Discovery in space of ethanolamine, the simplest phospholipid head group

Victor M. Rivilla,a,b,1, Izaskun Jiménez-Serra,a Jesús Martin-Pintado,a Carlos Briones,a Lucas F. Rodríguez-Almeida,a Fernando Rico-Villas,b Belén Tercero,3 Shaoshan Zeng,c Laura Colzi,b,pablo de Vicente,c, Sergio Martin,a,c, and Miguel A. Requena-Torresb,c

aCentro de Astrobiología, Consejo Superior de Investigaciones Científicas-Instituto Nacional de Técnica Aeroespacial “Esteban Terrazas”, 28850 Madrid, Spain; bOsservatorio Astrofisico di Arcetri, Istituto Nazionale di Astrofisica, 50125 Florence, Italy; cStar and Planet Formation Laboratory, Cluster for Pioneering Research, RIKEN, Wako 351-0198, Japan; dALMA Department of Science, European Southern Observatory, Santiago 763-0355, Chile; eDepartment of Science Operations, Joint Atacama Large Millimeter/Submillimeter Array Observatory, Santiago 763-0355, Chile; fDepartment of Astronomy, University of Maryland, College Park, MD 20742; and gDepartment of Physics, Astronomy and Geosciences, Towson University, Towson, MD 21252

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Cell membranes are a key element of life because they keep the genetic material and metabolic machinery together. All present cell membranes are made of phospholipids, yet the nature of the first membranes and the origin of phospholipids are still under debate. We report here the presence of ethanolamine in space, NH₂CH₂CH₂OH, which forms the hydrophilic head of the simplest and second-most-abundant phospholipid in membranes. The molecular column density of ethanolamine in interstellar space is N ≈ (1.51 ± 0.07) × 10¹³ cm⁻², implying a molecular abundance with respect to H₂ of (0.9 ± 1.4) × 10⁻¹⁰. Previous studies reported its presence in meteoritic material, but they suggested that it is synthesized in the meteorite itself by decomposition of amino acids. However, we find that the proportion of the molecule with respect to water in the interstellar medium is similar to the one found in the meteorite (10⁻⁵). These results indicate that ethanolamine forms efficiently in space and, if delivered into early Earth, could have contributed to the assembling and early evolution of primitive membranes.

Significance
The detection of ethanolamine (NH₂CH₂CH₂OH) in a molecular cloud in the interstellar medium confirms that a precursor of phospholipids is efficiently formed by interstellar chemistry. Hence, ethanolamine could have been transferred from the proto-Solar nebula to planetesimals and minor bodies of the Solar System and thereafter to our planet. The prebiotic availability of ethanolamine on early Earth could have triggered the formation of efficient and permeable amphiphilic molecules such as phospholipids, thus playing a relevant role in the evolution of the first cellular membranes needed for the emergence of life.

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1To whom correspondence may be addressed. Email: rivilla@cab.inta-csic.es.

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Results
We have detected EtA toward the molecular cloud G+0.693−0.027 (hereafter G+0.693), located in the SgrB2 complex in the Galactic Center, as shown in Fig. 2. This region is one of the

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most chemically rich reservoirs of molecules in the galaxy, with a plethora of organic species detected (21–25). The extremely rich gas-phase chemical composition of this region is due to erosion of the ice mantles of interstellar dust grains by large-scale low-velocity (<20 km·s⁻¹) shocks (26) induced by a collision between massive molecular clouds (27). For the typical (intermediate)
densities of G+0.693 of a few $10^{-3}$ cm$^{-3}$ (27), the emission is subthermally excited, yielding very low $T_{ex}$ in the range of 5 to 15 K (21, 22). Since only low-energy molecular transitions are excited, the density of molecular lines is substantially lower than in hotter sources such as massive molecular hot cores or low-mass hot corinos, alleviating the problems of line blending and line confusion. This, along with the effect of shock-induced desorption of interstellar ices, makes G+0.693 an excellent target for the detection of new molecular species in the ISM.

