Millimeter and submillimeter wave spectroscopy of propanal

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May 15, 2017

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Abstract

The rotational spectra of the two stable conformers syn- and gauche-propanal (CH$_3$CH$_2$CHO) were studied in the millimeter and submillimeter wave regions from 75 to 500 GHz with the Cologne (Sub-)Millimeter wave Spectrometer. Furthermore, the first excited states associated with the aldehyde torsion and with the methyl torsion, respectively, of the syn-conformer were analyzed. The newly obtained spectroscopic parameters yield better predictions, thus fulfill sensitivity and resolution requirements in new astronomical observations in order to unambiguously assign pure rotational transitions of propanal. This is demonstrated on a radio astronomical spectrum from the Atacama Large Millimeter/submillimeter Array Protostellar Interferometric Line Survey (ALMA-PILS). In particular, an accurate description of observed splittings, caused by internal rotation of the methyl group in the syn-conformer and by tunneling rotation interaction from two stable degenerate gauche-conformers, is reported. The rotational spectrum of propanal is of additional interest because of its two large amplitude motions pertaining to the methyl and the aldehyde group, respectively.

Keywords:
propanal, rotational spectroscopy, submillimeter wave spectroscopy, interstellar molecule, internal rotation, tunneling rotation interaction

1. Introduction

In 1964, Butcher and Wilson recorded the microwave spectrum of propanal, also known as propionaldehyde, and deuterated isotopic species up to 38 GHz. The existence of two stable conformers, syn (also called cis) and the doubly-degenerate gauche conformer (from here on simply syn and gauche) was established \[1\]. A sketch of syn is shown in Fig. 1. The two conformers differ mainly by the rotation of the aldehyde group with respect to the carbon atom plane of the molecule. Further transitions in low-lying excited vibrational states were also identified \[1\]. The potential energy surface of the rotation of the aldehyde group was studied in detail later \[2, 3\]. It was found that gauche is higher in energy by $\sim$420 cm$^{-1}$ and the aldehyde group is rotated by $\pm 128.2^\circ$ compared to the syn orientation \[3\]. The potential energy surface of propanal with respect to the rotation of the aldehyde group and sketches of the conformers are shown in Fig. 2. The torsional potentials were determined more accurately by Far-IR spectroscopy \[4\] and higher-lying vibrational modes were studied by Mid-IR spectroscopy \[5\]. In particular, the first aldehyde torsion $\nu_{24} = 1$ is 135.1 cm$^{-1}$ and the first excited methyl torsion $\nu_{23} = 1$ is 219.9 cm$^{-1}$ above the ground state of syn \[4\]; note that the methyl torsional assignments have been exchanged between syn and gauche from Ref. \[4\] to Ref. \[5\]. In the former work the energy difference between the conformers was redetermined as $\sim$421 cm$^{-1}$, whereas in the latter work it was determined to be $\sim$370 cm$^{-1}$.

Whereas the rotational spectrum of syn displays only small splittings caused by an internal rotation of the methyl group, the barrier between the two equivalent gauche conformations is sufficiently low (see Fig. 2) such that tunneling between them occurs, causing somewhat larger splittings \[1\].

Two groups measured further transitions of syn independently of each other in the frequency region from 8–38 GHz using a Stark-modulated and a Fourier transform microwave
Figure 2: Calculated potential energy surface of propanal with respect to the rotation of the aldehyde group. There are two stable conformers: syn- and the twofold degenerate gauche-conformer. White spheres in propanal sketches designate hydrogen, black ones carbon, and red ones oxygen atoms. The molecular axes c and b are aligned to the x- and y-axis, respectively. The point of view is shown for syn with the eye in Fig. [8]. Since syn and gauche conformers differ mainly by the rotation of the aldehyde group, this alignment was chosen for clarification. Their simplified Newman projections, where the three carbon atoms are shown as one cycle and hydrogen atoms are omitted, except the one from the aldehyde group, are highlighting this rotation. A more illustrative alignment of syn is shown in the supplementary material.

