Leveraging MMW-MMW Double Resonance Spectroscopy to Understand the Pure Rotational Spectrum of Glycidaldehyde and 17 of its Vibrationally Excited States

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Abstract

Broadband measurements of glycidaldehyde in the frequency ranges 75–170 GHz and 500–750 GHz were recorded to extend previous analyses of its pure rotational spectrum in the microwave region. The rotational parameters of the ground vibrational states for the main isotopologue and the three singly ^{13}C substituted isotopologues were considerably improved and additional higher-order parameters were determined.

To identify new vibrationally excited states in the dense and convoluted spectrum, an updated version of the double-modulation double-resonance spectroscopy technique was used. Connecting transitions with a shared energy level into series and expanding these via Loomis-Wood plots proved to be a powerful method, which allowed the identification of 11 new vibrationally excited states in addition to the already known aldehyde torsions, $v_{21} = 1$ to $v_{21} = 6$. Interactions between several vibrational states were observed and three interacting systems were treated successfully.

Rotational transitions of glycidaldehyde were searched for in the imaging spectral line survey ReMoCA obtained with the Atacama Large Millimeter/submillimeter Array (ALMA) toward the high-mass star-forming region Sgr B2(N). The observed spectra were modeled under the assumption of local thermodynamic equilibrium (LTE). Glycidaldehyde, an oxirane derivative, was not detected toward Sgr B2(N2b). The upper limit on its column density implies that it is at least six times less abundant than oxirane in this source.

Keywords

Absorption Spectroscopy, CCSD(T), Coriolis Interactions, Fermi Resonances, Double-Modulation Double-Resonance Spectroscopy, Vibrational Satellites

1 Introduction

To date, only a handful of ring molecules with heteroatoms in the ring have been detected in space. Beginning with the smallest possible ring molecules, the three triatomics c–SiC_2,[1] c–MgC_2,[2] and c–CaC_2[3] were first detected toward the carbon-rich asymptotic giant branch star CW Leo (IRC+10216) in

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1984, 2022 and 2024, respectively. SiC_2 was found recently also toward the Galactic Center molecular cloud G+0.693–0.027.[4] Similarly, the four-atom molecule $c-SiC_3$ was detected in 1999 in the circumstellar envelope of CW Leo. The two somewhat more complex ring molecules oxirane ($c-C_2H_4O$) and propylene oxide (CH_3CHCH_2O) were first detected toward the high-mass star-forming region Sagittarius B2(N) in 1997[5] and 2016,[6] respectively. Oxirane was later also observed toward hot core regions,[7] Galactic center molecular clouds,[8] a low-mass protostar,[9] and pre-stellar cores.[10]

The presence of oxirane in the interstellar medium gives rise to the question whether or not oxirane derivatives are astronomically abundant. Glycidaldehyde ((C_2H_3O)CHO), also known as oxiranecarboxaldehyde or 2,3-epoxy-propanal, is such a derivative in which one of oxirane's H atoms is substituted by a $-CHO$ functional group. Its rotational spectrum is known from a previous study in the microwave range (8–40 GHz) by Creswell et al. from 1977.[11] There, the authors analyzed the ground vibrational states of the main isotopologue and the three singly substituted ^{13}C isotopologues in natural abundance. Additionally, the lowest vibrational fundamental ν_{21}, the aldehyde torsion at about $125\,cm^{-1}$, was followed up to $v_{21} = 7$. However, even for the ground vibrational state only quartic centrifugal distortion parameters were determined, making frequency extrapolations to higher frequency ranges rapidly inaccurate.

In the present study, the frequency coverage was extended to the millimeter and submillimeter ranges reaching frequencies as high as 750 GHz. The dense and convoluted spectrum of glycidaldehyde makes it an ideal case study for double-modulation double-resonance (DM-DR) spectroscopy,[12] which allows to filter the spectrum for lines sharing an energy level. This simplified the analysis immensely, proved critical in identifying new vibrationally excited states, and understanding interactions between them. In total, 17 vibrationally excited states of the main isotopologue were analyzed along with the ground vibrational states of the main isotopologue and the three singly substituted ^{13}C isotopologues.

2 Experimental Details

Broadband as well as double-resonance (DR) measurements were recorded at two experimental setups in Cologne with a sample synthesized on a gram scale according to a previously reported procedure.[13] The broadband measurements cover the frequency ranges 75–170 GHz and 500–750 GHz. Double-resonance (DR) measurements in the frequency range 75–120 GHz were used to confirm relationships between lines, identify new series of transitions, and find pure rotational transitions between vibrationally excited states (so-called interstate transitions) that arise due to wavefunction mixing when vibrational states interact with each other. The DR measurements were performed with a modified version of the double-modulation double-resonance (DM-DR) method (see Sec. 2.2) described previously.[12]

2.1 Experimental Setups

Two absorption experiments were used to record the broadband spectra, each consisting of a source, an absorption cell, and a detector. The sources consist of synthesizers with subsequent amplifier-multiplier chains. The radiation is guided through the absorption cells and into the detector via lenses, mirrors, and horn antennas. For the higher frequency range of 500–750 GHz, the absorption cell consists of a single 5 m borosilicate glass cell in a double-pass setup for a total absorption path of 10 m. The lower frequency range setup (75–170 GHz) uses two 7 m borosilicate glass cells in a single-pass configuration for a total absorption path of 14 m. Double-pass configurations are foregone here as this lower-frequency experiment is also used for the DR measurements where the second polarization direction is used to align the pump and probe sources radiation co-spatially (see Sec. 2.2). Different Schottky detectors were used for frequencies below 500 GHz and a cryogenically cooled hot-electron bolometer (QMC QNbB/PTC(2+XBI)) was used for

measurements above 500 GHz. All experimental setups use frequency modulation with a *2f*-demodulation scheme to increase the signal-to-noise ratio (SNR). As a result, absorption features look similar to a second derivative of a Voigt profile. The lower frequency experimental setup is described in more detail elsewhere.[12]

Figure 1: Intensity-calibrated broadband spectrum of glycidaldehyde (black) from 75 GHz to 170 GHz in comparison with the simulated stick spectrum (blue). The ground vibrational state analysis was used for the intensity calibration. For better visual comparability, only experimental data points with positive signals are shown here. The stick-and-ball representation of glycidaldehyde is shown in the top left.

All measurements were performed at room temperature with filling pressures of around 10 µbar. Standing waves were removed from the measurements with a self-written Fourier filtering script[1]. Additionally, after completing the ground vibrational state analysis, the broadband measurements were intensity calibrated using the ground vibrational state predictions (see Fig. 1). All $v = 0$ transitions predicted to have an intensity $>10^{-5}$ nm^{2}MHz were fitted with a second derivative Voigt profile. Blends were considered by summing the intensities of all predictions within 200 kHz of the prediction of interest. The ratios of the predicted intensities and fitted intensities were then used to create a calibration curve with values in between the calibration points being interpolated. These post-processing steps greatly facilitated

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[1]Available at `https://pypi.org/project/fftfilter/` or with pip via *pip install fftfilter*

the visual detection of weak patterns in Loomis-Wood plots.

