

# Submillimeter spectroscopy of $\text{H}_2\text{C}^{17}\text{O}$ and a revisit of the rotational spectra of $\text{H}_2\text{C}^{18}\text{O}$ and $\text{H}_2\text{C}^{16}\text{O}$

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## Abstract

The rotational spectrum of the formaldehyde isotopologue  $\text{H}_2\text{C}^{17}\text{O}$  was investigated between 0.56 and 1.50 THz using a sample of natural isotopic composition. In addition, transition frequencies were determined for  $\text{H}_2\text{C}^{18}\text{O}$  and  $\text{H}_2\text{C}^{16}\text{O}$  between 1.37 and 1.50 THz. The data were combined with critically evaluated literature data to derive improved sets of spectroscopic parameters which include  $^{17}\text{O}$  or H nuclear hyperfine structure parameters.

## Keywords:

formaldehyde, rotational spectroscopy, terahertz spectroscopy, interstellar molecule, hyperfine structure

## 1. Introduction

As a simple four-atomic molecule, formaldehyde,  $\text{H}_2\text{CO}$ , also known as methanal, is of great fundamental interest. Its rotational spectrum is of great importance for radio astronomy. It was only the seventh molecule to be detected in the interstellar medium in 1969 [1], the fourth one that was detected by means of radio astronomy and only the third poly-atomic molecule; see, for example, the Interstellar & Circumstellar Molecules page<sup>1</sup> of The Astrochymist<sup>2</sup>. In the detection letter, the molecule was observed in absorption toward strong continuum sources, most of them dense and warm molecular clouds, so-called hot-cores. Formaldehyde was also detected in cold dark clouds, which are also dense, with the  $^1\text{H}$  hyperfine structure (HFS) splitting partially resolved [2], and in less dense translucent [3] and even less dense diffuse clouds [4]. It was also detected in the circumstellar envelopes of late-type stars, such as the C-rich protoplanetary nebula around V353 Aur [5], also known as AFGL 618, CRL 618, or the Westbrook Nebula, the O-rich protoplanetary nebula around QX Pup [6], also known as OH231.8+4.2 or the Rotten Egg Nebula, or the C-rich asymptotic giant branch star CW Leo [7], also known as IRC+10216 or the Peanut Nebula. The  $\text{H}_2\text{CO}$  molecule was the second molecule after OH to be detected in galaxies different from our Milky Way, here the two near-by galaxies NGC 253 and NGC 4945 [8]; it was also detected in more distant galaxies [9]. Formaldehyde is also one of the few molecules for which maser activity was not only detected in galactic sources [10], but also in extragalactic sources [11].

Numerous minor isotopic species were also detected in space, among them  $\text{H}_2^{13}\text{CO}$  [12],  $\text{H}_2\text{C}^{18}\text{O}$  [13], HDCO [14], and

$\text{D}_2\text{CO}$  [15] as the first multiply deuterated molecule in space. Unlabeled atoms refer to  $^1\text{H}$ ,  $^{12}\text{C}$ , and  $^{16}\text{O}$ . The detection of  $\text{D}_2\text{CO}$  was made in the Orion KL region, a site of high-mass star formation, where deuterium in formaldehyde was enriched by several orders of magnitudes with respect to the interstellar D/H ratio of  $\sim 1.5 \times 10^{-5}$ . Even higher degrees of deuteration were found in the molecular clouds surrounding low-mass proto-stars, such as IRAS 16293-2422 [16]. In fact, deuteration has become a means to investigate the evolutionary stage of low-mass proto-stars. The  $\text{H}_2\text{CO}$  main species may be used to probe the density in denser regions of the interstellar medium [17] and to determine the kinetic temperature [18]. The ratios of  $\text{H}_2^{13}\text{CO}$  to  $\text{H}_2\text{C}^{18}\text{O}$  have been used to infer the  $^{13}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$  double ratio in molecular clouds [19, 20], which in turn may be used to determine  $^{12}\text{C}/^{13}\text{C}$  and/or  $^{16}\text{O}/^{18}\text{O}$  ratios.

Formaldehyde was also seen in Earth's stratosphere employing microwave limb-sounding with the Odin satellite [21]; it is more commonly studied in the troposphere using infrared or UV/visible spectroscopy among other techniques [21]. The molecule was also detected in the comae of several comets, the first one being comet Halley, where it was identified tentatively by infrared spectroscopy [22, 23], later unambiguously using microwave spectroscopy [24].

Formaldehyde was among the first molecules whose rotational spectrum and dipole moment were studied by means of microwave spectroscopy [25]. A plethora of further studies on the rotational spectrum of  $\text{H}_2\text{CO}$ , its isotopologues, not only in the ground, but also excited vibrational states were published over the years. The rotational spectra of  $\text{H}_2\text{CO}$  and its isotopologues began to be explored in the terahertz region in the second half of the 1990s, starting with the main isotopologue [26]. Investigations of HDCO and  $\text{D}_2\text{CO}$  [27],  $\text{H}_2^{13}\text{CO}$  [28],  $\text{H}_2\text{C}^{18}\text{O}$  [29], and again  $\text{H}_2\text{CO}$  [30] followed. The most recent study involved studies of HDCO and  $\text{D}_2\text{CO}$  samples between 1.1 and 1.5 THz [31]. Important data were obtained for numerous iso-