spectrometer, respectively, but published it jointly [6]. They used a S-type centrifugal distortion analysis to guarantee a correct assignment of transitions involving states of large angular momentum $J$. Additionally, the height of the methyl barrier hindering internal rotation in syn was determined to $\sim 793.7 \text{ cm}^{-1}$. For gauche it is $\sim 886 \text{ cm}^{-1}$ and was determined by measuring c-type transitions [7]. This was crucial since b- and c-type transitions were predicted to split by internal rotation and only a-types were assigned before [1, 2]. Assignment of rotational transitions for syn were extended nearly up to 300 GHz with a spectrometer employing super-heterodyne detection [8]. Structural information on either conformer were derived from twelve isotopologues of syn and six of gauche [9].

In the homologous series of alkanales, the three smallest members, methanal, ethanal, and propanal were already detected in space [10, 11, 12]. The first detection of propanal was towards Sgr B2(N) [12]. Later, it was detected also in other galactic center molecular clouds [13] and very recently in the Protostellar Interferometric Line Survey (PILS) [14] of the low-mass protostellar binary IRAS 16293–2422 [15] using the Atacama Large Millimeter/submillimeter Array (ALMA). The first two detections indicated that the molecule is located in colder environments, whereas the most recent one is in a comparably warm one at around 125 K. Its detection is in the warm gas close to the protostar, where molecules desorb from the grain ice mantle and the column density is high. The lines toward one component in IRAS 16293–2422 are very narrow, approximately 1 km/s wide, and the PILS data indicated small discrepancies between some observed and predicted rotational lines of propanal [15]. The discrepancies may arise in part from the complexity of the astronomical spectrum itself, especially from presently unaccounted absorption lines affecting the emission lines. Furthermore, some of the lines in the observed frequency region (329–363 GHz) had non-negligible uncertainties. Finally, the identification of propanal in the survey was based on predictions which had ignored the small, often unresolved internal rotation splitting. Since higher accuracies are desired, especially in higher frequency regions, and propanal was also found in a warmer environment, the spectrum of propanal was measured from 75 up to 500 GHz at room temperature with the Cologne (Sub-)Millimeter wave spectrometer and analyzed with respect to the splittings of the lines and its energetically lowest lying vibrational states. Another incentive for us to revisit the rotational spectrum of propanal was the presence of the two large amplitude vibrations and their potential interaction. In the current work, we present results on the ground vibrational states of syn and gauche and the first excited aldehyde and methyl torsional states of syn.

2. Experimental details

The spectrum of propanal was measured continuously in the frequency regions of 75–129 GHz and 169.2–500.4 GHz with the Cologne (Sub-)Millimeter wave Spectrometer. The experimental setup is described in detail elsewhere [16]. In this work, a clean pyrex cell was used. A rooftop mirror was installed at one end of the 5 m long cell with a diameter of 10 cm to double the absorption path length. For covering the 75–129 GHz range, in-house developed electronics for operating an amplifier tripler chain (~10 mW) in full saturation mode and a low noise room temperature Schottky detector were used to improve the signal to noise ratio (SNR). The higher frequency range was operated with commercial multiplier chains [17]. Typical background pressures (vacuum) reached 0.1 μbar and the cell was filled with a commercially available sample of propanal (97 %) from Sigma-Aldrich to a total pressure of about 20 μbar (2 Pa). Frequency modulation (FM; ~50 kHz, amplitude usually between 180 and 300 kHz) was employed with 2f demodulation which causes isolated absorption signals to appear close to a second derivative of a Gaussian. The step size varied between 81 and 108 kHz, and the integration time was usually 50 ms. Approximately two gigahertz could be measured per hour. We assigned uncertainties of 20 kHz to strong and very symmetric lines, 40 or 80 kHz to weaker or less symmetric lines.