2.2 Improved DM-DR Setup

An improved version of the double-modulation double-resonance (DM-DR) setup originally described in Zingsheim et al.[12] was used for the DM-DR measurements. The great advantage of DM-DR measurements is their ability to filter the spectrum for lines (so-called probe transitions) sharing an energy level with an already known transition, the so-called pump transition. This greatly facilitates the assignment and analysis process as it allows filtering dense spectra for specific lines which is especially useful to unambiguously identify weak, blended and/or strongly perturbed transitions.

The DM-DR setup used here is based on the conventional 75–120 GHz absorption setup described in Sec. 2.1. A second, more powerful source, the pump source, is added covering the frequency range of 70–110 GHz and polarized orthogonally to the probe radiation allowing for co-spatial alignment of the probe and pump radiation via a polarizing grid. The probe frequency is tuned to record the spectrum whereas the radiation of the pump source is fixed to the frequency of a known pump transition and not measured by the detector. Instead, the pump radiation is used to split the energy levels of the pump transition via the Autler-Townes effect.[14,15] As a result, all transitions sharing an energy level with the pump transition split symmetrically into two transitions of half intensity. This is highlighted in the simulated 2D spectra in Fig. 2. The left half of the figure shows the case when the probe and pump transition share an energy level and the pump radiation is on. The heatmap shows the absorption of the probe radiation for the offsets of the probe and pump frequencies, i.e., that both sources are resonant with their respective transitions in the center of the heatmap. The plots to the left and the bottom show the 1D spectra along the dashed lines in the same colors. The right half shows the case when the probe and pump transitions do not share an energy level or the pump radiation is turned off. It is apparent that in this

Figure 2: Simulated 2D spectra of the probe radiation absorption for the cases of a shared energy level (left half) and no pump radiation or no shared energy level between probe and pump transition (right half). The x- and y-axes depict the frequency offsets of the probe and pump sources, respectively. The dashed lines in the heatmaps indicate the slices that are shown in the plots to the sides and on the bottom.

case, the 2D spectrum does not depend on the pump frequency.

A straight-forward way to determine if the probe and pump transitions share an energy level is to subtract the spectra measured with and without pump source - basically subtracting the left and right 1D slices in blue. The subtraction should be performed on a very short time scale to mitigate the influence of fluctuations in the experimental conditions which could otherwise lead to false positive signals (see Fig. 8 in Zingsheim et al.[12]). This was realized in the previous setup[12] by amplitude modulating the pump source and a corresponding $1f$-demodulation of the detector signal. Additionally, a frequency modulation of the probe source combined with a $2f$-demodulation of the detector signal was employed to increase the SNR.

The two consecutive demodulation steps are non-ideal for multiple reasons. Firstly, using a sine signal to realize a subtraction has an efficiency of only $2/\pi \approx 64\%$. Secondly, two lock-in amplifiers arranged in serial result in many of their parameters influencing each other (e.g.

the dependence of the signal on both time constants).

These shortcomings can be mitigated by using a digital DM-DR setup which performs the second demodulation in the measurement software. The intensity is measured with and without the pump source by digitally turning the pump source's radio frequency power on and off and subtracting the respective intensities on the computer. However, this procedure introduces additional overhead in the form of switching the radio frequency on and off[2].

Another possibility, applied here, is to operate the probe source in continuous wave mode and apply an FM to the pump source requiring only a single lock-in amplifier for the demodulation. The single FM of the pump source simultaneously increases the SNR and removes all transitions from the DM-DR spectrum that do not share an energy level with the pump transition. The working principle is explained

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[2]This overhead has greater efficiency than the $2/\pi \approx 64\%$ efficiency of the previous DM-DR setup for integration times $\geq 28\,\mathrm{ms}$. This integration time is well surpassed in our measurements.

by the red 1D slices along the pump frequency axis in Fig. 2. If the probe and pump transition share an energy level, the signal along the pump frequency axis has a strong dip at the center position whereas if no energy level is shared the signal is constant (left-most and right-most plots of Fig. 2, respectively). The two cases are distinguished via the FM of the pump source and subsequent *2f*-demodulation of the detector signal. For the pump-off case, this results in a zero signal after the lock-in amplifier but a strong signal for the pump-on case. Analogously to the conventional case, the FM also improves the SNR for the pump-on case. However, the FM amplitude has to be adjusted as the linewidth of the conventional case (bottom right plot of Fig. 2) depends on the different broadening effects but the linewidth along the pump frequency axis (left-most plot of Fig. 2) also strongly depends on the magnitude of the Autler-Townes splitting.

The simplicity of the new setup is highlighted by it differing from the conventional setup only in that the lock-in amplifier is connected to the pump instead of the probe source synthesizer (and the obvious addition of a pump source). This makes switching between the two measurement techniques as simple as changing a single cable connection.

Additionally, the current pump-modulated setup showed greater sensitivity to the detuning of the pump source in our measurements and simulations. Therefore, false positive signals (due to transitions close to the pump transition being pumped off-resonantly) are more easily distinguished. However, simulations also show that this behavior is very dependent on the magnitude of the Autler-Townes splitting and the chosen FM amplitudes. In summary, for molecules with similar (transition) dipole moments as glycidaldehyde, the new setup is noticeably more sensitive to false positive signals arising from off-resonant pumping than the previous setup.[12]

3 Quantum Chemical Calculations

Complementary quantum chemical calculations of glycidaldehyde have been performed at the coupled-cluster singles and doubles (CCSD) level augmented by a perturbative treatment of triple excitations, CCSD(T),[16] together with correlation consistent polarized valence and polarized weighted core-valence basis sets, as well as atomic natural orbital basis sets, specifically, cc-pVTZ,[17] cc-pwCVTZ,[18] and ANO0.[19] Equilibrium geometries have been calculated using analytic gradient techniques,[20] while harmonic frequencies have been computed using analytic second-derivative techniques.[21,22] For anharmonic computations using the cc-pVTZ and ANO0 basis sets second-order vibrational perturbation theory (VPT2)[23] has been employed and additional numerical differentiation of analytic second derivatives has been applied to obtain the third and fourth derivatives required for the application of VPT2.[22,24]

All calculations have been carried out using the CFOUR program package;[25,26] for some of the calculations the parallel version of CFOUR[27] has been used. The resulting rotation-vibration interaction constants, harmonic and fundamental wavenumbers, fundamental intensities, energy-dependence on the aldehyde torsional angle, and optimized molecular structures are given in Sec. 1 of the Supporting Information.