We analyzed the molecular data of a high-sensitivity unbiased spectral survey carried out with the Institut de Radioastronomie Millimétrique (IRAM) 30-m and the Yebes 40-m radio telescopes. Detailed information about the observations is presented in Materials and Methods. The identification of the rotational transitions of EtA was performed using the SLIM (Spectral Line Identification and Modeling) tool within the MADCUBA package (28). We predicted the synthetic spectrum of EtA under the assumption of local thermodynamic equilibrium (LTE) conditions. Among the numerous (23,655) transitions of EtA that fall in the spectral range covered by the survey, only tens of them are expected to be excited considering the low $T_{ex}$ measured in G+0.693 ($T_{ex} \sim$ 5 to 15 K) (21, 22).

We have detected the 45 brightest transitions of EtA, as predicted by the LTE simulation (with line intensities $T_{ex} > $ 5 mK), 14 of which appear either unblended or slightly blended with emission from other molecules. These transitions are shown in Fig. 2, and their spectroscopic information is provided in Table 1. The remaining 31 transitions are consistent with the observed spectra but appear blended with brighter emission lines from other molecular species already identified in this molecular cloud (see below). These transitions are shown in Fig. 3 and listed in Table 2.

To confirm that the spectral lines detected at the frequencies of the transitions of EtA are not produced by any other molecule, we have performed an extensive search for molecular species in our spectral survey, which includes all of the species detected so far in the ISM (29), and all other species reported toward G+0.693 in previous works (21–25). The predicted contribution from all molecular species is shown with a blue solid line in Fig. 2, confirming that 14 transitions of EtA are either clean or not significantly contaminated by the emission from other molecules. We have used these 14 transitions to perform the LTE fit and to derive the physical parameters of the emission of EtA. We used the AUTOFIT tool of MADCUBA–SLIM, which finds the best agreement between the observed spectra and the predicted LTE model (see details in Materials and Methods). To perform the fit we have considered not only the emission of EtA but also the predicted emission from all of the species identified in the region (blue line in Fig. 2). The best-fitting LTE model for EtA gives a molecular column density of $N = (1.51 \pm 0.07) \times 10^{13}$ cm$^{-2}$, an excitation temperature of $T_{ex} = 10.7 \pm 0.7$ K, and a velocity of $v_{LSR} = 63.8 \pm 0.4$ km s$^{-1}$ (the linewidth was fixed to 15 km s$^{-1}$; see details in Materials and Methods). The derived $T_{ex}$ and $v_{LSR}$ are very similar to those from other species previously analyzed in G+0.693 (21–25). To derive the abundance of EtA with respect to molecular hydrogen, we have used the H$_2$ column density inferred from observations of C$^{18}$O (26), obtaining a value in the range (0.9 to 1.4) × $10^{10}$.

We have also performed a complementary analysis using the rotational diagram method implemented in MADCUBA (see further description in Materials and Methods). Fig. 4 shows the rotational diagram obtained using the 14 EtA transitions from Fig. 2. We derived physical parameters fully consistent with the MADCUBA–AUTOFIT analysis: $N = (1.5 \pm 0.3) \times 10^{13}$ cm$^{-2}$, and $T_{ex} = 12 \pm 1$ K.

Discussion

We report a clear detection in the ISM of EtA, a precursor of phospholipids, with a relatively high abundance ($10^{-10}$ with respect to molecular hydrogen). This detection adds to that of precursors of ribonucleotides (23–25) and amino acids (30, 31) in the ISM. The building blocks of the three subsystems of life could therefore have been synthesized by interstellar chemistry, being part of the natal material that formed the Solar System.

The formation routes of EtA in the ISM are, however, poorly known. Grain-surface formation of EtA has been demonstrated by laboratory experiments of ultraviolet irradiation of interstellar ice analogs (32). In these experiments, photolysis of H$_2$O:CH$_3$OH:NH$_3$:HCN ices with a 20:2:1:1 mixture yields EtA as well as other prebiotic species such as the amino acids glycine, alanine, and serine. However, the detailed routes that result into the formation of EtA are still not understood. We discuss here several possible chemical pathways for the formation of EtA in the ISM, which are summarized in Fig. 5.