3. Spectroscopic analysis

The rotational spectrum of propanal is very rich even at the lowest frequencies of our study. In Figure 3 observed lines of ground vibrational states of syn and gauche and the first excited aldehyde and methyl torsional states of syn are shown. Even though spectra are quite dense, unambiguous assignments can be made. In general, intensity ratios and trends in deviations of observed and calculated lines for different series were used to unambiguously assign transitions to the observed lines. In fact, in the higher frequency region, this high density of lines is restraining our assignments for lines with large uncertainties.
3.1. syn-propanal

The lower energy syn conformer is an asymmetric top rotor with $\kappa = -0.7855$ in the ground vibrational state (prolate case: $\kappa = -1$). The dipole moment components of syn were determined from Stark-effect measurements as 1.71 D and 1.85 D along the $a$- and $b$-axis, respectively [11]. The $c$-component is zero owing to the $C_3$-symmetry of the conformer. Rotational lines may be split into $A$ and $E$ components with equal intensities due to the threefold degenerate potential of the methyl group for internal rotation. A full description of molecular symmetry, with symmetry tables for the rigid rotor assumption and allowing for internal rotation, as well as resulting energy levels and selection rules can be found in the supplementary material.

In general, for all studied syn states, lines in a frequency window of $\sim 30\text{ GHz}$ were assigned and then a new fit was performed, if necessary with additional parameters. In general, intensity ratios and trends in deviations of observed and calculated lines for different series were used to unambiguously assign transitions to the observed lines. With improved parameters, a prediction for the next frequency window was made and so on. Indeed, for both vibrationally excited states only limited microwave data were available. Thus assignments in the millimeter wave range were more challenging. Due to no overlapping frequency regions from literature and our spectra, centrifugal distortion constants were kept fixed to the ground state values as a starting point. In a first step, the rotational parameters $A$, $B$, $C$, and the energy tunneling parameter $\epsilon_{10}$ were fit to the literature data. Subsequently, strong and well separated lines could be assigned for the first few gigahertz. Improved centrifugal distortion constants led to improved predictions especially for lines slightly higher in $J$ or in $K_a$.

Groner’s ERHAM program [13] was used for predicting and fitting of the rotational spectrum, including splittings due to internal rotation (for the ground vibrational state an extended version was used, since the original version is limited to $8191$ transitions). To calculate an initial unitless internal rotation parameter $\rho$ and the angle $\Theta_{\text{RAM}}$ for applying the Rho-Axis Method (RAM), the formulas $\rho_{\lambda} = \lambda_\lambda I_\lambda / I_g$ and $\Theta_{\text{RAM}} = \arctan(\rho_{b}\rho_{c}/\rho_{a})$ were used ($g = a, b, c$) [19]. The direction cosines of the internal rotation axis $i$ of the top in the principal axis system $\lambda_j$, moments of inertia $I_j$, and moment of inertia of the top $I_\lambda$ were taken or calculated with rotational parameters and the angle $<(a,i)$ from the literature [6], resulting in $\rho = 0.06$ and $\Theta_{\text{RAM}} = 28^\circ$.

The ground vibrational state shows only small, whereas excited vibrational states show larger splittings. Hence, the ratio of observed lines to assigned transitions is higher for vibrationally excited states (specifically, ground state transitions are more frequently blended) and more tunneling parameters are required to reproduce the data within experimental uncertainties. In Table 1, rotational and tunneling parameters of the ground state and first excited aldehyde-torsion as well as first excited methyl-torsion of syn are listed.

3.1.1. the ground state, $v = 0$ ($E = 0 \text{ cm}^{-1}$)