4 Spectroscopic Fingerprint of Glycidaldehyde

Glycidaldehyde ($(C_2H_3O)CHO$) is an asymmetric rotor with Ray's asymmetry parameter of $\kappa = (2B - A - C)/(A - C) = -0.98$ which is very close to the prolate limit of -1. Creswell et al. determined its three dipole moment components to be $\mu_a = 1.932(5)\,\mathrm{D}$, $\mu_b = 1.511(17)\,\mathrm{D}$, and $\mu_c = 0.277(156)\,\mathrm{D}$ resulting in strong a- and b-type spectra accompanied by a considerably weaker c-type spectrum.[11] Additionally, four fundamental vibrational modes lie below

Figure 3: All vibrational states below $800\,\mathrm{cm^{-1}}$. The 18 analyzed states are shown in color or black. Interaction systems are indicated by mutual colors.

$500\,\mathrm{cm^{-1}}$ resulting in a plethora of vibrationally excited states below $800\,\mathrm{cm^{-1}}$ (see Fig. 3). The lowest vibrational state ν_{21}, the aldehyde torsion, has an energy of about $125\,\mathrm{cm^{-1}}$ only for which reason even multiply excited states up to $v_{21} = 6$ could be assigned in the spectrum. The combination of the many vibrational satellite patterns and the three non-zero dipole moments gives rise to a dense and feature-rich spectrum, making it difficult to identify weak series, especially by visual means. For brevity, vibrational states will also be given in the format $(v_{21}, v_{20}, v_{19}, v_{18})$.

The spectroscopic assignment process relied heavily on Loomis-Wood plots (LWPs) as implemented in the LLWP software[28] while Pickett's SPFIT and SPCAT[29] were used for line fitting and predicting the data with an asymmetric top Hamiltonian in the S-reduction[30] and $\mathrm{I^r}$ representation. Our Python library *Pyckett* was used to automate repetitive tasks carried out with SPFIT and SPCAT[3]. Line uncertainties were assigned with a semi-automatic procedure described previously.[31] Frequency uncertainties for the assignments by Creswell et al. were increased manually due to obvious systematic shifts in their data (see Sec. 2 of the Sup-

porting Information). Uncertainties of $200\,\mathrm{kHz}$ were found appropriate were found appropriate as then the assignments could be included with negligible effects on the $WRMS$ value.

The quantum chemical calculations described in Sec. 3 provided initial rotational parameters and estimates for the vibrational energies (see Sec. 1 of the Supporting Information). The ground vibrational state and the aldehyde torsion up to $v_{21} = 6$ were straightforward to assign due to the previous microwave study.[11] Further vibrational satellites were identified subsequently in Loomis-Wood plots or via DM-DR measurements. Candidates for the DM-DR measurements were found either visually in the LWPs or by an automated approach using a peakfinder. For the latter, the identified peaks were filtered for so-far unassigned peaks which were ordered by intensity and then tested for a shared energy level via DM-DR measurements. Furthermore, the DM-DR measurements were used to confirm and extend series showing strong deviations caused by interactions or series weak in intensity due to high vibrational energies. Once a few series belonging to the same vibrational state were assigned, the predictions were typically sufficient to extend the assignment by LWPs into regions where no DR spectroscopy was available.

To assign the identified vibrationally excited states the correct labels, their rotational constant differences ΔA, ΔB, and ΔC (which are to first order the negative rotation-vibration interaction constants $\alpha_v^{A,B,C}$) as well as their approximated vibrational energies[4] (see Tab. 1) were compared with the values from the quantum chemical calculations. As shown in Fig. 3, the 17 vibrationally excited states analyzed here were assigned to the 15 energetically lowest vibrational states as well as to $(1, 2, 0, 0)$ and $(6, 0, 0, 0)$. The experimental vibrational energies usually agree with the calculated anharmonic values within uncertainties. The devia-

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[3]Especially the interaction systems benefited from the ability to automatically test the influence of additional interaction parameters on the model via Pickett's CLI tool `pyckett_add`. See https://pypi.org/project/pyckett/ for more information or install with pip via `pip install pyckett`

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[4]The energies were approximated via a Boltzmann analysis comparing the amplitudes of the $J_{0,J} \leftarrow J - 1_{0,J-1}$ transitions for $J = 12$ to $J = 26$ with the respective ground vibrational state transitions. To make the results more robust, the three ratios with the highest deviation to the mean were iteratively removed.

Table 1: Approximated energies from the Boltzmann analysis $\tilde{\nu}_{\text{appr}}$ in cm^{-1}, rotational constant differences ΔA, ΔB, ΔC with respect to the ground vibrational state of the main isotopologue in MHz, the highest assigned frequency (in GHz), J value, and K_a value, the number of rejected lines, the number of transitions, RMS in kHz, and $WRMS$ values for the analyzed states. Comparison with the calculated values (see Sec. 1 of the Supporting Information) yielded the state labels given in the first column. Interaction systems are indicated by mutual colors analog to Fig. 3.

Vib. State	$\tilde{\nu}_{\text{appr}}$	ΔA	ΔB	ΔC	$\nu_{\max}$	$J_{\max}$	$K_{a,\max}$	Rej.	Trans.	RMS	$WRMS$
(0, 0, 0, 0)	0	0.00	0.00	0.00	749	114	24	0	6921	28.52	0.86
(1, 0, 0, 0)	125(27)	−138.84	12.89	5.16	749	115	24	0	5218	30.05	0.89
(2, 0, 0, 0)	257(42)	−273.89	25.64	10.27	747	103	24	0	3091	18.84	0.58
(0, 1, 0, 0)	312(14)	125.26	−1.82	−0.54	736	110	21	0	2356	17.98	0.59
(0, 0, 1, 0)	361(17)	−17.71	−0.73	−4.72	737	100	20	1[a]	2614[a]	28.13[a]	0.87[a]
(3, 0, 0, 0)	390(41)	−406.36	38.33	15.34	737	100	19	1[a]	2614[a]	28.13[a]	0.87[a]
(1, 1, 0, 0)	437(22)	−23.99	11.48	4.46	170	60	20	0	793	18.14	0.56
(1, 0, 1, 0)	469(20)	−132.47	10.50	0.32	170	52	21	0[b]	1930[b]	33.83[b]	0.94[b]
(0, 0, 0, 1)	516(14)	−3.18	−1.84	−2.01	168	51	19	0[b]	1930[b]	33.83[b]	0.94[b]
(4, 0, 0, 0)	538(54)	−533.90	50.87	20.47	170	45	19	0[b]	1930[b]	33.83[b]	0.94[b]
(2, 1, 0, 0)	584(37)	−166.96	24.45	9.34	170	54	19	0	676	25.11	0.74
(2, 0, 1, 0)	595(40)	−253.19	23.29	6.11	169	27	18	0[c]	1016[c]	23.74[c]	0.66[c]
(0, 2, 0, 0)	612(33)	250.42	−3.61	−1.05	168	50	18	15	541	54.72	1.48
(1, 0, 0, 1)	637(21)	−148.11	11.91	3.28	169	54	20	27	564	82.60	2.14
(5, 0, 0, 0)	640(75)	−666.26	63.13	25.08	170	26	19	0[c]	1016[c]	23.74[c]	0.66[c]
(0, 1, 1, 0)	677(22)	89.94	−1.36	−4.75	168	27	9	5	223	87.91	2.32
(1, 2, 0, 0)	754(24)	90.18	10.10	3.77	169	27	14	0	359	23.94	0.62
(6, 0, 0, 0)	767(61)	−682.75	65.89	24.96	170	26	9	110	269	195.76	4.22
$^{13}\mathrm{C}_2$ $v = 0$	0	−141.82	−5.77	−1.11	168	27	5	0	107	38.70	0.59
$^{13}\mathrm{C}_1$ $v = 0$	0	−333.54	−42.43	−48.41	168	27	12	0	354	30.18	0.59
$^{13}\mathrm{C}_4$ $v = 0$	0	−84.48	−22.40	−18.28	170	27	13	0	347	31.07	0.54