To our knowledge, the only route proposed in the literature (33, 34) is the hydrogenation chain of HNCO on dust-grain surfaces (see gray shaded area in Fig. 5). HNCO could be formed on grains by N addition to ketenyl (HCCO) (34). HNCCO could also be formed on dust grains from ketene (H$_2$CO), after two hydrogen abstractions, and with the imine radical NH (Fig. 5). G+0.693 presents a variety of imines with relatively high abundances (22, 23), which confirms that imine radicals are available on grain surfaces. This route is plausible since ketene is abundant toward G+0.693 (21) with a column density of $N = 2.9 \times 10^{14}$ cm$^{-2}$, a factor of $\sim$20 larger than that of EtA. Alternatively, the formation of HNCCO on grains could proceed as proposed by ref. 38 (Fig. 5) through the combination of HNC and CO, species expected to be abundant on grain surfaces.

The subsequent hydrogenation of HNCCO can form NH$_2$CHCO (Fig. 5). This species might also form through other
surface-chemistry routes. Ref. 39 proposed a barrierless reaction between NH$_3$, CO, and atomic C (Fig. 5). Given that three-body reactions are less efficient than two-body reactions, this route could contribute to the formation of NH$_2$CHCO only if a relatively high abundance of atomic C is available. Since it has been observed that the abundance of C is indeed large in Galactic Center molecular clouds, around half of that of CO (40), and considering that C is expected to be highly reactive, this route might be indeed viable in G+0.693. We note that the barrierless NH$_2$CH + CO reaction proposed by...
Table 2. Spectroscopic information (rest frequency, Einstein coefficients [$A_{ul}$], and energy of the upper levels [$E_{up}$]) of the transitions of EtA that appear blended in the observed spectra of G+0.693 (see Fig. 3)

| Frequency, GHz | Transition | log$_{10} A_{ul}$, s$^{-1}$ | $E_{up}$, K |
|---------------|------------|-----------------------------|-------------|
| 31.7653500    | 3(1,2)–(1,1) | -6.00114                     | 3.5         |
| 38.3746402    | 4(1,4)–(3,3) | -5.71626                     | 5.1         |
| 47.8493375    | 5(1,5)–(4,4) | -5.40899                     | 7.4         |
| 50.4153833    | 5(2,4)–(4,3) | -5.39849                     | 9.1         |
| 73.4680803    | 7(2,5)–(6,4) | -4.85633                     | 15.7        |
| 75.9126193    | 8(1,8)–(7,7) | -4.78270                     | 17.0        |
| 81.4338930    | 8(3,6)–(7,5) | -4.74841                     | 21.6        |
| 81.4392902    | 8(4,5)–(7,4) | -4.80721                     | 24.8        |
| 81.4863522    | 8(4,4)–(7,3) | -4.80646                     | 24.8        |
| 82.2698610    | 8(3,5)–(7,4) | -4.73500                     | 21.7        |
| 85.1653931    | 9(1,9)–(8,1) | -4.62876                     | 21.0        |
| 85.6467486    | 9(0,9)–(8,0) | -4.62059                     | 21.0        |
| 91.7192567    | 9(4,6)–(8,5) | -4.62007                     | 29.2        |
| 92.4964225    | 9(1,8)–(8,7) | -4.52562                     | 23.0        |
| 93.0416052    | 9(3,6)–(8,5) | -4.55708                     | 26.2        |
| 94.3281793    | 10(1,10)–9(1,9) | -4.49166                  | 25.6        |
| 95.0023981    | 9(2,7)–8(2,6) | -4.39975                     | 24.3        |
| 99.3388437    | 10(2,9)–9(2,8) | -4.43880                  | 28.3        |
| 101.7229298   | 10(3,8)–9(3,7) | -4.42905                   | 30.9        |
| 101.8639901   | 10(1,9)–9(1,8) | -4.39813                   | 27.9        |
| 102.0183989   | 10(4,7)–9(4,6) | -4.45929                   | 34.1        |
| 102.2528632   | 10(4,6)–9(4,5) | -4.45637                   | 34.1        |
| 103.5718907   | 11(1,11)–10(1,10) | -4.36815          | 30.5        |
| 103.7762062   | 11(0,11)–10(1,10) | -4.36532          | 30.5        |
| 103.9759166   | 10(3,7)–9(3,6) | -4.39964                   | 31.2        |
| 105.5481523   | 10(2,8)–9(2,7) | -4.35654                   | 29.4        |
| 108.8642389   | 11(2,10)–10(2,9) | -4.31491          | 33.5        |
| 111.0166375   | 11(1,10)–10(1,9) | -4.28448          | 33.2        |
| 111.7757005   | 11(3,9)–10(3,8) | -4.29721                   | 36.3        |
| 112.7422238   | 12(1,12)–11(1,11) | -4.25550          | 35.9        |
| 112.8692474   | 12(0,12)–11(0,11) | -4.25393          | 35.9        |

