



## Submillimeter wave spectroscopy of propanoic acid (CH<sub>3</sub>CH<sub>2</sub>COOH) and its ISM search

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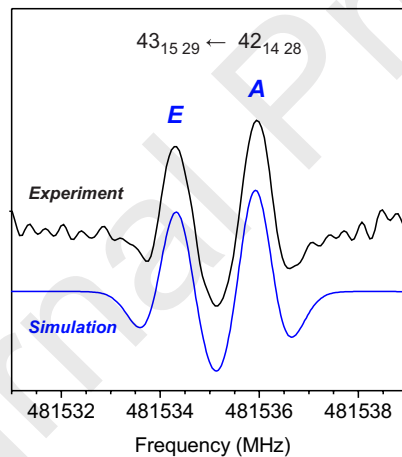
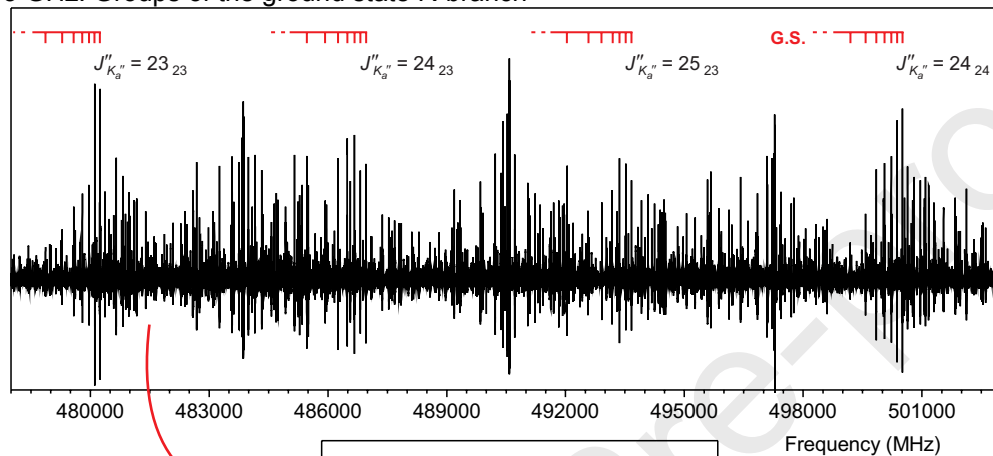
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## Highlights

- The higher thermodynamic stability of  $C_3H_6O_2$  isomer, propionic-acid, suggests that this molecule should be considered as a possible candidate for ISM detection
- report a non-detection of propanoic acid in these clouds and derive upper limits to the column density.
- study of the rotational spectrum of propanoic acid  $CH_3CH_2COOH$  was carried out in the frequency range of 150–545 GHz
- frequency predictions for astronomical use were produced up to 550 GHz

A section of the room-temperature rotational spectrum of propanoic acid between 478 and 503 GHz. Groups of the ground state R-branch



## Submillimeter wave Spectroscopy of Propanoic acid (CH<sub>3</sub>CH<sub>2</sub>COOH) and its ISM search

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### Abstract

Three compounds with a C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> formula have been detected in the Interstellar Medium (ISM): ethyl formate (CH<sub>3</sub>CH<sub>2</sub>OC(O)H), methyl acetate (CH<sub>3</sub>OC(O)CH<sub>3</sub>) and very recently hydroxyacetone (CH<sub>3</sub>C(O)CH<sub>2</sub>OH). **The higher thermodynamic stability of another isomer, the propanoic acid (CH<sub>3</sub>CH<sub>2</sub>C(O)OH), clearly suggests that this molecule should be considered as a possible candidate for ISM detection. To provide reliable predictions for astronomical use in the millimeter and submillimeter wave ranges we performed a new study of propanoic acid rotational spectrum up to 545 GHz. The analysis of large amplitude methyl top torsional motion in this molecule was carried out using the rho axis method and the RAM36 program code. More than 3200 lines corresponding to the rotational transitions in the ground and first excited methyl top torsional states were newly assigned and fit within experimental error. This enabled us to produce new predictions which were used to search**

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for propanoic acid in two high-mass star-forming regions: SgrB2 (public IRAM 30m) and Orion KL (ALMA Science Verification). We report a non-detection of propanoic acid in these clouds and derive upper limits to the column density.

*Keywords:*

ISM: molecules – methods: laboratory: molecular – submillimeter: ISM – molecular data – line: identification

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## 1. Introduction

More than 200 compounds have been detected in the interstellar medium (ISM)<sup>1</sup> [1] but thousands have been proposed. The choice of new candidates must come from scientific reasoning based on our knowledge of the chemistry occurring in the interstellar clouds, by analogy with the detected compounds or on the basis of the physical-chemical properties observed for many of them. The first way is to try to understand the chemistry of the ISM but each cloud seems to have its specific starting material and its own physical parameters. In addition, within the same cloud, a species can be found with notable differences in the column density depending on the studied part. This leads to too many imprecise parameters to satisfactorily understand the chemistry of these media and effectively predict the presence of new components. Therefore, the analogy with the detected compounds remains the most used tool. Adding "CH<sub>2</sub>" or "C≡C" between two atoms was particularly used and has led, for example, to the observation of many alkylcyanides or cyanopolyynes. The third approach takes into account certain properties of the detected compounds leading to a tool based on empirical observations. Most (but not all) of the detected compounds correspond to the most thermodynamically stable isomer. Many of the detected compounds have two and sometimes even three isomers that have been detected. In the case where several isomers are present in the ISM, the most thermodynamically stable one is often the most abundant. Many compounds satisfy this principle of minimum energy which can therefore be considered as a pragmatic tool for the choice of new candidates [2].

**We report here a study on propanoic acid, a compound selected taking into consideration the three approaches mentioned above. From the analogy with the detected compounds point of view propanoic acid may be considered**

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<sup>1</sup>[http://www.astrochymist.org/astrochymist\\_ism.html](http://www.astrochymist.org/astrochymist_ism.html)

<sup>2</sup><http://www.astro.uni-koeln.de/cdms/molecules>

as "CH<sub>2</sub>" derivative of already detected in the ISM acetic acid [3]. From a chemical modelling point of view propanoic acid may be formed via reaction of CO<sub>2</sub>H with C<sub>2</sub>H<sub>5</sub> by analogy with already detected in the ISM formic acid [4, 5] and acetic acid [3] which may have formed from CO<sub>2</sub>H and H [6] or CH<sub>3</sub> respectively. From thermodynamical stability point of view propanoic acid is the thermodynamically most stable compound in the isomeric family with a C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> formula [7] in which three isomers have already been detected in the ISM: methyl acetate [8], ethyl formate [9] and hydroxyacetone [10]. This fact makes propanoic acid a potential interstellar molecule that clearly deserves a thorough spectroscopic study as a prerequisite for its research in the ISM.

Microwave spectra of propanoic acid were first studied by O. Stiefvater in the 18-40 GHz range using the double resonance modulation technique [11, 12]. Transitions belonging to the ground vibrational state as well as to the first excited states of the five lowest normal vibrational modes have been assigned and analyzed to give rotational and quartic centrifugal distortion constants. He also determined dipole moment components of propanoic acid via standard Stark measurement procedure [11]. In addition, analysis of the A-E splittings in the first excited methyl top torsional state allowed to estimate the barrier height ( $\sim 818 \text{ cm}^{-1}$  [11]) hindering the methyl group internal rotation in propanoic acid. In 2008, Ouyang and Howard [13] provided new measurements of propanoic acid spectrum in the 6 - 18 GHz range using a Fourier Transform Microwave spectrometer. Transition frequencies of 26 lines belonging to the ground vibrational state were measured. Recently, Jaman et al. [14] provided measurements of propanoic acid in the 80 - 100 GHz range. 54 A-type transitions in the ground vibrational state with  $J_{max} = 50$ ,  $K_a^{max} = 12$  have been assigned and measured in this study [14]. The analysis of propanoic acid spectrum in [14] was supported by MP2 and DFT calculations.