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

<sup>2</sup><http://www.astrochymist.org/>

topic species with  $\text{HD}^{13}\text{C}^{18}\text{O}$  and  $\text{D}_2^{13}\text{C}^{18}\text{O}$  being the rarest ones. In addition, the data sets of the already well-characterized HDCO and  $\text{D}_2\text{CO}$  isotopic species were improved somewhat [31]. Excited vibrational states of  $\text{H}_2\text{CO}$  were also investigated up to terahertz frequencies [32]. The spectroscopic parameters were improved by ground state combination differences (GSCDs) for  $\text{H}_2\text{CO}$  [33] and by far-infrared spectra for  $\text{D}_2\text{CO}$  [34] and  $\text{D}_2^{13}\text{CO}$  [35]. In addition, the rotational spectra of formaldehyde in the ground and excited vibrational states were used to characterize a spectrometer system based on difference frequency generation [36].

The most abundant formaldehyde isotopic species, for which terahertz data are lacking, is  $\text{H}_2\text{C}^{17}\text{O}$ . Assuming that  $\text{H}_2^{13}\text{C}^{18}\text{O}$  is too rare to be detected at submillimeter wavelengths,  $\text{H}_2\text{C}^{17}\text{O}$  is the only one for which terahertz data are needed. Flygare and Lowe studied five  $a$ -type  $Q$ -branch transitions below 14 GHz which had  $K_a = 1$  and 2 and resolved the  $^{17}\text{O}$  HFS splitting almost completely [37]. Davies et al. extended the measurements up to 150 GHz with HFS resolved to a varying degree [38]. These data were superseded by more extensive and more accurate measurements by Cornet et al. which extended up to 294 GHz and which were reported only shortly thereafter [39].

In order to improve the predictions of the rotational spectrum of  $\text{H}_2\text{C}^{17}\text{O}$  especially for observations with the Atacama Large Millimeter/submillimeter Array (ALMA) [40], we recorded transitions from 0.56 THz up to 1.50 THz. Additionally, we recorded transitions of  $\text{H}_2\text{C}^{18}\text{O}$  and  $\text{H}_2\text{C}^{16}\text{O}$  in the region of 1.37 THz to 1.50 THz. We combined our new data with previously reported data for which the initially reported uncertainties were critically evaluated. This led to improved spectroscopic parameters which include  $^{17}\text{O}$  or H nuclear hyperfine structure parameters.

## 2. Experimental details

The rotational spectrum of  $\text{H}_2\text{C}^{17}\text{O}$  was recorded in selected regions between 568 and 658 GHz and between 848 and 927 GHz with the Cologne Terahertz Spectrometer (CTS) that is described in detail elsewhere [41]. Two phase-locked backward wave oscillators (OB 80, OB 82) were used as sources and a magnetically tuned, liquid-He-cooled InSb hot electron bolometer (QMC Instruments Ltd.) was used as detector. The measurements were carried out in a 4 m long glass cell at room temperature at pressures around 1 to 2 Pa. The cell was equipped with windows made from high density polyethylene (HDPE). Our study on  $\text{H}_2\text{CO}$  [30] may serve as an example for the accuracy achievable with the CTS.

Rotational spectra of  $\text{H}_2\text{C}^{17}\text{O}$ ,  $\text{H}_2\text{C}^{18}\text{O}$ , and  $\text{H}_2\text{C}^{16}\text{O}$  were recorded in selected regions between 1.35 and 1.50 THz using a VDI (Virginia Diodes, Inc.) Amplified Multiplier Chain driven by an Agilent E8257D microwave synthesizer as source and an InSb bolometer as detector. Measurements were carried out in a 3 m long glass cell at room temperature at pressures around 1 to 2 Pa for weaker lines, down to around 0.1 Pa for stronger lines. The cell was again equipped with HDPE windows. Our study on low-lying vibrational states  $v_8 \leq 2$  of methyl cyanide

[42] may serve as an example for the accuracy achievable with this spectrometer system.

Formaldehyde was generated by heating a small sample of commercial paraformaldehyde briefly with a heat-gun. Frequency modulation was used throughout with demodulation at  $2f$ , which causes an isolated line to appear approximately as a second derivative of a Gaussian.

## 3. Spectroscopic analysis

$\text{H}_2\text{C}^{16}\text{O}$  is an asymmetric top molecule close to the prolate limit ( $\kappa = -0.9610$  with a dipole moment of 2.3317 D [43]) along the  $a$  inertial axis, which is also the  $\text{C}_2$  symmetry axis. The asymmetry and the dipole moment change only slightly with isotopologue. The two equivalent H nuclei lead to spin-statistical weight factors of 1 and 3 for rotational states with  $K_a$  even (*para*) and odd (*ortho*), respectively. At high resolution, HFS splitting may be resolved for *ortho* transitions. This is usually only achieved at radio frequencies (RF) or in the microwave (MW) region. The splitting was also resolved in astronomical observations of colder environments, but only for  $K_a = 1$  and low values of  $J$ .