The rotational constant differences are defined as $\Delta A = A_v - A_0 \approx -\alpha_v^A$ (analog for B and C). The $\alpha_v^{A/B/C}$ are the first-order rotation-vibration interaction constants.
[a,b,c] Reported values are values for the respective combined fits.

tions are typically around $10\,\text{cm}^{-1}$ with a maximum deviation of $56\,\text{cm}^{-1}(1.04\,\sigma)$ for $(4, 0, 0, 0)$. The rejected lines and RMS values in Tab. 1 show that the vibrational states $(0, 2, 0, 0)$, $(1, 0, 0, 1)$, $(0, 1, 1, 0)$, and $(6, 0, 0, 0)^5$ could not be fit to experimental accuracy, hinting toward so far unaccounted interactions between these states and/or states not found yet. Therefore, these vibrational states were only fit to (incomplete) sets of quartic parameters as higher-order parameters had physically unreasonable values (see Sec. 3 of the Supporting Information). The obtained quartic distortion constants are prob-

ably highly effective and therefore should be viewed with caution. Lastly, we searched for the gauche rotamer which is calculated to lie about $2.4\,\text{kcal/mol}$ above the trans rotamer which is studied here (see Sec. 1.4 of the Supporting Information). However, it could not be identified in the spectrum due to its low relative intensity of about $1\,\%$.

4.1 Interactions

Three interacting systems, two dyads and one triad (see Fig. 3), were identified via mirror images in their resonance plots (see Fig. 4 for an example case). For the $(4, 0, 0, 0)$, $(0, 0, 0, 1)$, and $(1, 0, 1, 0)$ triad as well as the $(5, 0, 0, 0)$, and $(2, 0, 1, 0)$ dyad, the initial vibrational energy separations were approximated from the

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[5] The vibrational state $(6, 0, 0, 0)$ is most likely interacting with the not yet found $(3, 0, 1, 0)$ state, as $(3 + n, 0, 0, 0)$ and $(n, 0, 1, 0)$ are interaction partners for $n = 0, 1, 2$. Similarly, $(1, 0, 0, 1)$ could be interacting with $(5, 0, 0, 0)$ and $(2, 0, 1, 0)$. However, no conclusive evidence was found in the present analysis.

Table 2: Rotational parameters for the vibrationally excited states showing no signs of interactions.

Parameter		$(0,0,0,0)$	$(1,0,0,0)$	$(2,0,0,0)$	$(0,1,0,0)$	$(1,1,0,0)$	$(2,1,0,0)$	$(1,2,0,0)$
A	/MHz	18 241.103 99(19)	18 102.259 86(19)	17 967.217 15(20)	18 366.363 99(22)	18 217.111 77(70)	18 074.1420(16)	18 331.2800(78)
B	/MHz	3272.930 493(18)	3285.825 194(21)	3298.572 744(22)	3271.112 666(24)	3284.406 457(47)	3297.377 47(11)	3283.025 58(25)
C	/MHz	3137.715 975(18)	3142.876 045(20)	3147.986 349(21)	3137.177 292(23)	3142.173 621(47)	3147.053 16(10)	3141.481 99(23)
$-D_J$	/Hz	−562.8140(33)	−584.9656(39)	−609.5946(73)	−558.7139(73)	−579.461(37)	−603.725(99)	−574.30(13)
$-D_{JK}$	/kHz	−12.384 66(13)	−11.719 947(89)	−11.027 24(14)	−12.729 37(18)	−12.044 24(30)	−11.3339(11)	−12.3501(24)
$-D_K$	/kHz	−17.028 32(89)	−13.885 04(70)	−11.656 20(98)	−21.0938(12)	−16.643(31)	−14.020(72)	a
d_1	/Hz	−23.785 44(78)	−28.8834(11)	−35.1889(15)	−21.8177(19)	−25.6245(23)	−31.1607(65)	−22.27(13)
d_2	/Hz	−3.807 78(59)	−4.652 05(34)	−5.655 33(47)	−4.107 39(18)	−4.841 36(64)	−5.8702(38)	−4.952(88)
H_J	/µHz	135.01(19)	180.34(23)	225.13(70)	154.89(59)	a	a	a
H_{JK}	/mHz	74.081(31)	70.101(11)	65.710(21)	76.983(33)	a	60.39(47)	a
H_{KJ}	/Hz	−1.119 92(26)	−1.028 02(29)	−0.956 95(62)	−1.170 80(94)	−1.0776(11)	−1.1700(26)	−1.440(14)
H_K	/Hz	0.9334(23)	0.630 58(86)	0.4280(18)	1.0528(23)	a	a	a
h_1	/µHz	66.762(59)	86.997(91)	103.90(21)	80.33(24)	a	a	a
h_2	/µHz	65.81(19)	74.300(59)	80.97(12)	a	a	a	a
h_3	/µHz	3.146(17)	4.356(23)	5.788(29)	4.285(26)	a	a	a
L_{JJK}	/nHz	−431.2(21)	a	a	a	a	a	a
L_{JK}	/µHz	15.372(66)	a	a	a	a	a	a
L_{KKJ}	/µHz	−148.35(20)	−138.79(38)	−119.3(14)	−195.9(24)	a	a	a
L_K	/µHz	91.6(21)	a	a	a	a	a	a
l_2	/pHz	−456(12)	a	a	a	a	a	a
P_{JK}	/pHz	−182.4(51)	a	a	a	a	a	a

Fits performed with SPFIT in the S-reduction and I^r representation. Standard errors are given in parentheses. [a] Parameter was fixed to the ground vibrational state value.