Starting with the ground state of syn-propanal at $75\text{ GHz}$, assignments were more or less straightforward, since some transitions were already measured and assigned up to $290\text{ GHz}$. Great care had to be taken into account with some typos and bad lines from the literature, conspicuously large deviations from experimental to calculated frequencies. For example, the $A$ and $E$ components of transition $6a_2 - 5a_3$ were listed at $145035.5\text{ GHz}$, whereas we predict this line at $143035.5\text{ GHz}$, shifted by $2\text{ GHz}$. Since the bad lines were unknown at this point and due to a large overlap from literature data and ours, transitions from Ref. [8] were completely excluded from the fit.
after first assignments were done in the millimeter wave range. In the end, these 112 lines (with corrected typos) were included in an additional fit and only four show larger deviations, see supplementary material. One of them is the line mentioned above, for the other three lines the splitting due to internal rotation was neglected. Due to comparably strong dipole moment components along the $a$- and $b$-axis, mostly $a$- and $b$-type $R$- and $Q$-type transitions were assigned ($a - R$: 2963, $a - Q$: 542, $b - R$: 1567, $b - Q$: 2832, $b - P$: 4). ERHAM also labels some transitions as false (arising from mislabeling) or "forbidden" (mixed wavefunctions, i.e., when the tunneling splitting is approximately equal to the torsional splitting) $c$-type $R$- (186), $Q$- (163), and $P$-type (23) transitions plus 271 so called $x$-type $P$-type transitions, see Ref. [20]. In general, energy levels with higher angular momentum $J$ show smaller splittings for identical $K$'s. The $b$-type transitions with low $J$ and high $K_a$ are frequently split; splitting in $a$-type transitions was resolved for $R$-type transitions with large asymmetry splitting ($2K_a \approx J$) and lower values of $J$. The root mean square (RMS) error of the fit was quite constant up to 300 GHz. The deterioration of the fit quality with higher frequency assignments, up to $\sim 20\%$, was ameliorated with the inclusion of $L_{KK,J}$.

3.1.2. the $1^{st}$ excited aldehyde torsion, $v_{24} = 1 (E = 135.1 \text{cm}^{-1})$

In general, assignments and fitting were nearly straightforward for the first excited aldehyde torsion, similar to the ground state. Noticeable is that series of $b$-type transitions, with higher $K_a$ quantum numbers than were already implemented in the fit, needed to be weighted carefully step by step into the dataset. Sometimes, this was also observed in the ground state, albeit to a lesser extent. With a sufficient amount of new lines these transitions were fit satisfactorily, and assignments in the submillimeter wave region could be made. Eventually, all assigned lines from the first excited aldehyde torsion could be fit within experimental uncertainty.

3.1.3. the $1^{st}$ excited methyl torsion, $v_{23} = 1 (E = 219.9 \text{cm}^{-1})$

Assignment and fitting of transitions within the first excited methyl torsion of syn turned out to be much more complicated. First, observed lines are weaker, so lines are more frequently blended and, due to many weak lines in the spectra, special care had to be taken into account to avoid misassignments. Furthermore, larger splittings due to internal rotation hampered assignments by finding patterns. We have not been able to fit all assigned lines within experimental uncertainties. Nevertheless, out of the 3688 assigned transitions 2760 were reproduced satisfyingly. The observed deviations may originate from incorrect assignments, however, the discontinuities in our dataset are evidence of perturbed rotational energy levels. For example, an oblate pairing of transitions is observed for high $J$ values with $K_a = 3$, 4, and lines can be assigned up to $J_{\text{max}} = 51$. In the final fit lines with $J = 39 - 46$ are excluded and show deviations up to 5 MHz.

The present model treats the $v_{23} = 1 (A'' \text{ symmetry})$ state as isolated. However, its energy of 219.9 cm$^{-1}$ [3] is not only comparable to $v_{24} = 2$ at 269.3 cm$^{-1}$, the second excited state of the aldehyde torsion ($A'$), but also to the $A'$ CCC-bending fundamental $v_{13} = 1$ at 264.0 cm$^{-1}$ [4,5]. Thus, Coriolis interaction may occur between $v_{23} = 1$ and $v_{13} = 1$. In addition, rotational or Coriolis-type interaction may occur between $v_{23} = 1$ and $v_{24} = 2$, which is most likely less prominent because it is of higher order than the Coriolis interaction between two fundamentals, besides, $v_{24} = 2$ is farther away from $v_{23} = 1$ than is $v_{13} = 1$. The analysis likely becomes even more complex because of a possible Fermi resonance between $v_{13} = 1$ and $v_{24} = 2$.

As usual, the value of $J_{\text{max}}$ used in the fit is almost always decreasing for transitions involving energy levels with increasing $K_a$ quantum numbers. For $K_a = 0$, $J_{\text{max}}$ is 54, whereas for $K_a = 16$ it is 19. Excluded lines with higher quantum numbers are still unweighted in the fit file, but need to be treated with caution, considering that a proper treatment of interactions could lead to new assignments, since frequencies can be shifted up to several megahertz, and the spectra are crowded with lines. In this case, a new fit was performed by starting from scratch and increasing $J$ and $K_a$ step by step, with no improvement. A full treatment of interactions could enable to include all assigned lines in the future.

