Millimetre-wave laboratory study of glycinamide and a search for it with ALMA towards Sagittarius B2(N)*

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ABSTRACT

Context. Glycinamide (NH2CH2C(O)NH2) is considered to be one of the possible precursors of the simplest amino acid, glycine. Its only rotational spectrum reported so far has been in the centimetre-wave region on a laser-ablation generated supersonic expansion sample.

Aims. The aim of this work is to extend the laboratory spectrum of glycinamide to the millimetre (mm) wave region to support searches for this molecule in the interstellar medium and to perform the first check for its presence in the high-mass star forming region Sagittarius B2(N).

Methods. Glycinamide was synthesised chemically and was studied with broadband rotational spectroscopy in the 90–329 GHz region with the sample in slow flow at 50°C. Tunnelling across a low-energy barrier between two symmetry equivalent configurations of the molecule resulted in splitting of each vibrational state and many perturbations in associated rotational energy levels, requiring careful coupled state fits for each vibrational doublet. We searched for emission of glycinamide in the imaging spectral line survey ReMoCA performed with the Atacama Large Millimetre/submillimetre Array towards Sgr B2(N). The astronomical spectra were analysed under the assumption of local thermodynamic equilibrium.

Results. We report the first analysis of the mm-wave rotational spectrum of glycinamide, resulting in fitting – to experimental measurement accuracy – of over 1200 assigned and measured transition frequencies for the ground-state tunnelling doublet and of many lines for tunnelling doublets for two singly excited vibrational states. We also determine the precise vibrational separation in each doublet. We did not detect emission from glycinamide in the hot molecular core Sgr B2(N1S). We derived a column density upper limit of 1.6 × 1016 cm−2, which implies that glycinamide is at least seven times less abundant than aminoacetonitrile and 1.8 times less abundant than urea in this source. A comparison with results of astrochemical kinetics models for species related to glycinamide suggests that its abundance may be at least one order of magnitude below the upper limit obtained towards Sgr B2(N1S). This means that glycinamide emission in this source likely lies well below the spectral confusion limit in the frequency range covered by the ReMoCA survey.

Conclusions. Thanks to the spectroscopic data provided by this study, the search for glycinamide in the interstellar medium can continue on a firm basis. Targetting sources with a lower level of spectral confusion, such as the Galactic Center shocked region G+0.693-0.027, may be a promising avenue.

Key words. astrochemistry – ISM: molecules – astronomical databases: miscellaneous – ISM: individual objects: Sagittarius B2 – line: identification

1. Introduction

The quest for the simplest amino acid glycine in the interstellar medium (ISM) became a never-ending story for research in the fields of astrochemistry and astrophysics. More than 40 yr have passed since the first interstellar hunt for this molecule (Brown et al. 1979), during which glycine has been extensively searched for towards various interstellar sources in both the centimetre (cm) and millimetre (mm) wave regions of the electromagnetic spectrum (Hollis et al. 1980, 2003; Snyder et al. 1983; Berulis et al. 1985; Guélin & Cernicharo 1989; Combes et al. 1996; Ceccarelli et al. 2000; Kuan et al. 2003, 2004; Belloche et al. 2008). However, its presence in the ISM has never been confirmed (Snyder et al. 2005; Jones et al. 2007; Cunningham et al. 2007), even in the era of the Atacama Large Millimeter/submillimeter Array (ALMA). This is in spite of the fact that glycine has been discovered in meteorites (Pizzarello et al. 1991; Ehrenfreund et al. 2001b; Glavin et al. 2006), dust samples from comet Wild 2 (Elsila et al. 2009), and in the coma...
of comet 67P/Churyumov-Gerasimenko (Altwegg et al. 2016). In addition, several laboratory experiments demonstrated the synthesis of glycine, and other amino acids, when interstellar ice analogues were subjected to UV radiation (Bernstein et al. 2002; Caro et al. 2002; Lee et al. 2009; Zheng & Kaiser 2010; Kim & Kaiser 2011) or bombarded by energetic electrons (Holton et al. 2005). Numerous studies have been undertaken to throw light on this controversy. These have focused on plausible interstellar pathways to glycine, and its detectability and survival in the hostile ISM (see, e.g. Ehrenfreund et al. 2001a; Blagojevic et al. 2003; Largo et al. 2010; Pilling et al. 2011; Latelais et al. 2011; Rimola et al. 2012; Garrod 2013; Jimenez-Serra et al. 2014; Nhlabatsi et al. 2016; Aponte et al. 2017; Suzuki et al. 2018; Xavier et al. 2019). Particular emphasis has been placed on the formation routes of possible glycine precursors (see, e.g. Basiuk 2001; Largo et al. 2004; Koch et al. 2008; Knowles et al. 2010; Barrientos et al. 2012; Redondo et al. 2015, and references therein) which are exciting candidates for observations in the ISM as well. Some of them, such as methylamine (Kaifu et al. 1974), aminoacetanitrite (Belloche et al. 2008), and hydroxylamine (Rivilla et al. 2020) have been already detected. Rotational spectroscopic studies of potential glycine precursors hydantoin (Alonso et al. 2017; Ozeki et al. 2017) and hydantoic acid (Kolesnikova et al. 2019) were reported recently. Sanz-Novo et al. (2019) further computed the spectroscopic properties of glycine isomers of which methyl carbamate (Marstokk & Møllendal 1999; Bakri et al. 2002; Ilyushin et al. 2006; Groner et al. 2007) and glycolamide (Maris 2004; Sanz-Novos et al. 2020) were studied by microwave and mm wave spectroscopy that enabled dedicated searches in the ISM (Sanz-Novos et al. 2020; Sahu et al. 2020).

