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The Prebiotic Molecular Inventory of Serpens SMM1: II. The Building Blocks of Peptide Chains

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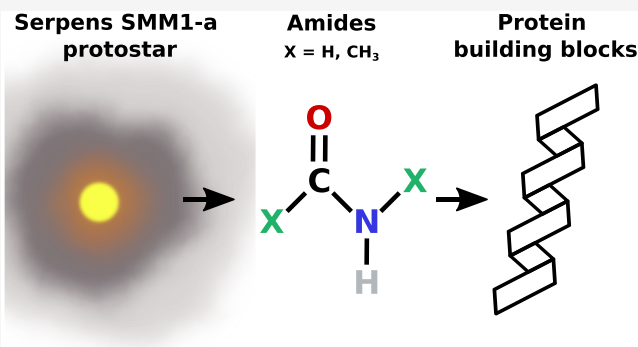


Article Recommendations



Supporting Information

ABSTRACT: This work aims to constrain the abundances of interstellar amides, by searching for this group of prebiotic molecules in the intermediate-mass protostar Serpens SMM1-a. ALMA observations are conducted toward Serpens SMM1. A spectrum is extracted toward the SMM1-a position and analyzed with the CASSIS line analysis software for the presence of characteristic rotational lines of a number of amides and other molecules. NH_2CHO , $\text{NH}_2\text{CHO } \nu_{12} = 1$, $\text{NH}_2^{13}\text{CHO}$, $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ $\nu = 0, 1$, CH_2DOH , CH_3CHO , and $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ are securely detected, while *trans*- NHDCHO , NH_2CDO , $\text{CH}_3\text{NHCHO } \nu = 0, 1$, CH_3COOH , and HOCH_2CHO are tentatively identified. The results of this work are compared with detections presented in the literature. A uniform $\text{CH}_3\text{C}(\text{O})\text{NH}_2/\text{NH}_2\text{CHO}$ ratio is found for a group of interstellar sources with vast physical differences. A similar ratio is seen for CH_3NHCHO , based on a smaller data sample. The D/H ratio of NH_2CHO is about 1–3% and is close to values found in the low-mass source IRAS 16293–2422B. The formation of $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ and NH_2CHO is likely linked. Formation of these molecules on grain surfaces during the dark cloud stage is a likely scenario. The high D/H ratio of NH_2CHO is also seen as an indication that these molecules are formed on icy dust grains. As a direct consequence, amides are expected to be present in the most pristine material from which planetary systems form, thus providing a reservoir of prebiotic material.



INTRODUCTION

Peptide chains, amino acids connected by a $\text{R}_1\text{-C}(=\text{O})\text{N-R}_2\text{R}_3$ group, are an essential component of life as we know it, since these molecules can fold into proteins, which, in turn, are the engines that life runs on. During protein biosynthesis, ribosomes catalyze condensation reactions between amino acids, resulting in the formation of a peptide bond, also called an amide, and a water molecule.¹ However, to understand how the peptide chains formed before life was present, abiotic processes need to be studied.

Several mechanisms have been proposed for abiotic peptide synthesis, involving catalysis by minerals,² in hydrothermal vents,^{3,4} with UV light,⁵ or by impact shocks.⁶ The last mechanism is particularly interesting, because it hints at an extraterrestrial origin of peptide chains. In fact, in the laboratory it has been demonstrated that dipeptides such as glycine–glycine and alanine–leucine can form in interstellar ice analogues.⁷ Incorporation of these interstellar peptides into planetary building material and subsequent delivery by impactors like comets could have helped start life on the Early Earth.

To understand interstellar peptide chemistry, observations of star-forming regions can help elucidate how these molecules

form. While observations of dipeptides and larger molecules are beyond current capabilities, several peptide-like molecules have been detected with radio and mm-wave observations. Formamide (NH_2CHO) has the same chemical structure as a peptide bond and is the simplest peptide-like molecule. It is the first peptide-like molecule to be detected in the interstellar medium (ISM) and is routinely found in extraterrestrial environments, ranging from star-forming regions to comets.^{8–10} Since the detection of formamide, several other peptide-like molecules have been detected, such as acetamide ($\text{CH}_3\text{C}(\text{O})\text{NH}_2$),¹¹ *N*-methylformamide (CH_3NHCHO),^{12–15} and urea (also known as carbamide, $\text{NH}_2\text{C}(\text{O})\text{NH}_2$).^{13,16} Searches for and tentative detections of several other peptide-like molecules have been reported, such as glycolamide ($\text{HOCH}_2\text{C}(\text{O})\text{NH}_2$),^{15,17} cyanoformamide ($\text{N}_2\text{C}(\text{O})\text{CN}$),¹⁵ and propionamide ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{NH}_2$).¹⁸

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Observations of these molecules provide insight into the chemical processes that result in their formation, which, in turn, indicate whether larger amides or even peptides are expected to form in the ISM. For example, correlations found between interstellar abundances of NH_2CHO and $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ hint that there is a physicochemical link between these two molecules.^{15,19} The similarity in the ratios of these molecules in a sample of sources with very different physical characteristics is explained by an early formation during the star formation cycle, presumably on ice-coated interstellar dust grains. Furthermore, this observation hints that these molecules form in related chemical reactions or even directly act as a precursor.

While observations of peptide-like molecules are valuable, detections of these molecules are still relatively sparse. Furthermore, detections are biased toward luminous high-mass protostars and star-forming regions. Peptide-like molecules detected toward low-mass protostars almost exclusively consist of NH_2CHO , with as the only exception a tentative detection of $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ toward the low-mass protostar IRAS 16293–2422B.²⁰ Identifications toward low-mass and Sun-like protostars will extend our knowledge of interstellar amide formation.

In this publication, observations of Serpens SMM1-a (hereafter SMM1-a), an intermediate-mass Class 0 protostar in the Serpens cloud ($D \approx 436.0 \pm 10 \text{ pc}^{21}$), are used. In particular, the outflows of the SMM1 region are well studied,^{22,23} but also its molecular inventory.^{24–27} The comparatively high luminosity of $\sim 100 L_\odot$ makes this an interesting source in the low-end protostellar mass range to search for weak spectral lines of prebiotic and peptide-like molecules.

This work presents the first detection of NH_2CHO , $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, and various isotopologues toward SMM1-a, combined with a tentative detection of CH_3NHCHO and upper limits of various other peptide-like molecules. The observations and analysis are presented in [Observations and Analysis](#), followed by the results in the [Results](#) section. These results are discussed in the [Discussion](#) section, and conclusions are given in the [Conclusions](#) section.

Observations and Analysis. The observations of Serpens SMM1 and the analysis methods are introduced in Ligterink et al.,²⁶ and only a brief overview will be given here.

Observations of SMM1 were conducted on March 27, 2019 in ALMA cycle 6 for project #2018.1.00836.S (PI: N.F.W. Ligterink). The source was observed toward the phase center $\alpha_{J2000} = 18:29:49.80$, $\delta_{J2000} = +01:15:20.6$ in select frequency windows between 217.59 and 235.93 GHz. The spectral resolution was 488.21 kHz ($\sim 0.33 \text{ km s}^{-1}$, several bands between 217.59 and 233.65 GHz) and 1952.84 kHz ($\sim 1.25 \text{ km s}^{-1}$, between 234.06 and 235.93 GHz) for the continuum band, while the spatial resolution was $1.32'' \times 1.04''$. The spectrum of the SMM1-a hot core was extracted toward position $\alpha_{J2000} = 18:29:49.793$, $\delta_{J2000} = +1.15.20.200$ in a beam of $1.32'' \times 1.04''$. The background temperature was determined to be $\sim 5 \text{ K}$.

