Observations of Interstellar Formamide: Availability of a Prebiotic Precursor in the Galactic Habitable Zone

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Abstract

We conducted a study on interstellar formamide, NH_2CHO , toward star-forming regions of dense molecular clouds, using the telescopes of the Arizona Radio Observatory (ARO). The Kitt Peak 12 m antenna and the Submillimeter Telescope (SMT) were used to measure multiple rotational transitions of this molecule between 100 and 250 GHz. Four new sources of formamide were found [W51M, M17 SW, G34.3, and DR21(OH)], and complementary data were obtained toward Orion-KL, W3(OH), and NGC 7538. From these observations, column densities for formamide were determined to be in the range of 1.1×10^{12} to $9.1 \times 10^{13} \text{ cm}^{-2}$, with rotational temperatures of 70–177 K. The molecule is thus present in warm gas, with abundances relative to H_2 of 1×10^{-11} to 1×10^{-10} . It appears to be a common constituent of star-forming regions that foster planetary systems within the galactic habitable zone, with abundances comparable to that found in comet Hale-Bopp. Formamide's presence in comets and molecular clouds suggests that the compound could have been brought to Earth by exogenous delivery, perhaps with an infall flux as high as $\sim 0.1 \text{ mol/km}^2/\text{yr}$ or 0.18 mmol/m^2 in a single impact. Formamide has recently been proposed as a single-carbon, prebiotic source of nucleobases and nucleic acids. This study suggests that a sufficient amount of NH_2CHO could have been available for such chemistry. Key Words: Formamide—Astrobiology—Radioastronomy—ISM—Comets—Meteorites. *Astrobiology* 13, 439–453.

1. Introduction

ACURRENT THEORY in the paradigm of the RNA world is that nucleobases originated from the condensation of HCN in the presence of water (Orgel, 2004). A tetramer arises from the polymerization, which then leads to adenine, guanine, and other products. However, there appear to be some issues in ascribing to HCN the role of “absolute protagonist” in the prebiotic chemistry of nucleic acids (*e.g.*, Saladino *et al.*, 2006). One issue is the thermodynamic instability of HCN polymers under hydrolytic conditions. At low concentrations ($<0.01 \text{ M}$), the hydrolysis of HCN to NH_2CHO prevails over its polymerization (Sanchez *et al.*, 1967). Higher concentrations needed to promote the polymerization route are hard to realize for HCN under early Earth temperature and pressure conditions, especially because it is more volatile than water and cannot simply be concentrated by evaporation. The competition between HCN polymerization and hydrolysis to formamide consequently favors the latter process (*e.g.*, Costanzo *et al.*, 2007). Furthermore, HCN condensation, unless in very specific conditions like eutectic freezing (Cleaves *et al.*,

2006), or with unrealistic prebiotic concentrations of reagents (Shapiro, 2002), only produces purines, not pyrimidines, in relevant yields. HCN therefore does not appear to have the multifunctional reactivity required to lead to the necessary nucleobases upon which life is built.

Recently, formamide, NH_2CHO , has been proposed as either an alternative to HCN in the prebiotic scheme (Costanzo *et al.*, 2007) or a possible nonvolatile source of HCN (Barks *et al.*, 2010), leading mainly to the synthesis of purines. Formamide has properties that overcome the difficulties arising in HCN. Upon heating at 110–160°C in the presence of metal oxides and mineral catalysts, neat formamide will condense into both purines and pyrimidines (Costanzo *et al.*, 2007). It has also been shown that purines can form from formamide at lower temperatures upon UV irradiation, with or without the presence of calcium carbonate or sodium pyrophosphate (Barks *et al.*, 2010). Moreover, unlike volatile HCN, formamide has a boiling point of 210°C and thus can be easily concentrated and accumulated by simple evaporation in a “drying lagoon” hypothesis, making the concentration threshold less of an issue. The reactivity of NH_2CHO goes

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beyond nucleobase synthesis as well; Costanzo *et al.* (2007) found that phosphorylation of nucleosides to produce nucleotides, the building blocks of nucleic acids, readily occurs in the presence of formamide and a phosphate donor. Finally, formamide in one molecule contains the four most important elements for biological systems: H, N, C, and O.

Based on these properties, a scenario for a prebiotic formamide-based synthesis of informational polymers has been proposed (Saladino *et al.*, 2006). In the presence of formamide, nucleobases would form in the crevices of a mineral catalyst based in clay with a phosphate surface in dry, moderately hot conditions. The bases would be washed into aqueous solution, and if TiO_2 is present, sugar chains would start to attach to them. If these simple polymers survive and phosphorylation occurs, they could lead to RNA strands.

While formamide appears to meet prebiotic requirements of stability and reactivity, another important criterion is availability and abundance as a starting material. Formamide can be created from the hydrolysis of dilute HCN in water, as mentioned. The quantity of formamide produced via this route is not known. Formamide could also be naturally available, delivered exogenously to Earth via comets, interplanetary dust particles (IDPs), and meteorites (*e.g.*, Costanzo *et al.*, 2007). Formamide has been observed in comet Hale-Bopp via the gas-phase detection of three rotational transitions, with abundance relative to water of 0.01% (Bockelee-Morvan *et al.*, 2000). Alkyl amides, such as acetamide and propionamide, have also been identified in carbonaceous chondrites (Cooper and Cronin, 1995). Exogenous delivery would require extraterrestrial synthesis, perhaps in molecular clouds.

Following the initial detection of formamide in the interstellar medium in the dense cloud SgrB2 by Rubin and co-workers (1971), studies of interstellar formamide have been sporadic, mostly in the context of spectral surveys. Multiple transitions of formamide have been identified in surveys of SgrB2(OH), SgrB2(N) (Cummins *et al.*, 1986; Turner, 1991; Nummelin *et al.*, 2000; Halfen *et al.*, 2011), and Orion-KL (Blake *et al.*, 1986; Turner, 1991). In addition, as part of a survey of organic species in young stellar objects, NH_2CHO was also found in six other molecular clouds, including NGC 7538 and W3(H₂O) (Bisschop *et al.*, 2007). Beam-corrected column densities of the molecule were typically found to be in the range of 10^{13} to 10^{15} cm^{-2} , with abundances relative to H₂ of $\sim 10^{-11}$ to 10^{-9} .

