Millimeter-wave and Submillimeter-wave Spectra of Aminoacetonitrile in the Three Lowest Vibrational Excited States

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Abstract

It is important to study possible precursors of amino acids such as glycine to enable future searches in interstellar space. Aminoacetonitrile (NH₂CH₂CN) is one of the most feasible molecules for this purpose. This molecule was already detected toward Sgr B2(N). Aminoacetonitrile has a few low-lying vibrational excited states, and transitions within these states may be found in space. In this study, the pure-rotational transitions in the three lowest vibrational states in the 80–450 GHz range have been assigned and analyzed. It was found to be very important to include Coriolis coupling between the two lowest vibrational fundamentals, while the third one was unperturbed. The partition function was evaluated considering these new results.

Key words: ISM: molecules – line: identification – molecular data – submillimeter: ISM – techniques: spectroscopic

Supporting material: machine-readable table

1. Introduction

Attempts to detect amino acids have so far been unsuccessful even for its simplest form, glycine, despite decades of devoted observational studies (Brown et al. 1979; Hollis et al. 1980; Bernstein et al. 1995; Combes et al. 1996; Ceccarelli et al. 2000; Hollis et al. 2003; Kuan et al. 2003; Snyder et al. 2005; Cunningham et al. 2007; Jones et al. 2007). There are several possible explanations for this failure. One is that rotational constants are relatively large and the line strength of each line is not very strong. Another is the expected spatial distribution of the molecule. Garrod (2013) developed his sophisticated chemical models for hot cores and indicated that glycine is formed almost exclusively within or upon dust-grain ice mantles. Since the high evaporation temperature of the molecule (200 K) makes the emission region extremely compact, it can be hardly expected to detect glycine with a single-dish telescope. The feasibility of detecting glycine highly depends on the selection of sources to be observed with ALMA at sub-arcsecond resolutions. Garrod (2013) proposed as a candidate source the hot core NGC 6334 IRS1, where relatively narrow emission lines are expected. In addition, Jiménez-Serra et al. (2014) claimed that glycine may be detectable in low-mass prestellar cores such as L1544 because the congestion of spectral lines can be avoided.

From a chemical point of view, it is also important to consider sources where possible glycine precursors are abundant. Aminoacetonitrile is one of the possible precursors of glycine via Strecker synthesis (Strecker 1880; Elsila et al. 2007). Belloche et al. (2008a) reanalyzed previous microwave spectroscopic studies of aminoacetonitrile in the millimeter-wave region (MacDonald & Tyler 1972; Pickett 1973; Bogey et al. 1990) and succeeded in the detection of this molecule toward Sgr B2(N) (Belloche et al. 2008b). They derived a column density of $2.8 \times 10^{16}$ cm$^{-2}$, or fractional abundance of $2.2 \times 10^{-8}$ at a temperature of 100 K. Garrod (2013) showed that the peak gas-phase fractional abundance of a few $10^{-9}$ to $10^{-8}$ is expected at around 120 K in each timescale model. At such a high kinetic temperature, it looks plausible that the molecule can be populated in the high $J$ rotational levels in the vibrational ground state, or in the low-lying vibrational excited states.

In our previous study, we extended the measurements of the rotational spectrum of aminoacetonitrile up to 1.3 THz, and found that several misassignments of $b$-type transitions were present in the literature (Bogey et al. 1990). Therefore, we provided firm spectroscopic data of aminoacetonitrile in the ground vibrational state by correcting these errors (Motoki et al. 2013). During the course of the measurements, we found several satellite bands near the ground-state line, due to the spectral lines of vibrational excited states (Fujita et al. 2015). Preliminary analyses of the satellite transitions belonging to six different vibrational states revealed the presence of perturbations in several spectra, also including those of the two states of lower energy (Fujita et al. 2016).