In this work, we focus on glycine precursor glycinamide (NH₂CH₂C(O)NH₂) which is predicted to be a feasible intermediate on the hydrolytic way from aminoacetanitrite to glycine (Zhu & Ho 2004; Ugliengo et al. 2011). Keeping in mind the presence of aminoacetanitrite in Sgr B2(N) (Belloche et al. 2008), glycinamide could be considered a good candidate for observations in the same source. Millimetre wave surveys of high-mass star-forming regions are known to present a forest of lines with a high level of line blending (see e.g. Tercero et al. 2010; Belloche et al. 2013). For this reason, the identification of a new molecule, such as glycinamide, in these sources has to be guaranteed by the detection of numerous features consistent with confident predictions of its spectrum over a broad frequency region. High-quality laboratory data and analysis are therefore the first and mandatory step before any interstellar search can be conducted.

It was only recently that the rotational spectrum of glycinamide was first studied. Alonso et al. (2018) investigated its conformational landscape in supersonic expansion by Fourier transform microwave spectroscopy between 6 and 16 GHz. The analysis of the spectrum revealed the existence of a single conformer whose configuration in the principal axis frame is shown in Fig. 1. In addition, an unexpected non-rigid behaviour of this conformer has been implied by abnormal values of quartic centrifugal distortion constants. Such behaviour has been attributed to a large-amplitude motion that combines C–N bond torsion, C–C torsion, and N,H₂ inversion. As this motion is governed by tunnelling through the central barrier in a double minimum potential function, rotational transitions in the ground vibrational state are expected to be split into two components associated with two torsion/inversion sublevels, usually labelled 0° and 0°. However, due to vibrational cooling accompanying supersonic expansion, only the transitions in the lowest-lying 0° substate were observed by Alonso et al. (2018). In order to interpret the dense mm wave surveys from interstellar sources, the rotational transitions in this 0° substate and also in the yet experimentally unobserved 0° substate may be of utmost importance. Furthermore, severe perturbations resulting from the 0° ↔ 0° coupling of the rotational manifolds may occur for higher J and K states transitions in the millimetre wave region. This situation is indeed the case for cyanamide (Read et al. 1986; Kraśnicki et al. 2011; Kisiel et al. 2013; Coutsens et al. 2019) in which the large-amplitude motion involves the inversion of the NH₂ group. It was only possible to detect the rotational transitions of cyanamide in the 0° and 0° substates towards solar-type protostars (Coutsens et al. 2018) after a successful laboratory analysis accounting for the 0° ↔ 0° interactions (Read et al. 1986; Kraśnicki et al. 2011; Kisiel et al. 2013). The latter studies highlighted that the common difficulties arising from extrapolations to higher frequencies are not the only problems that need to be faced in attempts to detect glycinamide in space.

In the course of the present work, the laboratory rotational spectrum of glycinamide was measured between 90 and 329 GHz. A comprehensive analysis of this mm wave spectrum made it possible to unambiguously assign the rotational transitions in the four lowest torsional/inversion substates 0°, 0°, 1° and 1°. In addition, rotational transitions in 0° and 0° substates for the ν₇s = 1 state were assigned and measured. Results of
this work deliver novel experimental information on the double minimum potential of glycinamide and provide a firm basis for searches for this molecule in space.

Section 2 describes the laboratory experiments performed to measure the rotational spectrum of glycinamide. The analysis of the laboratory spectra is presented in Sect. 3 and the search for glycinamide towards the hot molecular core Sgr B2(N1) with ALMA is reported in Sect. 4. Section 5 discusses the spectroscopic and astronomical results, and Sect. 6 summarises our conclusions.

2. Experiments

Pure glycinamide has the form of colourless crystals with a melting point of 63°C. A vapour pressure of 5–10 mTorr that was sufficient for measurements was generated when the sample was heated to 50°C, and signal stability was ensured using a slow flow through the three-metre free space absorption cell of the spectrometer. In a previous rotational spectroscopy study (Alonso et al. 2018), glycinamide was produced by laser ablation of a specially prepared hydrochloride glycinamide rod, whilst for this study we used pure glycinamide prepared from glycinamide hydrochloride, as purchased from Aldrich and used without further purification. Glycinamide hydrochloride (5.5 g, 50 mmol) and dry dichloromethane (100 mL) were introduced under nitrogen into a 250 ml three-necked flask. Dry ammonia was then bubbled through the stirred suspension for 30 min. The salt was filtered off and the solvent was removed under vacuum on a rotary evaporator and then on a vacuum pump (0.1 mbar, 2 h), leaving 2.5 g or 34 mmol glycinamide (68% yield). It showed long-term stability when stored in the freezer (−20°C) and there was also no discernible decomposition when heated for measurements.

Spectroscopic measurements were made in the region 90–329 GHz with the broadband backward wave oscillator (BWO) based spectrometer in Warsaw, which was described in Medvedev et al. (2004). The hardware configuration was later updated and augmented below 140 GHz with a harmonic generation source (Kisiel & Kraśnicki 2010). A frequency measurement accuracy of 50 kHz was assumed.

3. Rotational spectra and analysis

The mm-wave rotational spectrum of glycinamide posed a significant assignment challenge, which can be partly appreciated from the example shown in Fig. 2. Glycinamide is a rather asymmetric molecule (asymmetry parameter $\kappa = -0.68$, expected to give rise to strong pure-rotation $a$-type transitions accompanied by weaker $b$-type transitions (calculated dipole moment components are $\mu_a = 3.8$ D and $\mu_b = 1.5$ D, Alonso et al. 2018). However, there is a significant lack of characteristic line patterns that normally aid assignment. The most useful starting point was provided by the fact that the strongest lines in the spectrum would be quadruply degenerate, resulting from overlaps of pairs of $a$-type and $b$-type $R$-branch transitions for the lowest values of $K_a$. Unfortunately, such lines quickly proved to be poorly treatable with a single-state Watson’s asymmetric rotor Hamiltonian (Watson 1977). On the other hand, several sequences of such strong lines were identified with the use of the AABS graphical assignment package (Kisiel et al. 2005, 2012). Initial rotational constants, reported by Kisiel et al. (2010), were confirmed by measurement of the lowest-$J$ ground-state transitions in supersonic expansion (Alonso et al. 2018).