3.2. ground state of gauche-propanal, $v = 0 (E \approx 370 \text{cm}^{-1})$

The higher energy gauche conformer is an asymmetric top rotor with $\kappa = -0.9849$ quite close to the limiting prolate case. It is doubly-degenerate with $C_1$ symmetry. The low barrier between the two equivalent minima facilitates tunneling between them, lifting the degeneracy and creating a symmetric and an antisymmetric tunneling state which are often designated as $0^+$ and $0^-$, respectively. Since a non-vanishing transition dipole matrix element $\langle \psi_i \mid \mu_j \mid \psi_f \rangle$ is mandatory to observe a rotational transition, the wave functions $\psi_i$ and $\psi_f$ need to have the same symmetry for $a$- and $b$-type transitions ($x = a, b$). Hence, these transitions only occur within substates $0^+$ and $0^-$. However, the direction of $\mu_j$ is changing for the left and right handed version, for that reason c-type transitions occur between substates. The dipole moment components were determined as $\mu_{ax} = 2.645(5) \text{D}$, $\mu_{ay} = 0.417(6) \text{D}$, and $\mu_{az} = 1.016(3) \text{D}$, respectively [3]. The rotational spectrum of gauche with its Coriolis-type interactions was fit and predicted with Pickett’s SPFIT and SPCAT programs [21] and using Pickett’s reduced axis system [22]. We determined linear combinations of spectroscopic parameters $X^+$ and $X^-$ from the two substates, explicitly $X = (X^+ + X^-)/2$ and $\Delta X = (X^+ - X^-)/2$, see, e.g., Refs. [23, 24].

The two tunneling states may interact via Coriolis-type interaction of $a$- or $b$-type symmetry with the leading coefficients $F_{bc}$ and $F_{ac}$, respectively. The former connects in particular the upper energy asymmetry component of a given $J$ and $K_a$ with the lower energy asymmetry component of the same $J$ and $K_a$.

The strongest interactions occur for $K_a = 1$, $K_a = 2$, $K_a = 3$, $K_a = 4$, and $K_a = 5$ at $J = 2$, $J = 10$, $J = 22$, $J = 36$, and $J = 52$, respectively. Transitions involving these states are well described in our model. Due to a mixing of energy levels from $0^+$ and $0^-$ substates, also formal $x$-type transitions ($\Delta K_a$ and $\Delta K_e$ even) between these states are observed. The operator
Table 1: Spectroscopic parameters\(^a\) (MHz) of the ground state \((v = 0)\), first excited aldehyde \((v_{24} = 1)\) as well as first excited methyl torsion \((v_{23} = 1)\) of \(\text{syn-} \text{propanal}\).

| Parameter | \(v = 0\) | \(v_{24} = 1\) | \(v_{23} = 1\) |
|-----------|-----------|----------------|----------------|
| \(A\) | 16669.626420 (154) | 16712.057839 (167) | 16642.87187 (61) |
| \(B\) | 5893.503711 (49) | 5857.196275 (49) | 5871.180340 (171) |
| \(C\) | 4598.982111 (48) | 4595.250184 (50) | 4592.798935 (116) |
| \(\Delta K \times 10^4\) | 50.06226 (84) | 43.9445 (37) | 49.70451 (84) |
| \(\Delta JK \times 10^3\) | 19.370540 (153) | 17.5153 (34) | 18.097558 (232) |
| \(\delta K \times 10^4\) | 5.354247 (37) | 5.223946 (211) | 5.236678 (38) |
| \(\delta J \times 10^3\) | 4.211646 (164) | 1.6032 (32) | 4.22843 (30) |
| \(\Phi K \times 10^9\) | 986.40 (80) | −221.1 (104) | 1070.36 (179) |
| \(\Phi JK \times 10^9\) | −606.15 (37) | −143.2 (109) | −577.21 (64) |
| \(\Phi J \times 10^9\) | 77.271 (65) | −128.2 (92) | 62.316 (141) |