To further investigate the availability and distribution of formamide in our galaxy, we have conducted additional observations of this molecule toward star-forming clouds, using the telescopes of the Arizona Radio Observatory (ARO). Four new sources of NH_2CHO were found, and new transitions were measured in three additional sources. From these measurements, abundances of formamide were determined, which were then compared to that in comets. Here, these results are presented, as well as an estimate of the amount of extraterrestrial formamide that could have been released to Earth by comets, meteorites, and IDPs.

2. Quantum Mechanics of Formamide

The well-characterized rotational spectrum of formamide has been the subject of numerous studies (Blanco *et al.*, 2006; Kryvda *et al.*, 2009). Formamide is a near prolate asymmetric

FIG. 1. Chemical structure of formamide. NH_2CHO is a nearly flat prolate asymmetric top. The principal moments of inertia *a* and *b* are indicated.

top molecule with a nearly flat structure, as shown in Fig. 1. The molecule has a strong *a*-dipole moment component of 3.62 D and a smaller *b*-dipole moment of 0.85 D. Therefore, both *a*- and *b*-dipole-allowed transitions occur in this species, with the respective selection rules $\Delta J=0, \pm 1$, $\Delta K_a=0$, $\Delta K_c=\pm 1$ and $\Delta J=0, \pm 1$, $\Delta K_a=\pm 1$, $\Delta K_c=\pm 1$. Here, *J* is the quantum number describing the overall rotational energy of the molecule, while *K_a* and *K_c* represent the projection of the rotational angular momentum along two principal axes. The nuclear spin of the nitrogen atom (*I* = 1) also gives rise to a quadrupole hyperfine structure, although at millimeter wavelengths such splittings are generally not resolved. Formamide thus has a complex rotational spectrum. The rotational transitions observed in this work were chosen on the basis of their intensities, obtained from the CDMS catalogue (<http://www.astro.uni-koeln.de/cdms>) and were also checked for potential contamination from lines of other molecules.

3. Observations

The measurements were conducted at the facilities of the ARO: the 12 m telescope at Kitt Peak and the Submillimeter Telescope (SMT) on Mt. Graham, both in Arizona. The observations were carried out during a series of runs from May 2005 to June 2012. Sources and telescope parameters are listed in Tables 1 and 2. The 12 m telescope was employed for the 3 and 2 mm observations, while those at 1 mm were conducted with the SMT. The receivers used at 2 and 3 mm employed SIS mixers, operated in single-sideband mode with typical image rejection of ≥ 16 dB, achieved by tuning the mixers. For measurements made after 2008 May, a new receiver with ALMA-type Band 3 sideband-separating mixers was used. Image rejection in this case was typically ≥ 15 dB. The backends used were 256 channel filter banks with 500 or 1000 kHz resolution, configured in parallel mode (2×128) to accommodate the two perpendicular polarizations. The temperature scale at the 12 m is given in terms of T_R^* . The main beam brightness temperature is then defined as

TABLE 1. MOLECULAR CLOUDS IN OBSERVATIONAL SAMPLE

Source	α (B1950.0)	δ (B1950.0)	D_{GC} (kpc)
Orion-KL	05 ^h 32 ^m 46.8 ^s	−05°24′23″	8.3
W51M	19 ^h 21 ^m 26.2 ^s	14°24′43″	6.1
G34.3	18 ^h 50 ^m 46.4 ^s	01°11′14″	5.1
NGC 7538	23 ^h 11 ^m 36.6 ^s	61°11′47″	8.9
W3(OH)	02 ^h 23 ^m 17.0 ^s	61°38′54″	9.6
DR21(OH)	20 ^h 37 ^m 14.0 ^s	42°12′00″	8.0
M17 SW	18 ^h 17 ^m 31.0 ^s	−16°13′00″	6.1

$T_R = T_R^*/\eta_c$, where η_c is the beam efficiency corrected for forward spillover losses. In the 1 mm band at the SMT, a dual-channel receiver utilizing ALMA-type Band 6 side-band-separating mixers was used, with image rejection ≥ 15 dB. The backend used was a 2048 channel filter bank with 1 MHz resolution, configured in parallel mode (2×1024 channels) for the two receiver channels. The temperature scale at the SMT is defined in terms of T_A^* , where $T_R = T_A^*/\eta_B$, and η_B is the main beam efficiency. Data were taken in position-switching mode with the off position 30 arcmin west in azimuth. Pointing was checked every 1.5 h on nearby continuum sources, usually a planet. Local oscillator shifts were done for each line to protect against possible image contamination.

The celestial coordinates of all sources are provided in Table 1, as well as the distances of the objects from the Galactic Center, D_{GC} (in kiloparsecs). Figure 2 shows the location of the clouds in the Galaxy and with respect to the galactic habitable zone, which will be discussed later. Table 2 summarizes the transitions of NH_2CHO studied in this work.

 TABLE 2. OBSERVED TRANSITIONS OF NH_2CHO

Frequency	Transition	ΔE_{lower} (cm^{-1})	Beam efficiency
84542.5	4 _{0,4} $\rightarrow$ 3 _{0,3}	4.24	0.93
87849.0	4 _{1,3} $\rightarrow$ 3 _{1,2}	6.47	0.92
102064.5	5 _{1,5} $\rightarrow$ 4 _{1,4}	8.89	0.90
105464.4	5 _{0,5} $\rightarrow$ 4 _{0,4}	7.06	0.90
106108.3	5 _{4,2} $\rightarrow$ 4 _{4,1}	40.21	0.89
	5 _{4,1} $\rightarrow$ 4 _{4,0}		
106134.7	5 _{3,3} $\rightarrow$ 4 _{3,2}	25.72	0.89
106141.7	5 _{3,2} $\rightarrow$ 4 _{3,1}	25.72	0.89
106541.9	5 _{2,3} $\rightarrow$ 4 _{2,2}	15.37	0.89
109753.7	5 _{1,4} $\rightarrow$ 4 _{1,3}	9.40	0.89
131618.2	6 _{1,5} $\rightarrow$ 5 _{1,4}	13.06	0.84
142701.7	7 _{1,7} $\rightarrow$ 6 _{1,6}	16.37	0.82
146871.8	7 _{0,7} $\rightarrow$ 6 _{0,6}	14.79	0.81
148223.5	7 _{2,6} $\rightarrow$ 6 _{2,5}	23.14	0.80
148556.7	7 _{6,1} $\rightarrow$ 6 _{6,0}	89.39	0.80
	7 _{6,2} $\rightarrow$ 6 _{6,1}		
148567.5	7 _{5,3} $\rightarrow$ 6 _{5,2}	66.63	0.80
	7 _{5,2} $\rightarrow$ 6 _{5,1}		
148599.9	7 _{4,4} $\rightarrow$ 6 _{4,3}	48.00	0.80
	7 _{4,3} $\rightarrow$ 6 _{4,2}		
148667.8	7 _{3,5} $\rightarrow$ 6 _{3,4}	33.51	0.80
148709.5	7 _{3,4} $\rightarrow$ 6 _{3,3}	33.51	0.80
153432.5	7 _{1,6} $\rightarrow$ 6 _{1,5}	17.45	0.79
167321.1	8 _{0,8} $\rightarrow$ 7 _{0,7}	19.69	0.76
227606.4	11 _{0,11} $\rightarrow$ 10 _{0,10}	38.35	0.75
247391.6	12 _{0,12} $\rightarrow$ 11 _{0,11}	46.05	0.75