Complete assignment and analysis of the mm-wave spectrum became possible once it became clear that the observed sets of transitions belonged to coupled pairs of vibrational sublevels. As already mentioned, such pairs of levels typically arise from the example shown in Fig. 2. Glycinamide is a rather asymmetric molecule (asymmetry parameter $\kappa = -0.68$, expected to give rise to strong pure-rotation $a$-type transitions accompanied by weaker $b$-type transitions (calculated dipole moment components are $\mu_a = 3.8$ D and $\mu_b = 1.5$ D, Alonso et al. 2018). However, there is a significant lack of characteristic line patterns that normally aid assignment. The most useful starting point was provided by the fact that the strongest lines in the spectrum would be quadruply degenerate, resulting from overlaps of pairs of $a$-type and $b$-type $R$-branch transitions for the lowest values of $K_a$. Unfortunately, such lines quickly proved to be poorly treatable with a single-state Watson’s asymmetric rotor Hamiltonian (Watson 1977). On the other hand, several sequences of such strong lines were identified with the use of the AABS graphical assignment package (Kisiel et al. 2005, 2012). Initial rotational constants, reported by Kisiel et al. (2010), were confirmed by measurement of the lowest-$J$ ground-state transitions in supersonic expansion (Alonso et al. 2018).
is equivalent to a torsional motion (as in phenol, Kolesniková et al. 2013), or to inversion (as in cyanamide, Kisiel et al. 2013). For glycinamide, computations indicated that tunnelling between the most stable conformation depicted in Fig. 1 and its mirror image form obtained by reflection across the ab inertial plane is subject to a barrier of only ~100 cm$^{-1}$ (Alonso et al. 2018) and that such tunnelling has to involve a concerted combination of torsion and inversion. The molecule belongs to the lowest symmetry point group, C$_1$, and the general labelling used for vibrational levels split by double minimum inversion has been adopted (see Fig. 25.2 of Papoušek & Aliev 1982). Accordingly, the vibrational ground state, normally labelled $v_0 = 0$, splits into a pair of sublevels designated 0$^-$ (lower) and 0$^+$ (upper). Similarly, the usual first excited state, $v_0 = 1$, of the inversion motion, becomes a doublet labelled 1$^+$ (lower) and 1$^-$ (upper). This splitting structure is expected to be relatively unaffected by excitation of non-inverting vibrational motions. Accordingly, the first excited state of such a motion, for example labelled $v_0 = 1$, will be split by an amount comparable to that in the ground state, with labelling $v_0 = 1, 0^+$ (lower) and $v_0 = 1, 0^-$ (upper). Quantum chemistry vibrational calculations at both harmonic (Li et al. 2003) and anharmonic (Alonso et al. 2018) levels indicated, in agreement, that glycinamide has two low-frequency vibrational modes $v_{27}$ and $v_{26}$ with vibrational frequencies of near 100 and 200 cm$^{-1}$, respectively. Nevertheless, unambiguous attribution as to which of these modes is responsible for the tunnelling only became possible upon completion of the rotational analysis, as discussed below.

The most effective treatment of pairs of vibrational substates resulting from tunnelling is to use a $(2 \times 2)$ block diagonal Hamiltonian of the form:

$$H = \begin{pmatrix} \mathcal{H}_{00}^{(0)0} & \mathcal{H}_{00}^{(0)0} \\ \mathcal{H}_{00}^{(0)0} & \mathcal{H}_{00}^{(0)0} \end{pmatrix} + \Delta \mathcal{E}.$$ (1)

The two diagonal blocks, $\mathcal{H}_{00}^{(0)0}$ and $\mathcal{H}_{00}^{(0)0}$, are set up with the standard asymmetric rotor Hamiltonian (Watson 1977) for each of the two substates. The two off-diagonal blocks, $\mathcal{H}_{00}^{(0)0}$, connecting the two substates are set up with the reduced axis system (RAS) Hamiltonian (Pickett 1972). In the case where the tunnelling motion is around an axis in the $ab$ inertial plane, but at some angle to the principal axes, the RAS blocks are:

$$\mathcal{H}_{00}^{(0)0} = (F_{bc} + J F_{bc}^2 + F_{bc}^2 + \cdots)(P_b P_c + P_b P_a) + (F_{ca} + J F_{ca}^2 + F_{ca}^2 + \cdots)(P_c P_a + P_a P_c),$$ (2)

where $F_{bc}$ and $F_{ca}$ are the main adjustable parameters describing the interaction, each of which is further expanded empirically using centrifugal distortion-type terms $F_{bc}^2$, $F_{bc}^3$ and so on. Finally, $\Delta \mathcal{E}$ is the vibrational energy difference between the two substates, $E(0^-) - E(0^+)$. This approach was used, for example, for the singly deuterated species, HDNCO, of cyanamide (Kisiel et al. 2013). All fits and predictions were carried out with Pickett’s SPFIT/SPCAT package (Pickett 1991).

Assignment proceeded through analysis of $R$-branch transition sequences for successively higher values of $K_a$. Once these were understood for the ground-state tunnelling doublet, it was possible to also assign two vibrationally excited doublets. The success of the coupled state fit for each such pair of substates was critically dependent on the value of $\Delta \mathcal{E}$. In each case, the range of likely values had to be scanned with some care prior to using it as an adjustable parameter of fit.

The final understanding of the spectrum is illustrated in the lower part of Fig. 2. It can be seen from the pairs of lowest $K_a$ transitions marked in the top of Fig. 2 that the frequency differences between the same rotational transitions in the substates are considerable, which reflects the relatively low barrier to the tunnelling. Extensive relative intensity measurements allowed the energies above the ground state for the two excited vibrational states (energy differences between the lower substates) to be determined as 99(13) and 201(13) cm$^{-1}$, which was the initial basis for the $v_{27} = 1$ and $v_{26} = 1$ assignment marked in Fig. 2.