The previous spectroscopic measurements for propanoic acid are not enough to provide reliable predictions for astronomical use in the millimeter and sub-millimeter wave ranges. Whereas the results from [11, 12, 13] provide information on both A and E symmetry species in the propanoic acid spectrum, they are limited by the upper frequency of 40 GHz. Jaman et al. [14] extends the upper frequency limit up to 100 GHz, but only A-type transitions were analysed using Watson's S-reduction Hamiltonian model. Therefore, this study [14] does not provide a full picture of the spectrum even in the ground vibrational state. Since blends with emission lines of other species

may be a problem for firm identification of a molecule in space, availability of predictions for a full set of symmetry species present in a molecular spectrum is highly desired for the ISM search. Thus, the aim of this study is to provide for astronomical use reliable predictions of propanoic acid spectrum for both A and E type transitions in the millimeter and submillimeter wave ranges. With this aim we have performed new measurements of propanoic acid spectrum up to 545 GHz which were analysed using the rho axis method and the RAM36 program code [15, 16]. Finally, based on the improved frequency predictions provided by the present work we have carried out a search for  $\text{CH}_3\text{CH}_2\text{COOH}$  in two high-mass star-forming regions, Orion KL and Sgr B2.

## 2. Spectroscopic study

### 2.1. Experimental details

The sample purchased from Sigma-Aldrich with 99.5% purity was used. The propanoic acid absorption spectra were measured between 150 and 545 GHz using the Lille spectrometer [17]. **The absorption cell was a stainless- steel tube (6 cm in diameter, 220 cm in length).** The measurements were performed at typical pressures of 15 Pa at room temperature. The two frequency ranges used, 150–330 GHz and 400–550 GHz, were covered with various active and passive frequency multipliers with the Agilent synthesizer (12.5–18.33 GHz) used as the primary signal source. **To increase the sensitivity of the spectrometer, frequency modulation at 20.5 kHz of the reference source and lock-in detection are used. The demodulation of the detected signal may be performed either at 1f or 2f, but 2f demodulation is preferred because of simpler presentation of observed spectrum in this case.** Absorption signals were detected by an InSb liquid He-cooled bolometer (QMC Instruments Ltd.). Estimated uncertainties for measured line frequencies are 30 kHz, 50 kHz, and 100 kHz depending on the observed S/N ratio and the frequency range.

### 2.2. Analysis of the spectra

Propanoic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , in its preferred conformation has a planar heavy atom skeleton in which the  $\text{CH}_3$  group eclipses the carbonyl oxygen, and with the hydroxyl hydrogen lying in between the two oxygen atoms [11, 14]. It is a prolate asymmetric top (asymmetry parameter  $k \approx -0.74$ ) with *b*-type transitions dominating in the rotational spectrum ( $\mu_a = 0.19$  D and  $\mu_b = 1.54$  D [11]). Due to hindered internal rotation of the methyl group in

the molecule we have torsional  $A - E$  splittings in the spectrum. Relatively small rotational constants of this 11 atom molecule [11, 14] in the presence of a number of low lying vibrational modes [11] in combination with additional methyl torsion  $A-E$  splittings result in a rather congested spectrum of propanoic acid in the millimeter and submillimeter wave ranges.

The Hamiltonian used in the present work is the so-called rho-axis-method (RAM) torsion-rotation Hamiltonian, which has proved its effectiveness for a number of molecules containing the  $C_{3v}$  rotor and  $C_s$ ,  $C_{2v}$ , or  $C_1$  molecular frames (a detailed description of the rho-axis-method may be found for example in [18, 19]). Propanoic acid corresponds to the case of  $C_{3v}$  internal rotor and  $C_s$  molecular frame and allowed terms in its torsion-rotation Hamiltonian must be totally symmetric in the molecular symmetry group  $G_6$ . A strong point of the rho axis method is the global approach when the whole set of states associated with a torsional large amplitude motion coordinate is treated together. In this case interactions between different torsional states are taken into account automatically, i.e. they are intrinsically included in the RAM Hamiltonian model in contrast to those approaches which treat each torsional state separately (such as ERHAM for example [20, 21]). In the current study we employ the RAM36 (rho-axis-method for 3 and 6-fold barriers) program code [15, 16] that realizes the RAM approach for molecules with a  $C_{3v}$  top attached to a molecular frame of  $C_s$  or  $C_{2v}$  symmetry, which is thus suitable in the case of propanoic acid. A detailed description of the RAM36 program code may be found in [15, 16]. The RAM36 computer code uses the two step diagonalization procedure of Herbst et al. [22]. In the current case of propanoic acid, 21 torsional basis functions were used at the first diagonalization step and 9 torsional basis functions used at the second diagonalization step. For a molecule with  $C_s$  symmetry frame the RAM36 code defines the symmetry plane as the  $zx$  plane (molecule fixed-axis system). In the case of propanoic acid, the molecular Hamiltonian was established in  $I'$  coordinate representation:  $z = a$ ,  $x = b$ , and  $y = c$ .

Internal rotation of the methyl group in propanoic acid is hindered by a relatively high potential barrier ( $\sim 824 \text{ cm}^{-1}$  see Table 1). In addition due to rather heavy molecular frame  $-\text{CH}_2\text{CO}_2\text{H}$  coupling between internal rotation of the methyl group and the overall rotation of the molecule is quite low ( $\rho \approx 0.055$ ). As a result the  $A - E$  splittings due to the large amplitude methyl torsion motion in this molecule are rather small being in the order of few MHz (example in Fig. 1) or less in the ground vibrational state. The information extracted from the ground state  $A - E$  splittings of propanoic acid



is not enough to properly constrain pure torsional part of the RAM torsion-rotation Hamiltonian (one of the torsional parameters, e.g.  $F$ , should be fixed to avoid divergence of a fit). For a better constrain of the torsional parameters in the RAM Hamiltonian, data from excited methyl torsion states should be included. Here a complication may arise from a low lying skeletal torsion vibrational mode around the central carbon - carbon bond in this molecule ( $64(3) \text{ cm}^{-1}$  [11]), which is very likely to interact with the methyl torsion mode (see Fig.2 for corresponding energy level diagram).