4. Results

Four new sources of formamide were found: W51M, G34.3, DR21(OH), and M17 SW. Additional lines were observed in Orion-KL, W3(OH), and NGC 7538. Note that one line of NH_2CHO was also tentatively detected in G34.26+0.15 (Mookerjee *et al.*, 2007). All sources are sites of massive star formation and harbor compact hot core regions. Hot cores are warm (70–300 K), dense [$n(\text{H}_2) > 10^6 \text{ cm}^{-3}$] clumps of gas and dust near star-forming sites. The hot core phase lasts approximately 10^5 to 10^6 years (*e.g.*, Garrod and Herbst, 2006) and appears to be the most chemically rich in the interstellar medium. They are also where the collapsing gas and dust are giving rise to new stars, planetesimals, and possibly planets.

A summary of the spectral lines of formamide observed toward the seven molecular clouds is given in Table 3. All are a-type transitions and arise from levels < 130 K above ground state. The table lists the line intensities T_R^* (or T_A^*), the linewidths at half-maximum $\Delta V_{1/2}$, and the velocities with respect to the local standard of rest (LSR), V_{LSR} , for all observed features. The NH_2CHO lines appear to exhibit typical linewidths and LSR velocities of the given molecular clouds.

Representative spectra of formamide transitions measured toward each cloud are displayed in Figs. 3–5. The quantum numbers of the transition detected are given above each spectrum, and the actual formamide features are indicated by a line at the average LSR velocity for each cloud. Spectral lines arising from other complex organic molecules characteristic of hot cores, like $\text{C}_2\text{H}_5\text{CN}$ and CH_3COOH , are also visible in these data. Figure 3 displays representative lines measured toward the new sources G34.3 and W51M, while Fig. 4 shows those in DR21(OH) and M17 SW. Figure 5 presents data measured toward Orion-KL, NGC 7538, and W3(OH).

The W51 molecular cloud complex, located 7 kpc from the Sun, comprises several hot core regions, including W51M (Genzel *et al.*, 1982). For W51M, 14 transitions were observed, with intensities from 0.047 to 0.18 K. The LSR velocities are typically $V_{\text{LSR}} = 56$ –58 km/s, canonical values for this source, and the linewidths fall in the range of 8–12 km/s, also typical (*e.g.*, Bell *et al.*, 1993). This cloud is a new source for NH_2CHO .

Toward G34.3, nine transitions of NH_2CHO were detected. This cloud, at a distance of 4 kpc, contains a cometary-shaped ultracompact HII region and an isolated hot molecular core. The core region is known to be associated with numerous organic molecules, such as CH_3OH and CH_3CCH (Macdonald *et al.*, 1996; Kim *et al.*, 2000). Toward G34.3, line intensities of formamide range from 0.016 to 0.073 K; the linewidths are typically 5–8 km/s, with LSR velocities of 56–60 km/s, as also found for larger species such as CH_3OH , HCOOCH_3 , and CH_3OCH_3 by Mookerjee *et al.* (2007).

The M17 region is a prominent HII region–molecular cloud complex, located about 2.2 kpc from Earth, and is considered to be a prime example of triggered star formation (Wilson *et al.*, 2003). M17 SW is thought to contain young stellar objects and a photon-dominated region (PDR). Formamide appears to be associated with the general molecular cloud, rather than the PDR, judging from the measured linewidth near 10 km/s. Molecules associated with the

FIG. 2. Schematic representation of the Milky Way Galaxy. The Sun is indicated by the cross. The galactic habitable zone is indicated by the dashed, gray circles, based on work of Gowanlock *et al.* (2011). The approximate galactic positions of the molecular clouds where formamide has been detected are indicated by filled circles. The circle size indicates the relative amount of formamide. The figure summarizes the current work and past observations (*e.g.*, Cummins *et al.*, 1986; Bisschop *et al.*, 2007; Halfen *et al.*, 2011). The distances are in kiloparsecs, or kpc (1 kpc $\sim$ 3259 light-years).

PDR itself, such as HOC^+ , exhibit narrower lines, although they all have velocities near 20 km/s, as found for NH_2CHO (Apponi *et al.*, 1999). Larger molecules such as formamide may be less abundant in PDRs because the stronger UV field pervasive in those regions leads to their photodissociation (Apponi *et al.*, 1999).

DR21(OH) is a well-known high-mass star-forming region, with bright OH maser emission (*e.g.*, Zapata *et al.*, 2012). The source contains several dense clumps. The formamide line parameters ($V_{\text{LSR}} = -4$ km/s and $\Delta V_{1/2} = 4\text{--}5$ km/s) are typical for species such as CS and CH_3OH (Chandler *et al.*, 1993). High-velocity wings seen at certain positions near DR21(OH) are not apparently present in formamide.