Spectroscopic constants resulting from the fits are summarised in Table 1 and a breakdown of the statistics for individual substates is given in Table A.1. Data for the 0$^+$ substate also include hyperfine removed frequencies from supersonic expansion measurements reported in Alonso et al. (2018). For the two ground-state substates, some Q-branch transitions were also assigned and measured. In addition, nominal interstate transitions were observed. These result from strong mixing between perturbing rotational levels in two substates and are usually only identified in the final stages of the analysis.

For all of the identified substates, as well as for combined results for their pairs, it was possible to reproduce measured frequencies to within their assumed experimental accuracy of 50 kHz. The energy differences between the tunnelling substates were determined very precisely to sub-MHz precision. When combined with results of relative intensity measurements, these allow determination of the positions of the lowest vibrational energy levels in glycinamide, as summarised in Fig. 3. We now have further evidence concerning the proposed vibrational assignment. Tunnelling splitting is expected to increase significantly with vibrational excitation in a double minimum potential and can be successfully modelled with simple potentials, as described and carried out for cyanamide (Kisiel et al. 2013). The two splitting values in the $v_{27}$ column in Fig. 3 are consistent with a relatively low barrier, meaning that this mode is responsible for the tunnelling. On the other hand, the splitting
in the \( \nu_26 \) tunnelling pair is very close to that in the ground state, and therefore this appears to be a standard normal vibrational mode.

The coverage of values of rotational quantum numbers by the measured transitions is relatively comprehensive and can be assessed from the data distribution plots for the three studied doublets given in Figs. A.1–A.3. The values of quartic centrifugal distortion constants in the substates in each tunnelling pair are generally quite close to each other, which shows that the coupling behaviour has been largely accounted for by the parameters in Eq. (2). Two significant exceptions are \( \Delta K \) and \( \delta K \) for the upper substate of \( \nu_{26} = 1 \), suggesting that this substate may be interacting with some state outside the model, possibly \( 2^+ \) of \( \nu_{27} \). The dominance in magnitude of the \( F_{bc} \) over the \( F_{bc} \) parameter is similar to that for HDNCN (Kisiel et al. 2013) and can accordingly be taken to be an indicator that the effective axis around which tunnelling takes place is at a relatively small angle to the \( b \)-inertial axis.

It is at this stage that the difficulties faced during the analysis and possible pitfalls in searching for a new molecule in space on the basis of incomplete fits can be appreciated. Figure 4 illustrates a typical effect of perturbations on rotational transition frequencies in the two substates. Perturbations most efficiently followed in sequences of transitions for a given value of \( K_a \) and an unperturbed situation is characterised by smooth, near horizontal trace behaviour in a scaled frequency difference plot as in Fig. 4. The sharp spikes are due to contributions from resonances between rotational levels in the two vibrational

### Table 1. Spectroscopic constants determined for the three assigned tunnelling doublets in glycinamide.

| Parameter          | Ground state | \( \nu_{27} = 1 \) | \( \nu_{26} = 1 \) | \( \nu_{26} = 0 \) |
|--------------------|--------------|--------------------|--------------------|-------------------|
| \( A \) [MHz]      | 9631.65562(72) | 9690.18503(85)   | 9592.9536(13)     | 9560.8227(15)     |
| \( B \) [MHz]      | 3986.80416(25) | 3992.03664(20)   | 3984.61628(30)    | 3992.78766(28)    |
| \( C \) [MHz]      | 2925.57754(23) | 2931.88720(21)   | 2930.85963(37)    | 2939.30567(39)    |
| \( \Delta_J \) [kHz] | 0.82062(13)   | 0.79899(14)      | 0.75262(19)       | 0.81389(20)       |
| \( \Delta_K \) [kHz] | 3.13182(86)   | 3.42634(91)      | 4.338(12)         | 3.307(12)         |
| \( \delta_J \) [kHz] | 4.5931(23)    | 4.0563(26)       | 2.635(13)         | 4.562(16)         |
| \( \delta_K \) [kHz] | 1.82640(96)   | 1.88058(37)      | 0.18570(58)       | 0.17730(54)       |
| \( \Phi_J \) [kHz]  | 0.000185(37)  | 0.000505(39)     | 0.000407(43)      | 0.000244(46)      |
| \( \Phi_K \) [kHz]  | -0.05630(39)  | 0.01800(100)     | -0.1036(42)       | 0.0869(42)        |
| \( \phi_J \) [kHz]  | -0.0226(27)   | -0.0409(33)      | 0.0534(81)        | -0.2674(82)       |
| \( \phi_K \) [kHz]  | 0.00591(28)   | 0.0765(81)       | 0.082(14)         | 0.339(26)         |
| \( \delta E \) [MHz] | 287355.66(10) | 982174.88(42)    | 304943.46(32)     | 10.171818(11)     |
| \( \delta E \) [cm\(^{-1}\)] | 9.585186(3)   | 32.761828(14)    | 11.1549(28)       | -0.07722(63)      |
| \( F_{bc} \) [MHz]  | 4.2369(31)    | 11.573(17)       | 2.692(21)         | 0.00000308(27)    |
| \( F_{bc} \) [kHz]  | -0.040174(78) | 0.1309(25)       | 0.00000308(27)    | 0.0114(19)        |
| \( F_{bc} \) [kHz]  | 0.1352(90)    | 0.0765(81)       | 0.082(14)         | 0.339(26)         |
| \( F_{bc} \) [kHz]  | -0.339(69)    | 0.082(14)        | 0.339(26)         | 0.00000308(27)    |
| \( F_{bc} \) [kHz]  | 0.32775(79)   | 0.082(14)        | 0.339(26)         | 0.00000308(27)    |
| \( N_{lines} \)     | 1237          | 873              | 714               |
| \( \sigma_{fit} \) [kHz] | 43.76        | 44.32            | 50.31             |
| \( \sigma_{rms} \) [kHz] | 0.8865       | 0.8863           | 1.0056            |