We started our analysis of propanoic acid spectrum from refitting the results of [11, 13] using the RAM36 program [15, 16]. At the first stage, we decided to concentrate our efforts on the ground vibrational state. The initial fit of the data from [11, 13] allowed us to make predictions which were good enough to continue the assignment in the 150 - 545 GHz range of our measurements with the Lille spectrometer. The assignment was continued in the classical boot-strap manner, where newly assigned transitions were used to improve the frequency predictions and search for new ones. Transitions up to  $J = 94$  and  $K_a = 26$  in the ground vibrational state were assigned. **At this stage of our analysis the methyl top internal rotation constant  $F$  was kept fixed, since its varying lead to divergence of the fit.**

At the next stage of our analysis, transitions belonging to the first excited methyl torsion state  $v_t = 1$  were added to the fit. Since the transitions of the first excited methyl torsion state were included mainly with the purpose of better torsional parameter constrain in our Hamiltonian model, we decided to limit our assignments by the range of rotational quantum numbers  $J \leq 50$  and  $K_a \leq 10$ . This effectively limited the frequency range for the new assignments of the first excited methyl torsion state to 150 - 325 GHz. Our analysis showed that for transitions with higher  $J$  the avoided crossing interactions (presumably with the third excited skeletal torsion state, see Fig.2) occur quite often, reducing the quality of the fit. Based on our analysis 4 transitions belonging to the first excited methyl torsion state from [11] were excluded from the fit due to rather large deviations of the observed from the calculated line positions relative to the stated measurement uncertainty. **Inclusion of  $v_t = 1$  data gave us an opportunity to unfix and determine from the fit the methyl top internal rotation constant  $F$ . Besides this the main difference in the parameter sets of the first stage of our analysis (gs data only) and the second stage ( $v_t = 1$  data included) lie in the presence of a number of additional  $J$  and  $K$  dependencies of the  $V_3$  barrier height parameter (e.g.  $V_{3JJ}$ ,  $V_{3JJJ}$ ,  $V_{3JK}$ ,  $V_{3xyJ}$ ,  $V_{3xyK}$ ) and several octic centrifugal distortion parameters (see Table 1).**

At the final stage of our fitting process, the measurements **in the 80 - 100 GHz range** from Jaman et al. [14] were added to the fit. Although the transitions in [14] were assigned as A-type transitions **in the ground vibrational state**, our analysis showed that the measured lines more likely correspond to unresolved A-E doublets. Thus, we added to our fit the corresponding E-type component to each A-type transition from [14]. **Since we treat blends using an intensity-weighted average of calculated (but experimentally unresolved) transition frequency such augmenting by partners in blends provides an opportunity to better reproduce the observed spectrum.**

The final dataset treated in this work contains 3477 measured line frequencies, which due to the frequent blending correspond to 7951 transitions in the fit. From these transitions, 6592 correspond to the ground vibrational state and 1359 correspond to the first excited methyl torsion state. The full data set of the assigned lines is provided as supplementary material (Table S1). The RAM Hamiltonian model comprising 29 adjusted parameters fits the dataset at a weighted root mean square deviation of 0.82. Table 1 presents the parameters of our best-fit model for the current set of propanoic acid data. **If we compare our parameters with the previous results [11, 14] we will find rather good agreement for the torsional parameters ( $V_3 = 824.(13) \text{ cm}^{-1}$ ,  $F = 5.683(79) \text{ cm}^{-1}$  here versus  $V_3 = 818 \text{ cm}^{-1}$ ,  $F = 5.653 \text{ cm}^{-1}$  in [11]). The values for the angle between the methyl top symmetry axis and  $a$  principal axis is also rather close ( $32.26^\circ$  here versus  $33.10^\circ$  in [11]). A less good agreement for the rotational constants  $A = 10166.50 \text{ MHz}$ ,  $B = 3821.30 \text{ MHz}$ ,  $C = 2876.78 \text{ MHz}$  here (recalculated from rho axis system to principal axis system) versus  $A = 10155.358(2) \text{ MHz}$ ,  $B = 3817.887(1) \text{ MHz}$ ,  $C = 2875.174(1) \text{ MHz}$  in [14] presumably caused by the fact that the RAM model in a different way accounts for contribution from averaging over methyl top torsion motion.**

At the initial stage of the  $\text{CH}_3\text{CH}_2\text{COOH}$  spectrum analysis we anticipated that some problems with fitting high  $J$  transitions may occur due to the intervibrational interactions with a low lying skeletal torsion vibrational mode around the central carbon - carbon bond at  $64(3) \text{ cm}^{-1}$  [11]. But in fact, for the ground vibrational state only in a few cases we think that the observed increase in obs.-cal. values of order of several hundred kHz may be due to the weak avoided crossing interactions. The situation with the first excited methyl torsion state is quite different. For the transitions above  $J=50$  we observed shifts presumably due to the avoided crossing interactions quite often already for the lowest  $K_a$  values. Sometimes we even were not able to find a line of acceptable intensity in the vicinity of the predicted transition. That is why at the current stage of our analysis of

the propanoic acid spectrum we decided to limit ourselves with the range of rotational quantum numbers  $J \leq 50$  and  $K_a \leq 10$  in the first excited methyl torsion state. Also in our predictions for astronomical use we decided to limit ourselves by the ground vibrational state only and the range of rotational quantum numbers  $J \leq 95$  and  $K_a \leq 26$ , which we judge to be mainly free from avoided crossing interactions with other low lying vibrational states.

On the basis of the parameters from our final fit, we calculated a list of propanoic acid transitions for astronomical use. This list includes the information on transition quantum numbers, transition frequencies, calculated uncertainties, lower state energies, and transition strengths. We used dipole moment components obtained by Stiefvater [11]  $\mu_a = 0.19$  D and  $\mu_b = 1.54$  D, which were rotated from the principal axis system to the rho axis system of our Hamiltonian model ( $\theta_{RAM} = 13.344^\circ$ ,  $\mu_z = 0.565$  D and  $\mu_x = 1.445$  D). The predictions are made up to 550 GHz for the ground vibrational state and range of rotational quantum numbers  $J \leq 95$  and  $K_a \leq 26$ . We limit our predictions to the transitions with calculated uncertainties lower than 0.1 MHz. **Also we provide a calculation of the rotation-methyl torsion part of partition function for propanoic acid at different temperatures. In this calculation the torsion - rotation levels up to 8th excited methyl torsion-vibrational state and up to  $J_{max} = 120$  are taken into account.** The list of the predicted transitions for astronomical use (Table S2) and the rotation-torsion partition function for propanoic acid at different temperatures (Table S3) are provided as on-line Supplementary material with this article.

### 3. Search for propanoic acid in space

Using the improved frequency predictions provided by the present work, we have carried out a search for  $\text{CH}_3\text{CH}_2\text{COOH}$  in space. We focused the search on two high-mass star-forming regions, Orion KL and Sgr B2, in which acetic acid ( $\text{CH}_3\text{COOH}$ ) has been previously detected (see, e.g.[25, 26, 27, 28]). We used the MADEX code [29] to exploit the spectroscopic parameters presented in this work in deriving the synthetic spectrum of this species (assuming local thermodynamic equilibrium) according to the physical parameters of the source (see below) collected in Table 3. The column density was the only free parameter for these models. Corrections for beam dilution were applied to each line depending on its frequency.