Toward Orion-KL, 19 transitions were observed, with intensities ranging from 0.017 to 0.724 K (see Table 3 and Fig. 5). Orion-KL is an IR source contained in the giant Orion Molecular Cloud 1, located only at a distance of 450 pc. It is chemically rich, as attested by various spectral line surveys in the 3, 2, 1, and 0.8 mm bands (*e.g.*, Johansson *et al.*, 1984; Turner, 1991; Ziurys and McGonagle, 1993; Sutton *et al.*,

1995). The linewidths of the NH_2CHO features are typically between 4 and 6 km/s, while the LSR velocities are between 6 and 9 km/s. The warm gas core of the Orion A region consists of at least three distinct regions: the hot core, the plateau, and the compact ridge, with LSR velocities of 5, 8, and 7.5 km/s, and typical linewidths of $\Delta V_{1/2} \sim 10, 20\text{--}30$, and 4–6 km/s, respectively (*e.g.*, Sutton *et al.*, 1995; Lerate *et al.*, 2008). These regions are surrounded by a cooler quiescent extended ridge, with $\Delta V_{1/2} \sim 3$ km/s and LSR velocity of 10 km/s. Our results indicate that formamide emission comes mainly from the compact/extended ridge region.

NGC 7538 is an HII, star-forming region at a 2.7 kpc distance from Earth, which harbors three main activity centers containing massive stellar objects at different evolutionary stages (*e.g.*, Wright *et al.*, 2012). These observations focused on the gas associated with the massive young star IRS 1, which drives a molecular outflow (De Buizer and Minier, 2005). Four transitions of formamide were measured in NGC 7538, all of which had weak intensities (~ 10 mK) and

TABLE 3. OBSERVATIONS OF NH₂CHO

Transition	Orion-KL			W51M			G34.3			NGC 7538			M17 SW			W3(OH)			DR21(OH)		
$J''_{K_a, K_c} \rightarrow J'_{K_a, K_c}$	T_R^* (mK)	V_{LSR} (km/s)	$\Delta V_{1/2}$ (km/s)	T_R^* (mK)	V_{LSR} (km/s)	$\Delta V_{1/2}$ (km/s)	T_R^* (mK)	V_{LSR} (km/s)	$\Delta V_{1/2}$ (km/s)	T_R^* (mK)	V_{LSR} (km/s)	$\Delta V_{1/2}$ (km/s)	T_R^* (mK)	V_{LSR} (km/s)	$\Delta V_{1/2}$ (km/s)	T_R^* (mK)	V_{LSR} (km/s)	$\Delta V_{1/2}$ (km/s)	T_R^* (mK)	V_{LSR} (km/s)	$\Delta V_{1/2}$ (km/s)
$4_{1,3} \rightarrow 3_{1,2}$	27	7	5.1																		
$5_{1,5} \rightarrow 4_{1,4}$	60	7	6.8																		
$5_{0,5} \rightarrow 4_{0,4}$	80	7	4.3																		
$5_{4,2} \rightarrow 4_{4,1}$	17	9	4.2	82	58	11.2	16	58	8.4												
$5_{3,3} \rightarrow 4_{3,2}$	22	7	4.3	80	57	8.4	33	60	7.0												
$5_{3,2} \rightarrow 4_{3,1}$				95	61	12.8	25	57	8.4												
$5_{2,3} \rightarrow 4_{2,2}$	45	8	5.7	55	56	12.6	45	57	6.8												
$5_{1,4} \rightarrow 4_{1,3}$				95	56	9.6															
$6_{1,5} \rightarrow 5_{1,4}$	122	9	5.7																		
$7_{1,7} \rightarrow 6_{1,6}$	150	7	4.8	110	58	9.5	73	56	6.3												
$7_{0,7} \rightarrow 6_{0,6}$	724	6	5.1	180	57	11.2	70	59	8.0												
$7_{2,6} \rightarrow 6_{2,5}$	94	6	5.5	110	58	11.5															
$7_{6,1} \rightarrow 6_{6,0}$	80	9	4.0	47	58	8.1															
$7_{5,3} \rightarrow 6_{5,2}$	60	5	4.0	74	56	10.1															
$7_{4,4} \rightarrow 6_{4,3}$	110	7	6.0	103	59	9.1	46	60	4.9												
$7_{3,5} \rightarrow 6_{3,4}$	100	9	5.0	100	60	10.1															
$7_{3,4} \rightarrow 6_{3,3}$	54	8	6.0	93	59	11.1	50	58	6.3												
$7_{1,6} \rightarrow 6_{1,5}$	120	7	5.8																		
$8_{0,8} \rightarrow 7_{0,7}$	140	7	5.4																		
$11_{0,11} \rightarrow 10_{0,10}^a$	270	8	5.3																		
$12_{0,12} \rightarrow 11_{0,11}^a$	350	7	5.3																		

^aMeasured as T_A^* (K).

FIG. 3. Example spectra of formamide transitions observed toward G34.3 (left panels) and W51M (right panels) at 3 and 2 mm in wavelength with the ARO 12 m telescope. The spectral resolution is 500 kHz for all data, except the $J=7_{0,7} \rightarrow 6_{0,6}$ transition in W51M, where it is 1 MHz. The quantum numbers for each transition are shown on each panel. The vertical line under each spectrum indicates the average cloud LSR velocity, near 58 km/s for both regions. Other organic molecules can be seen in the data, such as C_2H_5CN and $HCOOCH_3$.

exhibited linewidths of ~ 5 km/s at a velocity of -59 to -60 km/s. Similar line parameters have been measured in CS in this source (Kameya *et al.*, 1986); they suggest that formamide does not participate in the molecular outflow centered on IRS 1. The molecule had been previously detected in NGC 7538 by Bisschop *et al.* (2007).

W3(OH) is a compact HII region 2 kpc distant, situated in the massive W3 cloud complex (Wright *et al.*, 2004). Within 2 arcmin of W3(OH) are over 100 near-IR sources that are presumed to be low-mass stars. W3(OH) and its close-by companion, W3(H₂O) (Turner and Welch, 1984), are two very dense hot cores surrounded by cooler material (Wilson *et al.*, 1991). The LSR velocities (near -48 km/s) and linewidths (~ 5 km/s) for formamide in this source are typical for molecules in the cooler gas (10–

60 K; Kim *et al.*, 2006). Formamide had been previously seen in W3(H₂O), which is 5 arcsec away from our position (Bisschop *et al.*, 2007).