Notes. \(^{a}\)A, B, and C are rotational constants. \( \Delta_J, \ldots, \phi_K \) are centrifugal distortion constants in Watson's A-reduced asymmetric rotor Hamiltonian, \( \Delta E \) is the fitted energy difference between the two levels of the tunnelling doublet, \( F_{bc} \) and \( F_{bc} \) are leading substate coupling terms in the RAS Hamiltonian, and the related superscripted versions are parameters in their empirical centrifugal distortion expansions. \(^{b}\)Errors in parentheses are standard errors in units of the last digit. \(^{c}\)Number of fitted lines. \(^{d}\)Standard deviation of the fit. \(^{e}\)Unitless (weighted) deviation of the fit.
Fig. 4. Perturbation shifts in selected "R-branch rotational transitions in the ground-state tunnelling doublet. The plotted quantity is the scaled difference between frequencies from the full spectroscopic model (ν) and perturbation-removed frequencies (ν0) calculated without the interstate coupling terms. The matching character of the observed resonance behaviour identifies the interacting Kq sequences in the two substates. Circles denote experimental measurements, and the perturbation contribution at the resonance peak at J″ + 1 = 30 is near 2.4 GHz. The 0+ sequence has a smaller resonance at J″ + 1 = 19, which we identify as resulting from a resonance with a different, Kq = 2 sequence in substate 0−. All measured transitions involved in the resonances are fitted to within their experimental uncertainty.

substates that arise within a Hamiltonian matrix for a given value of the J quantum number. A specific resonance between two rotational levels in perturbing substates will have the same magnitude but the opposite sign for the two partners. Mirror image behaviour such as that seen in Fig. 4 confirms identification of the resonance partners and, if consistent with observed frequencies, is also indicative of the quality of the fit. It is notable that resonances can be of considerable magnitude (2.4 GHz for the ground-state tunnelling doublet) and can also significantly affect transition intensities, as visible in Fig. 5. The vibrational effect for glycinamide is documented in Table 2. Glycinamide also has two other relatively low-frequency modes (ν25 and ν26 calculated at 303 and 384 cm−1 resp., Li et al. 2003). Combination of those modes with present information on ν27 and ν28 allows an estimate that up to 412 cm−1 it is necessary to account for populating a total of 19 sublevels, corresponding to a partition function correction of 2.4 at 200 K.

4. Search for glycinamide towards Sgr B2(N1)

4.1. Observations

We used the imaging spectral line survey ReMoCA (Re-exploring Molecular Complexity with ALMA) performed with ALMA towards Sgr B2(N). The observational setup and the method used to reduce this interferometric data set were described in Belloche et al. (2019). We summarise only the main features here. The field of view of the observations was centred between Sgr B2(N1) and Sgr B2(N2), the two
main hot molecular cores of Sgr B2(N), which are separated by 4.9" or ~0.2 pc in projection onto the plane of the sky. The equatorial coordinates of this phase centre are \((\alpha, \delta)_{2000} = (17^h 47^m 19^s 870', -28^\circ 22' 16'' 0')\). The survey has an angular resolution (HPBW) that varies between ~0.3" and ~0.8". The median angular resolution is 0.6" and corresponds to ~4900 au at the distance of Sgr B2 (8.2 kpc; Reid et al. 2019). Five frequency tunings of the receivers, which we call setups S1 to S5, were used to cover the frequency range from 84.1 to 114.4 GHz at a spectral resolution of 488 kHz (1.7–1.3 km s\(^{-1}\)). The observations achieved a sensitivity per spectral channel of 0.8 mJy beam\(^{-1}\) with a median sensitivity of 0.8 mJy beam\(^{-1}\). Following, Belloche et al. (2019) we selected the offset position Sgr B2(NIS) located at \((\alpha, \delta)_{2000} = (17^h 47^m 19^s 870', -28^\circ 22' 19' 48'')\) for this study. This position is about 1' to the south of the main hot core Sgr B2(N1). Its continuum emission has a lower opacity than the peak of the hot core, which allows for a deeper look into the molecular content of this source. We used an improved version of the data reduction here, as reported in Melosso et al. (2020).

We employed the software Weeds (Maret et al. 2011) to produce synthetic spectra under the assumption of local thermodynamic equilibrium (LTE). This assumption is appropriate for Sgr B2(N) because the regions where hot-core emission is detected in Sgr B2(N) have high densities (>1 \times 10^7 cm\(^{-3}\), see Bonfand et al. 2019). A best-fit synthetic spectrum was derived for each molecule separately, and then the contributions of all identified molecules were added together. Each species was modelled with a set of five parameters: size of the emitting region \((\theta_0)\), column density \((N)\), temperature \((T_{\text{rot}})\), line width \((\Delta V)\), and velocity offset \((V_{\text{off}})\) with respect to the assumed systemic velocity of the source, \(V_{\text{sys}} = 62\) km s\(^{-1}\).

### 4.2. Non-detection of glycinamide

We assumed a rotational temperature of 160 K, as derived for formamide, NH\(_2\)CHO, by Belloche et al. (2019), an emission size of 2", and an FWHM line width of 5 km s\(^{-1}\) to compute LTE synthetic spectra of glycinamide and search for rotational emission of this molecule towards Sgr B2(NIS). We found no evidence for emission of glycinamide towards this source. This non-detection is illustrated in Fig. 6. We also searched for rotational emission from within its vibrationally excited states \(v_{27} = 1\) and \(v_{26} = 1\) but did not detect any clear sign of it (see Figs. 7 and 8, respectively). The upper limit that we obtain for the column density of glycinamide is indicated in Table 3 along with the parameters derived by Belloche et al. (2019) for urea, NH\(_2\)C(O)NH\(_2\), and formamide, NH\(_2\)CHO, and by Melosso et al. (2020) for aminoacetonitrile, NH\(_2\)CH\(_2\)CN.