Even though formaldehyde's proximity to the prolate limit would make Watson's  $S$  reduction the natural choice for fitting of its rotationally resolved spectra to some spectroscopists, use of the  $A$  reduction is not so far-fetched. In fact, it was the  $A$  reduction that was most commonly applied until fairly recently [26, 27]. There was only one detailed consideration of the  $S$  reduction in earlier reports [44], but the results present for the main isotopologue were actually slightly worse in the  $S$  reduction. The advantage of the  $S$  reduction has only lately become increasingly apparent in most of the diagonal distortion parameters which are smaller in magnitude for the sextic distortion parameters in the  $S$  reduction compared to the  $A$  reduction, and the differences are more pronounced in the octic distortion parameters [28, 30, 33]. The situation is less clear for the off-diagonal distortion parameters,  $d_1$ ,  $d_2$ , etc. in the  $S$  reduction,  $\delta_K$ ,  $\delta_J$ , etc. in the  $A$  reduction. But it is the large number of off-diagonal distortion parameters needed to fit the formaldehyde spectra and their relatively large magnitudes which cause the pronounced differences between the two reductions.

Prediction and fitting of the rotational spectra were made with Pickett's SPCAT and SPFIT programs [45]. Our new data were fit together with previously reported line frequencies, and we consulted the original references to check for the reported uncertainties. In almost all instances, we used the initially reported uncertainties, which is different from some studies where uncertainties had been increased considerably, usually without justification. In very few cases of transition frequencies with larger residuals, the uncertainties were increased slightly or the transition frequencies were omitted from the line lists. Transitions with HFS splitting were used as such. In order to keep the line list short, each isotopic species was defined twice in its parameter file, with and without HFS. Overlapping HFS or asymmetry components were treated in the fit as intensity-weighted averages, in contrast to most other fitting programs

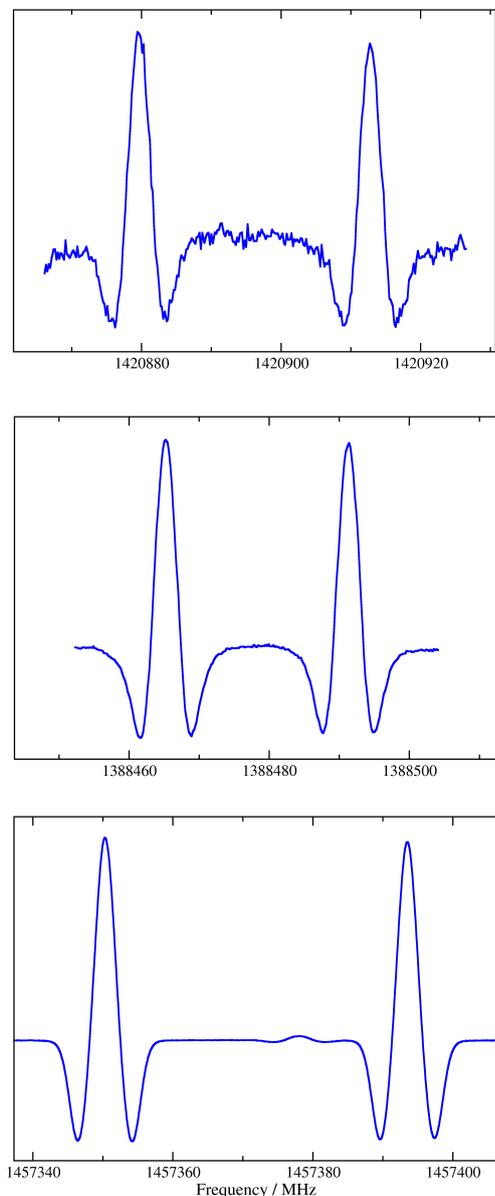


Figure 1: Detail of the formaldehyde terahertz spectrum displaying the  $J = 20 - 19$ ,  $K_a = 5$  rotational transitions of  $\text{H}_2\text{C}^{17}\text{O}$ ,  $\text{H}_2\text{C}^{18}\text{O}$ , and  $\text{H}_2\text{C}^{16}\text{O}$  (from top to bottom) with resolved asymmetry splitting. The asymmetry splitting of  $\text{H}_2\text{C}^{17}\text{O}$  is between those of the heavier and the lighter isotopologue, as can be expected. The weak feature near 1457378 MHz in the bottom panel is unassigned.

which treat each overlapping components as one piece of information with exactly the assigned frequency, which may increase the rms error unless uncertainties were increased beyond the usual extent.

Some higher order parameters were evaluated from other isotopic species, usually  $\text{H}_2\text{C}^{16}\text{O}$ , by scaling the parameters with appropriate powers of  $B + C$  and  $B - C$ ;  $A - (B + C)/2$  was very similar among the three species and was not considered for scaling. Even if such scaling is not the best choice for all parameters, it is often a good approximation. Such scaling was used, for example, for  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopic species of methyl cyanide [46].

There are different sign conventions concerning the nuclear spin-rotation parameters and the nuclear spin-nuclear spin coupling parameters. The sign conventions in SPFIT are such that in the first case the magnetic moment of H is positive. This convention is common nowadays in rotational spectroscopy, e.g., [43], but is opposite to nuclear magnetic resonance and to earlier rotational studies, e.g., [37, 39]. The sign convention in the second case is that the nuclear spin-nuclear spin coupling parameters of homo-diatomics are negative; there appears to be no clear preference for this or for the opposite sign convention.

### 3.1. $\text{H}_2\text{C}^{17}\text{O}$

The  $^{17}\text{O}$  isotope is the rarest of the stable oxygen isotopes with a terrestrial abundance of 0.00038 [47]. The isotope possesses a nuclear spin of 5/2 which gives rise to HFS splitting caused by the nuclear electric quadrupole and the nuclear magnetic dipole moments.