5. Analysis

For each source in which more than three rotational transitions were observed, a column density was calculated with the rotation diagram method, which assumes local thermodynamic equilibrium conditions (see Turner, 1991). Local thermodynamic equilibrium implies optically thin emission as well as a homogeneous distribution of molecules in an area of constant temperature and density. It is a reasonable approximation for molecules with extended distributions, as exhibited by formamide in Orion,

FIG. 4. Example spectra of formamide transitions observed toward DR21(OH) (left panels) and M17 SW (right panels) at 3 and 2 mm with the ARO 12 m telescope. The spectral resolution is 500 kHz. The quantum numbers for each transition are shown on each panel. The vertical line under each spectrum indicates the cloud average LSR velocity: -3 km/s for DR21(OH) and 18 km/s for M17 SW.

where it appears to arise from the more quiescent ridge material that traces the general molecular cloud. The molecule thus is likely produced by quiescent cloud chemistry and might be expected to be extended in other sources as well. Therefore, assuming a beam-filling factor of 1 for all the clouds studied here is reasonable. However, if beam dilution plays a role for the more distant clouds, the net effect would be to raise the column density and abundance of NH_2CHO in those objects, increasing the availability of the molecule.

The rotational diagram method is based on the following formula for total molecular column density N_T :

$$N_T = \left(\frac{3kT_R \Delta V_{1/2}}{8\pi^3 \nu S \mu^2} \right) Q_{\text{rot}} \exp\left(\frac{E_u}{T_{\text{rot}}}\right) \quad (1)$$

Here, S is the line strength of a given transition, μ the molecular dipole moment, Q_{rot} the rotational partition function, E_u the energy of the upper level of the transition, and T_{rot} the rotational temperature. The above equation can be rearranged to be the formula employed in the rotational diagram method:

$$\log\left(\frac{3kT_R \Delta V_{1/2}}{8\pi^3 \nu S \mu^2}\right) = \log\left(\frac{N_T}{Q_{\text{rot}}}\right) - \frac{E_u \log e}{k T_{\text{rot}}} \quad (2)$$

The quantity on the left, also called $\log I$, is then plotted versus E_u for each transition measured. The slope of the resulting line yields T_{rot} , and the y intercept is $\log(N_T/Q_{\text{rot}})$. Calculation of the partition function then directly leads to the total column density. The partition function for asymmetric tops with no particular symmetry is estimated by the following formula (Turner, 1991):

$$Q_{\text{rot}} = \left[\frac{\pi(kT)^3}{h^3 ABC} \right]^{1/2} \quad (3)$$

Here A , B , and C are the rotational constants of the molecule, in this case formamide, and $T = T_{\text{rot}}$.

Figure 6a displays the rotational diagrams derived for Orion-KL, G34.3, and W51M. Figure 6b shows the rotational diagrams for W3(OH) and NGC 7538, generated by combining these data with those of Bisschop *et al.* (2007). As expected for optically thin emission, the points

FIG. 5. Example spectra of formamide transitions observed toward Orion-KL (left panels), NGC 7538, and W3(OH) (right panels) at 3 and 2 mm with the ARO 12 m telescope. The spectral resolution is 500 kHz. The quantum numbers for each transition are shown on each panel. The vertical line under the data indicates the cloud average LSR velocity: 8 km/s for Orion-KL, -58 km/s for NGC 7538, and -48 km/s for W3(OH). Other molecular features are present in these spectra.

corresponding to the measured transitions approximately fall along a straight line. The derived rotational temperatures and column densities obtained from this method are presented in Table 4. As is seen in the table, the rotational temperatures fall in the range of 70–177 K for NH_2CHO , indicating its presence in warm gas.

For the sources when only a few transitions were measured [M17 SW and DR21(OH)], the total column density was calculated analytically from the transition with the highest upper state energy, with the equation

$$N_{\text{T}} = Q_{\text{rot}}(T) \frac{3kT_{\text{R}}4V_{1/2}}{8\pi^3\nu\mu^2S} \exp\left(\frac{E_{\text{u}}}{T_{\text{rot}}}\right) \quad (4)$$

In this case, a rotational temperature must be assumed; based on the values obtained by the rotational diagram method, $T_{\text{rot}} \sim 70$ K was used. The resulting column densities calculated by this method are also summarized in Table 4. To complete the sample, included in the table is N_{T}

FIG. 6. Rotational diagrams for Orion-KL, W51M, G34.3 (upper panels), and NGC 7538, W3(OH) (lower panels). The y axis represents $\log I$, where $I = \frac{3kT_R \Delta V_{1/2}}{8\pi^3 \nu S \mu^2}$. The rotational diagrams for NGC 7538 and W3(OH) were constructed by combining our measurements with those of Bisschop *et al.* (2007). Rotational temperatures derived from the plots lie in the range of 70–177 K, indicating that formamide is present in warm gas in molecular clouds.

obtained for formamide for the other known sources of this molecule, including SgrB2(N) and SgrB2(OH), as measured by Halfen *et al.* (2011) and Cummins *et al.* (1986), and four clouds from Bisschop *et al.* (2007). These values were also determined by the rotational diagram method. A uniform beam-filling factor was assumed in all cases.

6. Discussion

6.1. Abundances and distribution of interstellar NH_2CHO

The total column densities obtained for formamide in the seven sources studied are in the range of $0.1\text{--}9.1 \times 10^{13} \text{ cm}^{-2}$. The source with the highest value is W51M, and the smallest is DR21(OH). In comparison, the total column density found in SgrB2(N) is $1.7\text{--}4.0 \times 10^{14} \text{ cm}^{-2}$ (Halfen *et al.*, 2011). Here the range of values reflects the presence of two gas components, one cool and one warm, with $T_{\text{rot}} \sim 26 \text{ K}$ and 134 K , respectively. In SgrB2(OH), $N_{\text{T}} \sim 7.2 \times 10^{13} \text{ cm}^{-2}$ (Cummins *et al.*, 1986). SgrB2(N) clearly has the largest abundance of

formamide, with both components summing to almost $6 \times 10^{14} \text{ cm}^{-2}$. Note that Sutton *et al.* (1995) found a column density of $2.4 \times 10^{14} \text{ cm}^{-2}$ for NH_2CHO and $T_{\text{rot}} \sim 187 \text{ K}$ in the Orion-KL compact ridge, based on 10 higher energy lines in the 0.8 mm region. These authors also found weak emission in NH_2CHO arising from the Orion hot core and the southeast plateau. From 19 observed transitions at lower energies, we find $4.7 \times 10^{13} \text{ cm}^{-2}$ $T_{\text{rot}} \sim 168 \text{ K}$, somewhat in agreement. The factor of 5 difference is likely a result of the smaller beam size used by Sutton *et al.*, which samples higher-excitation material.