Table 3: Rotational parameters for perturbed vibrationally excited states. Interaction systems are indicated by mutual colors analog to Fig. 3.

Parameter		$(3,0,0,0)$	$(0,0,1,0)$	$(4,0,0,0)$	$(0,0,0,1)$	$(1,0,1,0)$	$(5,0,0,0)$	$(2,0,1,0)$
A	/MHz	17 834.740 75(93)	18 223.393 07(75)	17 707.207(32)	18 237.9197(18)	18 108.639(31)	17 574.848(64)	17 987.917(50)
B	/MHz	3311.259 31(48)	3272.204 55(49)	3323.7963(60)	3271.087 86(14)	3283.4264(60)	3336.0643(43)	3296.2156(44)
C	/MHz	3153.059 77(45)	3132.991 73(47)	3158.1879(37)	3135.706 94(14)	3138.0404(41)	3162.8007(46)	3143.8252(44)
$-D_J$	/Hz	−635.605(28)	−567.669(36)	−683.43(49)	−551.24(13)	−582.05(47)	−687.06(40)	−632.22(34)
$-D_{JK}$	/kHz	−10.331 09(79)	−12.196 93(61)	−9.2939(43)	−12.871 07(74)	−11.6037(31)	−8.8172(96)	−10.777(10)
$-D_K$	/kHz	−9.9572(27)	−18.3391(19)	−9.44(11)	−11.235(85)	−19.105(83)	−5.3(22)	−3.6(18)
d_1	/Hz	−42.790(10)	−29.1396(97)	−54.78(12)	−14.4779(93)	−39.04(11)	−56.96(24)	−51.52(21)
d_2	/Hz	−6.7420(23)	−4.2186(20)	−9.753(34)	−1.847(14)	−5.786(29)	−9.18(12)	−7.25(10)
H_J	/µHz	a	198.2(18)	a	a	a	a	a
H_{JK}	/mHz	62.31(22)	a	a	a	a	a	35.7(18)
H_{KJ}	/Hz	−0.8813(11)	a	a	−0.8042(31)	−0.9352(48)	−0.6181(59)	a
H_K	/mHz	330.0(53)	a	a	a	a	a	a
h_2	/µHz	100.30(93)	a	a	a	a	a	a

Fits performed with SPFIT in the S-reduction and I^r representation. Standard errors are given in parentheses. Parameters not shown here were fixed to the ground vibrational state values (see Tab. 2). [a] Parameter was fixed to the ground vibrational state value.

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Figure 4: Resonance plot for the $3\nu_{21}/\nu_{19}$ dyad. A $\Delta K_a = 2$ interaction for the $K_a = 5$ series of $v_{21} = 3$ and the $K_a = 7$ series of $v_{19} = 1$ is highlighted by the mirrored patterns. Here, the $J = K_a + K_c$ asymmetry components are shown but the figure is nearly identical for the other asymmetry component. The respective y-axes are shifted to highlight the mirror image nature of the two series which is a clear sign of an interaction between the two states centered around $J = 17$.

rotational energies of the strongest mirror images in the resonance plots[6]. The analysis of the $(3,0,0,0)$ and $(0,0,1,0)$ dyad was greatly simplified by finding interstate transitions between vibrationally excited states using the DM-DR method. This yielded their vibrational energy separation with rotational precision (see Fig. 5 for an example). Transitions between vibrationally excited states become allowed due to the interactions which result in the rovibrational levels being linear combinations of the rovibrational levels of the interacting vibra-

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[6]To approximate the initial vibrational energy separations, first, the energy levels at the center of the interaction are identified in resonance plots (e.g. $17_{7,10}$ of $v_{19} = 1$ and $17_{5,12}$ of $v_{21} = 3$ in Fig. 4). Their rovibrational energies, consisting of a calculated vibrational energy and the rotational energy from the best-fit rotational model, are retrieved from the *.egy* file produced by SPCAT.[29] Then, the rovibrational energies of the two states are equalized by adding an energy offset to one of the two vibrational states (in the example of $v_{21} = 3$ and $v_{19} = 1$ the calculated vibrational energies $E^{\text{calc}}_{v_{19}=1}$ and $E^{\text{calc}}_{v_{21}=3}$ are used together with the offset energy $\Delta E_{v_{21}=3}$). Once first interaction parameters are included in the combined fit, the offset energy can be floated in the fit and will result in a highly accurate value for the vibrational energy separation.

Table 4: Energy differences and interaction parameters for the three interacting systems. Interaction systems are ordered by increasing energy and are indicated by mutual colors analog to Fig. 3.

v_1	v_2	ID[a]	Parameter		Value
		$\tilde{\nu}_{(3,0,0,0)} - \tilde{\nu}_{(0,0,1,0)}$		/cm^{-1}	11.244 843(37)
(3,0,0,0)	(0,0,1,0)	$0v_1v_2$	W	/GHz	$-65.6207(14)$
(3,0,0,0)	(0,0,1,0)	$1v_1v_2$	W_J	/kHz	295.1(12)
(3,0,0,0)	(0,0,1,0)	$400v_1v_2$	W_2	/kHz	$-28.477(63)$
(3,0,0,0)	(0,0,1,0)	$401v_1v_2$	$W_{2,J}$	/Hz	$-1.848(22)$
(3,0,0,0)	(0,0,1,0)	$4000v_1v_2$	G_b	/MHz	$-164.86(29)$
(3,0,0,0)	(0,0,1,0)	$6000v_1v_2$	G_c	/MHz	177.28(27)
(3,0,0,0)	(0,0,1,0)	$6001v_1v_2$	$G_{c,J}$	/kHz	$-1.684(18)$
(3,0,0,0)	(0,0,1,0)	$6100v_1v_2$	F_{ab}	/MHz	$-2.585(15)$
		$\tilde{\nu}_{(0,0,0,1)} - \tilde{\nu}_{(4,0,0,0)}$		/cm^{-1}	25.8639(64)
(4,0,0,0)	(0,0,0,1)	$2100v_1v_2$	F_{bc}	/MHz	1.958(11)
(4,0,0,0)	(0,0,0,1)	$2101v_1v_2$	$F_{bc,J}$	/Hz	$-128.2(75)$
		$\tilde{\nu}_{(4,0,0,0)} - \tilde{\nu}_{(1,0,1,0)}$		/cm^{-1}	12.6795(50)
(4,0,0,0)	(1,0,1,0)	$0v_1v_2$	W	/GHz	134.42(10)
(4,0,0,0)	(1,0,1,0)	$10v_1v_2$	W_K	/MHz	$-9.71(14)$
(4,0,0,0)	(1,0,1,0)	$4000v_1v_2$	G_b	/MHz	422.7(11)
(4,0,0,0)	(1,0,1,0)	$4010v_1v_2$	$G_{b,K}$	/MHz	$-1.250(17)$
(4,0,0,0)	(1,0,1,0)	$4200v_1v_2$	G_{2b}	/kHz	$-4.421(77)$
(4,0,0,0)	(1,0,1,0)	$4210v_1v_2$	$G_{2b,K}$	/Hz	53.7(17)
(4,0,0,0)	(1,0,1,0)	$4100v_1v_2$	F_{ac}	/MHz	$-6.91(12)$
		$\tilde{\nu}_{(5,0,0,0)} - \tilde{\nu}_{(2,0,1,0)}$		/cm^{-1}	12.9327(37)
(5,0,0,0)	(2,0,1,0)	$0v_1v_2$	W	/GHz	$-198.920(58)$
(5,0,0,0)	(2,0,1,0)	$400v_1v_2$	W_2	/kHz	26.38(95)
(5,0,0,0)	(2,0,1,0)	$4000v_1v_2$	G_b	/MHz	432.455(39)
(5,0,0,0)	(2,0,1,0)	$4101v_1v_2$	$F_{ac,J}$	/Hz	313.9(22)

