low-mass star-forming regions. Our models show that radical–radical association on grains are necessary to explain the observed abundance of DCOOCH₃ in the protostar IRAS 16293–2422. H-D substitution reactions on grains significantly enhance the abundances of HCOOCHD₂, DCOOCHD₂, and HCOOCD₃. The observed abundance of HCOOCHD₂ in IRAS 16293–2422 can only be reproduced if H-D substitution reactions are taken into account. However, HCOOCH₂D remain underestimated in all of our models. The deuteration of methyl formate appears to be more complex than initially thought. Additional studies, both experimentally and theoretically, are needed for a better understanding of the interstellar formation of these species.

Key words: astrochemistry-stars: formation-stars: low-mass-ISM: abundances-ISM: molecules.

1 INTRODUCTION

Complex organic molecules (hereafter COMs) are defined as interstellar molecules that are made of six or more atoms (Herbst & van Dishoeck 2009), and accordingly, the simplest COM is methanol, CH₃OH. Several COMs have been detected in cores around massive and low-mass star-forming regions (SFRs) among which are methyl formate (HCOOCH₃, hereafter MF), dimethyl ether (CH₃OCH₃, hereafter DME), and formamide (NH₂CHO) (e.g. Ikeda et al. 2001; Cazaux et al. 2003; Bottinelli et al. 2004; Jørgensen et al. 2005; Bisschop et al. 2007; Kahane et al. 2013), as well as their isotopologues, in particular the deuterated ones, whether mono or multiply.

Most deuterated COMs have been detected towards the lowmass protostar IRAS 16293–2422 A and B (e.g. Coutens et al. 2016; Jørgensen et al. 2016, 2018; Manigand et al. 2019, 2020) among which are those of MF (hereafter DMF). Using IRAM-30 m and JCMT data from the TIMASSS program (Caux et al. 2011), Demyk et al. (2010) reported tentatively the first detection of the mono-deuterated methyl formate DCOOCH₃ with a column density of 6×10^{14} cm⁻² in both IRAS 16293A and IRAS 16293B where the column density of MF is estimated to be 1×10^{16} and 9×10^{15} cm⁻² in both cores, respectively. This data gives a deuterium fractionation ratio of around 6 per cent in IRAS 16293– 2422 A and B. The two singly deuterated forms HCOOCH₂D and DCOOCH₃ were later detected as part of the ALMA-PILS survey (Jørgensen et al. 2016) with D/H ratios of 1.7–2.8 per cent for the component A of IRAS 16293–2422 and 5.8–6.2 per cent for the component B (Jørgensen et al. 2018; Manigand et al. 2019). More recently, Manigand et al. (2019) identified for the first time the doubly deuterated form HCOOCHD₂ using the same survey. The species was detected towards both cores A and B with a D/H ratio of 8 and 12 per cent, respectively.

Species larger than methanol were initially thought to form through chains of warm gas-phase chemistry triggered by the evaporation of mantle CH₃OH during the warming-up phase ($T \ge 100$ K) of the star formation process (e.g. Garrod & Herbst 2006). MF was long thought to be a product of the gas-phase reaction sequence, equation (1) below, which was used in several chemical models such as Millar, Herbst & Charnley (1991), Caselli, Hasegawa & Herbst (1993), and Charnley et al. (1995).

$$\begin{array}{l} H_2 \text{CO} + \text{CH}_3 \text{OH}_2^+ \longrightarrow \text{HCOOCH}_4^+ \\ \text{HCOOCH}_4^+ + \text{e}^- \longrightarrow \text{HCOOCH}_3. \end{array}$$
(1)

However, the first step of reaction (1), $H_2CO + CH_3OH_2^+$, was later proved to be highly inefficient because it possesses a high activation energy of ~ 15 000 K (Horn et al. 2004).

Based on these findings, Garrod & Herbst (2006) and Garrod, Weaver & Herbst (2008) constructed a gas–grain chemical model to study the formation of MF and other related COMs via surface reactions that involve the reactions of heavy radicals, equation (2), when they become mobile during the heating up of the medium by the

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new protostar. The authors found that the formation of HCOOCH₃ is efficient on grains through the reaction

$$HCO + CH_3O \longrightarrow HCOOCH_3, \tag{2}$$

where both reactants are formed on grains through either the successive hydrogenation of CO (e.g. experiments by Watanabe & Kouchi 2002; Watanabe, Shiraki & Kouchi 2003) or the ultraviolet (UV) photodissociation of CH_3OH (e.g. experimental results by Bennett & Kaiser 2007; Watanabe & Kouchi 2008).

Modica & Palumbo (2010) showed that the formation of MF can occur, after cosmic ion irradiation, via the surface two-body reaction

$$CO + CH_3OH \longrightarrow HCOOCH_3.$$
 (3)

The authors also calculated the reaction rate constant for equation (3). These experimental results (the reaction and the rate constant) were implemented in chemical models and proved their efficiency in the formation of MF in the interstellar medium (Occhiogrosso et al. 2011).

In addition, Vasyunin & Herbst (2013) used a full macroscopic Monte Carlo gas-grain model to explore the influence of the formation of grain icy mantle species in a multilayer (layer-by-layer) manner, during the early cold stages of the prestellar evolution, on the gas-phase chemistry triggered by the evaporation of icy mantle species, during the warming-up phase of the protostellar evolutionary stage. The model results showed that species that are essentially formed on grains such as HCOOCH₃ are affected more by the multilayer treatment than other species such as HCOOH and DME that are formed by gas-phase chemistry. The authors attributed their failure in reproducing the observed abundances of gaseous MF to the fact that its formation on grain surfaces in their multilayer simulations is severely affected by the limitation in the photodissociation reactions to the first four layers unlike normal twophase models in which photochemistry occurs throughout the mantle. After that, Ruaud et al. (2015) studied the formation of COMs in cold dense environments by introducing the combination between the Eley-Rideal mechanism and the induced COMs formation on grain surfaces. The findings showed that including these mechanisms into gas-grain models increases the abundances of MF and related species 10 to 100 times compared to models without these mechanisms. More recently, Vasyunin et al. (2017) found that adding the chemical or reactive desorption (RD) to the non-thermal desorption processes, into their gas-grain chemical model, successfully enhances the amount of gaseous COMs produced in the prestellar core L1544 to $\sim 10^{-10}$ relative to the total H nuclei. These abundances depend on the efficiency of the RD mechanism, which in turn, rests on the icy composition of the first layer of the grain mantle where large abundances of CO and its hydrogenation products may reside.