Initial predictions of the rotational spectrum of  $\text{H}_2\text{C}^{17}\text{O}$  were generated from the data reported by Flygare and Lowe [37] and Cornet et al. [39]. Both studies resolved  $^{17}\text{O}$  HFS splitting to a different degree depending on the quantum numbers and the frequency region; no HFS splitting caused by the H nuclei was reported. Initial spectroscopic parameters were taken from the latter study which were converted to the  $S$  reduction subsequently. Additional higher order parameters were derived from  $\text{H}_2\text{C}^{16}\text{O}$  [30]. The initially reported uncertainties were used for essentially all transition frequencies and essentially all reported HFS information was used. Some modifications were made to the list of transition frequencies from Ref. [37]. There was a typographical error in the  $1_{10} - 1_{11}$  center frequency; an increase by 0.5 MHz is agrees almost within uncertainty with the frequency calculated from the final set of spectroscopic parameters and was used in the final line list. The remaining data were reproduced slightly outside the uncertainties on average. Therefore, uncertainties of the more poorly fitting data,  $2_{11} - 2_{12}$  center frequency and of two HFS splittings of the  $6_{24} - 6_{25}$  transition were doubled. In addition, one HFS splitting of the  $2_{11} - 2_{12}$  transition, involving a weak HFS component, was omitted. These modifications affected obviously the partial rms error of this data set and, to a lesser extent, the rms error of the entire fit; the parameter values and their uncertainties were only slightly affected.

Despite the low  $^{17}\text{O}$  isotopic abundance, the strengths of the formaldehyde absorption lines were sufficient to obtain reasonable signal-to-noise ratios for  $\text{H}_2\text{C}^{17}\text{O}$  lines in the present study,

see Fig. 1. The detected transitions involve  $\Delta K_a = 0$   $R$ -branch transitions with  $7 \leq J \leq 22$  and  $K_a$  up to 7. None of the observed transitions displayed HFS splitting, as may be expected.

The spectroscopic parameters determined in the final fit are almost complete up to sixth order, only  $H_K$  and  $H_J$  were kept fixed to the estimated values. In addition, two independent quadrupole parameters,  $\chi_{aa}$  and  $\chi_{bb}$ , were determined along with three nuclear spin-rotation parameters.  $C_{cc}$  was retained in the fit because its uncertainty is commensurate with those of  $C_{aa}$  and  $C_{bb}$ . The value and the uncertainty of  $\chi_{cc}$  were derived from the tracelessness of the quadrupole tensor. An edited version of the fit file is available as supplementary material. The final spectroscopic parameters of  $\text{H}_2\text{C}^{17}\text{O}$  are given in Table 1 together with those of  $\text{H}_2\text{C}^{18}\text{O}$  and  $\text{H}_2\text{C}^{16}\text{O}$ . The rms error of the final fit is 0.870, meaning that the experimental data have been reproduced within their uncertainties on average. The partial rms errors are 1.019, 0.793, and 0.903 for the data from Flygare and Lowe [37], from Cornet et al. [39], and from the present investigation, respectively.

### 3.2. $\text{H}_2\text{C}^{18}\text{O}$

The  $^{18}\text{O}$  isotope has a terrestrial abundance of 0.0020, more than five times that of  $^{17}\text{O}$  [47]. The abundance difference translates into a gain of signal-to-noise or a shorter integration time by a factor of  $\sim 30$  or an appropriate combination, see Fig. 1. Initial predictions of its rotational transitions were taken from the Cologne Database for Molecular Spectroscopy, CDMS [48, 49]; these data are based on our previous study of  $\text{H}_2\text{C}^{18}\text{O}$  [29]. The transitions recorded in the present study cover  $\Delta K_a = 0$   $R$ -branch transitions with  $19 \leq J \leq 22$  and  $K_a$  up to 11.

Among the previously published data, resolved HFS splitting was reported for two  $\Delta K_a = 0$   $Q$ -branch transition with  $K_a = 1$  and  $J = 1$  [50] and 2 [51], respectively. This HFS information was used in the present investigation especially to facilitate astronomical observations. Initial sets of  $^1\text{H}$  HFS parameters were derived from the main isotopic species, see Sect. 3.3. Neglecting vibrational effects, the spin-spin coupling parameters are expected to be equal, and the spin-rotation parameters  $C_{gg}$  scale with the respective rotational parameters  $B_g$ . A satisfactory fit was obtained with just the spin-spin coupling parameter  $S(\text{HH})$  and  $C_- = (C_{bb} - C_{cc})/4$  released. These are the parameters on which the HFS splitting of these transitions depends to first order. No combination of three or even four  $^1\text{H}$  HFS parameters yielded a significantly better fit. Moreover, the changes from the initial parameters were deemed to be too large for some of the parameters if more than two parameters were released in the fits. In case of the  $J = 1$  transition frequencies, the  $F = 0 - 1$  and  $F = 2 - 2$  HFS components differ by  $\sim 0.8$  kHz, and the transition frequency published for the latter component corresponded much better to the intensity-weighted average of the two components. Therefore, we assigned the frequency to the intensity-weighted average in the final fit. In case of the  $J = 2$  transitions, the  $F = 2 - 2$  and  $F = 2 - 3$  HFS components are close in frequency, and the frequency assigned to the stronger  $F = 2 - 2$  component differed considerably from the calculated position for this component as well as for the

intensity-weighted average of the two components. Therefore, this transition frequency was omitted from the final fit.