\(\Delta K \times 10^4\) | 0.94 | 0.93 | 1.06 |

\(\Delta JK \times 10^3\) | 65.681 (116) | 63.8032 (90) | 61.9026 (102) |
| \(\Delta J \times 10^3\) | 27.871 (60) | 28.5299 (48) | 28.4352 (82) |

\(\rho^b \times 10^3\) | 5084 | 2085 | 2860 |
| \(\Theta_{\text{RAM}}^c[\degree]\) | 5851 | 6823 | 2760 |

\(\text{Combined fit}\) | 3901 | 5084 | 2085 |
| \(\text{no. of lines}\) | 8551 | 6823 | 2760 |
| \(\text{rms error}^b\) | 0.94 | 0.93 | 1.06 |

\(^a\)Watson’s \(A\) reduction in the \(P\) representation was used in ERHAM. Numbers in parentheses are one standard deviation in units of the least significant figures. In the first block are rotational constants, in the second ERHAM tunneling parameters (in Watson’s \(S\) reduction), and in the last are general information about the fits.

\(^b\)Weighted unitless value for the entire fit.
with the $F_{ac}$ coefficient may connect levels of the same $J$ with $K_a$ and $K_c$ differing by an odd number. We did not have clear evidence for this type of interaction.

A splitting due to internal rotation of the methyl group was not observed in the present investigation.

Unfortunately, only $a$-type transitions could be assigned with confidence in our observed spectra, since intensities are proportional to the square of the dipole moment, and gauche is in general less populated than syn owing to Boltzmann statistics. The $b$-type transitions are by far too weak to be observed, but $c$-type transitions may have sufficient intensity to identify them in the spectrum. We found evidence for a $Q$-series type with $K'_b - K''_b = 5 - 4$, but the intensities of these lines were in some occasions too weak to assign them securely. Two $Q$-type $b$-type and one $R$-type $c$-type transition from the literature are unweighted in the fit due to conspicuously large deviations.

The fitting procedure was very different for gauche compared to syn. We started to fit all transitions with $K_a = 0$ up to $J = 45$, followed by series with $K_a = 1$, then $K_a = 2$, and so on. Later, transitions involving $J$ up to 60 were added. To assign and especially to fit transitions, originating in strongly perturbed energy levels, was quite challenging. For $K_a = 2$, transitions from unperturbed energy levels with higher $J$ quantum numbers were implemented earlier in the fit than those from perturbed ones. Otherwise the quality of the fit was too poor. It is possible that the fit converged into a different local minimum. In Figure 4 an easy assignable set of doublets, originating by tunneling rotation interaction, of $R$-type $a$-type transitions with $J' - J'' = 26 - 25$ is shown. Complications arose for transitions with $K_a = 12$, which should not be affected by Coriolis-type interactions. Here, the dataset could not be fit to the experimental uncertainties for $J > 38$, even though more transitions can be assigned securely still straightforwardly (517 in total). The strong lines in Fig. 4 illustrate the possibility of secure assignments to higher $K_a$ quantum numbers, up to $K_a = 22$. The observed deviations could originate from insufficiencies in our spectroscopic model or from interactions with other states, for example the first excited aldehyde torsion of gauche, and are shown exemplary for $K_a = 12$ in the supplementary material. The analysis of this excited state is beyond the scope of this paper. The fitting procedure was very different for gauche compared to syn. We started to fit all transitions with $K_a = 0$ up to $J = 45$, followed by series with $K_a = 1$, then $K_a = 2$, and so on. Later, transitions involving $J$ up to 60 were added. To assign and especially to fit transitions, originating in strongly perturbed energy levels, was quite challenging. For $K_a = 2$, transitions from unperturbed energy levels with higher $J$ quantum numbers were implemented earlier in the fit than those from perturbed ones. Otherwise the quality of the fit was too poor. It is possible that the fit converged into a different local minimum. In Figure 4 an easy assignable set of doublets, originating by tunneling rotation interaction, of $R$-type $a$-type transitions with $J' - J'' = 26 - 25$ is shown. Complications arose for transitions with $K_a = 12$, which should not be affected by Coriolis-type interactions. Here, the dataset could not be fit to the experimental uncertainties for $J > 38$, even though more transitions can be assigned securely still straightforwardly (517 in total). The strong lines in Fig. 4 illustrate the possibility of secure assignments to higher $K_a$ quantum numbers, up to $K_a = 22$. The observed deviations could originate from insufficiencies in our spectroscopic model or from interactions with other states, for example the first excited aldehyde torsion of gauche, and are shown exemplary for $K_a = 12$ in the supplementary material. The analysis of this excited state is beyond the scope of this paper.