The assignment of vibrational states of aminoacetonitrile (trans form, $C_s$ symmetry group) has been established by experimental and theoretical studies. Bak et al. (1975) observed and assigned the three lowest fundamental bands at 216 ($\nu_{11}$, $A'$ symmetry), 247 ($\nu_{18}$, $A''$ symmetry), and 370 cm$^{-1}$ ($\nu_{17}$, $A''$ symmetry), respectively, by gas-phase, low-resolution IR spectroscopy. Bernstein et al. (2004) performed density-functional theory calculations on aminoacetonitrile at the B3LYP/6–31+G(d) level. The harmonic frequencies computed for the three lowest modes were 204.9, 259.6, and 377.2 cm$^{-1}$, which were described as C–C≡N bend, $–\text{NH}_2$ torsion, and $\text{NH}_2$–$\text{CH}_3$ torsion, respectively.

Very recently, Kolesniková et al. (2017) reported rotational spectra for 29 vibrational excited states. Although perturbation effects were recognized, effective rotational and
centrifugal-distortion constants for each state were obtained by fitting their rotational spectra using the standard semi-rigid rotor model (Watson 1977). No vibration–rotation couplings between the excited states of the exhaustive list were considered, despite the remarkable effects in the higher rotational states they can produce. In this paper, we focused on the three lowest vibrational excited states. We have extended to a higher frequency than the previous study (Kolesniková et al. 2017), and have taken into account the Coriolis resonance existing between the two lowest states. This made it possible to include higher rotational states in the fitting, so that our obtained molecular constants have better predictive capabilities. The spectral data of these astronomically important states are essential for future observations of the molecule in relatively high kinetic temperature conditions.

2. Experiment

The present experiments were carried out in two laboratories, at Bologna and Toho Universities, respectively. The experiment at Bologna was conducted in the frequency ranges 80–115 and 240–290 GHz using a source-modulation millimeter/submillimeter-wave spectrometer. The main radiation sources were several Gunn-diode oscillators (Radiometer Physics GmbH, J.E. Carlstrom Co), which emit microwave radiation in the 80–130 GHz frequency range. Higher frequencies were generated using passive harmonic multiplication (Virginia Diodes, Inc.). The oscillators were stabilized through a suitable phase-lock loop to a computer-controlled frequency synthesizer, which was referenced to an external rubidium frequency standard. The frequency modulation of the radiation was obtained by sine-wave modulating (at 6 kHz) the reference signal of the wide-band Gunn synchronizer. Phase-sensitive detection at 2f is employed, so that the second derivative of the actual spectrum profile is recorded by the acquisition system. Two Schottky-barrier diodes (Millitech DXW-08 and Virginia Diodes, Inc. WR3.4R4ZBD) were used as detectors to record the spectra in the investigated frequency ranges. A 3.5 m long free-space glass absorption cell, filled with aminoacetonitrile vapor at a static pressure of ca. 15 mTorr (2 Pa), was employed for the measurements. The experiment at Toho University was conducted in frequency regions complementary to those investigated in Bologna, reaching a frequency as high as 450 GHz, with essentially the same apparatus and experimental conditions of the previous work (Motoki et al. 2013).

The aminoacetonitrile sample was purchased from a manufacturer (Sigma Aldrich) and used without further purification. All the spectra were taken at room temperature. The accuracy of each line frequency varies from 20 to 200 kHz, depending on the signal-to-noise ratio of the observed

Figure 1. Observed and calculated spectrum of aminoacetonitrile in its ground (denoted by “G”) and excited vibrational states (denoted by “11,” “17,” and “18” for \(v_{11} = 1, v_{17} = 1, \) and \(v_{18} = 1 \) states, respectively) around 150 GHz.

Figure 2. Portion of the \(J = 10 \leftrightarrow 9, a\)-type band of aminoacetonitrile in the \(v_{18}\) state. Splittings caused by electric quadrupole coupling are detectable for \(K_a = 7, 8, \) and 9. The \(K_a = 4\) transition shows the asymmetry splitting. An asterisk indicates a line of the \(v_{17}\) state.
spectrum, and line-blending due to unresolved hyperfine components enveloped in a single line profile.

3. Results and Analysis

At room temperature, all three lowest vibrationally excited states of aminoacetonitrile were sufficiently populated to assure the identification of the respective rotational spectra.