The abundances derived for formamide, relative to H_2 , are also shown in Table 4. These values were obtained by comparing the total column densities for NH_2CHO with values for H_2 from the literature. The abundances lie in the range of $0.1\text{--}1 \times 10^{-10}$. It appears that the abundance of formamide relative to H_2 is constant within one order of magnitude throughout the molecular cloud sample.

Formamide's known presence in 13 sources (Table 4) indicates that it is a fairly common species in molecular clouds

TABLE 4. COLUMN DENSITIES AND ABUNDANCES OF NH₂CHO IN MOLECULAR CLOUDS

Source	$N_{\text{tot}} \text{ (cm}^{-2}\text{)}$	$T_{\text{rot}} \text{ (K)}$	$N(\text{H}_2) \text{ (cm}^{-2}\text{)}$	$f(\text{NH}_2\text{CHO}/\text{H}_2)$
Orion-KL	$4.7 \text{ (1.7)} \times 10^{13}$	168	$1 \times 10^{24,a}$	5×10^{-11}
W51M	$9.1 \text{ (2.2)} \times 10^{13}$	130	$1 \times 10^{24,a}$	1×10^{-10}
G34.3	$1.2 \text{ (0.4)} \times 10^{13}$	70	$5 \times 10^{23,a}$	4×10^{-11}
NGC 7538	$4.8 \text{ (1.5)} \times 10^{12}$	177	$1 \times 10^{23,a}$	5×10^{-11}
M17 SW	$2.6 \text{ (0.9)} \times 10^{12}$	70 ^b	$2 \times 10^{23,c}$	1×10^{-11}
W3(OH)	$3.3 \text{ (0.8)} \times 10^{12}$	124	$1 \times 10^{23,a}$	3×10^{-11}
DR21(OH)	$1.1 \text{ (0.5)} \times 10^{12}$	70 ^b	$1 \times 10^{23,a}$	1×10^{-11}
SgrB2(N)	$1.7 \times 10^{14,d}$	26	$3 \times 10^{24,d}$	5×10^{-11}
	$4.0 \times 10^{14,e}$	134	$3 \times 10^{24,e}$	1.3×10^{-10}
SgrB2(OH)	$7.2 \text{ (0.3)} \times 10^{13,f}$	13 ^f	$1 \times 10^{24,g}$	7×10^{-11}
G24.78 ^h	1.4×10^{13}	169	4×10^{23}	3×10^{-11}
G75.78 ^h	2.5×10^{12}	77	1×10^{23}	2×10^{-11}
NGC 6334 IRS1 ^h	3.2×10^{13}	166	2×10^{23}	1×10^{-10}
W33 A ^h	1.3×10^{13}	45	2×10^{23}	6×10^{-11}
Comet Hale-Bopp				$1-2 \times 10^{-12,i}$

^aApponi and Ziurys, 1997.^bAssumed rotational temperature.^cStutzki *et al.*, 1988.^dHalfen *et al.*, 2011, cold component.^eHalfen *et al.*, 2011, hot component.^fCummins *et al.*, 1986.^gSutton *et al.*, 1991.^hBased on rotational diagrams of Bisschop *et al.* (2007), assuming a uniform beam-filling factor.ⁱDerived from the fractional abundance of formamide relative to H₂O, from Bockele-Morvan *et al.* (2000). See text.

associated with high-mass star formation. Its abundance in the Galaxy is illustrated in Fig. 2. Here, the sources of formamide are indicated by a filled circle, whose size is proportional to the [NH₂CHO]/[H₂] ratio. The molecule is present near the Galactic Center, to as far out as $R_G \sim 10$ kpc. It is unknown whether it exists in objects at larger galactic distances. H₂CO has been observed in gas as far as $R_G \sim 20$ kpc (Blair *et al.*, 2008). These observations have suggested that the galactic habitable zone (GHZ) could exist near the edges of the Galaxy.

The concept of the GHZ is clearly evolving. Criteria such as metallicity gradients, star formation, and supernova rates have been used to define its location in the Galaxy. Line-weaver *et al.* (2004), for example, modeled the GHZ as a time-evolving region, at the current time located in a ring roughly between 7 and 9 kpc from the Galactic Center. In this region, the probability of finding complex life is the highest. Prantzos (2008) argued that the whole galactic disk may be suitable for life, when considering the number of Earth-like planets that survive both the formation of “Hot Jupiters” and supernovae explosions. The most recent estimation of the GHZ, from Gowanlock *et al.* (2011), is based on the number of habitable planets. These authors predicted the GHZ to extend about 12 kpc from the Galactic Center, with the greatest possibility of life at a radius of about 2.5 kpc. At distances $D_G \leq 2.5$ kpc, however, habitability may sharply decrease as the stellar density rises. The extent of the GHZ of Gowanlock *et al.* is plotted on Fig. 2. It is interesting to see from the figure that formamide appears to exist throughout the proposed GHZ region.

6.2. Interstellar formation of formamide

The formation process of formamide in molecular clouds is not well understood. The molecule appears to be present

near hot cores, in gas that is warm. Halfen *et al.* (2011) suggested two basic routes to NH₂CHO formation. One route involves gas-phase processes, in particular radiative association and ion-molecule reactions that use common and abundant precursors like H₂CO and NH₄⁺; the alternative pathway is via grain chemistry, through hydrogenation and UV processing, followed by the evaporation of the icy grain mantles. It is difficult from our observations to reliably distinguish between these possible synthetic routes, but some insight can be gained from well-studied sources like Orion.

In the Orion-KL region, the center of the star-forming region is the dense “Hot Core,” where the gas kinetic temperature is greater than 200 K. The chemistry in the Hot Core is thought to be dominated by gas-grain interactions and the subsequent evaporation of ice mantles (Wright *et al.*, 1996). Surrounding this Hot Core is the Plateau, tracing material impacted by powerful outflows from the protostars near the Hot Core and the more quiescent ambient material (Lerate *et al.*, 2008). In the Plateau, shock chemistry is likely to be important. Finally, there is an extended layer of ambient material forming the so-called ridge; the “compact ridge” is material that is heated by the activities near the Hot Core (Ungerechts *et al.*, 1997). Each of these regions displays a different line profile. The V_{LSR} velocities and linewidths indicate that formamide emission likely arises from the warm ridge. Furthermore, the rotational diagram is consistent with one velocity component. These facts would suggest that gas-phase mechanisms lead to formamide in Orion, albeit at warm temperatures.