The CASSIS²⁸ line analysis software was used to analyze the spectra. Line lists taken from the Cologne Database for Molecular Spectroscopy (CDMS),^{29–31} the JPL database for molecular spectroscopy,³² and from the literature were used to identify and fit spectral lines. These databases are also used to identify the lines that are largely free of blending transitions originating from other molecules. Largely clean lines are

defined as transitions that have an almost negligible contribution of a blending transition (approximately 10% of the observed line intensity) or only blend with another species in the wing of the transition. Only largely clean lines were used for subsequent line fitting. A synthetic spectrum consisting of the emission of all 26 securely and tentatively detected species detected toward SMM1-a in this work and in Ligterink et al.²⁶ was generated to check against and verify that detected lines were unblended. An overview of the spectroscopic data of the species discussed in this paper are given in the spectroscopy [Supporting Information](#) section, [Table S1](#).

For a given column density (N_T), excitation temperature (T_{ex}), source velocity (V_{LSR}), line width (ΔV), background temperature ($T_{\text{BG}} = 5.2 \text{ K}$, derived from the average continuum flux density of $0.41 \text{ Jy beam}^{-1}$),²⁶ and source size, which is assumed to be equal to the beam size ($\theta_{\text{source}} = 1.2''$), a synthetic spectrum was generated, assuming Local Thermodynamic Equilibrium (LTE) conditions. This synthetic spectrum was initially fit by-eye to the rotational lines identified in the observed spectrum. Next, a χ^2 minimization routine in combination with the Monte Carlo Markov Chain (MCMC) algorithm was applied to find the best fit to the observed spectrum. The column density was given as a free parameter over 2 orders of magnitude around the by-eye fit column density, while $T_{\text{ex}} = 50\text{--}350 \text{ K}$, $\Delta V = 1.0\text{--}4.0 \text{ km s}^{-1}$, and $V_{\text{LSR}} = 6.0\text{--}9.0 \text{ km s}^{-1}$. In certain cases, T_{ex} , ΔV , or V_{LSR} could not properly be fit and instead estimated values were given. In most cases, these estimates were based on an average of values found for other molecules where a proper fit was possible or based on related species, for example isotopologues.

A secure identification is based on the detection of at least 3 largely unblended lines for species that have prominent spectral lines and are routinely observed in interstellar observations (e.g., NH_2CHO , CH_3OH), while 5 or more lines are required to claim a detection of species that are less routinely observed or have comparatively weak spectral lines (e.g., $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ or glycolaldehyde, HOCH_2CHO). If no lines are identified of a species, an upper limit is determined that is based on the 3σ noise level of a line of the species that is found in a line-free segment of the spectrum.

From the average continuum flux density ($0.41 \text{ Jy beam}^{-1}$),²⁶ the H_2 column density can be estimated following equation:^{33,34}

$$N(\text{H}_2) = \frac{F_\nu R}{B_\nu(T_D) \Omega \kappa_\nu \mu m_H} \quad (1)$$

where F_ν is the flux density, R the gas-to-dust mass ratio, $B_\nu(T_D)$ the Planck function for dust temperature T_D , Ω the beam solid angle, κ_ν the dust absorption coefficient, μ the mean molecular weight, and m_H the atomic hydrogen mass. R is assumed to be 100, $\kappa_{220 \text{ GHz}} = 0.9 \text{ cm}^2 \text{ g}^{-1}$,³⁵ and $\mu = 2.8$. The dust temperature is assumed to be coupled to the gas temperature. The excitation temperature of the dense gas tracer CH_3CN ²⁶ is adopted, resulting in $T_D = 190 \text{ K}$. From this, a hydrogen column density of $N(\text{H}_2) = (1 \pm 0.2) \times 10^{24} \text{ cm}^{-2}$ is estimated.

RESULTS

In the SMM1-a spectrum several lines originating from amides are identified, leading to the secure detection of NH_2CHO $\nu_{12} = 1$, $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ $\nu = 0, 1$, NH_2CHO $\nu = 0$, and $\text{NH}_2^{13}\text{CHO}$ (see [Figures 1 and 2](#), and [Supporting Information Figures S1](#),

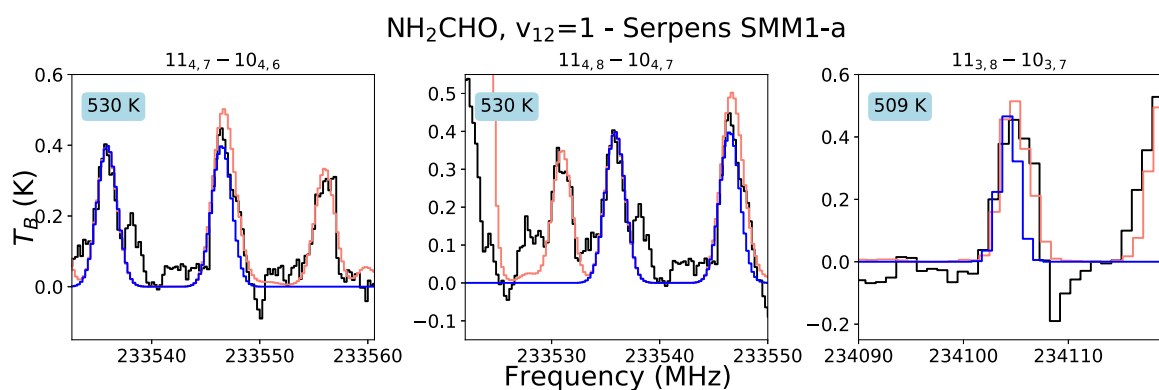


Figure 1. Identified lines of NH₂CHO, $\nu_{12} = 1$ toward SMM1-a. The observed spectrum is plotted in black, with the synthetic spectrum of the species overplotted in blue, and the synthetic spectrum of all fitted species combined in red. The transition is indicated at the top of each panel and the upper state energy is given in the top left of each panel. Detected transitions of NH₂CHO $\nu = 0$, NH₂¹³CHO, NH₂CDO, and NHDCHO are presented in the [Supporting Information](#) section.