The amides NH\(_2\)CH\(_3\)C(O)NH\(_2\) and NH\(_2\)C(O)NH\(_2\) could be seen as the partially hydrolysed counterparts of the nitriles NH\(_2\)CH\(_2\)CN and NH\(_2\)CN, respectively. It may therefore be instructive to compare the relative abundances of these two pairs of molecules. With this in mind, we modelled the emission spectrum of cyanoamide (aminomethanenitrile, NH\(_2\)CN) towards Sgr B2(NIS). The cyanoamide spectroscopic information was taken from the JPL catalogue (Pickett et al. 1998). This JPL entry (TAG 42003 version 1) is based mostly on microwave data from Read et al. (1986) along with far-infrared data from Birk et al. (1993). A few transitions of cyanoamide are clearly detected (see Fig. A.4), but unfortunately not enough to derive its rotational temperature from a population diagram. Therefore, we also assumed a temperature of 160 K to compute its column density, which is given in Table 3. The cyanoamide line around 100.070 GHz is contaminated by absorption from HC\(_3\)N \(J = 11\)–10, which is not accurately accounted for by our current complete model of Sgr B2(NIS).

### 5. Discussion

#### 5.1. Laboratory spectroscopy of glycinamide

The present experimental investigation of the rotational spectrum covers the most useful ALMA bands for a molecule of this size. We satisfactorily fitted many resonances between rotational levels in the three studied tunnelling doublets allowing reliable predictions, at least when these are interpolations within the acquired data sets. At the laboratory measurement temperature at 50°C, we accounted for all of the strongest observed lines, providing a comprehensive basis for any future searches.
Fig. 6. Selection of transitions of $\text{NH}_2\text{CH}_2\text{C(O)NH}_2$, $v = 0$ covered by our ALMA survey. The synthetic spectrum of $\text{NH}_2\text{CH}_2\text{C(O)NH}_2$, $v = 0$ used to derive the upper limit to its column density is displayed in red and overlaid on the observed spectrum of Sgr B2(N1S) shown in black. The blue synthetic spectrum contains the contributions from all molecules identified in our survey so far, but not from the species shown in red. The central frequency of each panel is indicated in MHz below its $x$-axis. Each panel has a width of 40 MHz, as indicated in brackets behind the central frequency. The angular resolution (HPBW) is also indicated. The $y$-axis is labelled in brightness temperature units (K). The dotted line indicates the $3\sigma$ noise level.

Fig. 7. Same as Fig. 6 but for $\text{NH}_2\text{CH}_2\text{C(O)NH}_2$, $v_{27} = 1$.

Fig. 8. Same as Fig. 6 but for $\text{NH}_2\text{CH}_2\text{C(O)NH}_2$, $v_{26} = 1$.

especially at the typically significantly lower interstellar temperatures. Clearly many more outstanding lines from higher vibrational states remain to be assigned and measured in the experimental spectrum, but their analysis is expected to be even more challenging than that reported presently.

5.2. Comparison of glycinamide to related molecules in Sgr B2(N)

Our non-detection of glycinamide, $\text{NH}_2\text{CH}_2\text{C(O)NH}_2$, towards Sgr B2(N1S) reported in Table 3 implies that it is at least
Table 3. Parameters of our best-fit LTE models of cyanamide, aminoacetonitrile, formamide, methylamine, and urea towards Sgr B2(N1S), along with column density upper limit for glycynamide.

| Molecule          | Status (a) | \( N_{\text{det}} \) (b) | \( \theta_k \) (c) (°) | \( T_{\text{rot}} \) (K) | \( N^c \) (cm\(^{-2}\)) | \( F_{\text{vib}} \) (f) | \( \Delta v \) (g) (km s\(^{-1}\)) | \( V_{\text{off}} \) (h) (km s\(^{-1}\)) |
|-------------------|------------|---------------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| \( \text{NH}_2\text{CN} \) | d          | 3                   | 2.0             | 160            | 2.6 (16)      | 1.03           | 5.5            | -0.3           |
| \( \text{NH}_2\text{CH}_2\text{CN} \) (i) | d          | 23                  | 2.0             | 200            | 1.1 (17)      | 1.00           | 5.0            | 0.0            |
| \( \text{NH}_2\text{CHO} \) (j) | d          | 34                  | 2.0             | 160            | 2.9 (18)      | 1.09           | 6.0            | 0.0            |
| \( \text{NH}_3\text{CH}_3 \) | d          | 15                  | 2.0             | 230            | 1.4 (18)      | 1.25           | 5.0            | 0.0            |
| \( \text{NH}_2\text{C(O)NH}_2 \) (j) | d          | 9                   | 2.0             | 160            | 2.7 (16)      | 1.86           | 5.0            | 0.0            |
| \( \text{NH}_2\text{CH}_2\text{C(O)NH}_2 \) n | 0          | 2.0                 | 160             | 1<16 (16)      | 1.27           | 5.0            | 0.0            |

Notes. (a): detection, n: non-detection. (b): Number of detected lines (conservative estimate, see Sect. 3 of Belloche et al. 2016). One line of a given species may mean a group of transitions of that species that are blended together. (c): Source diameter (FWHM). (d): Rotational temperature. (e): Total column density of the molecule. \( x \) \( y \) means \( x \times 10^y \). (f): Correction factor that was applied to the column density to account for the contribution of vibrationally excited states, in the cases where this contribution was not included in the partition function of the spectroscopic predictions. (g): Line width (FWHM). (h): Velocity offset with respect to the assumed systemic velocity of Sgr B2(N1S), \( V_{\text{sys}} = 62 \text{ km s}^{-1} \). (i): The parameters were derived from the ReMoCA survey by Melosso et al. (2020). (j): The parameters were derived from the ReMoCA survey by Belloche et al. (2019).