Close to each a-type \( R \) branch of the ground state, we were able to identify three different sequences of lines having the same \( K_a \) structure, but with reduced intensities, as expected for vibrational satellites produced by low-lying states, as shown in Figure 1. Preliminary fits to these sets of lines always provided \( B \) and \( C \) rotational constants that were a few MHz greater than those of the ground state. From intensity-ratio measurements, it was possible to make an approximate evaluation of the excited-state vibrational energies, which were found in the range from 200 to 400 cm\(^{-1}\), in qualitative agreement with the IR data (Bak et al. 1975; Bernstein et al. 2004). The measurements for the three excited states were then extended up to 450 GHz so that a fairly large set of \( a- \) and \( b- \)type transition frequencies could be obtained for each vibrational state. The measurements probed rotational energy levels in the \( J \) interval from 6 to 56 and in the \( K_a \) interval from 0 to 15. Small splittings due to the \( ^{14}\text{N} \)-nuclear spin of the two nitrogen atoms were observed for a few \( a- \)type \( R \) branch transitions with high \( K_a \) values measured in the 100 GHz region. An example is provided in Figure 2, which shows a \( K_a \) sequence for the \( J = 10 \rightarrow 9 \) a-type band in the \( \nu_{18} \) State, in which splittings due to the electric quadrupole coupling are detectable for \( K_a = 7, 8, \) and 9.

The complete data sets for the three excited states were then assembled by combining the millimeter-wave and submillimeter-wave transition frequencies measured at Bologna and Toho. They were analyzed using Pickett’s SPFIT program (Pickett 1991), adopting Watson’s \( S \)-reduced Hamiltonian in its \( l' \) representation (Watson 1977). In order to analyze the observed hyperfine-structure components, the following angular momenta coupling scheme between the \(^{14}\text{N} \)-nuclear spins \( I_I (\text{NH}_2 \) group) and \( I_C (\text{CN} \) group) and the rotational angular momentum \( J \) was adopted: \( I = I_I + I_C, F = J + I \). The required \(^{14}\text{N} \) electric quadrupole coupling constants were held fixed to the values determined by Brown et al. (1977) for the vibrational ground state, which are \( \chi_{aa} = -2.77 \text{ MHz} \) and \( \chi_{bb} - \chi_{cc} = -0.37 \text{ MHz} \) for \(^{14}\text{NH}_2 \), \( \chi_{aa} = -3.48 \text{ MHz} \) and \( \chi_{bb} - \chi_{cc} = -0.48 \text{ MHz} \) for \(^{14}\text{N} \).

The rotational lines of the weakest spectrum, corresponding to \( \nu_{21} \), could be fitted very well using the standard semirigid Hamiltonian. Centrifugal-distortion constant values close to those of the ground-state were determined.

The same procedure gave, however, unsatisfactory results when used to analyze the transition frequencies measured for the two states of lower energy. Large deviations, opposite in signs, were produced for \( a- \)type \( R \) branch lines with \( K_a \geq J/2 \), and strongly diverging values of the quartic centrifugal-distortion constants \( D_K \) and \( D_d \) resulted. This was a clear indication of the existence of some rovibrational interaction between these states. Since aminoacetonitrile has \( C_2 \) symmetry, its vibrations must belong to the \( A' \) or \( A'' \) irrep. Hamiltonian. Centrifugal-distortion constant values close to those of the ground-state were determined.

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Table 2
Molecular Constants of Aminocetanitriile in the Vibrational Ground and the Lowest Three Excited States