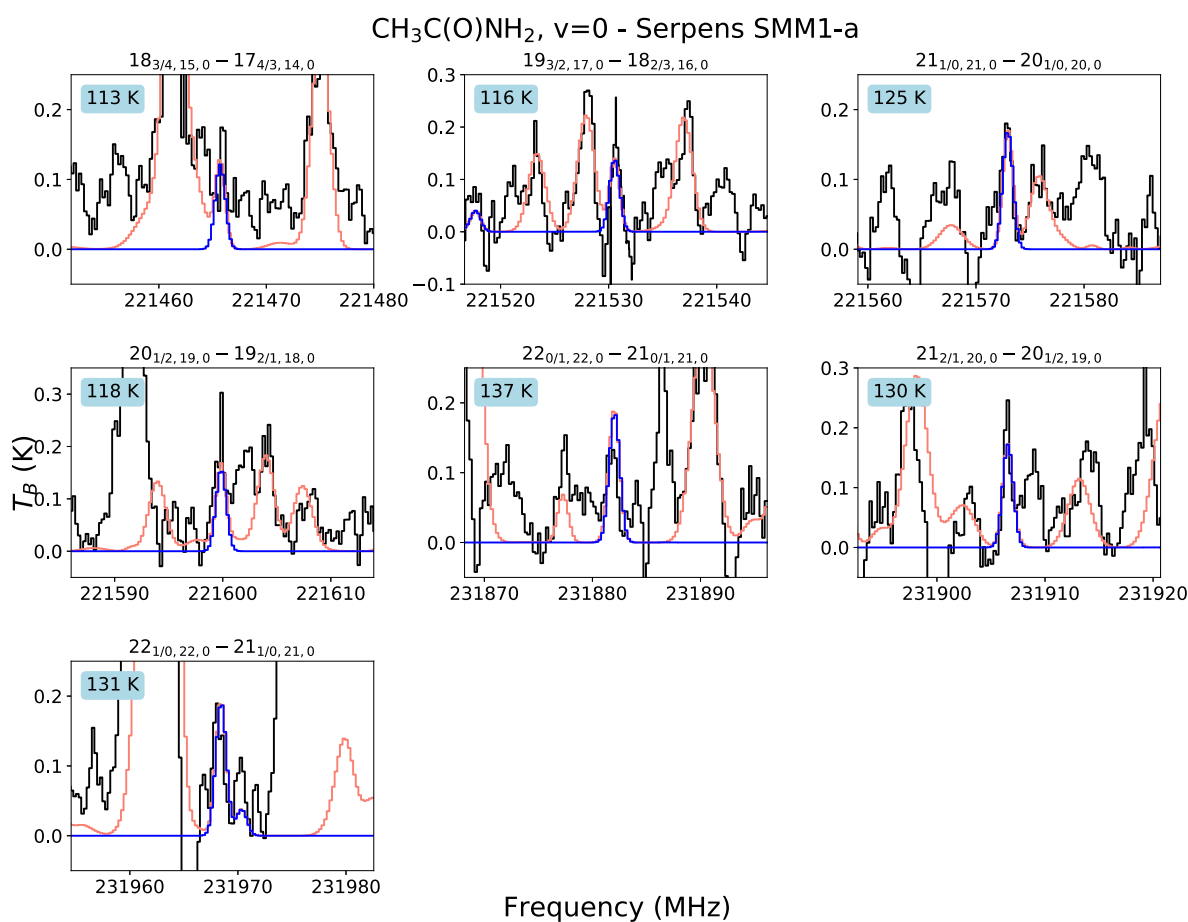


Figure 2. Identified lines of CH₃C(O)NH₂, $\nu = 0$ toward SMM1-a. The observed spectrum is plotted in black, with the synthetic spectrum of the species overplotted in blue, and the synthetic spectrum of all fitted species combined in red. The transition is indicated at the top of each panel and the upper state energy is given in the top left of each panel. Detected transitions of CH₃C(O)NH₂, $\nu = 1$ are presented in the [Supporting Information](#).

S2, and S3), while CH₃NHCHO $\nu = 0, 1$, NH₂CDO, and *trans*-NHDCHO are tentatively identified (see [Figure 3](#) and [Supporting Information Figures S4 and S5](#)). Moment 0 maps of the emission of selected NH₂CHO $\nu_{12} = 1$, NH₂CDO, CH₃C(O)NH₂ $\nu = 0$, and CH₃NHCHO $\nu = 0$ lines are shown in [Figure 4](#). These maps show compact emission of these amides toward the peak continuum of SMM1-a. The difference in the extent of the emission between the NH₂CHO

isotopologues and the larger CH₃C(O)NH₂ and CH₃NHCHO molecules, probably results from the lower line brightness of the latter two species, but may also be due to different chemical responses to the environment, for example the gas density.³⁶ The spatial resolution of these observations is insufficient to resolve finer features in the distribution of these molecules throughout the source and to give a definitive answer to this question.

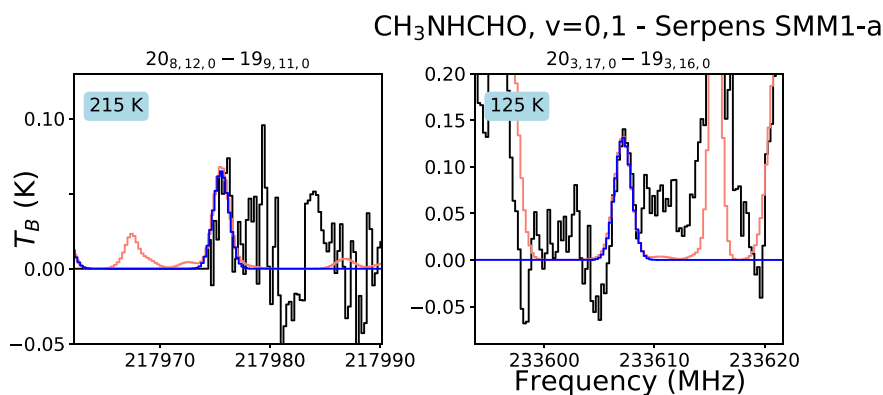


Figure 3. Identified lines of CH_3NHCHO , $\nu = 0, 1$ toward SMM1-a. The observed spectrum is plotted in black, with the synthetic spectrum of the species overplotted in blue, and the synthetic spectrum of all fitted species combined in red. The transition is indicated at the top of each panel and the upper state energy is given in the top left of each panel.