### Table 2: Spectroscopic parameters

| Parameter | $X$ | $\Delta X$ |
|-----------|-----|------------|
| $E$       | 237.7953 (98) | 237.7953 (98) |
| $B$       | 26250.6640 (148) | 26250.6640 (148) |
| $C$       | 4148.01846 (117) | 4148.01846 (117) |
| $\Delta K$ | 2.1000 (41) | 2.1000 (41) |
| $\Delta K_J$ | -0.1794215 (84) | -0.1794215 (84) |
| $\Delta_{1J}$ | 6.58936 (136) | 6.58936 (136) |
| $d_1$ | 1.082322 (88) | 1.082322 (88) |
| $d_2$ | -38.36 (41) | -38.36 (41) |
| $H_{KJ}$ | 9.613 (70) | 9.613 (70) |
| $H_{JK}$ | -3.3404 (164) | -3.3404 (164) |
| $H_J$ | 127.294 (252) | 127.294 (252) |
| $h_1$ | -52.463 (193) | -52.463 (193) |
| $h_2$ | -0.463 (40) | -0.463 (40) |
| $h_3$ | 0.01814 (181) | 0.01814 (181) |
| $L_{KJK}$ | -4.318 (220) | -4.318 (220) |
| $L_{JK}$ | -2.263 (73) | -2.263 (73) |
| $L_{J}$ | 145.05 (216) | 145.05 (216) |
| $I_1$ | 2.1031 (150) | 2.1031 (150) |
| $P_{JK}$ | -0.1243 (34) | -0.1243 (34) |
| $P_J$ | 0.07098 (299) | 0.07098 (299) |

$^a$Watson’s $S$ reduction was used with SPEFT in the $\overrightarrow{I}$-representation. Parameters were fit as linear combinations $X = (X^+ + X^-)/2$ and $\Delta X = (X^+ - X^-)/2$. Values of $F_{ac}$, etc., given between two columns, are associated with operators between both tunneling states; $\Delta X$ is not defined for these parameters. Numbers in parentheses are one standard deviation in units of the least significant figures.

$^b$Weighted unitless value for the entire fit.
4. Discussion and conclusion

The ground and first excited aldehyde torsion of syn can be assigned and modeled quite straightforwardly. The improvement of centrifugal distortion constants leads to faithful predictions even in higher frequency regions. The description of these states with a total of 15374 newly assigned and fitted transitions provides satisfactory synthetic spectra for state-of-the-art astronomical observation standards. Only predictions for b-type transitions with $K_a$ quantum numbers much higher than implemented in the fit should be treated with caution, see subsection 3.1.2.

Parameters describing the first excited methyl torsion are quite different compared to the other two states. Since it was treated as an isolated state, but there is evidence that it is perturbed, the model is adequate only for transitions with quantum numbers implemented in the fit. Varying magnitudes of the observed splittings due to internal rotation of the methyl group for the various studied states can be explained roughly with the classical tunneling scheme: Higher relative energies of vibrationally excited states, consequently, smaller energy differences to the potential barrier height of 793.7 cm$^{-1}$ lead in general to larger splittings. This results in increasing magnitude of the energy tunneling parameter $\epsilon_{10}$, from the ground state $\epsilon_{10} = -3.0941$ (57) MHz ($E_{rel} = 0$ cm$^{-1}$) to the first aldehyde torsion $\epsilon_{10} = 38.7984$ (68) MHz ($E_{rel} = 135.1$ cm$^{-1}$) up to the first excited methyl torsion $\epsilon_{10} = 130.5541$ (250) MHz ($E_{rel} = 219.9$ cm$^{-1}$).