In addition to the formation of HCOOCH₃ on grain surfaces, gas-phase routes have been also investigated in chemical models. Balucani, Ceccarelli & Taquet (2015) succeeded in reproducing the observed abundances of MF and DME in cold regions using pure gas-phase chemical models. In their models, the authors introduced a set of gas-phase reactions, equation (4), that forms MF from DME by converting the latter to the reactive intermediate radical CH₃OCH₂

$$\begin{array}{l} \mathrm{CH}_{3}\mathrm{OH} + \mathrm{OH} & \longrightarrow \mathrm{CH}_{3}\mathrm{O} + \mathrm{H}_{2}\mathrm{O}, \\ \mathrm{CH}_{3}\mathrm{O} + \mathrm{CH}_{3} & \longrightarrow \mathrm{CH}_{3}\mathrm{OCH}_{3} + \mathrm{photon}, \\ \mathrm{CH}_{3}\mathrm{OCH}_{3} + \mathrm{Cl}\left(\mathrm{F}\right) & \longrightarrow \mathrm{CH}_{3}\mathrm{OCH}_{2} + \mathrm{HCl}\left(\mathrm{HF}\right), \\ \mathrm{CH}_{3}\mathrm{OCH}_{2} + \mathrm{O} & \longrightarrow \mathrm{HCOOCH}_{3} + \mathrm{H} \ . \end{array}$$
(4)

The results of Balucani et al. (2015) models showed that gas-phase reactions are capable of reproducing the observed abundances of MF

and DME in cold environments down-to 10 K simulating the cold dense prestellar phase.

For the deuterated counterparts of methyl formate (hereafter DMF), Demyk et al. (2010) suggested that DCOOCH₃ is formed on grain surfaces via radical-radical reactions similar to those forming HCOOCH₃, with HCO replaced by DCO. Bennett & Kaiser (2007) experimental results suggested that the formation of DCO happens by the UV photodissociation of mantle CH₃OD. Other experiments suggested that H-D substitution reactions are important in the formation of partially deuterated methanol (Nagaoka, Watanabe & Kouchi 2005) and formaldehyde (Hidaka et al. 2009). Following the same approach, partially deuterated HCOOCH₃ might result from H-D substitution of HCOOCH₃ during the ice phase change when these grains are warmed up by stellar radiation. Taquet, Charnley & Sipilä (2014) investigated the formation and evolution of deuterated COMs including singly deuterated MF in low-mass SFRs with a multilayer approach. A gas-grain astrochemical model was coupled with a 1D dynamical model of a collapsing core. The model showed that, in the grain mantles, the deuterium fractionation increases towards the ice surface, which would lead to lower deuterium fractionation ratios in the warm inner regions of protostars compared to their cold outer regions. A good agreement is found between the observations and the predicted deuteration of water and COMs, but it fails to reproduce the high deuteration of the multiply deuterated formaldehvde and methanol.

To the best of our knowledge, none of the literature studies focused on investigating the best chemical pathway to form deuterated $HCOOCH_3$ among the proposed gas-phase and surface reactions, but most of them test a specific route and/or reaction mechanism. In this study, we focus on the formation of deuterated $HCOOCH_3$ in low-mass SFRs using a theoretical approach. We test both gas-phase and grain surface chemistries to evaluate their efficiency in forming these isotopologues.

The description of the chemical model used for this study is given in Section 2. We present and discuss our results and findings in Section 3. Finally, we summarize our main conclusions and remarks in Section 4.

2 THE MODEL

2.1 The physical and chemical model

In order to understand which chemical pathway is most responsible for the formation of the different forms of DMF in SFRs, we used the open-source publicly available astrochemical code UCLCHEM (Holdship et al. 2017).¹ UCLCHEM is a time-dependent, gas-grain chemical model which computes the fractional abundances of the species (with respect to the total number of H in all forms) by solving a set of rate equations. UCLCHEM has been used in previous studies of COMs in SFRs (e.g. Coutens et al. 2018; Quénard et al. 2018). However, we note that for simplicity, we neglect the temperaturedependent diffusion treatment of Langmuir-Hinshelwood reactions that is standard for UCLCHEM (Quénard et al. 2018) and instead use grain reactions with fixed rates. Besides the reactions we discuss below, most of the surface reactions included in this work involve mainly simple hydrogenation reactions, with hydrogen moving freely on the grains; hence the temperature dependence is not very important. Most of the non-hydrogenation reactions we include in the network are barrier-less (see Table 2) so, again, our simplification

¹link to UCLCHEM: https://uclchem.github.io/uclchem.html

seems justified. This allows us to investigate whether a path is viable without considering a large number of unknowns such as binding energy and energy barriers.

Briefly, the fractional abundances are computed in two successive phases; a collapsing phase (Ph I) followed by a warming-up phase (Ph II) which is representative of the hot cores we wish to model. In Ph I, we model the evolution of a diffuse atomic gas which undergoes a free-fall collapse (following Rawlings et al. 1992) until it reaches a final density suitable for a hot core at a constant temperature of 10 K. During this phase, the chemistry takes place both in the gas-phase and on grain surfaces with active non-thermal desorption processes as described in Roberts et al. (2007). As a result, this phase provides initial fractional abundances for Ph II that are realistic and consistent with the chemical network rather than assumed.

Once the gas reaches its final density, the second phase of the model starts in order to simulate the effect of the radiation emitted by the new star on the chemical evolution of the dense gas. This radiation gradually heats up its surrounding medium, based on its mass, and causes the thermal desorption of mantle species in a temperature-(hence time) dependent manner according to the experimental work by Collings et al. (2003). For this reason, Ph II is known as the warming-up phase (Viti et al. 2004). In this work, as in Viti et al. (2004) and in Awad et al. (2010), the dust temperature increases as a function of time according to the following equation:

$$T_{\rm dust} = 10.0 + (A \times t^B),\tag{5}$$

where the constant and the exponent were empirically fitted for a 1 solar mass star (see Awad et al. 2010 for full details). Sublimation of mantle species influences the evolution of the gas-phase chemistry during this phase. We note the exact temperature evolution of this phase can be important for temperature-dependent grain chemistry (Garrod 2013). However, as noted previously, we do not believe our surface reaction rates depend strongly on the temperature in this case. The initial chemical abundances of this stage (Ph II) are those obtained from the final time step of the collapsing phase (Ph I).