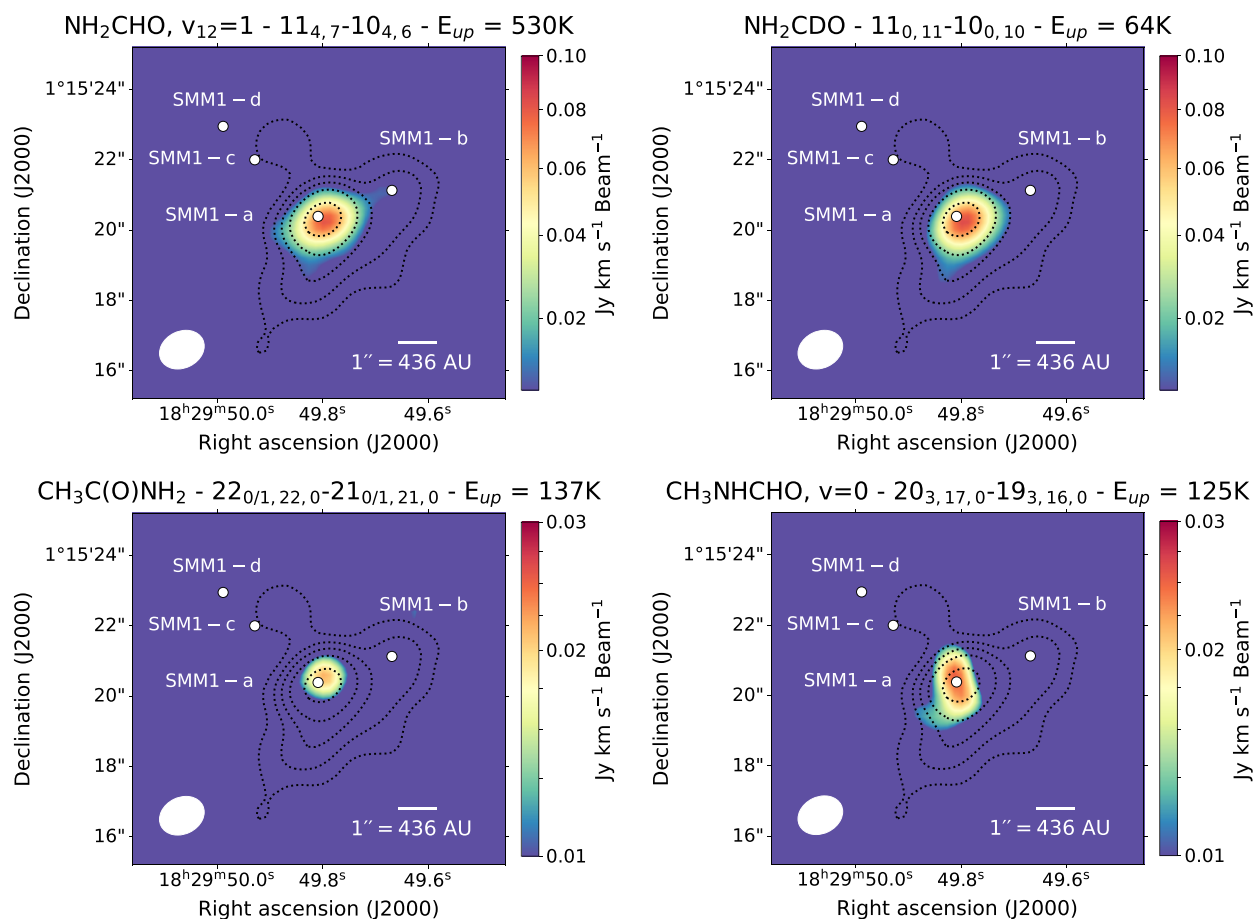


Figure 4. Moment 0 maps of lines of NH_2CHO , $\nu_{12} = 1$, NH_2CDO , $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, and CH_3NHCHO toward SMM1. All lines are integrated over eight velocity bins, centered on the peak frequency of each line as determined toward SMM1-a. Positions of protostars in the SMM1 region are indicated and the beam size ($1.32'' \times 1.04''$) is visualized in the bottom left corner. Dust continuum contours are given by the black dotted line at the levels of 0.02, 0.05, 0.1, 0.2, and 0.5 Jy Beam^{-1} .

The excitation temperature could only be determined for $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, $\nu = 0$, albeit with a large error bar, at $T_{\text{ex}} = 235 \pm 80$ K. For the $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, $\nu = 1$ fit the excitation temperature of its ground vibrational state is adopted. The remaining species were fit with $T_{\text{ex}} = 200$ K, the average temperature that could be securely determined from the detected molecular species toward SMM1-a.²⁶ Other excitation temperatures are possible, which can affect the derived column density. For T_{ex} of 100 to 300 K, temperatures that are

generally realistic for hot core and corinos, the column density can vary by about a factor of 2. This temperature variation may also affect $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, for which an excitation temperature is determined. The column densities of its ground and first excited vibrational states differ substantially at $(2.2 \pm 1.1) \times 10^{14}$ and $(6 \pm 3) \times 10^{14} \text{ cm}^{-2}$, respectively. Due to the large error bar on the determined excitation temperature it is possible that this species is excited at a substantially different temperature. While no other T_{ex} was found for which the

Table 1. Best Fit Parameters for the Molecules Investigated in This Work^a

Molecule	#Lines	N_{T} (cm ⁻²)	T_{ex} (K)	V_{LSR} (km s ⁻¹)	ΔV (km s ⁻¹)	$[X]/[\text{NH}_2\text{CHO}]^b$	$[X]/[\text{CH}_3\text{OH}]^c$	$[X]/[\text{H}_2]$
NH ₂ ¹³ CHO	2	(7.5 ± 1.2) × 10 ^{13,d}	[200]	6.8 ± 0.2	2.6 ± 0.4	—	(7 ± 3) × 10 ⁻⁵	(8 ± 4) × 10 ⁻¹¹
NH ₂ ¹² CHO ^d	7	[(3.9 ± 1.3) × 10 ^{15,d,f}]	—	—	—	1.0 × 10 ⁰	(3.5 ± 1.7) × 10 ⁻³	(3 ± 2) × 10 ⁻⁹
NH ₂ CHO, $\nu_{12} = 1$	3	(1.0 ± 0.2) × 10 ^{15,d}	[200]	6.9 ± 0.1	2.8 ± 0.2	(2.6 ± 1.0) × 10 ⁻¹	(9 ± 4) × 10 ⁻⁴	(1.0 ± 0.5) × 10 ⁻⁹
NH ₂ CDO	2	~(1.4 ± 0.3) × 10 ¹⁴	[200]	6.4 ± 0.2	3.0 ± 0.5	~(3.6 ± 1.4) × 10 ⁻²	~(1.3 ± 0.5) × 10 ⁻⁴	~(1.4 ± 0.7) × 10 ⁻¹⁰
<i>trans</i> -NHDCO	3	~(4.3 ± 1.6) × 10 ¹³	[200]	7.4 ± 0.6	3.3 ± 0.4	~(1.1 ± 0.6) × 10 ⁻²	~(4 ± 2) × 10 ⁻⁵	~(4 ± 3) × 10 ⁻¹¹
CH ₃ C(O)NH ₂ , $\nu = 0$	7	(2.2 ± 1.1) × 10 ¹⁴	235 ± 80	6.4 ± 0.2	1.5 ± 0.4	(6 ± 3) × 10 ⁻²	(2.0 ± 1.2) × 10 ⁻⁴	(2.2 ± 1.5) × 10 ⁻¹⁰
CH ₃ C(O)NH ₂ , $\nu = 1$	5	(6 ± 3) × 10 ¹⁴	[235]	6.9 ± 0.5	[1.5]	(1.4 ± 1.0) × 10 ⁻¹	(5 ± 3) × 10 ⁻⁴	(6 ± 4) × 10 ⁻¹⁰
CH ₃ NHCHO, $\nu = 0$	1	~(6 ± 3) × 10 ¹⁴	[200]	7.3 ± 0.6	2.3 ± 0.5	~(1.5 ± 0.9) × 10 ⁻¹	~(6 ± 3) × 10 ⁻⁴	~(6 ± 4) × 10 ⁻¹⁰
CH ₃ NHCHO, $\nu = 1$	1	~(6 ± 4) × 10 ¹⁴	[200]	7.5 ± 0.8	2.3 ± 0.5	~(1.5 ± 1.0) × 10 ⁻¹	~(5 ± 4) × 10 ⁻⁴	~(6 ± 4) × 10 ⁻¹⁰
¹⁵ NH ₂ CHO	0	≤1.5 × 10 ¹⁴	[200]	[7.0]	[3.0]	≤3.8 × 10 ⁻²	≤1.4 × 10 ⁻⁴	≤1.5 × 10 ⁻¹⁰
<i>cis</i> -NHDCO	0	≤1.0 × 10 ¹⁴	[200]	[7.0]	[3.0]	≤2.6 × 10 ⁻²	≤9.1 × 10 ⁻⁵	≤1.0 × 10 ⁻¹⁰
NH ₂ CH ¹⁸ O	0	≤1.5 × 10 ¹⁴	[200]	[7.0]	[3.0]	≤3.8 × 10 ⁻²	≤1.4 × 10 ⁻⁴	≤1.5 × 10 ⁻¹⁰
NH ₂ C(O)NH ₂	0	≤5.0 × 10 ¹³	[200]	[7.0]	[3.0]	≤1.3 × 10 ⁻²	≤4.5 × 10 ⁻⁵	≤5 × 10 ⁻¹¹
NH ₂ C(O)CN	0	≤2.0 × 10 ¹⁴	[200]	[7.0]	[3.0]	≤5.1 × 10 ⁻²	≤1.8 × 10 ⁻⁴	≤2.0 × 10 ⁻¹⁰
HOCH ₂ C(O)NH ₂	0	≤5.0 × 10 ¹³	[200]	[7.0]	[3.0]	≤1.3 × 10 ⁻²	≤4.5 × 10 ⁻⁵	≤5 × 10 ⁻¹¹
CH ₃ OH ^c	5	[1.1 × 10 ¹⁸] ^c	—	—	—	—	1.0 × 10 ⁰	(1.1 ± 0.3) × 10 ⁻⁶ (phantom)
CH ₂ DOH	4	(1.2 ± 0.2) × 10 ¹⁶	[250] ^e	7.5 ± 0.1	2.3 ± 0.2	(3.1 ± 1.1) × 10 ⁰	(1.1 ± 0.4) × 10 ⁻²	(1.2 ± 0.6) × 10 ⁻⁸
CH ₃ CHO	6	(1.5 ± 0.2) × 10 ¹⁵	170 ± 10	7.8 ± 0.1	3.4 ± 0.2	(3.8 ± 1.4) × 10 ⁻¹	(1.4 ± 0.5) × 10 ⁻³	(1.5 ± 0.7) × 10 ⁻⁹
CH ₃ C(O)CH ₃	4	(8 ± 3) × 10 ¹⁵	250 ± 40	7.4 ± 0.2	3.4 ± 0.3	(2.1 ± 1.0) × 10 ⁰	(7 ± 4) × 10 ⁻³	(8 ± 5) × 10 ⁻⁹
CH ₃ COOH	2	~(2.8 ± 0.7) × 10 ¹⁵	180 ± 40	7.4 ± 0.2	3.6 ± 0.6	~(7 ± 3) × 10 ⁻¹	~(2.5 ± 1.1) × 10 ⁻³	~(2.8 ± 1.4) × 10 ⁻⁹
HOCH ₂ CHO	4	~(1.6 ± 0.2) × 10 ¹⁵	220 ± 20	6.8 ± 0.3	4.6 ± 0.3	~(4.1 ± 1.5) × 10 ⁻¹	~(1.5 ± 0.6) × 10 ⁻³	~(1.6 ± 0.7) × 10 ⁻⁹
H ₂ CCO	0	≤1.5 × 10 ¹⁶	[200]	[7.0]	[3.0]	≤3.8 × 10 ⁰	≤1.4 × 10 ⁻²	≤1.5 × 10 ⁻⁸