**Orion KL:** Science Verification (SV) data from the Atacama Large Millimeter/submillimeter Array (ALMA) interferometer towards Orion KL [30, 28] have been explored to search for propanoic acid. The ALMA SV data allow us to obtain

Table 1: Molecular parameters of propanoic acid obtained with the RAM36 program.

ntr <sup>a</sup>	Parameter <sup>b</sup>	Operator <sup>c</sup>	Value (this study) <sup>d</sup>
220	$F$	$p_\alpha^2$	5.683(79)
220	$V_3$	$\frac{1}{2}(1 - \cos 3\alpha)$	824.(13)
211	$\rho$	$J_z p_\alpha$	0.055263(16)
202	$A_{RAM}$	$J_z^2$	0.327844(10)
202	$B_{RAM}$	$J_x^2$	0.138739(10)
202	$C_{RAM}$	$J_y^2$	0.0959590862(46)
202	$D_{zx}$	$\{J_z, J_x\}$	-0.047530(20)
422	$V_{3J}$	$J^2(1 - \cos 3\alpha)$	$-0.61366(61) \times 10^{-3}$
422	$V_{3K}$	$J_z^2(1 - \cos 3\alpha)$	$-0.26534(46) \times 10^{-2}$
422	$V_{3xy}$	$(J_x^2 - J_y^2)(1 - \cos 3\alpha)$	$-0.15262(20) \times 10^{-3}$
404	$\Delta_J$	$-J^4$	$0.223983(31) \times 10^{-7}$
404	$\Delta_{JK}$	$-J^2 J_z^2$	$0.98022(55) \times 10^{-7}$
404	$\Delta_K$	$-J_z^4$	$0.17420(18) \times 10^{-6}$
404	$\delta_J$	$-2J^2(J_x^2 - J_y^2)$	$0.46676(21) \times 10^{-8}$
404	$\delta_K$	$-\{J_z^2, (J_x^2 - J_y^2)\}$	$0.11390(71) \times 10^{-7}$
642	$F_{mK}$	$J_z^2 p_\alpha^4$	$0.969(11) \times 10^{-7}$
624	$V_{3JJ}$	$J^4(1 - \cos 3\alpha)$	$0.1800(27) \times 10^{-8}$
624	$V_{3JK}$	$J^2 J_z^2(1 - \cos 3\alpha)$	$-0.511(30) \times 10^{-8}$
624	$V_{3xyJ}$	$J^2(J_x^2 - J_y^2)(1 - \cos 3\alpha)$	$-0.4240(83) \times 10^{-8}$
624	$V_{3xyK}$	$\frac{1}{2}\{J_z^2, (J_x^2 - J_y^2)\}(1 - \cos 3\alpha)$	$0.2929(33) \times 10^{-7}$
624	$D_{3xyJ}$	$\frac{1}{2}J^2\{J_x, J_y\} \sin 3\alpha$	$-0.1490(25) \times 10^{-6}$
606	$\Phi_{JK}$	$J^4 J_z^2$	$-0.8312(64) \times 10^{-12}$
606	$\Phi_K$	$J_z^6$	$0.652(25) \times 10^{-12}$
606	$\phi_J$	$2J^4(J_x^2 - J_y^2)$	$-0.396(26) \times 10^{-14}$
606	$\phi_{JK}$	$J^2\{J_z^2, (J_x^2 - J_y^2)\}$	$0.719(14) \times 10^{-12}$
826	$V_{3JJJ}$	$J^6(1 - \cos 3\alpha)$	$-0.560(41) \times 10^{-13}$
808	$L_{JK}$	$J^6 J_z^2$	$0.688(12) \times 10^{-16}$
808	$L_{JK}$	$J^4 J_z^4$	$-0.4470(43) \times 10^{-15}$
808	$l_{JK}$	$J^4\{J_z^2, (J_x^2 - J_y^2)\}$	$-0.298(13) \times 10^{-16}$
Number of parameters			29
Number of lines			3477
$\nu_{max}$ in GHz			542
$J_{max}, K_{a,max}$			94, 26
rms in kHz			61.4
wrms unitless			0.82

<sup>a</sup>  $n = t + r$ , where  $n$  is the total order of the operator,  $t$  is the order of the torsional part and  $r$  is the order of the rotational part, respectively.

<sup>b</sup> Parameter nomenclature based on the subscript procedures of [24].

<sup>c</sup>  $\{A, B\} = AB + BA$ . The product of the operator in the third column of a given row and the parameter in the second column of that row gives the term actually used in the torsion-rotation Hamiltonian of the program, except for  $F$ ,  $\rho$  and  $A_{RAM}$ , which occur in the Hamiltonian in the form  $F(p_\alpha - \rho J_z)^2 + A_{RAM} J_z^2$ .

<sup>d</sup> All values are in  $\text{cm}^{-1}$  (except  $\rho$  which is unitless). Statistical uncertainties are shown as one standard uncertainty in the units of the last two digits.

the spectrum between 213.7 GHz and 246.7 GHz for different positions within the source characterized by different chemistries and physical parameters. We focus on the location where  $\text{CH}_3\text{COOH}$  has been identified in this region, the south hot core [26, 27, 28]. To model the  $\text{CH}_3\text{CH}_2\text{COOH}$  emission in this component, we have adopted physical parameters derived for  $\text{CH}_3\text{COOH}$  by [28]. Figure 3 shows selected frequencies of these data together with the model derived by MADEX that demonstrates the lack of propanoic acid lines above the confusion limit of these data. Table 2 lists the spectroscopic parameters of the lines shown in Fig. 3.

**Sgr B2:** We also searched for this species in the public IRAM 30 m data available for Sgr B2 at 3 mm provided by [25]. We did not find this species above the detection limit of these data. To estimate upper limits to the  $\text{CH}_3\text{CH}_2\text{COOH}$  column density in the region, we adopted the physical parameters derived by [25] for  $\text{CH}_3\text{COOH}$ . Figure 3 shows the model provided by MADEX together with the IRAM 30 m data of Sgr B2(N). Spectroscopic parameters of the depicted  $\text{CH}_3\text{CH}_2\text{COOH}$  lines are shown in Table 2.

Table 3 also shows the  $\text{CH}_3\text{COOH}/\text{CH}_3\text{CH}_2\text{COOH}$  column density ratios in Orion KL and Sgr B2. It is worth noting that the derived lower limit ratios are extremely low ( $\sim 0.5 - 2$ ). As we discuss previously for other species [31, 32, 33], the  $\text{CH}_3\text{CH}_2\text{COOH}$  partition function is  $\sim 3$  times larger than that of  $\text{CH}_3\text{COOH}$  at  $\sim 100$  K. As a result, the propanoic acid lines appear weaker than those of  $\text{CH}_3\text{COOH}$  assuming similar abundances. Moreover, [34] discussed the column density ratios between other Methyl(Met)/Ethyl(Et) species identified in Orion KL and Sgr B2: Met-CN/Et-CN, Met-OH/Et-OH, and Met-OCOH/Et-OCOH. Only for the  $-\text{CN}$  bearing species they found a ratio in agreement with these presented here. On the other hand, the provided Met/Et ratios for the O-bearing species range between 10 – 120 depending on the source and the particular species. These facts, together with the high level of line blending, specially in the IRAM 30 m data of Sgr B2, which prevents us from determining a constrained upper limit for the  $\text{CH}_3\text{CH}_2\text{COOH}$  column density, suggest that the derived lower limit to the abundance ratio is probably far from its real value in the considered regions.

#### 4. Discussion

It is interesting to discuss why the thermodynamically most stable propanoic acid [7] was not detected in the ISM whereas its three less stable isomers were. From a spectroscopic point of view ethyl formate ( $\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{H}$ ), methyl acetate ( $\text{CH}_3\text{OC}(\text{O})\text{CH}_3$ ), hydroxyacetone ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ ), and propanoic acid ( $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OH}$ ) should have relatively close values for partition functions and

Table 2: Spectroscopic parameters of lines depicted in Fig. 3.