Table 4. Rotational temperature of methylamine derived from its population diagram towards Sgr B2(N1S).

| Molecule | States (a) | \( T_{\text{fit}} \) (b) (K) |
|----------|------------|-------------------------------|
| \( \text{NH}_2\text{CH}_3 \) v = 0 | 223.0 (5.9) |

Notes. (a): Vibrational states that were taken into account to fit the population diagram. (b): The standard deviation of the fit is given in parentheses. As explained in Sect. 3 of Belloche et al. (2016) and in Sect. 4.4 of Belloche et al. (2019), this uncertainty is purely statistical and should be viewed with caution. It may be underestimated.

\(~1.8\) times less abundant than urea, \( \text{NH}_2\text{C(O)NH}_2 \), which is markedly different from the pair of nitriles \( \text{NH}_2\text{CH}_3\text{CN/NH}_2\text{CN} \) for which the longer molecule is a factor four more abundant than the shorter one. In other words, \( \text{NH}_2\text{C(O)NH}_2 \), the partially hydrolysed counterpart of \( \text{NH}_2\text{CN} \), has the same abundance as the latter, while \( \text{NH}_2\text{CH}_3\text{C(O)NH}_2 \), the partially hydrolysed counterpart of \( \text{NH}_2\text{CH}_3\text{CN} \), is at least seven times less abundant than the latter. The analysis reported in Sect. 4 also shows that glycynamide is at least two orders of magnitude less abundant than its potential precursors formamide and methylamine.

5.3. Glycinamide chemistry

Glycinamide is not presently included in any astrochemical models, but the results of recent chemical simulations of hot cores may nevertheless be informative. Garrod (2013) constructed a chemical network for glycine (\( \text{NH}_2\text{CH}_2\text{COOH} \)), which included the related species glycin (\( \text{NH}_2\text{CH}_2\text{CHO} \)). These species could be formed on interstellar dust grains through the addition of radicals produced mainly by photodissociation of simpler solid-phase molecules, a process which itself is driven by the enhanced surface mobility of the radicals, as the result of grain heating induced by the star-formation process. Complex organic molecules including glycine and glycin would later sublime entirely from the dust grains. The chemical network included mechanisms for those molecules to be subsequently destroyed in the gas phase through ion–molecule reactions.

The more recent models by Garrod et al. (2021), which incorporate the same glycine-related chemistry, allow a broader range of grain-surface and bulk-ice kinetic processes to bring together reactive radicals and thus form complex organics. This includes the possibility of radicals reacting non-diffusively on dust-grain surfaces at very low temperatures, when the icy grain mantles are still gradually building up. In this scenario, the radicals themselves need only be formed close to each other, allowing their reactions to proceed immediately by thermal diffusion. Furthermore, the initially translucent conditions under which the dust-grain ices build up may allow some degree of UV processing of the young ices by the ambient interstellar UV field, converting a small fraction of simple solid-phase molecules into more complex organics. The Garrod et al. models indicate that a substantial fraction of glycine production may occur at this very early stage, with glycinal acting as a precursor. Although it is not included in those models, glycynamide could plausibly be produced through a similar mechanism, such as the photodissociation of solid-phase glycinal to produce the radical \( \text{NH}_2\text{CH}_2\text{CO} \), with which \( \text{NH}_2 \) would react to form \( \text{NH}_2\text{CH}_2\text{CONH}_2 \).

If such a mechanism is active in producing solid-phase glycynamide, then the observed ratio of formamide to urea might be somewhat indicative of the expected ratio of glycinal to glycynamide, which share similar molecular structures. Towards Sgr B2(N1S), the former ratio is approximately 100. Although glycinal has not yet been detected in the interstellar medium, with dedicated searches being hindered by a lack of spectroscopic predictions, the model of Garrod et al. (2021) suggests that its peak gas phase abundance should be around a factor 100 less than that of formamide. On this basis, one might therefore expect an abundance of glycynamide around 10\(^4\) times lower than formamide, or 100 times lower than urea. However, it is plausible that the efficiency of the conversion of glycinal to glycynamide on the grains could be greater than the above crude comparison might suggest; in the models, glycine itself reaches a peak gas-phase abundance as great as around half that of glycinal, implying substantial conversion. This corresponds to an approximately 40 times lower abundance than that of urea produced by the model. If we were to take this abundance of glycine as the maximum possible allowed abundance for glycynamide, which assumes that glycine and glycynamide are produced in equal amounts from glycinal, then the implied 40:1 ratio of urea to glycynamide would produce a glycynamide column density of around 20 times lower than the observed upper limit. Even efficient conversion from glycinal would therefore still
produce a smaller amount of glycaminide than might plausibly be detectable at this time.

However, the above production mechanism is not the only possible means by which glycaminide could form through radical addition; alternatives would include the reaction of the acetamide-related radical NH₂COCH₂ with NH₂, or the addition of NH₂CH₂ to NH₂CO. The latter pair of radicals can be formed through cosmic-ray-induced UV photodissociation of, or chemical H-atom abstraction from, solid-phase NH₂CH₃ and NH₂CHO, both of which are detected towards Sgr B2(N1S) in the gas phase. A similar reaction between radicals NH₂CH₂ and COOH indeed produces a substantial quantity of glycine in the models; this process occurs much later, at around the time when water itself is beginning to desorb rapidly from the grains, releasing trapped radicals onto the surface of the warm ice, where they may react diffusively. The sizeable abundances of NH₂CH₃ and NH₂CHO detected towards Sgr B2(N1S) suggests this could be a plausible route to glycaminide production.

The above reaction mechanisms nevertheless remain entirely conjectural, at least until they have been tested explicitly in the astrochemical models. The closure of the existing chemical network surrounding glycine in order to incorporate glycaminide seems a plausible goal for future investigation.