Fig. 4. Rotational diagram of EtA. The analysis procedure is described in Materials and Methods. The red dots correspond to the 14 EtA transitions shown in Fig. 2 and Table 1. The black line is the best linear fit to the data points. The derived values for the molecular column density (N) and the $T_{ex}$, along with their uncertainties, are indicated in blue in the upper right corner.

Fig. 5. Summary of the chemical routes proposed for the formation of EtA in the ISM. The molecular species in red have been detected toward the G+0.693 molecular cloud. The gray shaded area corresponds to a hydrogenation chain. The chemical reactions indicated with colored arrows have been proposed in previous work: magenta (36), blue (38), orange (41), cyan (39), and green (41, 47). In black, we show the formation routes proposed in this work. The solid arrows indicate surface chemistry reactions, and dashed arrows denote gas-phase chemistry.
material (19). Considering that the abundance of water in the ISM is of the order of \(10^{-5}\) (49), the EtA/H\(_2\)O abundance ratio measured in G+0.693 is of the order of \(10^{-6}\). The Almahata Sitta meteorite, where EtA was detected (19), has been classified as a ureilite with an anomalously high fraction of other materials, the enstatite chondrites (EC) being the most abundant (50). Interestingly, EC meteorites have recently been proposed as the origin source of most of Earth’s water (51). Therefore, meteorites such as Almahata Sitta could have simultaneously delivered to Earth not only water but also prebiotic chemicals such as EtA. From the concentration of EtA measured in the Almahata Sitta meteorite of 20 ppb (19), and the average concentration of water in EC meteorites (~7,500 ppm) (51), we derive a meteoritic EtA/H\(_2\)O abundance ratio of \(3 \times 10^{-6}\). This value is consistent with that derived in the ISM. Although isotopic analysis of EtA would be needed to confirm its interstellar origin in meteorites, our results suggest that phospholipid precursors such as EtA formed in the ISM could have been stored in planetesimals and minor bodies of the Solar System, to be subsequently transferred to early Earth.

Once EtA was available on Earth’s surface, it could form phospholipids (in particular PE; see Fig. 1C) under plausible early Earth conditions, as proposed by ref. 6 and confirmed by prebiotic experiments (7). It is commonly assumed that the first cell membranes could have been composed of amphiphilic molecules such as fatty acids/alcohols, which are chemically simpler than phospholipids (3, 8). However, the availability of EtA in an early Earth could have enabled the progressive replacement of fatty acids/alcohols by more efficient and permeable amphiphilic molecules such as phospholipids. In this scenario, the protocols could have been able to incorporate from the environment the precursor molecules required to start the synthesis of RNA and eventually other polymeric molecules (52, 53) needed for the first replicative and metabolic processes of life. This has important implications not only for theories of the origin of life on Earth but also on other habitable planets and satellites anywhere in the universe.