Symmetry	Transition $J''_{K_a, K_c} - J'_{K_a, K_c}$	Frequency (MHz)	Error (MHz)	$E_{\text{upp}}$ (K)	$S_{ij}\mu^2$ (D <sup>2</sup> )
Orion KL					
E	$37_{0,37} - 36_{1,36}$	215298.559	0.003	198.6	85.71
E	$37_{1,37} - 36_{0,36}$	215298.559	0.003	198.6	85.71
A	$37_{0,37} - 36_{1,36}$	215298.564	0.003	198.6	85.71
A	$37_{1,37} - 36_{0,36}$	215298.564	0.003	198.6	85.71
E	$38_{0,38} - 37_{1,37}$	221041.967	0.003	209.2	88.12
E	$38_{1,38} - 37_{0,37}$	221041.967	0.003	209.2	88.12
A	$38_{0,38} - 37_{1,37}$	221041.974	0.003	209.2	88.12
A	$38_{1,38} - 37_{0,37}$	221041.974	0.003	209.2	88.12
E	$39_{0,39} - 38_{1,38}$	226785.019	0.003	220.1	90.53
E	$39_{1,39} - 38_{0,38}$	226785.019	0.003	220.1	90.53
A	$39_{0,39} - 38_{1,38}$	226785.024	0.003	220.1	90.53
A	$39_{1,39} - 38_{0,38}$	226785.024	0.003	220.1	90.53
E	$40_{0,40} - 39_{1,39}$	232527.700	0.003	231.2	92.94
E	$40_{1,40} - 39_{0,39}$	232527.700	0.003	231.2	92.94
A	$40_{0,40} - 39_{1,39}$	232527.705	0.003	231.2	92.94
A	$40_{1,40} - 39_{0,39}$	232527.705	0.003	231.2	92.94
E	$41_{0,41} - 40_{1,40}$	238270.002	0.003	242.7	95.35
E	$41_{1,41} - 40_{0,40}$	238270.002	0.003	242.7	95.35
A	$41_{0,41} - 40_{1,40}$	238270.007	0.003	242.7	95.35
A	$41_{1,41} - 40_{0,40}$	238270.007	0.003	242.7	95.35
E	$42_{0,42} - 41_{1,41}$	244011.915	0.004	254.4	97.76
E	$42_{1,42} - 41_{0,41}$	244011.915	0.004	254.4	97.76
A	$42_{0,42} - 41_{1,41}$	244011.920	0.004	254.4	97.76
A	$42_{1,42} - 41_{0,41}$	244011.920	0.004	254.4	97.76
Sgr B2					
E	$14_{0,14} - 13_{1,13}$	83107.168	0.002	30.7	29.59
A	$14_{0,14} - 13_{1,13}$	83107.175	0.002	30.7	29.59
E	$14_{1,14} - 13_{0,13}$	83146.607	0.002	30.7	29.59
A	$14_{1,14} - 13_{0,13}$	83146.615	0.002	30.7	29.59
E	$15_{0,15} - 14_{1,14}$	88864.555	0.003	35.0	31.96
A	$15_{0,15} - 14_{1,14}$	88864.563	0.003	35.0	31.96
E	$15_{1,15} - 14_{0,14}$	88885.340	0.003	35.0	31.96
A	$15_{1,15} - 14_{0,14}$	88885.348	0.003	35.0	31.96
E	$16_{0,16} - 15_{1,15}$	94617.689	0.003	39.5	34.34
A	$16_{0,16} - 15_{1,15}$	94617.696	0.003	39.5	34.34
E	$16_{1,16} - 15_{0,15}$	94628.555	0.003	39.5	34.34
A	$16_{1,16} - 15_{0,15}$	94628.563	0.003	39.5	34.34
E	$17_{0,17} - 16_{1,16}$	100368.507	0.003	44.3	36.71
A	$17_{0,17} - 16_{1,16}$	100368.514	0.003	44.3	36.71
E	$17_{1,17} - 16_{0,16}$	100374.149	0.003	44.3	36.71
A	$17_{1,17} - 16_{0,16}$	100374.157	0.003	44.3	36.71
E	$18_{0,18} - 17_{1,17}$	106118.050	0.003	49.4	39.08
A	$18_{0,18} - 17_{1,17}$	106118.058	0.003	49.4	39.08
E	$18_{1,18} - 17_{0,17}$	106120.962	0.003	49.4	39.08
A	$18_{1,18} - 17_{0,17}$	106120.970	0.003	49.4	39.08
E	$19_{0,19} - 18_{1,18}$	111866.866	0.003	54.8	41.45
A	$19_{0,19} - 18_{1,18}$	111866.873	0.003	54.8	41.45
E	$19_{1,19} - 18_{0,18}$	111868.361	0.003	54.8	41.45
A	$19_{1,19} - 18_{0,18}$	111868.368	0.003	54.8	41.45

Table 3: Physical parameters of the considered cloud cores

Source	Coordinates (J2000.0)	HPBW <sup>(a)</sup> (")	Frequencies <sup>(b)</sup> (GHz)	$v_{\text{LSR}}$ <sup>(c)</sup> (km s <sup>-1</sup> )	$\Delta v_{\text{FWHM}}$ <sup>(d)</sup> (km s <sup>-1</sup> )	$d_{\text{sou}}$ <sup>(e)</sup> (")	$T_{\text{rot}}$ <sup>(f)</sup> (K)	$N^{(g)}$ $\times 10^{15}$ (cm <sup>-2</sup> )	$R^{(h)}$
Orion KL (ALMA SV) Hot core	$\alpha=05^{\text{h}}35^{\text{m}}14.5^{\text{s}}$ $\delta=-05^{\circ}22'32.5''$	$\sim 1.9 \times 1.4$	213.7-246.7	8.0	3.0	3.0	150	$\leq (2.0 \pm 0.6)$	$\geq 2^{(i)}$
Sgr B2(N)	$\alpha=17^{\text{h}}47^{\text{m}}20.0^{\text{s}}$ $\delta=-28^{\circ}22'19.0''$	30-21	80-115.5	63 72	7.0 7.0	4.0 4.0	100 100	$\leq (20 \pm 6)$ $\leq (10 \pm 3)$	$\geq 0.5^{(j)}$ $\geq 0.5^{(j)}$

**Notes.** <sup>(a)</sup> HPBW (half power beam width) for observations with single dish telescope (IRAM 30m) and synthetic beam for the ALMA SV observations. <sup>(b)</sup> Range of frequencies considered in the analysis. <sup>(c)</sup> Radial velocity with respect the Local Standard of Rest. <sup>(d)</sup> Full Width at Half Maximum. <sup>(e)</sup> Source diameter assuming a uniform disc-type model. <sup>(f)</sup> Rotational Temperature. <sup>(g)</sup> Column density for  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$  (A+E) in the ground state. <sup>(h)</sup>  $N(\text{CH}_3\text{COOH})/N(\text{CH}_3\text{CH}_2\text{CO}_2\text{H})$  column density ratio. <sup>(i)</sup>  $\text{CH}_3\text{COOH}$  column density in Orion KL from [28]. <sup>(j)</sup>  $\text{CH}_3\text{COOH}$  column density in Sgr B2 from [25].

whereas the propanoic acid dipole moment has the lowest value of  $\sim 1.55$  D among the compounds considered, it is not that different from the dipole moment value of methyl acetate ( $\sim 1.7$  D). Thus, the characteristic order of magnitude for transition intensities of all four considered  $\text{C}_3\text{H}_6\text{O}_2$  isomers should be more or less the same.

We can note that the thermodynamically most stable  $\text{C}_2\text{H}_4\text{O}_2$  isomer, the acetic acid, is less abundant than the less stable isomer methyl formate (in some clouds even less abundant than glycolaldehyde [35]). That could be attributed to a stronger absorption on the grains due to the presence of the carboxylic acid group. A similar absorption of propanoic acid could thus be predicted making its detection more hypothetical if it is present in the ISM. Moreover the increase of the alkyl moiety has known strong limitations since neither ethylamine nor propanol have yet been detected although methylamine and ethanol are present. Nevertheless, being the thermodynamically most stable isomer with the formula  $\text{C}_3\text{H}_6\text{O}_2$  for which three isomers have already been observed, propanoic acid clearly should be considered as a possible candidate for ISM detection.