All further rotational data were used as in our previous analysis [29]. These involve a large body of MW and mmW data from Cornet and Winnewisser [52] along with three RF transition [53] and one mmW transition [54]. The set of spectroscopic parameters determined for  $\text{H}_2\text{C}^{18}\text{O}$  is almost the same as for  $\text{H}_2\text{C}^{17}\text{O}$ , except that  $H_J$  was released in the fit of the former. An edited version of the fit file is available as supplementary material. The final spectroscopic parameters of  $\text{H}_2\text{C}^{18}\text{O}$  are also given in Table 1. The rms error of the entire fit is 0.735, indicative of conservative uncertainties in some data sets. The partial rms error of the HFS containing data [50, 51] in the fit is 1.065, that from Refs. [52, 53] are 0.825 and 0.567, respectively. Finally, the rms errors of our previous [29] and present studies are 0.556 and 0.903, respectively.

### 3.3. $\text{H}_2\text{C}^{16}\text{O}$

Initial predictions of the rotational transitions of the main isotopic species were also taken from the CDMS [48, 49]; these data are based on our previous study of  $\text{H}_2\text{C}^{16}\text{O}$  [30]. In the present investigation, frequencies were determined for  $\Delta K_a = 0$   $R$ -branch transitions with  $18 \leq J \leq 21$  and  $K_a$  up to 15, for four  $\Delta K_a = 2$  transitions, and for one  $\Delta K_a = 0$   $Q$ -branch transition with  $J = 26$  and  $K_a = 1$ .

In order to determine the best possible set of HFS parameters, in particular for astronomical observations, we evaluated the information in the available original reports because effects of HFS were usually omitted in previous studies [26, 30, 52, 54]. In the course of this process, we noticed that uncertainties of previous data were increased in Ref. [26] to usually 1 kHz in cases in which the originally reported uncertainties were smaller than this value. The most likely explanation would be the difficulty to reproduce the data to within the reported uncertainties. This, in turn, may be explained by the reluctance to use a sufficiently large set of off-diagonal distortion parameters or by the adherence to the A reduction. In addition, uncertainties appeared to have been increased for transitions with unresolved asymmetry splitting for which the calculated asymmetry splitting was much larger than the uncertainties.

As in the case of  $\text{H}_2\text{C}^{18}\text{O}$ , resolved HFS splitting was reported for two  $\Delta K_a = 0$   $Q$ -branch transition with  $K_a = 1$  and  $J = 1$  [50] and 2 [51], respectively; the  $J = 2$ ,  $F = 2 - 2$  transition frequency omitted for  $\text{H}_2\text{C}^{18}\text{O}$  was also omitted for  $\text{H}_2\text{C}^{16}\text{O}$ . Further HFS information originated from an RF investigation of  $\text{H}_2\text{C}^{16}\text{O}$  [55].

Hyperfine free transition frequencies were taken from Ref. [26] with additional original data [52, 54, 55, 56, 57, 58, 59]. Further data come from our previous study [30], from a study of a spectrometer system employing difference frequency generation [36], and from GSCDs generated from IR spectra in the  $3.5 \mu\text{m}$  region [60] which were used in a previous ground states study [33].

In almost all instances, we use here the originally reported uncertainties; only in very few cases uncertainties were increased slightly if residuals were larger than the reported uncer-

Table 1: Spectroscopic parameters<sup>a</sup> (MHz) of formaldehyde isotopologues with <sup>17</sup>O, <sup>18</sup>O, and <sup>16</sup>O along with number of lines and rms error (both unit less).

Parameter	H <sub>2</sub> C <sup>17</sup> O	H <sub>2</sub> C <sup>18</sup> O	H <sub>2</sub> C <sup>16</sup> O
$A - (B + C)/2$	246452.397 (95)	247253.578 (54)	245551.4495 (40)
$(B + C)/2$	35513.40370 (32)	34707.84108 (25)	36419.11528 (25)
$(B - C)/4$	1148.454801 (90)	1097.2174152 (59)	1207.4358721 (33)
$D_K$	19.448 (33)	19.5203 (151)	19.39136 (53)
$D_{JK}$	1.257644 (30)	1.2021350 (85)	1.3211073 (93)
$D_J \times 10^3$	67.10965 (90)	64.30788 (135)	70.32050 (50)
$d_1 \times 10^3$	-9.70379 (87)	-9.08202 (31)	-10.437877 (47)
$d_2 \times 10^3$	-2.27013 (64)	-2.07709 (38)	-2.501496 (33)
$H_K \times 10^3$	4.03	4.03	4.027 (22)
$H_{KJ} \times 10^6$	6.13 (56)	2.615 (77)	10.865 (79)
$H_{JK} \times 10^6$	6.949 (25)	6.380 (9)	7.465 (16)
$H_J \times 10^9$	5.70	9.41 (170)	3.54 (33)
$h_1 \times 10^9$	26.67 (135)	27.23 (51)	32.272 (58)
$h_2 \times 10^9$	43.47 (50)	37.60 (27)	47.942 (74)
$h_3 \times 10^9$	13.87 (27)	12.135 (67)	15.966 (15)
$L_K \times 10^6$	-0.610	-0.610	-0.610 (177)
$L_{KKJ} \times 10^9$	-5.7	-5.5	-5.85 (19)
$L_{JK} \times 10^9$	0.35	0.33	0.367 (85)
$L_{JJK} \times 10^9$	-0.098	-0.091	-0.1057 (92)
$l_2 \times 10^{12}$	-0.30	-0.26	-0.345(50)
$l_3 \times 10^{12}$	-0.36	-0.31	-0.427(19)
$l_4 \times 10^{12}$	-0.126	-0.104	-0.1520 (32)
$p_5 \times 10^{18}$	2.60	2.06	3.33
<sup>17</sup> O hyperfine parameters			
$\chi_{aa}$	-1.903 (16)		
$\chi_{bb}$	12.381 (10)		
$\chi_{cc}^b$	-10.478 (10)		
$C_{aa} \times 10^3$	-366.4 (25)		
$C_{bb} \times 10^3$	-26.5 (8)		
$C_{cc} \times 10^3$	0.4 (8)		
<sup>1</sup> H hyperfine parameters			
$S(\text{HH}) \times 10^3$		-17.933 (98)	-17.685 (42)
$C_{  *} \times 10^3{}^c$		-3.391	-3.368 (46)
$C_{\perp} \times 10^3{}^c$		-0.2481	-0.2603 (135)
$C_{-} \times 10^3{}^c$		1.0943 (136)	1.1292 (80)
$C_{aa} \times 10^3{}^b$			-3.629 (35)
$C_{bb} \times 10^3{}^b$			1.998 (20)
$C_{cc} \times 10^3{}^b$			-2.519 (22)
no. of lines <sup>d</sup>	181	147	2043 <sup>f</sup>
rms error <sup>e</sup>	0.870	0.735	0.904