**Materials and Methods**

**Astronomical Observations.** We have analyzed a high-sensitivity spectral survey of the molecular cloud G+0.693-0.027 conducted with the Yebes 40-m telescope (Guadalajara, Spain) and the IRAM 30-m telescope (Granada, Spain). The observations were centered at the equatorial coordinates of G+0.693: RA(J2000) = 17 h 47 m 22 s, DEC(J2000) = 28° 21’ 27’’.

**Yebes 40-m telescope.** The observations were carried out with the Yebes 40-m telescope located in Yebes (Guadalajara, Spain), during six observing sessions in February 2020, as part of the project 20A008 (Principal Investigator J.M.-P.) and 018-19 (Principal Investigator V.M.R.). We used the broad-band Eight Mixer Receiver (EMIR) and the fast Fourier transform spectrometers in FTS200 mode, which provided a channel width of ~200 kHz. The final spectra were smoothed to a peak brightness (HPBW) of the telescope is 48° at 36 GHz.

**IRAM 30-m telescope.** We have carried out a spectral survey at 3 mm using the IRAM 30-m telescope. The observations were performed in two observing runs during 2019: 10 to 16 April and 13 to 19 August, from project numbers 172-18 (Principal Investigator J.M.-P.) and 018-19 (Principal Investigator V.M.R.). We used the broad-band Eight Mixer Receiver (EMIR) and the fast Fourier transform spectrometers in FTS200 mode, which provided a channel width of ~200 kHz. The final spectra were smoothed to a 609 KHz, i.e., a velocity resolution of 1.8 km s\(^{-1}\) at 100 GHz. The full spectral coverage is 71.770 to 116.720 GHz. The telescope pointing and focus were checked every 1 h toward bright sources. The spectra were also measured in units of antenna temperature, \(T_A\), the noise of the spectra depends on the frequency range, reaching values as low as 1.0 mK, while in some intervals it increases up to 4.0 mK. The half-power beam width (HPBW) of the telescope is 48° at 36 GHz.

**Table 3. Spectroscopic information (rest frequency, Einstein coefficients \([A_{ul}\]), and energy of the upper levels \([E_{up}\]) of the rotational transitions of ketenyl (HCCO) tentatively detected toward the G+0.693 molecular cloud (shown in Fig. 6).**

| Frequency, GHz | Transition | \(\log A_{ul}\), s\(^{-1}\) | \(E_{up}\), K |
|----------------|------------|------------------|-----------|
| 43.3176674    | 2(3,3)–1(2,2) | -0.0192         | 3.1       |
| 43.3211451    | 2(3,2)–1(2,1) | -0.1404         | 3.1       |
| 43.3295421    | 2(2,2)–1(1,1) | -0.0634         | 3.1       |
| 43.3546257    | 2(2,1)–1(1,0) | -0.2739         | 3.1       |
| 43.3368615    | 2(3,2)–1(2,2) | -0.6741         | 3.1       |
| 43.3373040    | 2(2,1)–1(2,1) | -0.4207         | 3.1       |
| 86.6191857    | 4(4,3)–3(3,3) | -0.9202         | 10.4      |
| 86.6423419    | 4(5,5)–3(4,4) | -0.9073         | 10.4      |
| 86.6438483    | 4(4,4)–3(4,3) | -0.9042         | 10.4      |
| 86.6558306    | 4(4,4)–3(3,3) | -0.0772         | 10.4      |
| 86.6574849    | 4(4,3)–3(3,2) | -0.1070         | 10.4      |
| 86.6652791    | 4(5,4)–3(4,4) | -0.3845         | 10.4      |
| 108.2823800   | 5(5,4)–4(4,4) | -0.7293         | 15.6      |
| 108.3040553   | 5(6,5)–4(5,5) | -0.7698         | 15.6      |
| 108.3051187   | 5(6,5)–4(5,4) | -0.7480         | 15.6      |
| 108.3178903   | 5(5,5)–4(4,4) | -0.7474         | 15.6      |
| 108.3190248   | 5(6,5)–4(5,3) | -0.7916         | 15.6      |
| 108.3280559   | 5(6,5)–4(5,5) | -0.2997         | 15.6      |
115 GHz, and ~10 mK in the range 115 to 116 GHz. The HPBW of the observations varies between 21.1° and 34.3°. The position switching mode was used in all observations with the off position located at (−88.5°, +290°) from the source position.