| Parameter | Ground State | \( \nu = 1 \) | \( \nu = 4 \) | \( \nu = 7 \) |
|-----------|--------------|--------------|--------------|--------------|
| A         | 30246.48871(102) | 30279.631(148) | 30366.319(148) | 30143.70415(279) |
| B         | 4761.002547(139) | 4775.685772(133) | 4769.41045(152) | 4764.237310(128) |
| C         | 4310.748574(139) | 4316.85665(127) | 4314.508679(139) | 4316.43367(93) |
| \( D_\ell \times 10^3 \) | 3.06687(108) | 3.048626(79) | 3.070470(136) | 3.072421(106) |
| \( D_{\ell K} \times 10^3 \) | –55.29457(138) | –52.555(85) | –55.690(85) | –55.02910(216) |
| \( D_{\ell K} \times 10^3 \) | 714.0755(78) | 649.868(148) | 779.287(233) | 695.850(188) |
| \( \delta_1 \times 10^3 \) | –0.67353(41) | –0.674571(61) | –0.675957(75) | –0.6762041(62) |
| \( \delta_2 \times 10^3 \) | –0.02999382(96) | –0.0336185(89) | –0.0297107(156) | –0.0267621(125) |
| \( H_\ell \times 10^6 \) | 0.0095530(304) | 0.0091135(216) | 0.009503(42) | 0.0099613(33) |
| \( H_{\ell K} \times 10^6 \) | –0.12406(51) | –0.13109(89) | –0.11199(145) | –0.12406(51) |
| \( H_{\ell K} \times 10^6 \) | –2.7126(81) | –2.7126(81) | –2.7126(81) | –2.6604(164) |
| \( H_{\ell K} \times 10^6 \) | 53.2285(189) | 53.2285(189) | 53.2285(189) | 53.2285(189) |
| \( h_1 \times 10^9 \) | 3.8722(146) | 3.6369(142) | 3.6833(270) | 3.7659(223) |
| \( h_2 \times 10^9 \) | 0.4749(62) | 0.4749(62) | 0.4749(62) | 0.4749(62) |
| \( h_3 \times 10^9 \) | 0.0522(210) | 0.0522(210) | 0.0522(210) | 0.0522(210) |
| \( L_g \times 10^{12} \) | –0.03596(284) | –0.03596(284) | –0.03596(284) | –0.03596(284) |
| \( L_{\ell K} \times 10^{12} \) | 0.488(63) | 0.488(63) | 0.488(63) | 0.488(63) |
| \( L_{\ell K} \times 10^{12} \) | –5.39(133) | –5.39(133) | –5.39(133) | –5.39(133) |
| \( L_{\ell K} \times 10^{10} \) | 0.1858(157) | 0.1858(157) | 0.1858(157) | 0.1858(157) |
| \( L_{K} \times 10^9 \) | –4.4049(176) | –4.4049(176) | –4.4049(176) | –4.4049(176) |
| \( l_1 \times 10^3 \) | –0.02095(64) | –0.02095(64) | –0.02095(64) | –0.02095(64) |
| \( l_2 \times 10^3 \) | –5.05(90) | –5.05(90) | –5.05(90) | –5.05(90) |
| \( l_3 \times 10^3 \) | –0.61(41) | –0.61(41) | –0.61(41) | –0.61(41) |

\[ \Delta E(\nu_{18} - \nu_{11}) \quad 102880.7(79) \]
\[ G_\alpha \quad 16401.4(46) \]
\[ G_\beta \quad 0.03303(269) \]
\[ G_\alpha^R \times 10^3 \quad -0.03308(54) \]

Rms error of residuals: 0.0415 \[ \sigma \] = 0.894

Notes.
- a Units are in MHz. \(^14\text{N}\) electric quadrupole coupling constants were held fixed to the value determined by Brown et al. (1977).
- b Values in parenthesis denote one standard deviation and apply to the last digits of the constants.
- c Fixed to the ground-state value (Motoki et al. 2013).
- d Dimensionless fit standard deviation.

by more than a factor of ten, even if small systematic obs.-calc. deviations still remained, indicating the need to improve the coupling model. No significant effect was obtained, either considering a b-axis Coriolis interaction or higher-order terms deriving from \( H_{22} \) (Papoûsek & Aliev 1982), while a further lowering of the standard deviation of the fit was achieved by taking into account small dependences of \( G_{\alpha\gamma} \) from the rotational quantum numbers \( J \) and \( K \). The best results were obtained using two more adjustable parameters, adopting an off-diagonal Coriolis operator of the form \((G_{\alpha\gamma} + G_{\alpha\beta}P^2 + G_{\alpha\gamma}^R P^2 P^2)C_l\). The effectiveness of an \( a\)-type Coriolis coupling demonstrates that the two lowest vibrational states of aminocetanitriile must be of different symmetry, as stated in Bak et al. (1975) and confirmed by the ab initio calculations of Bernstein et al. (2004). In the fitting procedure, the experimental data were weighted according to the inverse square of their uncertainty.