<sup>a</sup>Watson's  $S$  reduction was used in the representation  $I'$ . Numbers in parentheses are one standard deviation in units of the least significant figures. Parameter values without uncertainties were estimated and kept fixed in the analyses, see end of general part of section 3.

<sup>b</sup>Derived parameter.

<sup>c</sup> $C_{||*} = C_{aa} - (C_{bb} + C_{cc})/2$ ;  $C_{\perp} = (C_{bb} + C_{cc})/2$ ;  $C_{-} = (C_{bb} - C_{cc})/4$ .

<sup>d</sup>Different pieces of information; i.e., a small number of multiple measurements of, e.g., one transition have been counted separately.

<sup>e</sup>Value for the entire fit. Additional details at the end of Sections 3.1, 3.2, and 3.3.

<sup>f</sup>Including 1609 GSCDs.

tainties and if the partial rms error of a given data set was substantially larger than 1.0. If residuals were much larger than the reported uncertainties, the corresponding transition frequencies were omitted from the final fit. Besides the HFS component mentioned before, this applies to three  $K_a = 2$  RF transitions [43]. Multiple data with MW accuracy were retained in the line list if the uncertainties were similar in magnitude. The omitted transitions involve mostly far-infrared laser-sideband data with uncertainties around 1 MHz [26].

The set of rotational and centrifugal distortion parameters is essentially identical to that of our previous study [30]; the only difference is the inclusion of an estimate of  $p_5$  as only parameter that was kept fixed in the fit. This parameter was derived from our study on  $\text{H}_2^{13}\text{CO}$  [28]. In addition, the nuclear spin-nuclear spin coupling parameter  $S(\text{HH})$  and two sets (in two different fits) of three nuclear spin-rotation parameters were determined. An edited version of one fit file is available as supplementary material. The final spectroscopic parameters of  $\text{H}_2\text{C}^{16}\text{O}$  are also given in Table 1. The rms error of the entire fit is 0.904, this value is dominated by the GSCDs, for which the partial rms error is 0.947. Numerous other subsets of the data have rms errors around 0.7, the remaining RF data from Tucker et al. [50, 51] are at the upper end (1.006), among the larger subsets, rather low values were obtained for the Kiel lines (0.333) [26] and the Cologne lines (0.506) from the same study [26]. The rms error of our new lines is 0.726.

#### 4. Discussion and conclusion

The rotational and centrifugal distortion parameters of  $\text{H}_2\text{C}^{17}\text{O}$ , which have been determined through fitting, compare favorably with those of  $\text{H}_2\text{C}^{18}\text{O}$  and  $\text{H}_2\text{C}^{16}\text{O}$ , their values are essentially in all instances between those of the heavier and the lighter isotopologue, see Table 1. The value of  $h_1$  appears to be an exception, but its uncertainty is large, and an increase by two to three times the uncertainty would bring it to the expected value. The  $\text{H}_2\text{C}^{18}\text{O}$  value of  $H_J$  is larger than the  $\text{H}_2\text{C}^{16}\text{O}$  value, but the uncertainty of the former is quite large. Also, the decrease of  $H_{KJ}$  from  $\text{H}_2\text{C}^{16}\text{O}$  over  $\text{H}_2\text{C}^{17}\text{O}$  to  $\text{H}_2\text{C}^{18}\text{O}$  is more pronounced than would be expected from the scaling mentioned above, but the change in the remaining parameters is rather close to what would be expected from such scaling.

The improvement in the distortion parameters of  $\text{H}_2\text{C}^{17}\text{O}$  are quite obvious as the  $R$ -branch transitions were extended from  $J = 4 - 3$  near 300 GHz to  $J = 22 - 21$  near 1500 GHz. In addition,  $K_a$  extends now to 7, up from previously 4. The improvement is also pronounced for  $\text{H}_2\text{C}^{18}\text{O}$  as most of the previous data was limited to below 835 GHz with two additional transitions near 1.87 THz. The situation is more complex for  $\text{H}_2\text{C}^{16}\text{O}$ . The uncertainties of some parameters changed only slightly, decreased by factors of around 1.5 to 2 for several others, and even by factors of  $\sim 4$  for  $d_1$  and  $L_{KKJ}$ .