**SLIM Molecular Line Fitting.** The identification of the molecular lines was performed using the SLIM tool of the MADCUBA package. SLIM solves the radiative transfer equation, as described in detail in ref. 28, and generates the expected synthetic spectra of the molecular species under the assumption of LTE conditions. SLIM implements a stand-alone HyperSQL database (https://hsqldb.org/) that contains the spectral line catalogs of the Jet Propulsion Laboratory (https://spec.jpl.nasa.gov/) (JPL) and the Cologne Database for Molecular Spectroscopy (CDMS) (https://cdms.astro.uni-koeln.de/) (57, 58).

For the case of EtA, we have used the spectroscopic entry 61004 (version September 2003) of the JPL database, based on different laboratory works (59–61). The value of the partition function (Q) at the temperatures of the fit (T_e = 11 K) has been interpolated from the values reported in the JPL catalog in the logQ-logT plane, using the two adjacent temperatures: Q(9.375 K) = 254.2935 and Q(18.75 K) = 716.8160.

To derive the physical parameters from the molecular emission, we have used the AUTOFIT tool of SLIM (28), which performs a nonlinear least-squares fitting of simulated LTE spectra to the observed data. It uses the Levenberg–Marquardt algorithm (62, 63), which combines the gradient descent method and the Gauss–Newton method to minimize the χ² function.

For the analysis of EtA, we fixed the linewidth (full width at half maximum, FWHM) to 15 km s⁻¹, which reproduces well the observed spectral profiles of the EtA transitions and is consistent with those measured for other molecules in the region (22, 24, 25). We note that the upper level energies (E_u) of the transitions used in the analysis span a range between 4.8 and 29.2 K, allowing us to determine the T_e of the emission. The molecular column density (N_e), T_e, and the velocity (v_lsr) were left as free parameters. The best-fitting LTE model gives N_e = (1.51 ± 0.07)×10^{13} cm⁻², T_e = 10.7 ± 0.7 K, and v_lsr = 68.3 ± 0.4 km s⁻¹.

To compute the relative molecular abundance with respect to molecular hydrogen we have used the value of the H2 column density inferred from observations of C18O, 1.35 × 10^{15} cm⁻² (26). We have assumed a 20% error uncertainty in the determination of the H2 column density and propagated the error accordingly. The EtA molecular abundance falls in the range (0.9 to 1.4)×10⁻⁴.

**Rotational Diagram Method.** The rotational diagram is calculated following the standard procedure (64) implemented in MADCUBA (28). For the case of optically thin emission the velocity integrated intensity over the plane, using the two adjacent temperatures:

\[
\Delta v = \frac{\Delta v}{c} \times \frac{\text{FWHM}}{5} \times \text{FWHM},
\]

where \(\Delta v\) is the noise of the spectra and \(\Delta v\) is the spectral resolution of the data in velocity units. The coefficients of the straight line that fits the data points (black line in Fig. 4) provide the values for log(N/Q) and log(e)/T_e, from which MADCUBA derives N and T_e, calculating Q(T_e) as explained above.

**Blended Transitions of EtA.** We present in Fig. 3 the transitions of EtA with line intensities I_v > 5 mK, as predicted by the LTE simulation described in the main text, that appear blended with emission from other molecular species already identified in the G+0.693 molecular cloud. The spectroscopic information of these transitions is shown in Table 2.

**Data Availability.** Molecular spectra and fits of the unblended transitions of ethanolamine have been deposited in the Centro de Astrobiología repository at https://cab.inta-csic.es/astrochem/data.html (68).

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*Madrid Data Cube Analysis on Imagi is a software developed at the Center of Astrobiology (CAB) in Madrid. https://cab.inta-csic.es/madcuba/.

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