Quan and Herbst (2007) proposed that NH₂CHO is created from the radiative association reaction:

Dissociative recombination then leads to the neutral product:

The rate of the radiative association process is not known, however. Halfen *et al.* (2011) proposed another gas-phase process involving an ion-molecule reaction, followed by dissociative electron recombination:

Reaction rates and branching ratios for these reactions are also unknown. In the best case scenario, Reaction 7 would proceed near the Langevin rate of $\sim 2 \times 10^{-9} \text{ cm}^3/\text{s}$, while typical dissociation electron recombination rates, as would apply to Eq. 8, are $\sim 10^{-7} \text{ cm}^3/\text{s}$ (Bardsley and Biondi, 1970). The above scheme in principle could be feasible, if the branching ratios were favorable.

Garrod *et al.* (2008) had an alternative mechanism for gas-phase formamide production, namely, neutral-neutral reactions. These processes often have a small barrier, which could be overcome in the warmer gas that characterizes NH_2CHO , making it an attractive possibility. The reaction involves formaldehyde and the NH_2 radical, both abundant species in interstellar clouds (*e.g.*, Persson *et al.*, 2012):

Because one of the reactants is a radical, the process should be faster than typical neutral-neutral pathways. The rate could be as high as $k \sim 10^{-11} \text{ cm}^3/\text{s}$ (Woodall *et al.*, 2007).

Another avenue for NH_2CHO synthesis would involve dust grain reactions. The tentative identification of formamide features in the ISO-SWS infrared spectra of interstellar ices in the young stellar objects NGC 7539 IRS9 (Raunier *et al.*, 2004) and W33A (Schutte *et al.*, 1999) suggests its presence on dust grain surfaces. It is postulated that hydrogenation of HNCO leads to formamide on grains (Charnley and Rodgers, 2009). Experimental irradiation of CO - and NH_3 -rich interstellar ice analogues has also been shown to produce this molecule (Jones *et al.*, 2011). Garrod *et al.* (2008) generated formamide in ices by hydrogenation of OCN and also by the reaction of HCO and NH_2 . However, these processes lead to an overproduction of formamide, with $f = 1.3\text{--}2.4 \times 10^{-6}$ (Garrod *et al.*, 2008), at least 4 orders of magnitude more abundant than in the most favorable source.

6.3. Links to comets, asteroids, and early Earth

During the formation of the Solar System, gas-phase formamide may have condensed and been incorporated in accreting asteroids, planetesimals, comets, and meteorites. Oort Cloud comets are believed to be residuals of planetary accretion and therefore reflect the pristine composition of grains and icy bodies in the presolar nebula (Irvine *et al.*, 2000). Such objects could contain unprocessed formamide from the nascent molecular cloud in which the Solar System formed. Observational evidence of comet Hale-Bopp supports this hypothesis. Hale-Bopp, discovered in 1995, is the

brightest Oort Cloud comet yet to be studied. Several organics were detected by millimeter radio observations, including formamide, which had an abundance, relative to water, of $[\text{NH}_2\text{CHO}]/[\text{H}_2\text{O}] \sim 1\text{--}2 \times 10^{-4}$ (Bockelee-Morvan *et al.*, 2000). This abundance is not negligible.

For comparison with the interstellar abundance measured here, a value for the $[\text{H}_2\text{O}]/[\text{H}_2]$ ratio in the molecular cloud predating our solar system must be assumed. Modeling the physical and chemical properties of H_2O and using observations of the 557 GHz line from the Submillimeter Wave Astronomy Satellite as a benchmark, Hollenbach *et al.* (2009) estimated the average abundance of water vapor within a dense, star-forming cloud to be $[\text{H}_2\text{O}]/[\text{H}_2] \sim 10^{-8}$. The $[\text{NH}_2\text{CHO}]/[\text{H}_2]$ would then be around $1\text{--}2 \times 10^{-12}$ for the Oort Cloud comets, if Hale-Bopp is representative. This value is within an order of magnitude of the abundances observed in molecular clouds (see Table 4).

It is not clear whether formamide in comets is pristine interstellar material or produced from chemical reactions in the coma on solar approach (Irvine *et al.*, 2000). It has been shown that the abundance of HCN and HNC within comets is highly dependent on their distance from the Sun and may not reflect interstellar abundances (Biver *et al.*, 1997; Rodgers and Charnley, 1998). The similarity between the gas-phase abundances for NH_2CHO in the interstellar medium and in Hale-Bopp, however, suggests a possible connection between interstellar clouds and comets.

Meteorites are also known to be sources of potentially prebiotic compounds (Pizzarello and Shock, 2010). Alkyl amides, such as acetamide, propionamide, and more complex species up to 12 carbon atoms have been identified in carbonaceous chondrites, although exact quantities have not been determined (Cooper and Cronin, 1995; Pizzarello *et al.*, 2006). However, smaller amides, such as formamide, are easily lost in the preparation process and are difficult to detect in meteoritic material. It is perhaps not unreasonable to assume that formamide is part of the meteoritic amide suite. Interplanetary dust particles are another source of interstellar organic compounds. However, due to their size, they are more difficult to analyze, and few techniques have the sensitivity and spatial resolution to study the organic content of IDPs in detail. The methods typically are only functional group-specific but seem to indicate the presence of amides or amines in IDPs (Pizzarello *et al.*, 2006).

The large prebiotic inventory of comets and meteorites has led to a renewed interest in estimating the role of extraterrestrial material in the emergence of life on Earth (*e.g.*, Whittet, 1997). The objects delivering extraterrestrial material can be classified into three general categories according to their size: large impactors, meteorites, and IDPs (*e.g.*, Pasek and Lauretta, 2008). Upon entry in the atmosphere, the organic matter in such objects faces multiple hazards, such as vaporization and destruction by heating (Anders, 1989; Pasek and Lauretta, 2008). However, it is now known that meteorites that survive passage through Earth's atmosphere without breaking apart do not lose their organic content, as it is preserved by an icy fusion crust (*e.g.*, Pizzarello *et al.*, 2001).