The present  $^{17}\text{O}$  HFS parameters are slightly better determined than those from the initial investigation [37] as can be expected because of additional data from a later study [39]; uncertainties in the later study are surprisingly worse in part

than those in the earlier study. The spin-spin coupling parameters  $S(\text{HH})$  may appear quite different among the two isotopic species  $\text{H}_2\text{C}^{18}\text{O}$  and  $\text{H}_2\text{C}^{16}\text{O}$ , but the differences are less than two times the combined uncertainties. Because of the uncertainties, one should take with a grain of salt that the value calculated from the ground state HH distance, derived from  $A_0$ , is  $-17.907$  kHz and thus closer to the value of  $\text{H}_2\text{C}^{18}\text{O}$ . Inclusion of higher  $K_a$  HFS splitting information in the fit improved the uncertainty of  $C_{aa}$  by almost a factor of 3 and those of  $C_{bb}$  and  $C_{cc}$  by factors of  $\sim 4$ .

Predictions of the rotational spectra of the three formaldehyde isotopologues will be available in the catalog section<sup>3</sup> of the CDMS [48, 49]. Edited fit files are deposited as supplementary material. In addition, line, parameter, and fit files, along with other auxiliary files, will be available in the spectroscopy data section<sup>4</sup> of the CDMS.

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#### Appendix A. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jms.2016.10.004>.

#### References

- [1] L.E. Snyder, D. Buhl, B. Zuckerman, P. Palmer, Phys. Rev. Lett. 22 (1969) 679–681.
- [2] P. Palmer, B. Zuckerman, D. Buhl, L.E. Snyder, Astrophys. J. 156 (1969) L147–L150.
- [3] A. Heithausen, U. Mebold, H.W. de Vries, Astron. Astrophys. 179 (1987) 263–267.
- [4] A.G. Nash, Astrophys. J. Suppl. Ser. 72 (1990) 303–322.
- [5] J. Cernicharo, M. Guélin, J. Penalver, J. Martín-Pintado, R. Mauersberger, Astron. Astrophys. 222 (1989) L1–L4.
- [6] M. Lindqvist, H. Olofsson, A. Winnberg, L.-Å. Nyman, Astron. Astrophys. 263 (1992) 183–189.
- [7] K.E.S. Ford, D.A. Neufeld, P. Schilke, G.J. Melnick, Astrophys. J. 614 (2004) 990–1006.
- [8] F.F. Gardner, J.B. Whiteoak, Nature 247 (1974) 526–527.
- [9] K.M. Menten, M.J. Reid, Astrophys. J. 465 (1996) L99–L102.
- [10] D. Downes, T.L. Wilson, Astrophys. J. 191 (1974) L77–L78.
- [11] W.A. Baan, R. Güsten, A.D. Haschik, Astrophys. J. 305 (1986) 830–836.
- [12] P.G. Wannier, A.A. Penzias, R.A. Linke, R.W. Wilson, Astrophys. J. 157 (1969) L167–L171.
- [13] F.F. Gardner, J.C. Ribes, B.F.C. Cooper, Astrophys. Lett. 9 (1971) 181–183.
- [14] W.D. Langer, M.A. Frerking, R.A. Linke, R.W. Wilson, Astrophys. J. 232 (1979) L169–L173.
- [15] B.E. Turner, Astrophys. J. 362 (1990) L29–L33.
- [16] C. Ceccarelli, A. Castets, L. Loinard, E. Caux, A.G.G.M. Tielens, Astron. Astrophys. 338 (1998) L43–L46.
- [17] A. Wootten, R. Snell, N.J. Evans II, Astrophys. J. 240 (1980) 532–546.