^aValues of T_{ex} , V_{LSR} , and ΔV in square brackets are estimated. The \sim symbol indicates a tentative identification and \leq an upper limit. ^bThe $[X]/[\text{NH}_2\text{CHO}]$ values are determined based on the NH₂CHO column density, which is derived from the column density of the optically thin NH₂¹³CHO isotopologue. ^cThe CH₃OH main isotopologue column density is taken from Ligtnerink et al.,²⁶ which is based on the CH₃¹⁸OH column density of (2.0 ± 1.1) × 10¹⁵ cm⁻² multiplied by a ¹⁶O/¹⁸O ratio of 560.³⁷ ^dThe NH₂¹²CHO column density is determined from the NH₂¹³CHO column density, multiplied by a ¹²C/¹³C ratio of 52.5 ± 15.4.³⁸ The number of lines listed are those identified of NH₂CHO. ^eThe fit of CH₂DOH makes use of the T_{ex} determined for CH₃¹⁸OH by Ligtnerink et al.²⁶

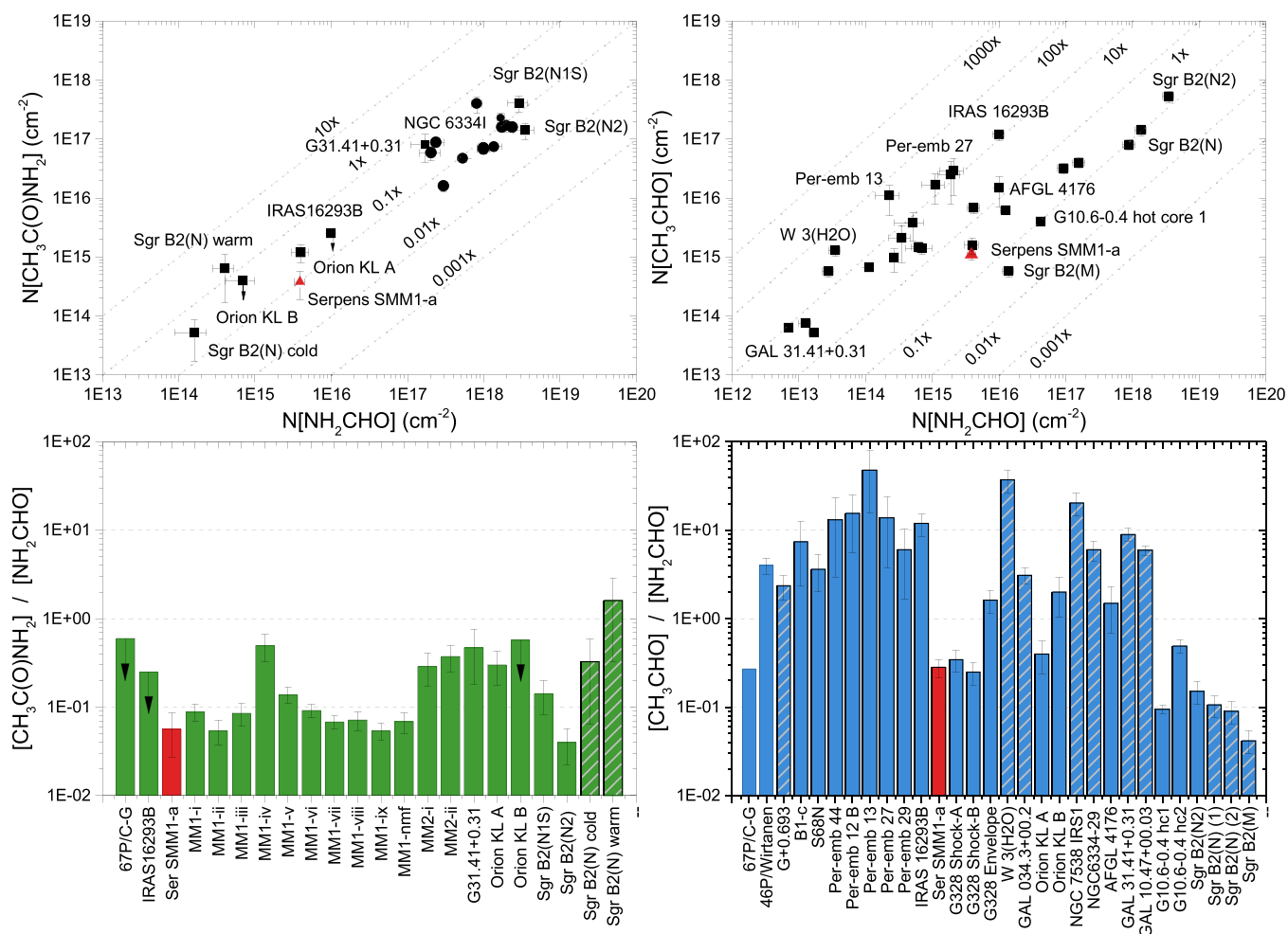


Figure 5. Scatter plots and bar graphs of the $\text{CH}_3\text{C}(\text{O})\text{NH}_2/\text{NH}_2\text{CHO}$ ratio (left) and $\text{CH}_3\text{CHO}/\text{NH}_2\text{CHO}$ ratio (right) toward various interstellar sources. Serpens SMM1-a is indicated with a red triangle or red bar. For readability the NGC 6334I sources are grouped together and indicated with a circle and abbreviated as MM1-i to MM2-ii in the bar graphs. Also for readability, only a select number of sources are labeled in the $\text{CH}_3\text{CHO}/\text{NH}_2\text{CHO}$ scatter plot. The sources in the bar plot are roughly ordered by luminosity. Single dish observations are indicated with striped bars. Column densities taken from the literature^{9,10,12,13,15,16,19,20,40–55} are presented in Table S3 in the Supporting Information.

column densities of the two states converged, the column densities are consistent within the uncertainties.