6. Conclusions

We performed a comprehensive laboratory rotational study of the potential glycine precursor glycaminide, up to 329 GHz. In total, over 2800 transition lines were assigned and measured for the ground state and two lowest lying excited-state tunnelling doublets. Newly derived spectroscopic constants were used to search for spectral signatures of glycaminide in Sgr B2(N) by millimetre-wave astronomy. Lists of experimental frequencies and their observed–calculated differences are provided in Tables 5–7, only available in electronic form.

Glycaminide was not detected towards the hot molecular core Sgr B2(N1S) with ALMA. The upper limit derived for its column density implies that it is at least seven times less abundant than aminoacetonitrile and 1.8 times less abundant than urea towards Sgr B2(N1S) with ALMA. The upper limit derived for its column density implies that it is at least seven times less abundant than aminoacetonitrile and 1.8 times less abundant than urea towards Sgr B2(N1S). This would likely be well below the spectral confusion limit of the ReMoCA survey of Sgr B2(N). Further progress in the search for glycaminide in the ISM could be made by targeting sources with a lower level of spectral confusion. The Galactic centre source G0.69+0.027, a shocked region close to Sgr B2(N) with a rich chemical content characterised by low excitation temperatures, should be a promising target to continue the search for interstellar glycaminide.

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Appendix A: Complementary Tables and figures

Table A.1 contains subset statistics for substates in each torsional/inversion doublet, including numbers of fitted lines, ranges of the values of the key quantum numbers, and frequency ranges of the measurements.

The plots in Figs. A.1, A.2, and A.3 are distribution plots of obs.-calc. frequencies as a function of the values of $J^\tau$ and $K_a^\tau$ quantum numbers, illustrating the comprehensive quantum number coverage achieved in the measurements.

Figures A.4 and A.5 show the transitions of NH$_2$CN and NH$_2$CH$_3$ that are covered by the ReMoCA survey and contribute significantly to the signal detected towards Sgr B2(N1S). Figure A.6 shows the population diagram of NH$_2$CH$_3$ towards Sgr B2(N1S).

Table A.1. Subset statistics for the coupled state fits of the three tunnelling doublets for glycinamide.

| Substate        | $N_{\text{lines}}$ | $\sigma^2$/MHz | $\sigma_{\text{rms}}$ | $J$ min | $J$ max | $K_a$ min | $K_a$ max | Frequency /GHz min | Frequency /GHz max |
|-----------------|---------------------|----------------|-----------------------|---------|---------|-----------|-----------|-------------------|-------------------|
| ground state, 0$^+$ | 635$^d$           | 0.0405         | 0.8353                | 0       | 55      | 0         | 36        | 6.706             | 328.902           |
| ground state, 0$^-$ | 602$^e$           | 0.0469         | 0.9354                | 11      | 55      | 0         | 37        | 90.620            | 328.918           |
| $v_{27}$, 1$^+$   | 438                | 0.0457         | 0.9129                | 11      | 55      | 0         | 31        | 112.147           | 328.889           |
| $v_{27}$, 1$^-$   | 435                | 0.0429         | 0.8578                | 11      | 55      | 0         | 31        | 112.210           | 328.346           |
| $v_{26}$, 0$^+$   | 381                | 0.0491         | 0.9822                | 11      | 55      | 0         | 26        | 112.148           | 328.787           |
| $v_{26}$, 0$^-$   | 333                | 0.0516         | 1.0316                | 12      | 55      | 0         | 26        | 112.238           | 326.637           |

Notes.

$^a$(a) Number of distinct measured frequencies. $^b$(b) Standard deviation of the fit. $^c$(c) Unitless (weighted) deviation of the fit. $^d$(d) Including 18 nominal 0$^-$ $\leftrightarrow$ 0$^+$ transitions. $^e$(e) Including 15 nominal 0$^+$ $\leftrightarrow$ 0$^-$ transitions.
Fig. A.1. Distribution plot of quantum numbers of rotational transitions measured and fitted for the ground-state doublet of glycinamide. Symbol diameter is proportional to the value of \(|f_{\text{obs}} - f_{\text{calc}}|/\sigma\) where \(f_{\text{obs}} - f_{\text{calc}}\) is the residual of fit for a given line and \(\sigma\) is its measurement uncertainty. Red colour identifies outliers with \(|f_{\text{obs}} - f_{\text{calc}}|/\sigma > 3\). The few outliers are all for confidently assigned transitions and may be due either to blends with unassigned lines or incompletely treated perturbation contributions.

Fig. A.2. Same as Fig. A.1 but for the \(v_{27} = 1\) doublet of glycinamide.
Fig. A.3. Same as Fig. A.1 but for the $v_{26} = 1$ doublet of glycinamide.

Fig. A.4. Transitions of NH$_2$CN, $v = 0$ covered by our ALMA survey. The synthetic spectrum of NH$_2$CN, $v = 0$ is displayed in red and overlaid on the observed spectrum of Sgr B2(N1S) shown in black. The blue synthetic spectrum contains the contributions from all molecules identified in our survey so far, including the species shown in red. The central frequency of each panel is indicated in MHz below its $x$-axis. Each panel has a width of 40 MHz, as indicated in brackets behind the central frequency. The angular resolution (HPBW) is also indicated. The $y$-axis is labelled in brightness temperature units (K). The dotted line indicates the 3$\sigma$ noise level.
Fig. A.5. Same as Fig. A.4 but for \( \text{NH}_2\text{CH}_3 \), \( v = 0 \).
Fig. A.5. continued.
Fig. A.5. continued.

Fig. A.6. Population diagram of NH$_2$CH$_3$ towards Sgr B2(N1S). The observed datapoints are shown in black while the synthetic populations are shown in red. No correction is applied in panel a. In panel b, the optical depth correction has been applied to both the observed and synthetic populations and the contamination by all other species included in the full model has been removed from the observed datapoints. The purple line is a linear fit to the observed populations (in linear-logarithmic space).