## 5. Conclusions

A new study of the rotational spectrum of propanoic acid  $\text{CH}_3\text{CH}_2\text{COOH}$  was carried out in the frequency range of 150–545 GHz in order to provide accurate predictions for astronomical use. The rotational transitions of the ground and first excited methyl torsional states were assigned up to  $J = 94$  and fit within experi-



mental accuracy (the overall weighted rms deviation of the global fit is 0.82). **Our work represents a significant improvement over previous results [11, 13, 14] extending the frequency range and quantum number range coverage and providing for the first time a joint analysis of the ground and first excited methyl torsion states of the propanoic acid molecule.** Based on our results, frequency predictions for astronomical use were produced up to 550 GHz. The predictions, as well as data set treated in our study, are available as supplementary material to this article. Unfortunately, despite the fact that three less thermodynamically stable isomers with the formula  $C_3H_6O_2$  were already detected in the ISM, our first attempt to search for the thermodynamically most stable isomer  $CH_3CH_2COOH$  in two high-mass star-forming regions SgrB2 (public IRAM 30m) and Orion KL (ALMA Science Verification) was not successful.

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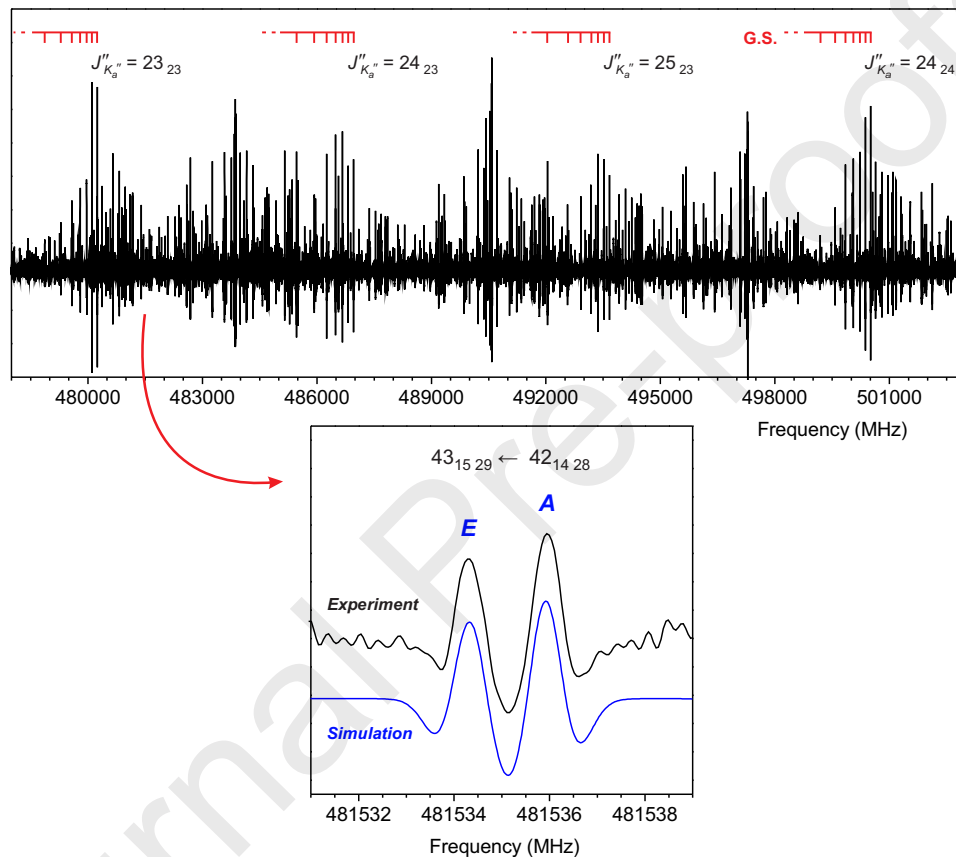


Figure 1: A section of the room-temperature rotational spectrum of propanoic acid between 478 and 503 GHz. Groups of the ground state R-branch transitions with high values of  $K_a$  quantum numbers are labeled with the red combs. The values of  $J''$  and  $K_a''$  are indicated for leading lines in these groups. Then, with each successive line running to lower frequencies, the value of  $J$  increases by 2 while the value of  $K_a$  decreases by 1. The lower inset shows an example of the methyl group internal rotation splitting in the ground vibrational state.