[a] The specified IDs are the respective parameter IDs used in the *.par* and *.var* files of SPFIT and SPCAT.[29,32]

tional states. This means the rovibrational levels shown on the right-hand side of Fig. 5 are linear combinations with the labels corresponding to the largest contribution. For example, the rovibrational level labeled $17_{7,10}$ $v_{19} = 1$ is a linear combination of $17_{7,10}$ $v_{19} = 1$ and $17_{5,12}$ $v_{21} = 3$ (similarly $16_{5,11}$ $v_{21} = 3$ will also contain parts of $16_{7,9}$ $v_{19} = 1$). As a result, the transition between the states labeled $16_{5,11}$ $v_{21} = 3$ and $17_{7,10}$ $v_{19} = 1$ becomes allowed.

As glycidaldehyde has C_1 symmetry, a-, b-, and c-type Coriolis interactions as well as Fermi resonances are allowed by symmetry considerations between any combination of vibrational modes. For each interaction system, the leading parameters for the different interaction types were tested with *Pyckett* and the influence on the *RMS*, *WRMS*, and rejected lines were monitored. When lower-order parameters were added, subsequently higher-order parameters of the same interaction type were tested.

Figure 5: DM-DR (top) and conventional measurement (bottom) of the same frequency range. On the right, the transition of interest, an interstate transition, is indicated in blue and the pump transition is indicated in red. Due to the DM-DR scheme, only lines sharing an energy level with the pump transition have a signature in the top plot, unambiguously identifying the weak interstate transition. As can be seen from the zoom into the gray marked area, there are many candidate lines in the conventional spectrum but only a single line in the DM-DR spectrum.

Table 5: Rotational parameters for the ground vibrational states of the three singly substituted ^{13}C isotopologues of glycidaldehyde.

Parameter		$^{13}C_2$	$^{13}C_1$	$^{13}C_4$
A	/MHz	18 099.286(30)	17 907.566(26)	18 156.623(12)
B	/MHz	3267.164 09(56)	3230.498 76(47)	3250.529 51(16)
C	/MHz	3136.601 01(42)	3089.309 08(45)	3119.439 23(15)
$-D_J$	/Hz	−559.12(21)	−554.49(12)	−561.65(11)
$-D_{JK}$	/kHz	−12.1451(91)	−11.914 66(91)	−11.900 03(72)
$-D_K$	/kHz	a	a	a
d_1	/Hz	−22.16(24)	−26.93(21)	a
d_2	/Hz	a	a	a

Fits performed with SPFIT in the S-reduction and I^r representation. Standard errors are given in parentheses. Parameters not shown here were fixed to the main isotopologue values (see Tab. 2). ^{a} Parameter was fixed to the main isotopologue value.

The final interaction parameter set includes Fermi, a-, b-, and c-type Coriolis terms. The absolute signs of the interaction parameters could not be determined from the fit, only their relative signs.[33,34]

To find the regions where the interactions have the strongest influence, the shifts in transition frequency between predictions with and without interactions were calculated (see Sec. 4 of the Supporting Information). When comparing these plots for coupled vibrational states, mirror images highlight the rotational states that are interaction partners. For all three in-

teracting systems the trends were very similar as ΔK_a decreases with increasing K_a value. Exemplary for the energetically lowest dyad, there are clear mirror image patterns for $K_a = 2$ of $(3, 0, 0, 0)$ and $K_a = 6$ of $(0, 0, 1, 0)$ resulting in $\Delta K_a = 4$ for these lower K_a values. For higher K_a values mirror image patterns can be seen e.g. for $K_a = 11$ and $K_a = 12$, respectively, resulting in $\Delta K_a = 1$ for these higher K_a values.

For low K_a values the interactions between $(3, 0, 0, 0)$ and $(0, 0, 1, 0)$ are most prominent around $J = 16$ for $K_a = 5$ and $K_a = 7$, respectively (see Fig. 4). Further strong interactions are found around $J = 32$ between $K_a = 11$ and $K_a = 12$ in addition to $\Delta K_a = 0$ interactions for the highest measured values of K_a, being 15 to 20.

For the $(4, 0, 0, 0)$, $(0, 0, 0, 1)$, and $(1, 0, 1, 0)$ triad, the dominant shifts are between $(4, 0, 0, 0)$ and $(1, 0, 1, 0)$. At low K_a values, the prominent interactions are around $J = 32$ between $K_a = 7$ and $K_a = 9$. For higher K_a values $\Delta K_a = 1$ interactions dominate with the biggest shifts around $J = 37$ between $K_a = 14$ and $K_a = 15$, respectively.

For the $(5, 0, 0, 0)$, and $(2, 0, 1, 0)$ dyad the strongest interactions are around $J \geq 50$ be-

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tween $K_a = 17$ and $K_a = 18$, respectively.

Due to the limitations in the frequency coverage, a-type transitions of the interacting systems are typically assigned up to $J = 26$. As a consequence, the centers of some perturbations lie outside our quantum number range and are determined via the predictions with and without interaction parameters.

The resulting rotational parameters (see Tab. 3) are deemed to be effective, particularly for the $(4, 0, 0, 0)$, $(0, 0, 0, 1)$, and $(1, 0, 1, 0)$ triad, as can be seen in the parameter progression for the quartic parameters (see Sec. 5 of the Supporting Information). This could result from so far unaccounted interactions with other states where the effects are too weak to be identified in the residuals or the corresponding quantum number ranges have not been observed yet.

Lastly, both $(2, 1, 0, 0)$, and $(1, 2, 0, 0)$ show hints for perturbations at higher K_a values but no interaction partners were identified as of yet.