In this work, the basic gas-phase chemical network is taken from the KIDA 2014 rate-file² (Wakelam et al. 2015); updated to include the MF formation route proposed by Balucani et al. (2015); equation (4). We generated the deuterium network from this gasphase network following the recipe described in Aikawa et al. (2012) and Furuya et al. (2013). Nuclear spin states of H_2 , H_3^+ , and their deuterated isotopologues are included and taken from Hincelin et al. (2014). The grain chemical network relies on simple hydrogenation and deuteration of depleted species, during the collapsing phase, in addition to simple two-body reactions to account for the formation of MF and its deuterated counterparts; see equations (2 and 3). The binding energy of HCOOCH₃ was taken from the recent experimental work by Burke et al. (2015) while we revised all of the desorption energy of our species set from Wakelam et al. (2017). For all the models performed in this study, the chemical network features a total of 8772 reactions, both in the gas-phase and on grain surfaces, linking 252 species (52 of which are mantle species). Differences between the models lie in the active formation route of DMF, but not on the physical conditions which we hold constant for all the performed models.

The species in the network used for this study include all deuterated isotopes of a given species up to the third level (i.e. 3 D atoms per

Table 1. Initial elemental abundances with respect to the total H content (taken from Asplund et al. 2009), and physical conditions adopted in our models.

Initia	l abundances	Physical parameters				
Helium	8.50×10^{-2}	Initial density (cm ⁻³)	400			
Carbon	2.69×10^{-4}	Initial temperature (K)	10			
Oxygen	4.90×10^{-4}	Final density (cm ⁻³)	10^{8}			
Nitrogen	6.76×10^{-5}	Final temperature (K)	100			
Chlorine	3.16×10^{-7}	Core radius (AU)	150			
Fluorine	3.63×10^{-8}	Core mass (M_{\odot})	1			
HD	1.50×10^{-5}	[†] Depletion	full			

[†]By full depletion we mean that by the end of collapsing phase more than 90 per cent of the gas is accreted on to grain surfaces.

molecule). The initial elemental abundance of atomic D is set to 10^{-5} to reflect the standard interstellar D/H ratio (Oliveira et al. 2003). The formation of HD on the grains is assumed to occur at the same rate as H₂. However, Kristensen et al. (2011) found that the abundance of D₂ molecules on the surface is an order of magnitude higher than HD. Thus, we assume D₂ forms at a rate tens times that of HD and H₂. Moreover, we adopt the statistical value of molecular hydrogen ortho-to-para ratio (H₂ OPR) to be 3.

Table 1 lists the initial chemical elemental abundances and physical parameters used for the performed grid of models. The description of the grid of models we ran is given below in Section 2.2.

2.2 The grid of models

For the purpose of this work, we ran eight models, in addition to the reference model (**RM**), to investigate which formation routes of DMF are capable of reproducing the observed abundances in the warm inner regions of low-mass SFRs. Apart from **RM**, we name each model as 'M + number', where the number refers to the active routes of DMF formation and corresponds to those listed in Table 2.

The RM, in this study, is the model in which none of the new included routes (equations 2, 3, and 4) are active and hence it is somehow chemically equivalent to the model described in Awad et al. (2014). In model M1, the formation of MF and DMF is active through the surface two-body reaction ($CH_3OH + CO$; equation 3) from Occhiogrosso et al. (2011). For model M2, the formation of these species occurs through the surface radical-radical reaction $(CH_3O + HCO; equation 2)$ from Garrod & Herbst (2006) while they are formed by the gas-phase scheme (equation 4; taken from Balucani et al. 2015) in model M3. These three different routes of formation in the three models are denoted R1, R2, and R3, respectively, in Tables 2 and 3. In reality, the formation of species often takes place through a combination of more than one route. For this reason, we performed a set of three models in which each model combines more than one route to form MF and its DMF. These models are model M12 in which the formation involves only surface reactions (pathways R1 and R2), and models M13 and M23 that combine gas- and solid-phase routes. A model in which the three proposed formation schemes are activated is model M123.

Finally, we ran model **Mex** that includes some simple enrichment mechanism such as the H-D exchange (substitution) reactions (listed in Table 4) that have been proven, experimentally, to be important in enhancing the deuteration of interstellar species (e.g. Nagaoka et al. 2005; Hidaka et al. 2009; Oba et al. 2016). The lack of the inclusion of these reactions in chemical models led to a deficiency in the relative abundances of HCOOCH₂D and HCOOCHD₂ with respect to MF as claimed by Manigand et al. (2019).

²KIDA website: http://kida.obs.u-bordeaux1.fr

Table 2. Summary of the main grid of models, the new pathways included into our chemical network to form MF, and their rate coefficients (α , β , and γ). The rate constants (k, in cm³ s⁻¹) are calculated using the UMIST formula $k = \alpha (T/300)^{\beta} exp(-\gamma/T)$ as described in McElroy et al. (2013). These reactions are used to generate the pathways of the formation of the different forms of DMF and their rate constants are calculated statistically following Aikawa et al. (2012).