As far as the \( \nu_{17} \) state is concerned, 352 different line frequencies measured in the frequency interval from 80 to 450 GHz were analyzed. They correspond to transitions between rotational levels for which \( J \) ranges from 6 to 50, and \( K \), from 0 to 15. The three rotational constants, the full set of quartic centrifugal-distortion constants, and the sextic centrifugal-distortion constants \( H_\alpha, H_{KF} \), and \( h_1 \) were fitted to the measured frequencies, obtaining a standard deviation value of 25.4 kHz. The remaining sextic centrifugal-distortion constants, not useful for a further improvement of the fit, were held fixed to the respective ground-state values (Motoki et al. 2013), and the \(^14\text{N}\) electric quadrupole coupling constants (Brown et al. 1977) as well.

For the \( \nu_{11}/\nu_{18} \) resonance system, a total number of 866 distinct line frequencies were measured, corresponding to rotational transitions spanning nearly the same \( J \) and \( K \) ranges previously mentioned for the the \( \nu_{17} \) state. The measured frequencies were analyzed by fitting all rotational and quartic centrifugal-distortion constants, and three sextic distortion constants \( H_{J}, H_{KF}, \) and \( h_1 \) of each interacting state. In addition, the vibrational energy difference \( \Delta E_{\gamma\beta} \) and the Coriolis coupling coefficients \( G_{\alpha\beta}, G_{\beta\gamma}, \) and \( G_{\alpha\gamma}^R \) were optimized to achieve a satisfactorily low standard deviation standard deviation of 29.8 kHz. The vibrational energy difference between the two interacting states is accurately determined to be 34.31731(26) cm\(^{-1}\). The observed and calculated transition frequencies are listed in Table 1; the complete list is included in the online machine readable version of this table. The determined molecular constants, including interaction parameters and the energy difference \( \nu_{18} - \nu_{11} \), are summarized in Table 2. As seen in Figure 1, many satellite lines remained unassigned in the
The rotational spectra of aminoacetanitrile in the three lowest vibrational states ($\nu_{11} = 1, \nu_{18} = 1$, and $\nu_{17} = 1$) were clearly identified. The $\nu_{17} = 1$ state was almost isolated and inclusion of any perturbation was not necessary, while the $\nu_{11} = 1$ and $\nu_{18} = 1$ states proved to be interacting through an $\alpha$-type Coriolis coupling, thus leading to a careful revision of the initial assignments. The determined vibrational energy difference between the two interacting states compares fairly well with the value from the previous infrared study of Bak et al. (1975) and with the computational result of Bernstein et al. (2004). In addition, the values of the centrifugal-distortion constants determined for the two interacting states are very close to those of the ground state, thus confirming the effectiveness of our analysis.

The fitted value of the main Coriolis coupling coefficient is $16.401 \pm 5$ MHz. It was compared with the corresponding ab initio computed value that was obtained using the Gaussian 09 program (Frisch et al. 2013) at the MP2/6–311++G(d, p) level. The $G_\alpha$ Coriolis coefficient that couples the $\nu_{11}$ and $\nu_{18}$ vibrational states has the following theoretical expression (Papoušek & Aliev 1982):

$$G_\alpha = A\frac{\omega_{11} + \omega_{18}}{\sqrt{\omega_{11}\omega_{18}}} a_{\nu_{11},\nu_{18}}$$

(1)

$A_\alpha$ is the equilibrium value of the rotational constant $A$, $\omega_{11}$ and $\omega_{18}$ are the harmonic frequencies of the interacting states, and $a_{\nu_{11},\nu_{18}}$ is the corresponding Coriolis coupling constant. Using the ab initio computed values for all the parameters ($A_\alpha = 30155.6$ MHz, $\omega_{11} = 209.16$ cm$^{-1}$, $\omega_{18} = 264.77$ cm$^{-1}$, $a_{\nu_{11},\nu_{18}} = 0.20622$), it results in $G_\alpha = 12.524$ MHz. A very negligible change is obtained using experimental vibrational frequencies and the ground-state value of the rotational constant $A$. It seems, therefore, that the 30% disagreement between $\nu_{11} = 1$ and $\nu_{18} = 1$ states.