For amides for which accurate spectroscopic laboratory data are available, but no convincing lines are found in our observed spectra, upper limits on the column density have been derived. This applies to the following amides (between brackets the line frequency is listed from which the upper limit is calculated): $^{15}\text{NH}_2\text{CHO}$ (233 523.8 MHz), *cis*-NHDCO (234 776.2 MHz), $\text{NH}_2\text{CH}^{18}\text{O}$ (231 843.5 and 235 678.6 MHz), $\text{NH}_2\text{C}(\text{O})\text{NH}_2$ (221 615.8 MHz), $\text{NH}_2\text{C}(\text{O})\text{CN}$ (217 621.9 and 218 497.0 MHz), and $\text{HOCH}_2\text{C}(\text{O})\text{NH}_2$ (234 277.2 MHz).

Finally, lines of several oxygen-COMs are also detected. While not the aim of this work, these species are analyzed to account for line blending with the amides. Furthermore, some species are of considerable prebiotic interest, such as glycolaldehyde (HOCH_2CHO), the simplest sugar-like molecule. In the SMM1-a spectrum CH_2DOH , acetaldehyde (CH_3CHO), and acetone ($\text{CH}_3\text{C}(\text{O})\text{CH}_3$) are securely identified (see Supporting Information Figures S6, S7, and S8), while acetic acid (CH_3COOH) and HOCH_2CHO are tentatively detected (see Supporting Information Figures S9 and S10).

The number of identified lines and fit parameters of all species are presented in Table 1, while the line parameters of the identified transitions are listed in Table S2 in the Supporting Information.

DISCUSSION

The detected molecules presented in the Results substantially expand the number of identified species in Serpens SMM1. Particularly noteworthy is the detection of $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, making SMM1-a the lowest luminosity and mass object where acetamide is securely identified, with only a tentative detection of the molecule in the low-mass protostar IRAS 16293–2422B.²⁰ Also, the tentative identification of deuterated formamide and CH_3NHCHO in SMM1-a add constraints to two molecules for which not many detections are found in the literature.^{9,12,13,15,19}

In the following three sections, comparisons are made with the molecular inventories of other extraterrestrial sources. An overview of these sources, including relevant molecular abundances and column densities, is found in the Supporting Information Table S3. The list covers a diverse set of objects, such as the comets 67P/Churyumov-Gerasimenko (hereafter 67P/C-G) and 46P/Wirtanen or the giant molecular cloud G

+0.693, where the molecular complexity is driven by shocks resulting from a cloud–cloud collision.³⁹ Data from the low-mass protostars Perseus B1-c (hereafter B1-c), Serpens S68N (hereafter S68N), Per-emb 44, Per-emb 12 B, Per-emb 13, Per-emb 27, Per-emb 29, and IRAS 16293–2422B are used. High-mass protostars and star-forming regions are represented in G328.2551–0.5321 (hereafter G328), W3(H₂O), NGC 6334I, G31.41 + 0.31, GAL 034.3 + 00.2, Orion KL, NGC 7538 IRS1, NGC 6334–29, AFGL 4176, GAL 10.47 + 00.03, G10.6–0.4, and Sagittarius B2 (hereafter Sgr B2). Most of these objects have been observed with interferometric observations, but data for 46P/Wirtanen, G+0.693, W3(H₂O), GAL 034.3 + 00.2, NGC 7538 IRS1, NGC 6334–29, GAL 31.41 + 0.31, GAL 10.47 + 00.03, Sgr B2(M), and Sgr B2(N) has been obtained with a variety of single dish telescopes. Data for 67P/C-G was obtained by the Rosetta space exploration mission.

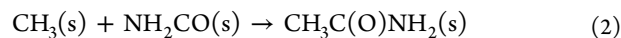
The NH₂CHO–CH₃C(O)NH₂ Link. Since the first detection of acetamide it has been suggested that CH₃C(O)NH₂ forms in reactions starting from NH₂CHO.¹¹ If this is the case, a column density correlation between the two species may be observed. In the left side panels of Figure 5 the results of this study and literature data are collected and the ratios between NH₂CHO and CH₃C(O)NH₂ are presented in a scatter plot and bar graph. Literature data are taken from a variety of sources, ranging from comets to protostars and star-forming regions, with vastly varying luminosities and masses.

From Figure 5 it becomes apparent that NH₂CHO and CH₃C(O)NH₂ column densities strongly correlate. A CH₃C(O)NH₂/NH₂CHO ratio of approximately 0.1 with a scatter of less than an order of magnitude is found, in particular when single dish data are omitted. The correlation is especially prominent when contrasted to CH₃CHO/NH₂CHO ratios, which easily scatter over 2 to 3 orders of magnitude, see right side panels of Figure 5. Furthermore, it is interesting to point out that this ratio is similar in a diverse set of objects with very different physical characteristics, such as luminosity and protostellar mass, as these sources range from the low end of the mass range and low-luminosity, such as IRAS 16293–2422B ($\sim 3L_{\odot}$)⁵⁶ and Ser SMM1-a ($\sim 100L_{\odot}$) to complex, multiprotostar, high-mass star-forming regions with luminosities of 1000s or 10000s L_{\odot} (e.g., NGC 6334I, Sgr B2(N)). In line with the conclusions of Colzi et al.,¹⁵ derived from a similar set of data, this points to a chemical link between the two species and/or a similar response of reaction pathways to physical conditions.⁵⁷ Formation of CH₃C(O)NH₂ and NH₂CHO in the ice mantles of grains in dark clouds or during warm-up toward the protostellar stage followed by release to the gas-phase due to thermal desorption is a likely scenario. This is in line with modeling work of Quénard et al.,⁵⁷ who find that NH₂CHO production at high temperatures (i.e., in or near a hot core/corino) is primarily the result of desorbing ice mantles. In contrast, the large differences seen in the CH₃CHO/NH₂CHO ratio, hint at a more complex interplay of reaction pathways and response to physical conditions for one or both of these species. Prominent gas-phase formation pathways are known for CH₃CHO, such as CH₃CH₂ + O → CH₃CHO + H,^{58,59} and its gas-phase formation has been hinted at in other interstellar sources, such as the L1157-B1 shock.⁶⁰

Formation of acetamide by gas-phase reactions and the possible chemical link with formamide have been relatively well investigated, mainly by computational studies.^{11,55,61–65}

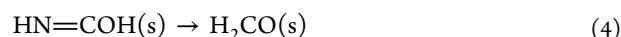
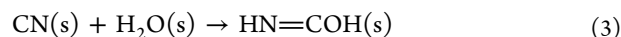
While solid-state formation of acetamide has been seen in various experiments,^{20,66–68} formation pathways and the chemical link with NH₂CHO are less well established.

Reactions involving the NH₂CO (carbamoyl) radical have been suggested as solid-state pathways to form amides in the literature.^{20,69} One solid-state link between formamide and acetamide is found in the reaction between the methyl and carbamoyl radical:

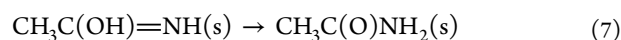
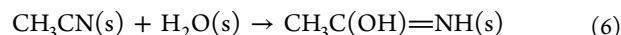


The carbamoyl radical links acetamide and formamide, since this radical can be formed by abstraction, radiolysis, and photolysis of NH₂CHO, via the NH₂ + CO radical addition, via the radical reaction CN + H₂O,⁷⁰ or by hydrogenation of HNCO.⁷¹ Variations on above reaction may be possible, for example by exchanging CH₃ with the methylene (CH₂) radical and an additional hydrogenation step. To further elucidate reactions involving carbamoyl, matrix isolation experiments should be conducted to determine to which extent this and related reactions contribute to the formation of acetamide with formamide.