				Sing	le Pathway Models				
Model	Route	Re1 ¹	Re2 ¹	-	P1 ¹	P2 ¹	α	β	γ Remarks
M1	R1	mCH ₃ OH	mCO	\rightarrow	mHCOOCH3		6.20×10^{-18}	0	0 Occhiogrosso et al. 2011
		mCH ₃ OD	mCO	\rightarrow	mDCOOCH3		1.55×10^{-18}	0	0 This work
		mCH ₃ OD	mCO	\rightarrow	mHCOOCH2D		4.65×10^{-18}	0	0
		mCH ₂ DOH	mCO	\rightarrow	mDCOOCH3		1.55×10^{-18}	0	0
		mCH ₂ DOH	mCO	\rightarrow	mHCOOCH2D		4.65×10^{-18}	0	0
		mCH ₂ DOD	mCO	\rightarrow	mDCOOCH2D		3.10×10^{-18}	0	0
		mCH ₂ DOD	mCO	\rightarrow	mHCOOCHD ₂		3.10×10^{-18}	0	0
		mCHD ₂ OH	mCO	\rightarrow	mHCOOCHD ₂		3.10×10^{-18}	0	0
		mCHD ₂ OH	mCO	\rightarrow	mDCOOCH2D		3.10×10^{-18}	0	0
M2	R2	mCH ₃ O	mHCO	\rightarrow	mHCOOCH3		1	0	0 Garrod et al. 2008
		mCH ₃ O	mDCO	\longrightarrow	mDCOOCH3		1	0	0 This work
		mCH ₂ DO	mHCO	\longrightarrow	mHCOOCH2D		1	0	0
		mCH ₂ DO	mDCO	\longrightarrow	mDCOOCH2D		1	0	0
		mCHD ₂ O	mHCO	\longrightarrow	mHCOOCHD ₂		1	0	0
$M3^2$	R3	CH ₃ OH	OH	\rightarrow	CH ₃ O	H_2O	3.60×10^{-12}		0 Antiñolo et al. 2016
								-1	
		CH ₃ O	CH ₃	\longrightarrow	CH ₃ OCH ₃	photon	3×10^{-10}	0	0 Balucani et al. 2015
		CH ₃ OCH ₃	Cl	\longrightarrow	CH ₃ OCH ₂	HCl	2×10^{-10}	0	0 Balucani et al. 2015
		CH ₃ OCH ₃	F	\longrightarrow	CH ₃ OCH ₂	HF	2×10^{-10}	0	0 Balucani et al. 2015
		CH ₃ OCH ₂	0	\longrightarrow	HCOOCH ₃	Н	2×10^{-10}	0	0 Balucani et al. 2015
		The deuterated	reactions a	re listed ir	1 Table <mark>3</mark> .				
				Mult	ipathways Models	5			
M12	R1 + R2	The formation o	f MF and DI	MF is dom	inated by surface ro	outes.			
M13	R1 + R3	The model com	bines gas and	l surface fo	ormation routes.				
M23	R2 + R3	The model com	bines gas and	l surface fo	ormation routes.				
M123	R1 + R2 + R3	The model repre	esents the ful	l set of for	mation pathways or	n grain surfaces	and in the gas-pl	nase.	
Mex	Rex	The set of reacti	ons we adde	d to our ch	emical network is	listed in Table 4			Oba et al. 2016

¹The prefix '**Re**, **P**, and **m**' refers to reactants, products, and mantle species, respectively.

²For the **'CH₃OH + OH'** reaction, the values of the rate coefficients (α , β , γ) represent the case T \leq 100 K. When T > 100 K, these values are 2.85 × 10⁻¹², 0, and 345, respectively (Atkinson et al. 2006).

We adopt the statistical branching ratio $DCOOCH_3$:HCOOCH₂D = 1:3 (Hincelin et al. 2014).

Table 2 lists all the models we ran and their associated MF and DMF formation pathways. For the combined models, we indicate the routes included by showing their label indicated in column 2 of the table; e.g. for model **M12** the activated routes for formation are R1 and R2.

3 RESULTS AND DISCUSSION

The time evolution of the fractional abundances during the warmingup phase (Ph II) of MF and its deuterated isotopologues (DMF) are shown in Figs 1 to 3 under the physical conditions of a typical $1 M_{\odot}$ hot corino. Different curves in each figure indicate different chemical models (see figure keys and Table 2). In all the plots, different models are displayed with different line styles where the (RM is denoted by dash-dotted lines; thick straight lines, parallel to the x-axis, represent the upper limits of the abundances of MF and DMF derived for IRAS 16293 B (see Section 3.2). In addition, if a species peaks above 1×10^{-12} in abundance and has been observed, we limit y-axis to 1×10^{-12} , otherwise the lower limit of the y-axis is set to 1×10^{-20} . Tables 5 and 6 summarize the predicted abundances of MF and its different forms and the associated D/H ratios during the warming up phase (Ph II) at time $t = 1-2 \times 10^5$ yr. For comparison, the observed values in the protostellar object IRAS 16293-2422 are also indicated.

3.1 Sensitivity to formation pathways

As illustrated in the figures, the obtained evolutionary trends of the species, from all performed models, show similarities. All the species are detectable at times around 10^5 yr that correspond to the time of their thermal evaporation from grains. At these times, the fractional abundances increase until they reach a maximum value. After that, the abundances decline until they become undetectable at times around $(3-4) \times 10^5$ yr. None of our single pathway models (**M1**, **M2**, and **M3**) shown in Fig. 1 nor the **RM** is able to form HCOOCD₃ with detectable abundances.

Model M2, dash lines in Fig. 1, produces significantly more DCOOCH₃ and DCOOCH₂D (1–2 orders of magnitude), and it is capable of forming very small amounts of HCOOCHD₂ and DCOOCHD₂ than the other models. This shows the efficiency of radical–radical reactions (route R2) in the formation of isotopologues of COMs.

In model **M3**, where the formation of MF and DMF occur via gas-phase chemistry, we found that the abundances of MF and both of its mono-deuterated forms, DCOOCH₃ and HCOOCH₂D, remain in the gas for longer times compared to the other models, and the abundance of MF remain relatively high for times up to $\sim 2.5 \times 10^6$ yr. The analysis of HCOOCH₃, DCOOCH₃, and HCOOCH₂D showed that, at these longer times, the species are mainly formed in the gas-phase via oxidisation reactions of CH₃OCH₂, CH₃OCHD,

Table 3. A list of the deuterated pathways of the reaction set of R3 used in the network of Model M3 as given in Table 2.