4.2 Fit Results

Except for the aforementioned vibrationally excited states, $(0, 2, 0, 0)$, $(1, 0, 0, 1)$, $(0, 1, 1, 0)$, and $(6, 0, 0, 0)$, all analyses reproduce the spectrum with about experimental uncertainty and only a single line was rejected from the fit due to $|\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}|/\Delta\nu > 10$ (see Tab. 1). The resulting rotational parameters are given in Tab. 2 for vibrational states showing no signs of interactions, in Tab. 3 for the interacting vibrational states, and the interaction parameters in Tab. 4.

In their previous study, Creswell et al. presented fits for $v_{21} = 0, 1, 2$ with full sets of quartic rotational constants. The relative deviations for the rotational constants are all below 10^{-5} even though not within their uncertainties. The quartic parameters differ by a few percent except d_2 which differs by up to 45%. For $v_{21} = 3, 4, 5, 6$ Creswell et al. fitted only rigid rotor Hamiltonians without accounting for any interactions. Thus, even the rotational constants differ greatly (up to 150σ[7]).

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[7]The values for $v_{21} = 6$ agree the best as in this work the interaction partner of $v_{21} = 6$ was not found meaning two highly effective fits were compared.

However, their study was much more limited in frequency coverage, only 8–40 GHz, and quantum number coverage, with only 31 transitions with $J_{\mathrm{max}} = 31$ for $v_{21} = 0, 1, 2$ and 10 transitions with $J_{\mathrm{max}} = 6$ for $v_{21} = 3, 4, 5, 6$. Furthermore, no interactions were accounted for at all by Creswell et al.[11].

The values for the ground vibrational state also show good agreement with values obtained from quantum chemical calculations (see Tab. S2 of the Supporting Information). The three parameters H_J, h_1, and d_2 show the highest relative deviations at 27%, 26%, and 21%, respectively.

4.3 Singly substituted ^{13}C Species

The singly substituted ^{13}C species were more difficult to analyze because of their low natural abundance resulting in a smaller number of assignable lines. This is especially apparent for the ^{13}C$_2$ species, for which only about 100 lines could be assigned due to its A and B values being close to the main isotopologue values (see Tab. 1). As a result, many of its a-type transitions are close to or blended with much stronger transitions. The resulting parameters are shown in Tab. 5 with the notation from Creswell et al.[11] being used to label the carbon atoms.

The rotational constants agree nicely with the values obtained by Creswell et al.[11] as the relative deviations are below 10^{-5} and all deviations are within 1.5σ. Higher order parameters were included by Creswell et al.[11] only as fixed values of the main isotopologue's ground vibrational state.

4.4 Estimation of the c-type Dipole Moment

Creswell et al. determined the c-type dipole moment to be $0.277(156)$ D. To derive a more accurate value, in the present study, the c-type dipole moment was determined via comparison of experimental line intensities. A selection of 28 c-type transitions was compared with b-type transitions close in frequency by fitting a second derivative Voigt profile to the

experimental lineshapes. The resulting c-type dipole moment, calculated as the mean value and the standard deviation of the 28 transition pairs, is 0.334(39) D. Additionally, the calculated equilibrium c-type dipole moment (ae-CCSD(T)/cc-pwCVTZ level, 0.276 D) was corrected for effects of zero-point vibrations (fc-CCSD(T)/cc-pVTZ, 0.023 D) resulting in a vibrationally averaged dipole moment of $\mu_c = 0.253$ D, which is about 2σ smaller than the experimental value.

The new experimental value agrees with the previously determined value within their uncertainties but has a significantly smaller uncertainty. Systematic errors occur as (among other things) the power of the probe source is frequency dependent, and the pressure, which influences the lineshape and thereby center intensities, rises over time. These effects were not taken into account but their impact was minimized by comparing transitions nearby in frequency (and thereby also in time). Additionally, lines might be blended with other lines so-far not assigned and therefore their amplitudes might be influenced. The systematic uncertainty might thus be slightly higher than the reported statistical uncertainty.

5 Search for Glycidaldehyde toward Sgr B2(N)

5.1 Observations

We used the imaging spectral line survey Re-exploring Molecular Complexity with ALMA (ReMoCA) that targeted the high-mass star-forming protocluster Sgr B2(N) with the Atacama Large Millimeter/submillimeter Array (ALMA) to search for glycidaldehyde in the interstellar medium. Details about the data reduction and the method of analysis of this survey can be found elsewhere.[35,36] The main features of the survey are the following. It covers the frequency range from 84.1 GHz to 114.4 GHz at a spectral resolution of 488 kHz (1.7 to 1.3 km s^{-1}). This frequency coverage was obtained with five different tunings of the receivers. The

phase center was located halfway between the two hot molecular cores Sgr B2(N1) and Sgr B2(N2), at the equatorial position $(\alpha, \delta)_{\mathrm{J2000}} = (17^{\mathrm{h}}47^{\mathrm{m}}19\overset{\mathrm{s}}{.}87, -28°22'16\overset{''}{.}0)$. The observations achieved a sensitivity per spectral channel ranging between 0.35 mJy beam^{-1} and 1.1 mJy beam^{-1} (rms) depending on the tuning, with a median value of 0.8 mJy beam^{-1}. The angular resolution (HPBW) varies between $\sim$0.3$''$ and $\sim$0.8$''$ with a median value of 0.6$''$ that corresponds to $\sim$4900 au at the distance of Sgr B2 (8.2 kpc).[37]

For this work we analyzed the spectra toward the position called Sgr B2(N2b) by Belloche et al.[36] It is located in the secondary hot core Sgr B2(N2) at $(\alpha, \delta)_{\mathrm{J2000}} = (17^{\mathrm{h}}47^{\mathrm{m}}19\overset{\mathrm{s}}{.}83, -28°22'13\overset{''}{.}6)$. This position was chosen as a compromise between getting narrow line widths to reduce the level of spectral confusion and keeping a high enough H_2 column density to detect less abundant molecules.

Like in our previous ReMoCA studies,[35,36] we compared the observed spectra to synthetic spectra computed under the assumption of local thermodynamic equilibrium (LTE) with the astronomical software Weeds.[38] This assumption is justified by the high densities of the regions where hot-core emission is detected in Sgr B2(N) $> 1 \times 10^7$ cm^{-3}, see Bonfand et al.[39] The calculations take into account the finite angular resolution of the observations and the optical depth of the rotational transitions. We derived by eye a best-fit synthetic spectrum for each molecule separately, and then added together the contributions of all identified molecules. Each species was modeled with a set of five parameters: size of the emitting region (θ_{s}), column density (N), temperature (T_{rot}), linewidth (ΔV), and velocity offset (V_{off}) with respect to the assumed systemic velocity of the source, $V_{\mathrm{sys}} = 74.2$ km s^{-1}. The linewidth and velocity offset were obtained directly from the well-detected and not contaminated lines. The size of the emission of a given molecule was estimated from integrated intensity maps of transitions of this molecule that were found to be relatively free of contamination from other species.