Another chemical link between formamide and acetamide is found in reactions starting from cyanides. With quantum chemical calculations, Rimola et al.⁷⁰ found a formamide formation pathway starting from the CN radical and water:



There exists an analogue of this reaction for the formation of acetamide, starting from acetonitrile (CH₃CN) and water, which also has been proposed as a gas-phase reaction pathway:⁶⁴



Important to note is that above reactions start with two closed shell species (eq 6), while the pathway to form NH₂CHO begins with the CN radical (eq 3). However, if the CH₃CN reaction proceeds, this could explain a chemical link between NH₂CHO and CH₃C(O)NH₂, if there is a relation between (H)CN and CH₃CN formed in interstellar ices and their abundances are high enough. In the literature, there is some experimental evidence that acetamide can be formed from CH₃CN. Bulak et al.⁷² investigated the photoprocessing of CH₃CN:H₂O ice mixtures with laser desorption postionization time-of-flight mass spectrometry and identified mass signatures that can be assigned to acetamide. However, an unambiguous identification was not made. Furthermore, Duvernay et al.⁷³ investigated the solid-state formation and photoprocessing of alpha-aminoethanol (CH₃C(OH)NH₂) a molecule that shows some chemical similarity to the CH₃C(OH)=NH intermediate produced in eq 6. Photoprocessing of this species resulted in the formation of acetamide, hinting that eq 7 may result in the same product.

Several other reactions that form CH₃C(O)NH₂ are possible, albeit that none of these show a direct chemical link with NH₂CHO. Among them, the reaction between ketene (H₂CCO) and ammonia (NH₃) is an interesting one that warrants further investigations. The gas-phase reaction of

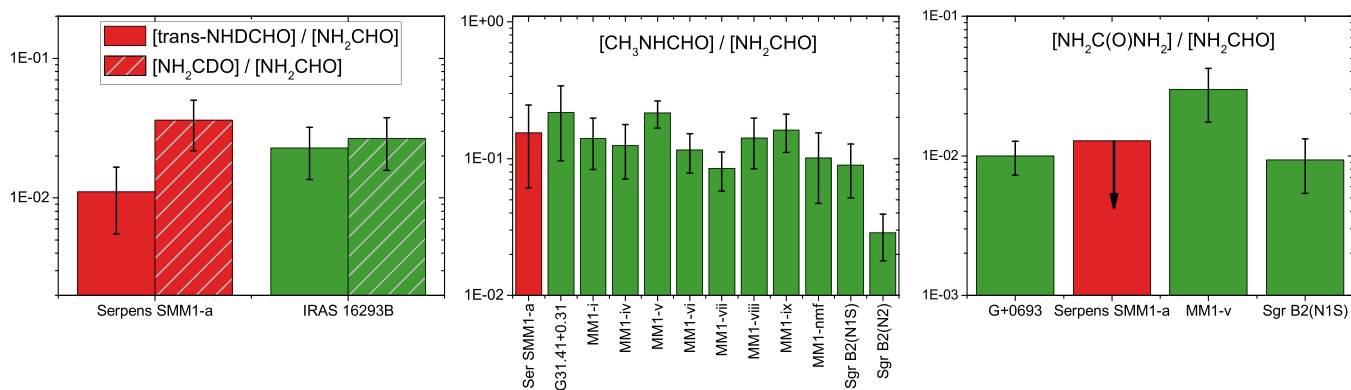


Figure 6. Bar graph plots of deuterated formamide (left), *N*-methylformamide (middle), and carbamide (right) abundances with respect to NH_2CHO toward SMM1-a (red) and IRAS 16293–2422B,⁹ G31.41 + 0.31,¹⁵ NGC 6334I MM1,¹⁹ Sgr B2(N),^{12,13} and G+0.693¹⁶ (all in green). This work and Coutens et al.⁹ use different values for the $^{12}\text{C}/^{13}\text{C}$ ratio.^{38,79} For consistency, the NH_2CHO column density has been determined in both sources with the $^{12}\text{C}/^{13}\text{C} = 52.5 \pm 15.4$ ³⁸ ratio in order to compare the formamide D/H ratios. For readability the NGC 6334I sources MM1-i to MM1-nmf are listed by their abbreviated names. The SMM1-a detection of deuterated NH_2CHO and CH_3NHCHO are tentative, while $\text{NH}_2\text{C(O)NH}_2$ is not detected and an upper limit is derived. The literature data used in this figure are presented in the Supporting Information Table S3.

these two molecules has been investigated,⁶⁵ but limited experimental evidence for a solid-state equivalent exists. Haupa et al.⁷⁴ investigated the hydrogen abstraction of $\text{CH}_3\text{C(O)NH}_2$, resulting in the formation of the $\text{CH}_2\text{C(O)NH}_2$ radical. Photoprocessing of this radical resulted in ketene formation. This can hint that a reverse pathway, starting from H_2CCO may be possible. It is worth noting that only one H_2CCO line is covered in the SMM1-a spectrum, which is not detected, making it difficult to assess ketene as a precursor of acetamide from these observations.

To conclude, observations indicate that the column densities of NH_2CHO and $\text{CH}_3\text{C(O)NH}_2$ might be correlated. However, the exact nature of this correlation is as of yet unknown and could be due to linked chemical processes, either in the gas-phase or in the solid-state, or production of these species under similar physical conditions.

Deuterated Formamide. Lines of two deuterated forms of formamide are tentatively detected in the SMM1-a spectrum, namely *trans*-NHDCHO and NH_2CDO , see Figures S4 and S5. While the number of detected lines of these species is insufficient to claim a secure detection, they can be used to give an indication of D/H fraction of NH_2CHO in SMM1-a and be compared with the values of IRAS 16293–2422B, the only source for which formamide D/H is thoroughly analyzed.⁹

Deuterium fractions of $\sim(1.1 \pm 0.5) \times 10^{-2}$ and $\sim(3.6 \pm 1.0) \times 10^{-2}$ are found for *trans*-NHDCHO and NH_2CDO , respectively, toward SMM1-a, which agree reasonably well with the $\text{CH}_2\text{DOH}/\text{CH}_3\text{OH}$ ratio of $(1.1 \pm 0.4) \times 10^{-2}$. The difference in abundance between *trans*-NHDCHO and NH_2CDO of a factor of 3 is peculiar. This can indicate something about the underlying chemistry, but additional observations of deuterated formamide spectral lines are needed to further constrain the synthetic fit and in turn their abundances. Within the error bars, the SMM1 abundances with respect to NH_2CHO match those found toward IRAS 16293–2422, see left panel of Figure 6. This hints that similar physicochemical processes are taking place in both sources that result in the formation of formamide and its deuterium isotopomers.

The formation of formamide is still strongly debated, with proponents for gas-phase and solid-state chemistry.⁷⁵ Traditionally,

deuteration levels of several percent, as found for SMM1-a, are seen as an indication that ice chemistry is producing these species.⁷⁶ For formamide, Skouteris et al.⁷⁷ showed that the gas-phase reaction $\text{NH}_2 + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO} + \text{H}$ can also be efficient in forming deuterated formamide. However, in this scenario, the high deuteration levels of H_2CO and NH_2 (or its precursor) have to be set on the grains. This raises the question whether one set of species can form on grains (H_2CO , NH_2) and the other will not (NH_2CHO), while laboratory evidence shows that both can simultaneously be formed in simulated interstellar ice mantles.⁷⁸ Exclusive gas-phase formation of formamide in hot cores seems unlikely.

Other Amides. The last couple of years have seen a boost in searches for and detections of amides, especially *N*-methylformamide and carbamide. In the middle and right panel of Figure 6 the tentative detection of CH_3NHCHO and upper limit of $\text{NH}_2\text{C(O)NH}_2$ toward SMM1-a are compared with interstellar detections of these molecules available from the literature.