Table 3 compares the values of the spectroscopic constants determined in the present work with those recently published by Kolesniková et al. (2017). Large discrepancies do obviously appear for the $\nu_{11} = 1$ and $\nu_{18} = 1$ states, because of the substantial difference of the fitting procedures. We have measured and analyzed transition frequencies corresponding to higher $J$ and $K_a$ values, so the $\alpha$-type Coriolis coupling existing between these two states had to be necessarily taken into account to obtain a reasonably good fit. In this way the contribution of the corresponding resonant term that is inversely proportional to $\pm (\omega_{11} - \omega_{18})$ is removed from the

| Parameter | $\nu_{11} = 1$ | $\nu_{18} = 1$ | $\nu_{17} = 1$ |
|-----------|----------------|----------------|----------------|
| Present Work | Previous Work | Present Work | Previous Work | Present Work | Previous Work |
| $A$ | $30279.631(148)^c$ | $30181.544(62)$ | $30366.319(148)$ | $30627.738(71)$ | $30143.701(279)$ | $30143.698(10)$ |
| $B$ | $4776.485772(133)$ | $4776.36759(43)$ | $4769.414045(152)$ | $4769.29434(62)$ | $4764.237310(128)$ | $4764.23280(41)$ |
| $C$ | $4316.655665(127)$ | $4316.76886(41)$ | $4314.508679(139)$ | $4314.62273(64)$ | $4316.436367(93)$ | $4316.43101(36)$ |
| $D_\ell \times 10^3$ | $3.046620(79)$ | $3.06106(33)$ | $3.070470(136)$ | $3.03501(35)$ | $3.072421(106)$ | $3.062103(31)$ |
| $D_{\ell k} \times 10^3$ | $−52.559(85)$ | $−50.298(10)$ | $−55.690(85)$ | $−57.563(14)$ | $−55.0210(216)$ | $−55.003(56)$ |
| $D_{\ell k} \times 10^3$ | $649.866(148)$ | $558.80(23)$ | $779.287(233)$ | $862.77(15)$ | $695.850(188)$ | $984.863(99)$ |
| $d_1 \times 10^4$ | $−0.675471(61)$ | $−0.675632(27)$ | $−0.675957(75)$ | $−0.67519(50)$ | $−0.672041(62)$ | $−0.67163(14)$ |
| $d_2 \times 10^3$ | $0.0091135(216)$ | ... | $0.009503(42)$ | ... | $0.009616(33)$ | ... |
| $H_{\ell k} \times 10^6$ | $0.013109(89)$ | $−0.25232(27)$ | $−0.11199(145)$ | $0.294(13)$ | $−0.12406(4d) | $−0.1134(33)$ |
| $H_{\ell k} \times 10^6$ | $53.2285d$ | ... | $53.2285d$ | ... | $53.2285d$ | ... |
| $h_1 \times 10^9$ | $3.6369(142)$ | $4.34(13)$ | $3.6833(270)$ | $2.25(27)$ | $3.7659(223)$ | $3.8722(4d) |
| $h_2 \times 10^9$ | $0.4749d$ | ... | $0.4749d$ | ... | $0.4749d$ | ... |
| $h_3 \times 10^9$ | $0.05229d$ | ... | $0.05229d$ | ... | $0.05229d$ | ... |

Rms error of residuals: $0.030^p = 0.048, 0.030^p = 0.046, 0.025, 0.040$

Notes.