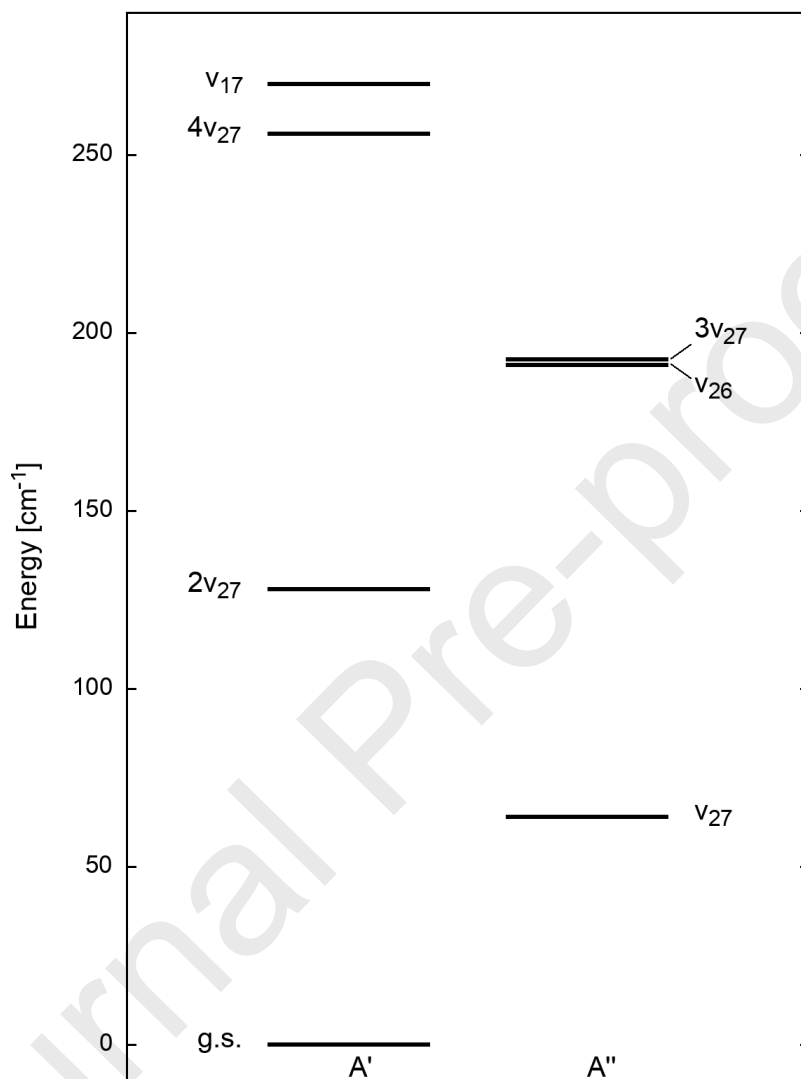


Figure 2: Excited vibrational states of propanoic acid below  $300\text{ cm}^{-1}$  and their symmetries in  $C_s$  point group. The vibrational mode labeling is the following:  $v_{27}$  - skeletal torsion,  $v_{26}$  - methyl torsion,  $v_{17}$  - in plane CCO bending. The fundamental frequencies of  $v_{27}$  and  $v_{17}$  modes are taken from Stiefvater [11]. The fundamental frequency of methyl torsional mode  $v_{26}$  is taken from the current study. The energies of the excited vibrational states for  $v_{27}$  mode are calculated in the harmonic oscillator approximation. Note rather close positions of the first excited methyl torsion state  $v_{26}$  and the third excited skeletal torsion excited state  $3v_{27}$ . It should be noted however that the  $v_{27}$  mode is likely to be characterized by a quartic-quadratic potential function which may notably deviate from harmonic approximation (as it happens for example in the case of similar molecule propionamide [23]). Such anharmonic correction would push up higher excited vibrational states of skeletal torsion mode starting from  $v_{27} = 2$  and the energy difference between  $v_{26} = 1$  and  $v_{27} = 3$  states may be up to about  $15 - 25\text{ cm}^{-1}$ .<sup>20</sup>

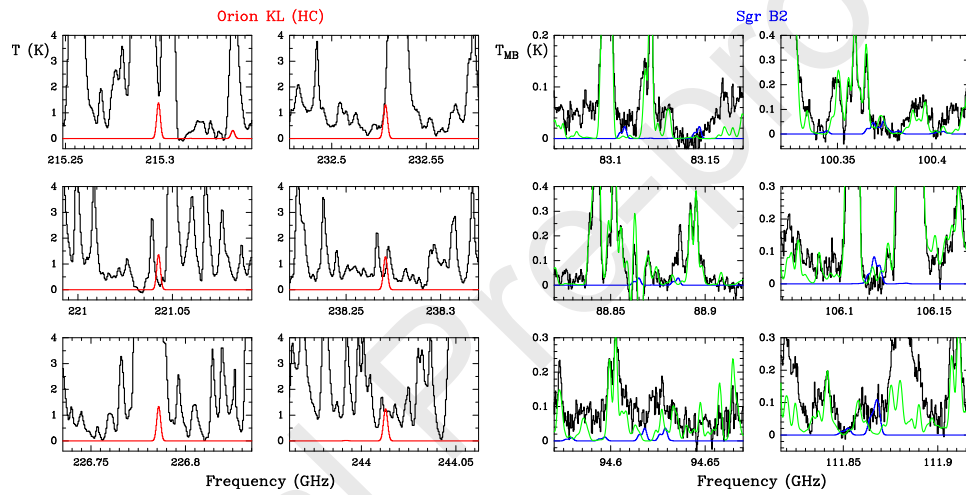
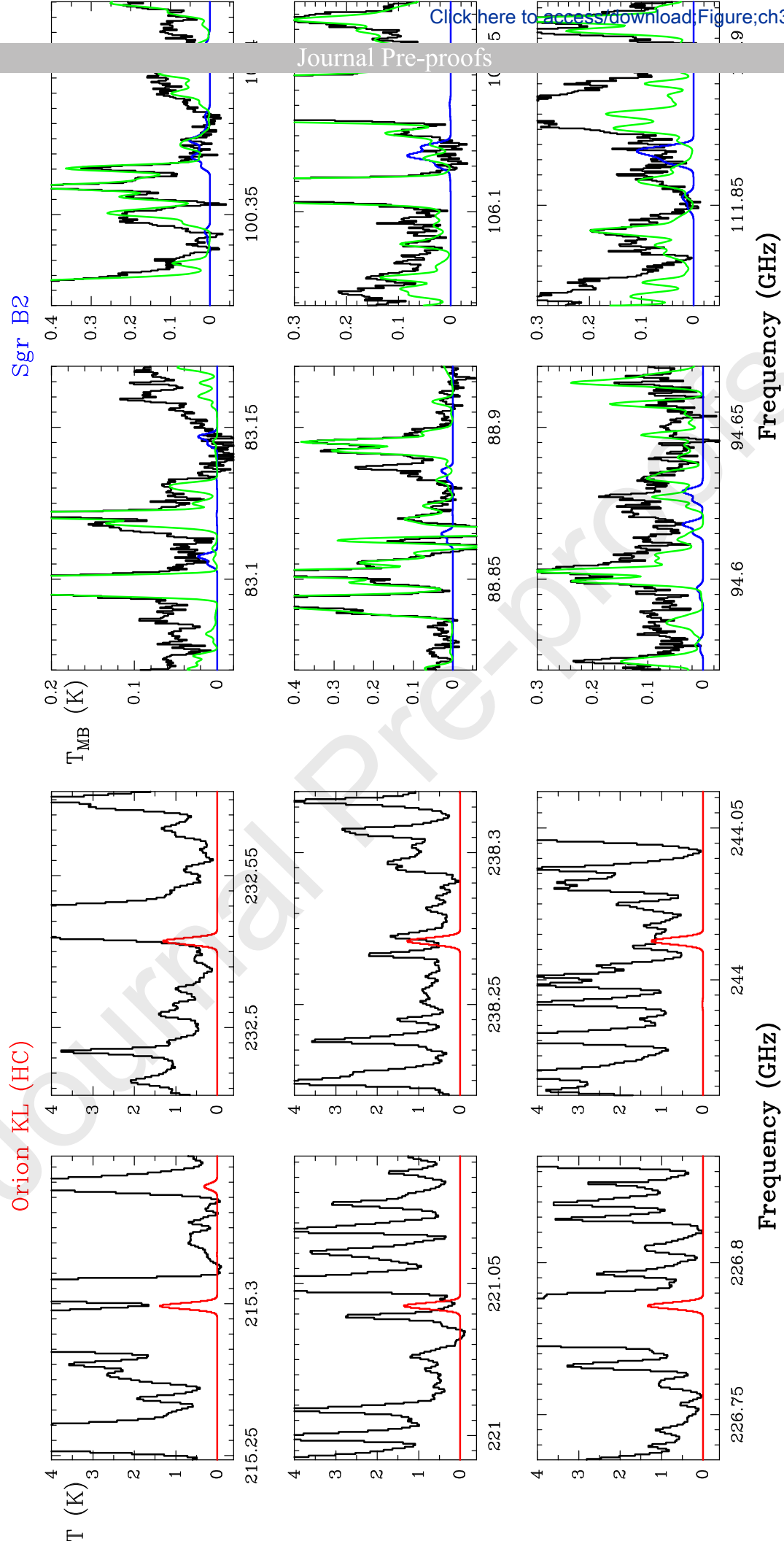
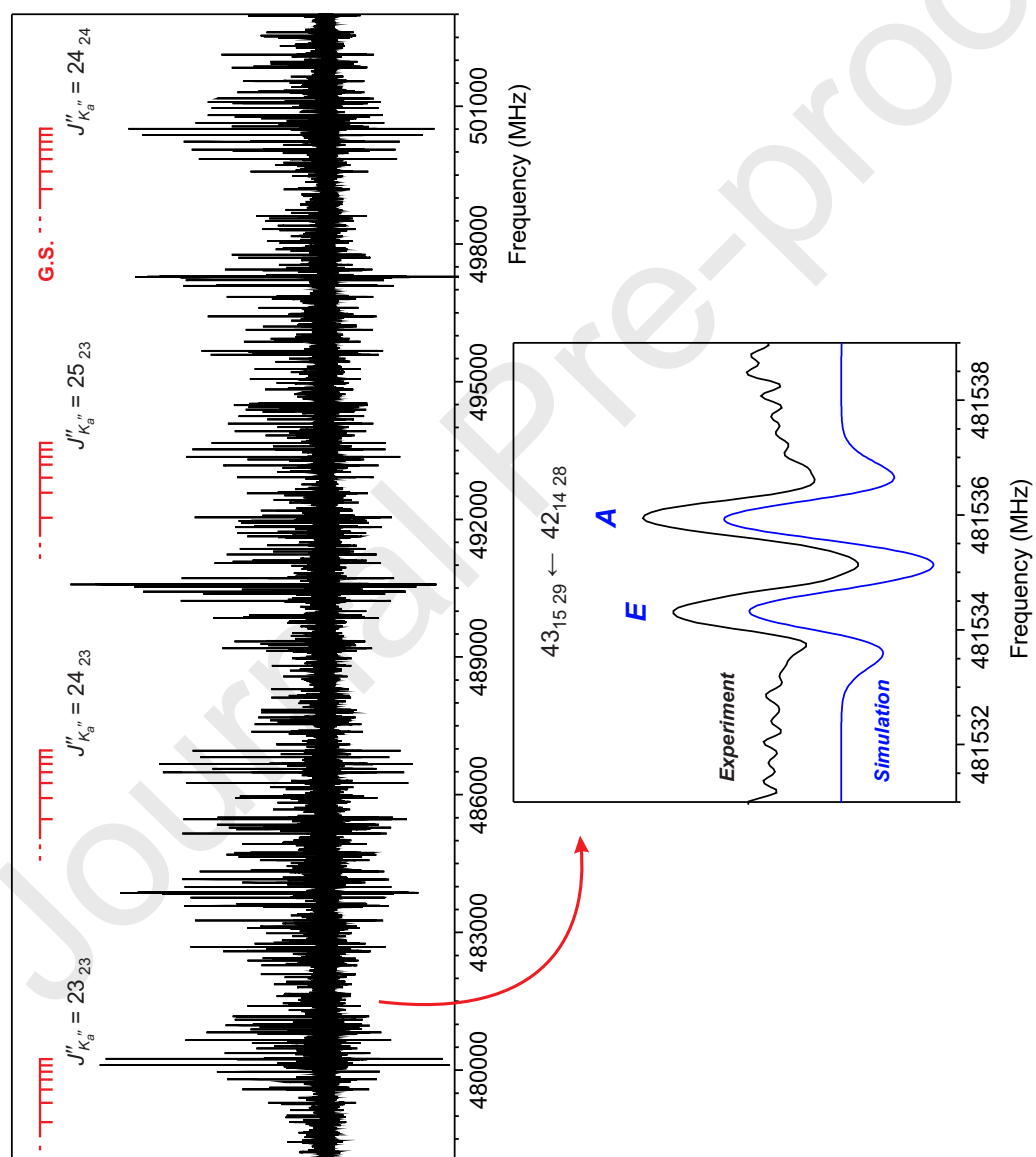