	Single Pathway Models - Deuteration of R3 in Table 2								
Model	¹ Re1	Re2		P1	P2	α	β	γ	Remarks
² M3	CH ₃ OH	ОН	\rightarrow	CH ₃ O	H ₂ O	3.60×10^{-12}	1	0	$T \le 100$ K, Antiñolo et al. 2016
	CH ₃ OH	OD	\rightarrow	CH ₃ O	HDO	3.60×10^{-12}	-1	0	This work
	CH ₃ OD	ОН	\rightarrow	CH ₃ O	HDO	3.60×10^{-12}	-1	0	
	CH ₃ OD	OD	\rightarrow	CH ₃ O	D_2O	3.60×10^{-12}	-1	0	
	CH ₂ DOH	OH	\rightarrow	CH ₂ DO	H_2O	3.60×10^{-12}	-1	0	
	CH ₂ DOH	OD	\rightarrow	CH ₂ DO	HDO	3.60×10^{-12}	-1	0	
	CHD ₂ OH	ОН	\rightarrow	CHD ₂ O	H_2O	3.60×10^{-12}	-1	0	
	CHD ₂ OH	OD	\rightarrow	CHD ₂ O	HDO	3.60×10^{-12}	-1	0	
	CH ₂ DOD	OH	\rightarrow	CH ₂ DO	HDO	3.60×10^{-12}	-1	0	
	CH ₂ DOD	OD	\rightarrow	CH ₂ DO	D_2O	3.60×10^{-12}	-1	0	
	CH ₃ O	CH ₃	\longrightarrow	CH ₃ OCH ₃	photon	3×10^{-10}	0	0	Balucani et al. 2015
	CH ₂ DO	CH ₃	\longrightarrow	CH ₂ DOCH ₃	photon	3×10^{-10}	0	0	This work
	CH ₃ O	CH ₂ D	\longrightarrow	CH ₂ DOCH ₃	photon	3×10^{-10}	0	0	
	CH ₂ DO	CH_2D	\longrightarrow	CH ₂ DOCH ₂ D	photon	3×10^{-10}	0	0	
	CH ₃ OCH ₃	Cl	\longrightarrow	CH ₃ OCH ₂	HCl	2×10^{-10}	0	0	Balucani et al. 2015
	CH ₂ DOCH ₃	Cl	\longrightarrow	CH ₂ DOCH ₂	HCl	1×10^{-10}	0	0	This Work
	CH ₂ DOCH ₃	Cl	\longrightarrow	CH ₃ OCH ₂	DCl	3.33×10^{-11}	0	0	
	CH ₂ DOCH ₃	Cl	\longrightarrow	CH ₃ OCHD	HCl	6.67×10^{-11}	0	0	
	CH ₂ DOCH ₂ D	Cl	\longrightarrow	CH ₂ DOCHD	HCl	1.33×10^{-10}	0	0	
	CH ₂ DOCH ₂ D	Cl	\longrightarrow	CH ₂ DOCH ₂	DCl	6.67×10^{-11}	0	0	
	CH ₃ OCH ₃	F	\longrightarrow	CH ₃ OCH ₂	HF	2×10^{-10}	0	0	Balucani et al. 2015
	CH ₂ DOCH ₃	F	\longrightarrow	CH ₂ DOCH ₂	HF	1×10^{-10}	0	0	This Work
	CH ₂ DOCH ₃	F	\longrightarrow	CH ₃ OCH ₂	DF	3.33×10^{-11}	0	0	
	CH ₂ DOCH ₃	F	\longrightarrow	CH ₃ OCHD	HF	6.67×10^{-11}	0	0	
	CH ₂ DOCH ₂ D	F	\longrightarrow	CH ₂ DOCHD	HF	1.33×10^{-10}	0	0	
	CH ₂ DOCH ₂ D	F	\longrightarrow	CH ₂ DOCH ₂	DF	6.67×10^{-11}	0	0	
	CH ₃ OCH ₂	0	\longrightarrow	HCOOCH ₃	Н	2×10^{-10}	0	0	Balucani et al. 2015
	CH ₂ DOCH ₂	0	\longrightarrow	HCOOCH ₂ D	Н	2×10^{-10}	0	0	This Work
	CH ₃ OCHD	0	\rightarrow	DCOOCH ₃	Н	1×10^{-10}	0	0	
	CH ₃ OCHD	0	\rightarrow	HCOOCH ₃	D	1×10^{-10}	0	0	
	CH ₂ DOCHD	0	\longrightarrow	DCOOCH ₂ D	Н	1×10^{-10}	0	0	
	CH ₂ DOCHD	0	\longrightarrow	HCOOCH ₂ D	D	1×10^{-10}	0	0	

¹The prefix **'Re, P, and m'** refers to reactants, products, and mantle species, respectively.

²For the **'CH₃OH + OH'** reaction and its deuterated pathways at T > 100 K, the values of the rate coefficients α , β , and γ are 2.85 × 10⁻¹², 0, and 345, respectively, according to Atkinson et al. (2006).

and CH₂DOCH₂, respectively. It also revealed that the main source of destruction of MF and DMF are the HCO⁺ and DCO⁺ ions which compete with H₃O⁺ up to 3.2×10^5 yr, after which the abundance of H₃O⁺ becomes around 30 times higher than them, and hence it dominates the destruction of these species. For the time interval up to $\sim 2 \times 10^5$ yr, the formation rate of the three species is 10–20 times higher than that of the destruction, and therefore, we see an increase in their abundance. After that and until 3.2×10^5 yr, the formation and destruction rates of the three species become comparable and hence, we see the plateau feature in the plots. When the abundance of H₃O⁺ becomes higher than that of the main parents, at 3.2×10^5 yr, the destruction rate increases leading to a decline of the molecular abundances until they disappear from the medium at a time of $\sim 4 \times 10^5$ (for mono-DMFs) or 2.5×10^6 yr (for MF).