5.2 Search for glycidaldehyde toward Sgr B2(N2b)

Figure 6: Population diagram of $c-C_2H_4O$ toward Sgr B2(N2b). The observed data points 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 subtracted from the observed data points. The purple line is a linear fit to the observed populations (in linear-logarithmic space). The fit yields a temperature of 132 ± 10 K.

Before searching for glycidaldehyde toward Sgr B2(N2b), we modeled the rotational emission of the related cyclic molecule oxirane, $c-C_2H_4O$. We used the spectroscopic predictions available in the Cologne database for molecule spectroscopy (CDMS)[40] for the vibrational ground state (version 3 of entry 44504), which are mainly based on work by Müller et al.[41]. Oxirane is well detected toward Sgr B2(N2b), with two dozens of lines in its vibrational ground state easily identified (see Sec. 6 of the Supporting Information). Integrated intensity maps of lines of oxirane that are free of contamination suggest an emission size on the order of 0.7″. Fig. 6 shows the population diagram of oxirane. A fit to this population diagram yields a rotational temperature of 132 ± 10 K. Assuming a temperature of 130 K, we adjusted a synthetic LTE spectrum to the observed spectrum and obtained the best-fit column density of oxirane reported in Tab. 6

that corresponds to the spectrum shown in red in Sec. 6 of the Supporting Information.

To search for glycidaldehyde toward Sgr B2(N2b) using the spectroscopic predictions obtained in Sec. 4, we computed a synthetic LTE spectrum assuming the same velocity offset, linewidth, emission size, and rotational temperature as those derived for oxirane (Tab. 6) and keeping the column density of glycidaldehyde as the only free parameter. We did not find any evidence for glycidaldehyde in this source. The synthetic spectrum used to estimate the upper limit to its column density is shown in red in Fig. 7. This upper limit is reported in Tab. 6. We conclude from this analysis that glycidaldehyde is at least 6 times less abundant than oxirane in Sgr B2(N2b).

Figure 7: Selection of rotational transitions of glycidaldehyde, $c-(C_2H_3O)CHO$ covered by the ReMoCA survey. The LTE synthetic spectrum of $c-(C_2H_3O)CHO$ used to derive the upper limit on its column density toward Sgr B2(N2b) is displayed in red and overlaid on the observed spectrum shown in black. The blue synthetic spectrum contains the contributions of all molecules identified in our survey so far, but not the species shown in red. The values written below each panel correspond from left to right to the half-power beam width, the central frequency in MHz, the width in MHz of each panel in parentheses, and the continuum level in K of the baseline-subtracted spectra in brackets. The y-axis is labeled in brightness temperature units (K). The dotted line indicates the 3σ noise level.

Table 6: Parameters of our best-fit LTE model of oxirane toward Sgr B2(N2b) and upper limit for glycidaldehyde.

Molecule	Status[a]	N_{det} [b]	Size[c] ('')	T_{rot} [d] (K)	N [e] (cm^{-2})	F_{vib} [f]	F_{conf} [g]	ΔV [h] (km s^{-1})	V_{off} [i] (km s^{-1})	$\frac{N_{\mathrm{ref}}}{N}$ [j]
$c-\mathrm{C_2H_4O}$, $v = 0^\star$	d	28	0.7	130	4.0 (16)	1.00	1.00	3.5	0.0	1
$c-(\mathrm{C_2H_3O})\mathrm{CHO}$, $v = 0$	n	0	0.7	130	< 7.1 (15)	1.43	1.00	3.5	0.0	> 5.6

[a] d: detection, n: nondetection. [b] Number of detected lines conservative estimate, see Sect. 3 of [42]. 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] Correction factor that was applied to the column density to account for the contribution of other conformers in the cases where this contribution could be estimated but was not included in the partition function of the spectroscopic predictions. [h] Linewidth ($FWHM$). [i] Velocity offset with respect to the assumed systemic velocity of Sgr B2(N2b), $V_{\mathrm{sys}} = 74.2$ km s^{-1}. [j] Column density ratio, with N_{ref} the column density of the previous reference species marked with a $\star$.

6   Conclusions

In the present study, coverage of the experimental rotational spectrum of glycidaldehyde has been extended greatly by measuring 345 GHz of broadband spectra in frequency intervals reaching as high as 750 GHz. The ground vibrational state, 17 vibrationally excited states, and the three singly substituted ^{13}C isotopologues were analyzed by combining the powers of LWPs and DM-DR measurements, which act as precise filters on the rather complicated spectrum. Additionally, DM-DR measurements facilitated measuring interstate transitions between vibrationally excited states, yielding their vibrational energy separation with rotational precision. In total, three interacting systems were examined and could be reproduced to about experimental accuracy. The presented data allow for radio astronomical searches over a wide range of frequencies and quantum numbers. Searches of glycidaldehyde's ground vibrational state with ALMA toward Sgr B2(N2b) were not successful implying that glycidaldehyde is at least six times less abundant than oxirane in this source. For future laboratory studies and astronomical searches of vibrationally excited states toward warm regions, the explicit interaction description in combined fits will be essential. [43] In the present study, foregoing the explicit interaction treatment and using only single-state fits would have resulted in about 20 % of the approximately 16 000 total lines being rejected (due to $|\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}|/\Delta\nu > 10$) and considerably worse RMS and $WRMS$ values.

Future studies might be targeted at filling the remaining frequency gaps and analyzing so-far untreated interactions. Future steps for the DM-DR method include implementing a demodulation scheme with the sum (or difference) of the *1f*- and *2f*-demodulation frequencies or in the ideal case with a custom function being the product of a sine function with the *2f*-demodulation frequency and a ±1 rectangle function for the subtraction.

Now that the rotational spectrum of glycidaldehyde is known very well, it might be worthwhile to check for the status of other substituted oxiranes, $c-\mathrm{C_2H_3O}-X$. A current census of the spectroscopic knowledge of six selected species has been given recently. [44] While rotational spectroscopic data have been collected for four of those ($X = \mathrm{CH_3}$, $\mathrm{C_2H}$, CN, and CHO), at least two simple representatives (X=OH, $\mathrm{NH_2}$) still await their microwave spectroscopic characterization.

Data availability

The input and output files of SPFIT will be provided as supplementary material. These files as well as auxiliary files will be deposited in the data section of the CDMS. Calculations of rotational spectra of the main isotopic species will be available in the catalog section of the CDMS.

Supporting Information Available

The calculated structures, rotation-vibration interaction constants, vibrational energies, and intensities. Residuals histograms for assignments from this work and Creswell et al.[11] The transition shift due to interactions for one exemplary interaction system. Parameter progression plot for the $v_{21} = n$ states. Additional figure of the ReMoCA survey illustrating the detection of oxirane.

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