$^a$ Units are in MHz.
$^b$ Kolesniková et al. (2017).
$^c$ Values in parentheses denote one standard deviation and apply to the last digits of the constants.
$^d$ Fixed to the ground-state value (Motoki et al. 2013).
$^e$ Root mean square deviation of a single fit for the lines of the $\nu_{11} = 1$ and $\nu_{18} = 1$ states.
$^f$ Number of distinct line frequencies analyzed for each vibrational state.
\( \delta_{011} \) and \( \delta_{018} \) vibration–rotation interaction constants, and this explains the differences of ca. \( \pm 261 \) MHz between the effective \( A \) constants determined in the present work and those published by Kolesniková et al. (2017) for the same states. Very significant changes are also produced for some centrifugal-distortion constants which converge to rather unreliable values (i.e., too far from those of the ground state) if the resonance is neglected. Anomalous values of the quartic centrifugal-distortion constants \( D_K \) and \( d_2 \), and of the sextic \( H_{6K} \) and \( h_1 \) are apparent in the results of Kolesniková et al. (2017), although they analyzed transition frequencies corresponding to lower \( J \) and \( K_a \) values. On the contrary, normal values are obtained by our analysis for these constants. Note that if the spectroscopic constants determined by Kolesniková et al. (2017) are used to predict the whole set of transition frequencies that we have measured for the \( \nu_{11} = 1 \) and \( \nu_{18} = 1 \) states, then obs.-calc. values greater than 1 MHz are produced for nearly all transitions recorded above 273 GHz, and for 33 transitions the frequency discrepancies are larger than 10 MHz. For the unperturbed \( \nu_{17} = 1 \) state, the molecular constants determined in the present work are essentially the same as those reported by Kolesniková et al. (2017). Small discrepancies beyond the quoted uncertainties are anyway observable, probably due to (a) the extension of our measurements into a higher frequency region, (b) a different choice of the sextic centrifugal-distortion constants released in the fits, and (c) a better accuracy of our frequency measurements when hyperfine splittings due to the electric quadrupole coupling were resolved.

The vibration–rotation partition function of aminoacetonitrile was calculated for several temperatures by taking the three lowest vibrational excited states into account. The observed vibrational frequencies in the gas phase (216, 247, and 370 cm\(^{-1}\) for \( \nu_{11} = 1, \nu_{18} = 1, \) and \( \nu_{17} = 1 \) states, respectively) were used as term values for these states. The results are listed in Table 4. According to Bak et al. (1975), the vibrational frequency next to the lowest three modes is 558 cm\(^{-1}\), and the effect of this mode on the vibrational partition function can contribute to the uncertainties of the present data by 6% at 300 K and less than 1% at 100 K.

In order to calculate the spectral intensity of the molecule for conducting a search in the interstellar medium, we needed to assume the components of the dipole moment in the vibrational excited states to be the same as those in the ground state, which are \( \mu_e = 2.5777 \) and \( \mu_p = 0.5754 \) Debye (Pickett 1973). The spectral line catalog was then constructed with Pickett’s SPCAT program (Pickett 1991).

Using these data, an initial attempt to detect these transitions in the ALMA survey toward Sgr B2 showed that there are some weak hints of their presence (A. Belloche 2016, private communication). All the lines were blended and we need more sensitive data to confirm the first detection. The previous study (Belloche et al. 2008a, 2008b) indicates that the emission of aminoacetonitrile came from a compact source and ALMA’s high spatial resolution provides an ideal tool to observe this species.

## 5. Conclusion

Rotational spectral lines in the astronomically important vibrational excited states, \( \nu_{11}, \nu_{17}, \) and \( \nu_{18} \) of aminoacetonitrile, which is considered a possible precursor of glycline, were observed. Among the three vibrational states, \( \nu_{11} \) and \( \nu_{18} \) states are mixed through an \( a \)-type Coriolis interaction. The standard deviation of the fit is around our experimental accuracy, leading to a calculated frequency error for the spectral lines lower than 100 kHz, which is suitable for the line identification of aminoacetonitrile in the vibrational excited states. Our spectral line list will be cataloged in a spectral line database (Toyama Microwave Atlas (ToyaMA); [http://www.sci.u-toyama.ac.jp/phys/4ken/atlas/](http://www.sci.u-toyama.ac.jp/phys/4ken/atlas/)). Our initial attempt for detection of aminoacetonitrile in the vibrationally excited state is still inconclusive, and further consideration will be needed.

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**Software:** SPCAT (Pickett 1991), SPFIT (Pickett 1991), Gaussian 09 (Frisch et al. 2013).

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