It can be argued that IDPs are the main contributors of extraterrestrial prebiotic compounds (Anders, 1989; Pasek and Lauretta, 2008). Based on the analysis of the crater record on the Moon, two delivery scenarios can be inferred: a

gradual decrease of the flux of impactors after the creation of Earth 4.4 billion years ago (Hartmann, 2003); alternatively, a cataclysmic event at 3.8–4 Ga, where the flux of impactors greatly increased, that is, the Late Heavy Bombardment (Ryder, 2003). Depending on the chosen hypothesis, the flux of prebiotic carbon from IDPs on early, pre-life Earth has been estimated to be in the range of $\sim 0.1 \text{ kg/km}^2/\text{yr}$ to $\sim 10 \text{ kg/km}^2/\text{yr}$ (Whittet, 1997; Pasek and Lauretta, 2008).

There has only been one estimate of the IDP flux of prebiotic nitrogen, by Pasek and Lauretta (2008). These authors calculated the influx of extraterrestrial nitrogen delivered to earth from IDPs during the Late Heavy Bombardment to be $\sim 0.2 \text{ kg/km}^2/\text{yr}$, or $14.3 \text{ mol/km}^2/\text{yr}$. Considering the inventory in Hale-Bopp (Bockelee-Morvan *et al.*, 2000), nitrogen-bearing molecules are $\sim 1.1\%$ of the H_2O abundance. Formamide itself is 0.01% and thus about 1% of the nitrogen molar content in Hale-Bopp. If the assumption is made that formamide composes roughly 0.5% of all nitrogen molecules brought to Earth during the Late Heavy Bombardment, then the maximum annual terrestrial flux of formamide from IDP infall is $\sim 0.07 \text{ mol/km}^2/\text{yr}$. Even though it is likely that most of this material was deposited in the oceans and thus largely dissolved and diluted, some formamide also could have found its way to the surface of a mineral catalyst or thin freshwater environments.

It is hard to evaluate whether such a flux of NH_2CHO would be sufficient to influence prebiotic chemistry. In the case of HCN, concentrations of 10^{-2} M are needed to produce the tetramer leading to purine synthesis (Orgel, 2004). It is hard to imagine that such a concentration on early Earth could be realized, given the volatility of HCN. On the other hand, mixtures of 10% formamide in water have been shown experimentally to yield purine, adenine, and hypoxanthine at 100°C over a 96 h period (Barks *et al.*, 2010). It is possible that this concentration of formamide in water could have occurred on early Earth, given the low volatility of NH_2CHO and the lack of azeotrope mixtures between the two substances. However, formamide would have to be accumulated over a long period of time without disruption—an improbable scenario. It is therefore unlikely that the formamide flux from IDPs would be sufficient to start significant production of purines in the RNA world.

Locally, however, meteorites also may have delivered a significant amount of NH_2CHO (Pasek and Lauretta, 2008). Renazzo-type or CR carbonaceous chondrites are remarkably rich in small, nitrogen-bearing soluble organic molecules, including ammonia, amino acids, and amines (Pizzarello *et al.*, 2011). Recently, GRA95229 and other meteorites were found to contain large amounts of ammonia in the insoluble organic material, or IOM (Pizzarello and Williams, 2012). HCN now has also been extracted from the Murchison meteorite (Pizzarello, 2012). These results suggest that meteorites were the main source of nitrogen-containing material needed for prebiotic synthesis. Formamide could be part of this nitrogen source.

If the atmosphere during the early Earth epoch was denser than it is today, say of the order of 10 bar, the organic content of impactors up to 100 m in size would be preserved (Whittet *et al.*, 1997). A carbonaceous chondrite fragment of 1 m in radius, hitting early Earth at a speed of 15 km/s and at an angle of 15° from the horizontal (Pierazzo and Chyba, 1999), would have formed a crater of $\sim 2.5 \times 10^3 \text{ m}^2$, in accordance

with the crater energy-diameter scaling law given by Popova *et al.* (2003). Assuming this hypothetical meteorite to have the same density as that of Murchison (2.5 g/cm^3 ; Fuchs *et al.*, 1973), it would have delivered a total mass of $\sim 1.05 \times 10^4 \text{ kg}$ of material, or 4.2 kg/m^2 . Considering a meteorite such as GRA 95229, about 1% of this mass would be in the IOM, or about 105 kg. The amount of nitrogen found in the IOM phase of GRA 95229 is about $27.9 \text{ } \mu\text{g/mg}$ (Pizzarello *et al.*, 2011). Roughly speaking, the IOM composes about 70% of the organic material in typical carbonaceous chondrites, with 30% in the soluble organic material phase. Therefore, about $12.0 \text{ } \mu\text{g/mg}$ of nitrogen is contained in the soluble organic material, assuming that the nitrogen content is the same in both phases. If about 0.5% of the molar nitrogen content is contained in the form of formamide (approximately the percent in comet Hale Bopp), then of the original $\sim 10^4 \text{ kg}$ of material, $\sim 0.45 \text{ mol}$ of NH_2CHO would be delivered to Earth in one impact, or 0.18 mmol/m^2 . Given formamide's relatively high stability, with a low boiling point (210°C), it is conceivable that on local sites, over several years, the concentration of formamide could reach levels necessary for prebiotic synthesis. As mentioned, 10% formamide in water can produce detectable amounts of purines (Barks *et al.*, 2010).

7. Conclusion

Formamide has been proposed as a unique, prebiotic source of nucleobases and informational polymers. Past work has shown that the compound has the necessary reactivity and stability to fulfill this role. This study of interstellar formamide indicates that the molecule is a common constituent of star-forming regions and is prevalent within the GHZ. The abundance found in molecular clouds is comparable to what has been observed in comet Hale Bopp, suggesting that formamide is incorporated into planetesimals in the pre-solar nebula. Oort Cloud comets may be a potential source of prebiotic formamide, as could be meteorites and IDPs. The flux of formamide brought to Earth during the period of the Late Heavy Bombardment by IDPs could have been on average $0.07 \text{ mol/km}^2/\text{yr}$, and a single meteorite impact could deliver as much as a few tenths of a millimole per square meter. Considering the low volatility and hydrolysis rate of formamide, these amounts are not negligible and may have contributed importantly to the synthesis of the first prebiotic polymers.

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Abbreviations

ARO, Arizona Radio Observatory; GHZ, galactic habitable zone; IDPs, interplanetary dust particles; IOM, insoluble organic material; LSR, local standard of rest; PDR, photon-dominated region; SMT, Submillimeter Telescope.

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