The $\text{CH}_3\text{NHCHO}/\text{NH}_2\text{CHO}$ ratio in SMM1-a matches with those found in the high-mass sources G31.41 + 0.31,¹⁵ NGC 6334I,¹⁹ and Sgr B2(N1S).¹³ This supports the idea that the underlying physicochemical processes that result in CH_3NHCHO formation in SMM1-a are similar to those in the high-mass objects.

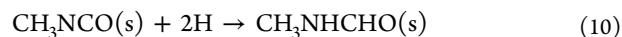
In ice mantles, several CH_3NHCO formation pathways are available,^{12,80} such as the radical–radical addition reactions



and



and the hydrogenation reaction



The tentative correlation between CH_3NHCHO and NH_2CHO can hint that the formation of these two species is linked and that eq 9 is involved in its formation. It would be of interest to determine the $\text{CH}_3\text{NHCO}/\text{NH}_2\text{CHO}$ toward the giant molecular cloud G+0.693 to see if this correlation also

holds at an early stage of star formation. At the same time, parallel detections of CH_3NCO and CH_3NH_2 , of which currently a limited number exist in the literature, may provide insight into the other two formation pathways.

Of the amides that are not detected in SMM1-a, the upper limit abundance of $\text{NH}_2\text{C}(\text{O})\text{NH}_2$ can be compared with detections of this molecule in G+0.693 and Sgr B2(N1S) and a tentative identification in NGC 6334I MM1-v,^{13,16,19} see right panel of Figure 6. The upper limit abundances are found to be similar to those of the detections. This suggests that a slightly deeper search that targets prominent spectral lines of $\text{NH}_2\text{C}(\text{O})\text{NH}_2$ may result in a detection of this molecule toward SMM1-a.

Two other complex amides that are searched for in SMM1-a, $\text{NH}_2\text{C}(\text{O})\text{CN}$ and $\text{HOCH}_2\text{C}(\text{O})\text{NH}_2$, are not detected and at present they have not been detected toward other sources either.^{15,17} The $\text{NH}_2\text{C}(\text{O})\text{CN}/\text{NH}_2\text{CHO}$ upper limit ratios are similar in SMM1-a and G31.41 + 0.31 at ≤ 0.05 and ≤ 0.02 ,¹⁵ respectively. For $\text{HOCH}_2\text{C}(\text{O})\text{NH}_2$ the upper limits toward SMM1-a, G31.41 + 0.31, and Sgr B2(N2) are ≤ 0.01 , ≤ 0.004 ,¹⁵ and ≤ 0.007 ,¹⁷ respectively, with respect to NH_2CHO . Compared to the abundances of $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ and CH_3NHCHO with respect to NH_2CHO , which are approximately 0.1, this shows that $\text{NH}_2\text{C}(\text{O})\text{CN}$ and $\text{HOCH}_2\text{C}(\text{O})\text{NH}_2$ are substantially less abundant by at least a factor 5–25.

It is interesting to note that $\text{NH}_2\text{C}(\text{O})\text{CN}$ and $\text{HOCH}_2\text{C}(\text{O})\text{NH}_2$ are much less abundant, while their chemical complexity seems to be similar or marginally greater than that of $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ and CH_3NHCHO . This suggests that reactions forming these molecules are substantially less efficient than the pathway(s) leading to $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ and CH_3NHCHO or that these molecules are much more readily destroyed.

Prebiotic Chemistry and Planetary Exploration. The results of this study suggest that SMM1-a has a rich inventory of amides, which have been primarily formed in the ice mantles of interstellar grains and are sublimated in the hot corino. Recent studies indicate that ice formed in the dark cloud is inherited into the planet-forming disk.⁸¹ Chemical inventories, including NH_2CHO , of several hot corinos have indeed been shown to be similar to the composition of comet 67P/Churyumov-Gerasimenko.^{82,83} If amides are formed in the dark cloud or during the onset of the protostellar stage, when ice mantles warm up, they can survive into the planet-forming disk and be available as planet building material. Remnants of planet building, such as comets and asteroids, can bombard newly formed planets and seed it with a cocktail of prebiotic molecules, including amides.⁸⁴

More studies of comets and asteroids are needed to determine the amount of amides that are present in these objects. Radio telescope observations may help with this by analyzing the coma gas,¹⁰ but observational tools are generally not sensitive enough to detect larger amides, since they are usually less abundant and not very volatile. Space exploration missions are required to explore these chemical inventories in situ, for example with the Organics Information Gathering Instrument (ORIGIN)¹⁴ space instrument, which is intended to detect large nonvolatile prebiotic molecules and biomolecules.

CONCLUSIONS

In this publication the amide inventory of the hot corino around the intermediate-mass protostar Serpens SMM1-a is

studied. The first detections of $\text{NH}_2\text{CHO } \nu = 0$, $\text{NH}_2\text{CHO } \nu_{12} = 1$, $\text{NH}_2^{13}\text{CHO}$, and $\text{CH}_3\text{C}(\text{O})\text{NH}_2 \nu = 0, 1$ toward this source are presented, as are the tentative identifications of *trans*-NHDCHO, NH_2CDO , and $\text{CH}_3\text{NHCHO } \nu = 0, 1$. Serendipitous detections of the oxygen COMs CH_3CHO and $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ are made, while CH_3COOH and HOCH_2CHO are tentatively identified. Ratios of the detected molecules are derived with respect to NH_2CHO and compared with molecular inventories of a varied sample of other sources.

For $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ and CH_3NHCHO a ratio of approximately 0.1 and a scatter of less than an order of magnitude is found. For $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, for which a larger sample of detections is available, this uniform ratio suggests that there is a link in the formation of this molecule and NH_2CHO and that the ratio must already be set at an early stage of star formation, presumably in ice mantles on dust grains that are present in dark clouds. The D/H ratio of NH_2CHO is found to be about 1–3% and is similar to the ratio derived for IRAS 16293–2422B. This is a strong clue that ice mantle reactions are involved in the formation of NH_2CHO , but further studies are required to assess the extent to which gas-phase reactions are involved. A comparison of the upper limit abundance derived for $\text{NH}_2\text{C}(\text{O})\text{NH}_2$ toward Serpens SMM1-a with those in other sources, suggests that this is a suitable source for follow-up searches for this relevant prebiotic molecule.

The rich amide inventory of Serpens SMM1-a is further evidence for the widespread availability of these molecules in star-forming regions. This increases the likelihood that these molecules are inherited into comets and other planetesimals and subsequently delivered to planetary surfaces, where they can aid the formation of biomolecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.1c00330>.

Spectroscopic line lists of CH_2DOH , H_2CCO , CH_3CHO , $\text{NH}_2\text{CHO } \nu = 0$, $\text{NH}_2\text{CHO } \nu_{12} = 1$, $\text{NH}_2^{13}\text{CHO}$, NH_2CDO , *cis*-NHDCHO, *trans*-NHDCHO, $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, $\text{CH}_3\text{C}(\text{O})\text{NH}_2$, CH_3NHCHO , CH_3COOH , HOCH_2CHO , $\text{NH}_2\text{C}(\text{O})\text{NH}_2$, $\text{NH}_2\text{C}(\text{O})\text{CN}$, $\text{HOCH}_2\text{C}(\text{O})\text{NH}_2$ (Section S1, Table S1); Their observed lines toward Serpens SMM1 (Section S2, Table S2); Spectral line fits of CH_2DOH , CH_3CHO , $\text{NH}_2\text{CHO } \nu = 0$, $\text{NH}_2^{13}\text{CHO}$, NH_2CDO , *trans*-NHDCHO, $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, CH_3COOH , HOCH_2CHO (Section S3, Figures S1–S10); Literature data used in Figures 5 and 6 (Section S4, Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

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