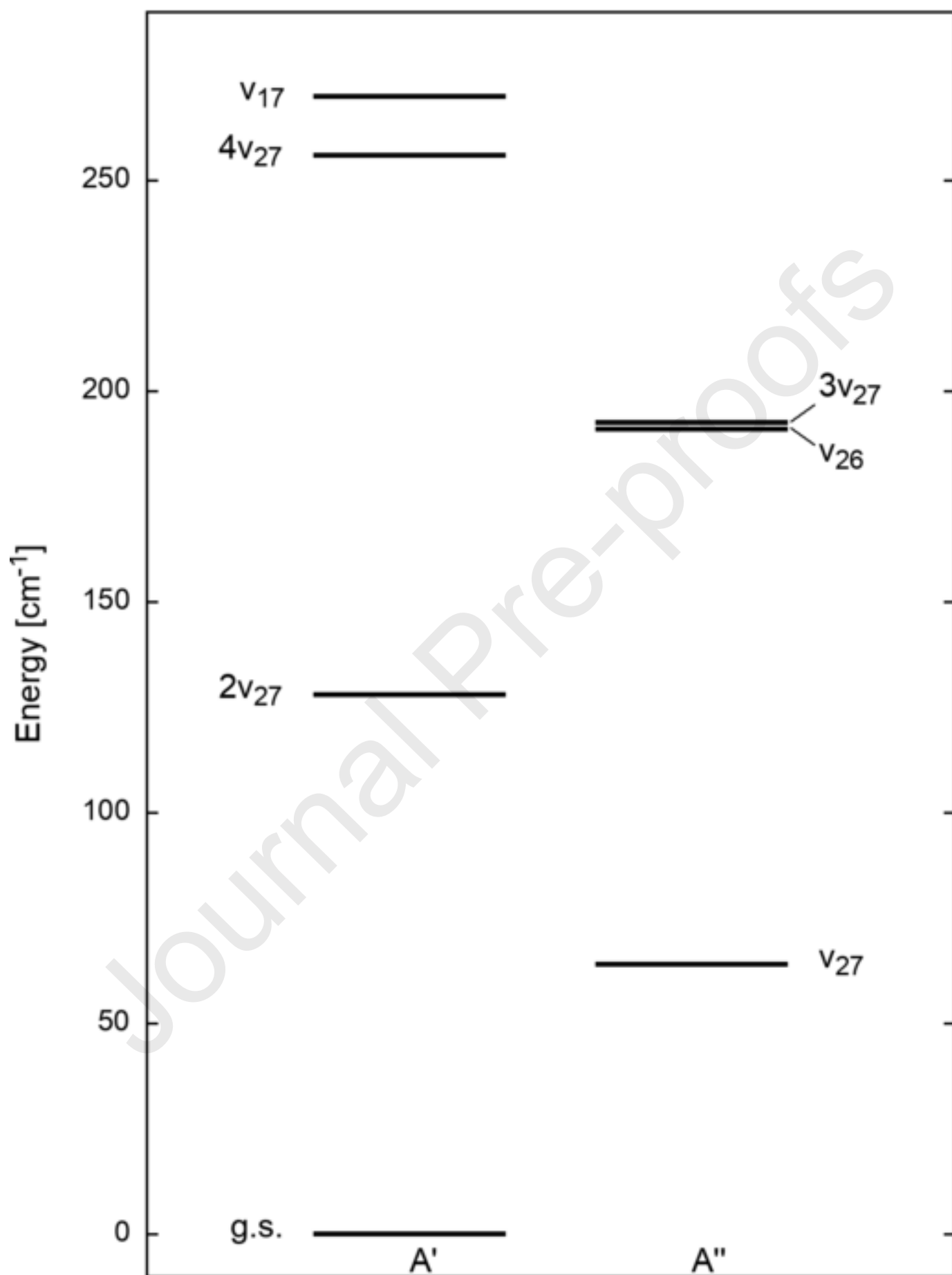
Figure 3: Observed data of Orion KL and Sgr B2 taken with the ALMA interferometer and the IRAM 30 m telescope, respectively (histogram black spectrum), together with the synthetic spectra obtained using the column densities given as upper limits in Table 3 (red and blue thin curves). The synthetic total model for the 30 m data of Sgr B2(N) (see [25]) is overlaid in green. A  $v_{LSR}$  of  $+9.0 \text{ km s}^{-1}$  and  $+64.0 \text{ km s}^{-1}$  is assumed for Orion KL and Sgr B2, respectively.



Figure3







**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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