Modelling of gauche is somewhat more difficult. Most of the lines can be assigned confidently, but the treatment, even with Coriolis interaction, seems insufficient. The large residuals may be caused by perturbations caused by a yet unidentified state. Wrong assignments not yet identified could also be an explanation as could be the inadequacy of the effective Hamiltonian, or that the large parameter space causes the fit to not converge into the global minimum. Sometimes the fit is converging and the parameter values are reasonable with different sets of parameters, so the right choice is not obvious, nor unambiguous. Missing b- and c-type transitions may affect the description of the $K$-level structure, and may, in turn, be a reason for our inability to determine $F_{ac}$ with confidence. The magnitude of $F_{ac}$ may well be larger than that of $F_{bc}$, as, for example, in ethanethiol [24] or hydroxyacetone [25]; see also the theoretical treatment of the reduced axis system [22]. The omission of $F_{ac}$ may influence the ability to determine higher order parameters or affect their values. Complications by describing molecules with two stable degenerate forms and necessary treatment of Coriolis interactions occurred already before [26, 27]. For conformer I of cyanacetaldehyde only transitions up to $K_a = 2$ for $0^+$ and up to $K_a = 8$ for $0^-$-state are employed in the fit and moreover transitions with $J$ equal to 30, 31, and 32 needed to be excluded [26]. For synclinal mercaptoacetone, the standard deviation is four times larger than the expected experimental uncertainty and again special kinds of transitions were excluded, regarding large deviations between experimental and calculated frequencies [27]. For gauche propanal, a first model is now available into the submillimeter wave region.

![Figure 5: Sections of the ALMA-PILS radio astronomical spectrum toward a position offset from one of the components in the protostellar binary (see Refs. 13 and 15 for details) displaying selected emission features of propanal. The observed spectrum is shown in solid gray lines, the initial model is indicated by dashed blue lines, and the new model by solid red lines. The upper state observed spectrum is shown in solid gray lines, the initial model is indicated by symbols, and the new model by solid red lines. The position of the transitions are indicated. The high-$J$, low-$K_a$ transitions are blends of two $a$-type and two $b$-type $R$-type transitions which all have $K_c = J - K_a$, where $K_a$ is the lower one of two and the one shown.](image-url)
This extensive study of propanal could lead to a better understanding of the behavior of complex molecules with two large amplitude motions, here originating from its two functional groups, the aldehyde and methyl groups.

With the newly derived constants of this work the synthetic spectra of syn and gauche should satisfy the requirements in sensitivity and accuracy of astronomical observations nowadays, even for warm environments. We have modeled the propanal emission lines with the new predictions and compare them with those previously available. As can be seen in Fig. 5 (b-type) transitions with high \( K_a \) and low \( J \) appear weaker, broader, and slightly shifted because of the consideration of the methyl internal rotation in the present predictions. Overprediction of line intensities does not occur anymore. Transitions with high \( J \) and low \( K_a \), on the other hand, are shifted by up to half a line-width; whenever the shift is large, the agreement is much better with the new predictions.

Predictions of the rotational spectra of syn- and gauche-propanal are available in the catalog section\(^2\) of the CDMS\(^2\)\(^9\). In addition, line, parameter, and fit files, along with other auxiliary files, are available in the spectroscopy data section\(^2\) of the CDMS.

Acknowledgments

We thank Hanno Schmiedt for group theory discussions and Matthias Ordu for the extended version of ERHAM. This work has been supported by the Collaborative Research Centre 956, project B3, and the Gerätezentrum “Cologne Center for Terahertz Spectroscopy”, both funded by the Deutsche Forschungsgemeinschaft (DFG). OZ acknowledges support from the Bonn-Cologne-Graduate School of Physics and Astronomy (BCGS). JKJ acknowledges support from the European Union’s Horizon 2020 research and innovation programme through ERC Consolidator Grant “S4F” (grant agreement No 646908).

Appendix A. Supplementary Material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi: xyz.

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\(^2\)http://www.astro.uni-koeln.de/cdms

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