We defined the multipathway models to be those in which the chemical network includes more than one formation route of MF and DMF; see Table 2. Model calculations are represented in Fig. 2 together with those of the RM. The results show that the peak abundances of most of the species are not significantly affected by combining more than one formation route. Models **M12**, **M23**, and **M123** (where route R2 is common) show the highest abundances. These findings support the results by Garrod et al. (2008) in which the authors showed that radical–radical reactions may dominate the formation process of complex molecules on grain surfaces in dense interstellar regions. Indeed, the chemical analysis of DCOOCH₃ and DCOOCH₂D in models **M12**, **M23**, and **M123** revealed that the surface radical–radical route (R2) dominates their formation pathways during both phases Ph I and Ph II. During the cold collapsing phase (Ph I), where deuteration may occur efficiently,

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Table 4.	List of exchange	reactions we addee	l to our network	for model Mer	x following	Oba et al. (2016).
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Model	¹ Re1	Re2		P1	P2	α	β	γ	Remarks
Mex	mHCOOCH3	mHDO	\rightarrow	mHCOOCH ₂ D	mH ₂ O	0.5	0	0	
	mHCOOCH3	mHDO	\longrightarrow	mDCOOCH3	mH_2O	0.5	0	0	
	mHCOOCH3	mD_2O	\longrightarrow	mHCOOCH2D	mHDO	0.5	0	0	
	mHCOOCH3	mD_2O	\longrightarrow	mDCOOCH3	mHDO	0.5	0	0	
	mHCOOCH2D	mH_2O	\longrightarrow	mHCOOCH3	mHDO	1	0	0	
	mHCOOCH2D	mHDO	\longrightarrow	mHCOOCH3	mD_2O	0.2	0	0	
	mHCOOCH2D	mHDO	\longrightarrow	mHCOOCHD ₂	mH_2O	0.6	0	0	
	mHCOOCH2D	mHDO	\longrightarrow	mDCOOCH2D	mH_2O	0.2	0	0	
	mHCOOCH2D	mD_2O	\longrightarrow	mHCOOCHD ₂	mHDO	0.75	0	0	
	mHCOOCH2D	mD_2O	\longrightarrow	mDCOOCH2D	mHDO	0.25	0	0	
	mHCOOCHD ₂	mH_2O	\longrightarrow	mHCOOCH2D	mHDO	1	0	0	
	mHCOOCHD ₂	mHDO	\longrightarrow	mHCOOCD3	mH_2O	0.2	0	0	
	mHCOOCHD ₂	mHDO	\longrightarrow	mDCOOCHD ₂	mH_2O	0.2	0	0	
	mHCOOCHD ₂	mHDO	\longrightarrow	mHCOOCH2D	mD_2O	0.6	0	0	
	mHCOOCD3	mH_2O	\longrightarrow	mHCOOCHD ₂	mHDO	1	0	0	
	mHCOOCD3	mHDO	\longrightarrow	mHCOOCHD ₂	mD_2O	1	0	0	
	mDCOOCH3	mH_2O	\longrightarrow	mHCOOCH3	mHDO	1	0	0	
	mDCOOCH3	mHDO	\longrightarrow	mHCOOCH3	mD_2O	0.25	0	0	
	mDCOOCH3	mHDO	\longrightarrow	mDCOOCH2D	mH ₂ O	0.75	0	0	
	mDCOOCH3	mD_2O	\longrightarrow	mDCOOCH2D	mHDO	1	0	0	
	mDCOOCH2D	mH_2O	\rightarrow	mHCOOCH2D	mHDO	0.25	0	0	
	mDCOOCH2D	mH_2O	\rightarrow	mDCOOCH3	mHDO	0.75	0	0	
	mDCOOCH2D	mHDO	\longrightarrow	mHCOOCH2D	mD_2O	0.2	0	0	
	mDCOOCH2D	mHDO	\rightarrow	mDCOOCH3	mD_2O	0.4	0	0	
	mDCOOCH2D	mHDO	\longrightarrow	mDCOOCHD ₂	mH ₂ O	0.4	0	0	
	mDCOOCH2D	mD_2O	\longrightarrow	mDCOOCHD ₂	mHDO	1	0	0	
	mDCOOCHD ₂	mH_2O	\rightarrow	mHCOOCHD ₂	mHDO	0.25	0	0	
	mDCOOCHD ₂	mH_2O	\longrightarrow	mDCOOCH2D	mHDO	0.75	0	0	
	mDCOOCHD ₂	mHDO	\longrightarrow	mHCOOCHD ₂	mD_2O	0.25	0	0	
	mDCOOCHD ₂	mHDO	\longrightarrow	mDCOOCH2D	mD_2O	0.75	0	0	

¹The prefix 'Re, P, and, m' refers to reactants, products, and mantle species, respectively.

the analysis showed that the formation rates of these species in the three models are at least 100 times higher than their destruction rates, especially towards the end of the collapse. During these late times, the density of the core becomes more than 10^6 cm⁻³, which weakens the non-thermal evaporation processes of mantle species. This would allow longer residence time for the parent molecules of these species on grain surfaces and hence would increase their yield. As a consequence, when DCOOCH₃ and DCOOCH₂D evaporate from grain mantles in the warming up phase, they enrich the medium with higher abundances compared to other models.

The results of the model, Mex, with those from M12 (only surface pathways) and M123 (full gas-grain pathways), are illustrated in Fig. 3. We observe for Mex an increase in the molecular abundances of the forms of multiple DMF (DCOOCH₂D, HCOOCHD₂, $DCOOCHD_2$, and $HCOOCD_3$) and a significant decrease (at the time of evaporation) in the abundance of DCOOCH₃ (2-3 orders of magnitude). HCOOCH₂D is insensitive to the inclusion of the H-D exchange reactions. The chemical analysis of the results of model Mex revealed that DCOOCH3 forms DCOOCH2D that acts as the parent molecule of DCOOCHD₂. This sequence shows that the deuteration occurs for the CH₃ group. In addition, the same analysis was obtained for HCOOCD₃ which is the daughter of HCOOCHD₂. These results are inline with those obtained experimentally by Nagaoka et al. (2005). The authors reported that the H-D substitution occur in the CH₃ group of methanol (CH₃OH) and not on the OH group and that is why they did not observe any molecules on the form Me- d_n -OD, where Me- d_n represents the deuteration in CH₃ group with n = 0-3. Our model shows that, in addition to radicalradical reactions on grain surfaces, H-D substitution reactions can play a major role in the enrichment of the medium with deuterated complex molecules.

3.2 Comparison with observations

This work focuses on the formation pathways of the deuterated isotopologues of MF under physical and chemical conditions comparable to those observed in hot corinos, in particular the one in the Class 0 protostar IRAS 16293–2422 (hereafter IRAS 16293). In this section, we are going to discuss our model calculations in light of the most recent ALMA PILS observations of MF and DMF in IRAS 16293 (Jørgensen et al. 2018; Manigand et al. 2019). We may also shed light on these species in other low-mass protostellar objects such as NGC 1333 IRAS4A (Bottinelli et al. 2004) and SVS13-A (Bianchi et al. 2019).

