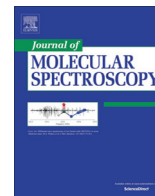




Contents lists available at ScienceDirect

## Journal of Molecular Spectroscopy

journal homepage: [www.elsevier.com/locate/jms](http://www.elsevier.com/locate/jms)

## Millimeter and submillimeter wave spectroscopy of propanal

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## ARTICLE INFO

## Article history:

Received 12 May 2017

In revised form 28 June 2017

Accepted 6 July 2017

Available online xxxxx

## Keywords:

Propanal

Rotational spectroscopy

Submillimeter wave spectroscopy

Interstellar molecule

Internal rotation

Tunneling rotation interaction

## ABSTRACT

The rotational spectra of the two stable conformers *syn*- and *gauche*-propanal (CH<sub>3</sub>CH<sub>2</sub>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.

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## 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. Furtheron 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<sup>-1</sup> 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<sup>-1</sup> and the first excited methyl torsion  $\nu_{23} = 1$  is 219.9 cm<sup>-1</sup> above the ground state of *syn* [4]; note that the methyl torsional assignments have been exchanged between *syn*

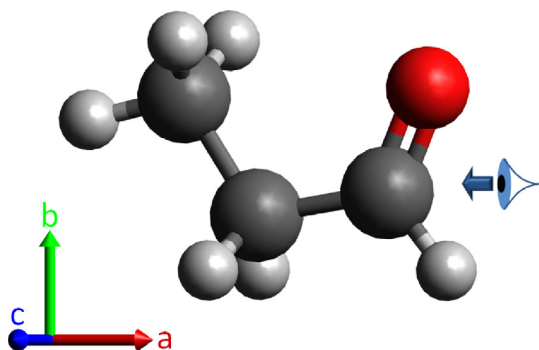
and *gauche* from Ref. [4] to Ref. [5]. In the former work the energy difference between the conformers was redetermined as  $\sim 421$  cm<sup>-1</sup>, whereas in the latter work it was determined to be  $\sim 370$  cm<sup>-1</sup>.

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].

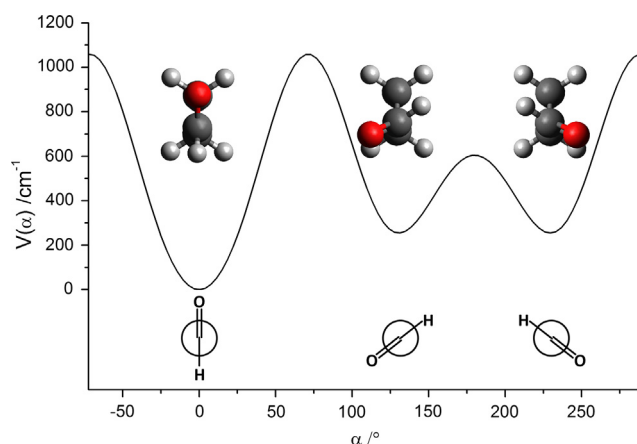
Two groups measured further transitions of *syn* independently of each other in the frequency region from 8 to 38 GHz using a Stark-modulated and a Fourier transform microwave spectrometer, respectively, but published it jointly [6]. They used a S-type centrifugal distortion analysis to guarantee a correct 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  $\sim 793.7$  cm<sup>-1</sup>. For *gauche* it is  $\sim 886$  cm<sup>-1</sup> 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 superheterodyne detection [8]. Structural information on either conformer were derived from twelve isotopologues of *syn* and six of *gauche* [9].

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**Fig. 1.** Sketch of *syn* propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$ . White spheres designate hydrogen, black ones carbon, and the red one oxygen atoms. All heavy atoms, three carbon and one oxygen, are in the *ab*-plane. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Calculated potential energy surface of propanal with respect to the rotation of the aldehyde group [4]. 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. 1. 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](#). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the homologous series of alkanals, the three smallest members, methanal, ethanal, and propanal were already detected in space [10–12]. 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  $1 \text{ km s}^{-1}$  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 ( $\sim 10 \text{ mW}$ ) 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  $0.1 \mu\text{bar}$  and the cell was filled with a commercially available sample of propanal (97%) from Sigma-Aldrich to a total pressure of about  $20 \mu\text{bar}$  (2 Pa). Frequency modulation (FM;  $\sim 50 \text{ kHz}$ , 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 Fig. 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 more often than limitations in the signal-to-noise ratio. Figs. 3 and 4 already give a hint of the line confusion, however they were chosen to clarify different aspects of the spectra, so there are much more crowded frequency regions. Thus far, about 15% of the observed lines could be assigned to the ground states of both conformers and to the two lowest vibrationally excited states of *syn*.

### 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

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