The fractional abundances, x(X), obtained with our chemical models are expressed with respect to the total hydrogen density of the core, n_H . In order to compare our results with observations, we converted the observed column densities of the species, N(X), into fractional abundances with respect to the total hydrogen density. For IRAS 16293B, Jørgensen et al. (2016) derived an H₂ column density N(H₂) of $\gtrsim 1.2 \times 10^{25}$ cm⁻². We computed the fractional abundances of MF and DMF in IRAS 16293B by dividing the column densities determined by Jørgensen et al. (2018) and Manigand et al. (2019) by the lower limit of N(H₂). The abundance is multiplied by two to take into account the fact that the position analysed in these studies is shifted by one beam offset with respect to the continuum peak position (Jørgensen et al. 2016, 2018). These fractional abundances



Figure 1. The time evolution of the computed fractional abundances of MF and DMF in models in which we test the effect of including a single formation pathway to the network either on grain surfaces, M1 and M2, or in the gas-phase, M3. The results are compared to the RM, dash-dotted line, where neither of the three routes is included; see figure key. Straight grey lines represent the upper limits of the MF and DMF abundances in IRAS 16293B (Manigand et al. 2019; Jørgensen et al. 2016); see Table 5.

Table 5. Comparison between the observed fractional abundances of MF and DMF in the protostellar object IRAS 16293B and those obtained with our models after the evaporation of the grain ices (t $\sim 1-2 \times 10^5$ yr) in Ph-II. a(b) means a $\times 10^b$.

Species	[†] IRAS 16293B	This work	Corresponding Model
(1)HCOOCH ₃	≲ 2.2 (-8)	1.4 (-8)	All
(1)DCOOCH ₃	≲ 1.3 (-9)	9 (-10)	M2, M12
(1)HCOOCH ₂ D	≲ 4.0 (-9)	≤ 4.0 (-11)	All
⁽²⁾ HCOOCHD ₂	≲ 9.1 (-10)	≤ 4.0 (-13)	All except Mex
		1.7 (-9)	Mex
⁽³⁾ CH ₃ OH	≲ 8.3 (-7)	2.3 (-6)	RM, M1, M2, M12
		3.0 (-7)	Mex, M3, M13, M23, M123

Notes.[†]Observations are converted into fractional abundances with respect to the total number of H as described in Section 3.2.

References: (1) Jørgensen et al. (2018), (2) Manigand et al. (2019), (3) Jørgensen et al. (2016).

Table 6. Comparison between the DMF-to-MF column density ratios in IRAS 16293 and the theoretically calculated ratios during Ph-II at a time of $1-2 \times 10^5$ yr. The last two columns of the table list the ratios obtained with the model by Taquet et al. (2014). a(b) means $a \times 10^b$.

Abundance ratios	IRAS 16293		This Work	Corresponding Model	Other Model ⁽³⁾		
	A ⁽¹⁾	B ^(1, 2)			Early time	Late time	
DCOOCH ₃ /HCOOCH ₃	1.7 per cent	5.7 per cent	6.2 per cent	M2, M12	9.2 per cent	0.0025 per cent	
HCOOCH ₂ D/HCOOCH ₃	8.5 per cent	18.0 per cent	0.3 per cent	All	21 per cent	0.65 per cent	
	2.0 per cent	4.2 per cent	0.003 per cent	All except Mex	2.4 per cent	0.0016 per cent	
[†] HCOOCHD ₂ /HCOOCH ₃		*	*		•	*	
			12 per cent	Mex			
[‡] HCOOCH ₃ /CH ₃ OH	2.1 per cent	2.7 per cent	0.6 per cent	RM, M1, M2, M12	_	_	
			4.7 per cent	Mex, M3, M13, M23, M123	—	_	

[†]Taken from Table 2 in Manigand et al. (2019).

^{\ddagger} The observed ratio in IRAS 16293A is taken from Manigand et al. (2020) while for IRAS 16293B, we computed the ratio by adopting N(HCOOCH₃) and N(CH₃OH) observations from Manigand et al. (2019) and Jørgensen et al. (2016), respectively.

References: (1) Manigand et al.(2019), (2) Jørgensen et al. (2018), (3) Taquet et al. (2014).

are then computed with respect to the total H following a simple expression $n(X)/n_{\rm H} = 0.5 n(X)/n_{\rm H_2}$ (Pety et al. 2005).

The abundance of HCOOCH₃ (with respect to H) is estimated to be $\leq 2.2 \times 10^{-8}$ in IRAS 16293 (Jørgensen et al. 2018; Manigand et al. 2019). All of our models predict abundances in agreement with the observations (~ 1.4×10^{-8} during the warming up phase at t~ $1-2 \times 10^5$ yr). These results are also inline with the observed abundances in NGC 1333 IRAS4A (4 × 10^{-8} ; Bottinelli et al. 2004) and in the more chemically evolved Class I protostar SVS13-A (2.2×10^{-8} ; Bianchi et al. 2019).

None of the computed models can reproduce the observed abundances of MF and all the detected forms of DMF, at once, during the warming-up phase of the hot corino. All the models reproduce well the observed abundances of MF, but only the models including R2 (M2, M12, M23, and M123) and Mex are able to reproduce the observed amounts of DCOOCH₃ and HCOOCHD₂, respectively. In addition, all of our models predict abundances of HCOOCH₂D that are about 100 times lower than the observations. More details can be found below for the different isotopologues (see also Tables 5 and 6).

DCOOCH₃ was detected in IRAS 16293 with an abundance of $\leq 1.3 \times 10^{-9}$ and a D/H ratio of 1.7 per cent in IRAS 16293A and 5.7 per cent in IRAS 16293B (Jørgensen et al. 2018; Manigand et al. 2019). Models **M2**, **M12**, **M23**, and **M123** that include a formation through radical–radical association on grains (R2), reproduce well these observations, once the species evaporate from grains at 1.1×10^5 yr. These models predict abundances of 9×10^{-10} – 5×10^{-9} at a time of $\sim 1-2 \times 10^5$ yr (when MF best-fitting observations).

The DCOOCH₃/HCOOCH₃ abundance ratios predicted by Models **M2** and **M12** (\sim 6.3 per cent) is in perfect agreement with the value measured towards IRAS 16293B (5.7 per cent) and only 3.7 times higher than the ratio determined in IRAS 16293A (Jørgensen et al. 2018; Manigand et al. 2019) while the ratios estimated from the other models (**M23** and **M123**; 35 per cent) are about six times larger than observations for IRAS 16293B. These results indicate the importance of radical–radical reactions, route R2 in Table 2, in the formation of this molecule. It also implies that R2 dominates the other chemical routes of formation of DCOOCH₃ as reflected by the comparable abundances predicted in the four models that best fit the observations (Models **M2**, **M12**, **M23**, and **M123**). It is worth noting that the DCOOCH₃/HCOOCH₃ ratios for models **M2** and **M12** are inline with the predictions of the so-called early-time model (\sim 9.2 per cent at 1.1 \times 10⁵ yr) by Taquet et al. (2014).

The predicted abundances of HCOOCH₂D and HCOOCHD₂ are found to be lower than the observations by a factor of 10^2 and 10^3 , except for the model **Mex** for HCOOCHD₂ which is discussed later. HCOOCH₂D is detected with an abundance of $\leq 4 \times 10^{-9}$, while the models predict abundances of $\leq 4 \times 10^{-11}$. Similarly for HCOOCHD₂, which has an observed abundance of $\leq 9 \times 10^{-10}$, while the models (except for Mex) predict no more than 4×10^{-13} . The abundances ratios of HCOOCHD₂ with respect to MF are 8 and 18 per cent and those of HCOOCHD₂ are 2 and 4 per cent, in IRAS 16293A and B, respectively. The equivalent ratios predicted by our models are significantly lower (0.3 per cent for HCOOCH₂D and 0.003 per cent for HCOOCHD₂), which would mean that some deuteration reaction pathways are missing in our network. In comparison, Taquet et al. (2014) predicted for HCOOCH₂D an



Figure 2. Similar to Fig. 1, but for models that examine combining more than one formation pathway; see Table 2. The results are also compared to the RM denoted by dash-dotted line.



Figure 3. The chemical evolution of MF and DMF in hot corinos assuming that only H-D substitution/exchange reactions are their formation routes. The results are compared to the abundances of these species in models where the formation is dominated by surface chemistry, M12, or models that reflect the mutual gas–grain interaction pathways, M123; see figure key.

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abundance ratio with respect to MF of 21 per cent at a time of 1.1×10^5 yr but much smaller (0.6 per cent) and comparable to our results at a time of 2×10^5 yr. Based on these results, the radical-radical reactions included in our models are not sufficient to explain the observed abundances of these two molecules.

When introducing the H-D exchange reactions (Table 4, Model **Mex**), we see a surprising enhancement of the abundance of HCOOCHD₂ (~ 1.7×10^{-9} at 1.5×10^{5} yr) which is about 4 orders of magnitude higher than the results of the other models in the grid. The predicted abundance is twice the observed value in IRAS 16293B ($\leq 9 \times 10^{-10}$), but it decreases with time and at a time of 2.5×10^{5} yr, a good agreement is obtained with respect to the observed value. As a consequence, we obtain a high HCOOCHD₂/MF abundance ratio of 12 per cent at a time of $1-2 \times 10^{5}$ yr. The H-D substitution reactions can explain the high abundance of HCOOCHD₂ but they are, however, not sufficient to reproduce the observed abundance of HCOOCH₂D.

In summary, the comparison of our models with the observations of IRAS 16293 shows that the formation of the different forms of DMF relies on both radical-radical associations and H-D exchange reactions on grains. Surface reactions involving radicals (R2; Garrod et al. 2008) are sufficient to explain the observed abundance of DCOOCH₃, but H-D exchange reactions are also necessary to reproduce the abundance of the doubly deuterated form HCOOCHD₂ in IRAS 16293. It should be noted that H-D exchange reactions would also imply high abundances of DCOOCHD₂, which could consequently be detectable. To the best of our knowledge, this isotopologue is, however, not available in the spectroscopic data bases. The deuteration pathways of MF may be more complex than expected given the difficulty in reproducing the observations of HCOOCH₂D. The chemical network may be missing some effective formation pathways or it may be that temperature dependent diffusion is indeed needed to achieve a higher abundance of HCOOCH₂D.

4 CONCLUSIONS

This work examined the formation of DMF in light of the proposed chemical pathways to form MF both in the gas phase and on grain surfaces in low-mass SFRs.

The main conclusion here is that the formation of all forms of DMF cannot be explained by a single scenario, at once, because species respond differently to changes in the chemistry. It is clear therefore that any future astrochemical modelling ought to include a more rigorous surface network where, not only all the reactions explored here need to be included, but also the temperature dependence of the diffusion treatment of the Langmuir-Hinshelwood reactions, as well as surface reactions during the warm-up phase, should be included. Our models succeed in reproducing the observed abundances of HCOOCH₃, DCOOCH₃ and HCOOCHD₂ after their evaporation from grains at times of $1-2 \times 10^5$ yr. However, they always underestimate the abundances of HCOOCH₂D by a factor of \sim 100. Our results show that radical-radical reactions often dominate over other chemical pathways. Models with H-D substitution reactions are capable of producing doubly and multiply deuterated MF such as DCOOCHD₂ and HCOOCD₃. In addition, we found that the deuteration of the OH group is more sensitive to changes in the chemistry than the one of the CH₃ group. The calculations also showed that the abundance ratio between D(CH₃) and D(OH) deviates from the initially assumed statistical value of three.

Our models predict the existence of multiply deuterated isotopologues of methyl formate, $DCOOCH_2D$, $DCOOCHD_2$, and $HCOOCD_3$ in low-mass SFRs with abundances up to an order of 10^{-10} , 10^{-9} and 10^{-12} , respectively, assuming that substitution reactions are enhancing the molecular abundances as suggested experimentally (e.g. Nagaoka et al. 2005; Hidaka et al. 2009; Oba et al. 2016).

It is clear that the chemistry of DMF is more complicated than the simple picture we presented here. Comprehensive work, experimentally as well as theoretically, is needed for a better understanding of the interstellar chemistry of these species, especially reactions on grain surfaces.

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DATA AVAILABILITY

The model outputs underlying this article will be freely shared on request to the corresponding author.

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