<sup>3</sup><https://cdms.astro.uni-koeln.de/classic/entries/>

<sup>4</sup><https://cdms.astro.uni-koeln.de/classic/predictions/daten/H2CO/>

- [18] J.G. Mangum, A. Wootten, *Astrophys. J. Suppl. Ser.* 89 (1993) 123–153.
- [19] F.F. Gardner, J.B. Whiteoak, *Mon. Not. R. astr. Soc.* 194 (1981) 37P–41P.
- [20] R. Güsten, C. Henkel, W. Batrla, *Astron. Astrophys.* 149 (1985) 195–198.
- [21] P. Ricaud, D. Alexandre, B. Barret, E. Le Flochmoën, E. Motte, G. Berthet, F. Lefèvre, D. Murtagh, *J. Quant. Spectrosc. Radiat. Transfer* 107 (2007) 91–104; and references therein.
- [22] R.F. Knacke, T.Y. Brooke, R.R. Joyce, *Astrophys. J.* 310 (1986) L49–L53.
- [23] A.C. Danks, T. Encrenaz, P. Bouchet, T. Le Bertre, A. Chalabaev, *Astron. Astrophys.* 184 (1987) 329–332.
- [24] L.E. Snyder, P. Palmer, I. de Pater, *Astron. J.* 97 (1989) 246–253.
- [25] J. K. Bragg, A.H. Sharbaugh, *Phys. Rev.* 75 (1949) 1774–1775.
- [26] R. Bocquet, J. Demaison, L. Poteau, M. Liedtke, S. Belov, K.M.T. Yamamada, G. Winnewisser, C. Gerke, J. Gripp, T. Köhler, *J. Mol. Spectrosc.* 177 (1996) 154–159.
- [27] R. Bocquet, J. Demaison, J. Cosléou, A. Friedrich, L. Margulès, S. Macholl, H. Mäder, M.M. Beaky, G. Winnewisser, *J. Mol. Spectrosc.* 195 (1999) 345–355.
- [28] H.S.P. Müller, R. Gendriesch, L. Margulès, F. Lewen, G. Winnewisser, R. Bocquet, J. Demaison, U. Wötzel, H. Mäder, *Phys. Chem. Chem. Phys.* 2 (2000) 3401–3404.
- [29] H.S.P. Müller, R. Gendriesch, F. Lewen, G. Winnewisser, *Z. Naturforsch.* 55a (2000) 486–490.
- [30] S. Brünken, H.S.P. Müller, F. Lewen, G. Winnewisser, *Phys. Chem. Chem. Phys.* 5 (2003) 1515–1518.
- [31] O. Zakharenko, R.A. Motiyenko, L. Margulès, T.R. Huet, *J. Mol. Spectrosc.* 317 (2015) 41–46.
- [32] L. Margulès, A. Perrin, R. Janečková, S. Bailleux, C.P. Endres, T.F. Giesen, S. Schlemmer, *Can. J. Phys.* 87 (2009) 425–435.
- [33] H.S.P. Müller, G. Winnewisser, J. Demaison, A. Perrin, A. Valentin, *J. Mol. Spectrosc.* 200 (2000) 143–144.
- [34] J. Lohilahti, V.-M. Horneman, *J. Mol. Spectrosc.* 228 (2004) 1–6.
- [35] J. Lohilahti, H. Mattila, V.-M. Horneman, F. Pawłowski, *J. Mol. Spectrosc.* 234 (2005) 279–285.
- [36] S. Eliet, A. Cuisset, M. Guinet, F. Hindle, G. Mouret, R. Bocquet, J. Demaison, *J. Mol. Spectrosc.* 279 (2012) 12–15.
- [37] W.H. Flygare, J.T. Lowe *J. Chem. Phys.* 43 (1965) 3645–3653
- [38] D.T. Davies, R.J. Richards, M.C.L. Gerry, *J. Mol. Spectrosc.* 80 (1980) 307–319.
- [39] R. Cornet, B.M. Landsberg, G. Winnewisser, *J. Mol. Spectrosc.* 82 (1980) 253–263.
- [40] A. Wootten, *Astrophys. Space Sci.* 313 (2008) 9–12.
- [41] G. Winnewisser, A.F. Krupnov, M.Y. Tretyakov, M. Liedtke, F. Lewen, A.A. Saleck, R. Schieder, A.P. Shkaev, S.V. Volokhov, *J. Mol. Spectrosc.* 165 (1994) 294–300.
- [42] H.S.P. Müller, L.R. Brown, B.J. Drouin, J.C. Pearson, I. Kleiner, R.L. Sams, K. Sung, M.H. Ordu, F. Lewen, *J. Mol. Spectrosc.* 312 (2015) 22–37.
- [43] B. Fabricant, D. Krieger, J.S. Muentner *J. Chem. Phys.* 67 (1977) 1576–1586.
- [44] L. Halonen, A.G. Robiette, *J. Mol. Spectrosc.* 101 (1983) 440–443.
- [45] H.M. Pickett, *J. Mol. Spectrosc.* 148 (1991) 371–377.
- [46] H.S.P. Müller, B. J. Drouin, J. C. Pearson, M. H. Ordu, N. Wehres, F. Lewen, *Astron. Astrophys.* 586 (2016) A17.
- [47] M. Berglund, M.E. Wieser, *Pure Appl. Chem.* 83 (2011) 397–.
- [48] H.S.P. Müller, S. Thorwirth, D.A. Roth, G. Winnewisser, *Astron. Astrophys.* 370 (2001) L49–L52.
- [49] H.S.P. Müller, F. Schlöder, J. Stutzki, G. Winnewisser, *J. Mol. Struct.* 742 (2005) 215–227.
- [50] K.D. Tucker, G.R. Tomasevich, P. Thaddeus, *Astrophys. J.*, 169 (1971) 429–440.
- [51] K.D. Tucker, G.R. Tomasevich, P. Thaddeus, *Astrophys. J.*, 174 (1972) 463–466.
- [52] R. Cornet, G. Winnewisser, *J. Mol. Spectrosc.* 80 (1980) 438–452.
- [53] J.C. Chardon, C. Genty, D. Guichon, N. Sungur, J.G. Théobald, *Rev. Phys. Appl.*, 9 (1974) 961–965.
- [54] D. Dangoisse, E. Willemot, J. Bellet, *J. Mol. Spectrosc.* 71 (1978) 414–429.
- [55] J.C. Chardon, D. Guichon *J. Phys.*, 34 (1973), 791–803.
- [56] M. Takami, *J. Phys. Soc. Japan*, 24 (1968) 372–376.
- [57] J.C. Chardon, D. Guichon *J. Phys.*, 38 (1977) 113–120.
- [58] J.C. Chardon, J.J. Miller, *Can. J. Phys.* 59 (1981) 378–386.
- [59] D.R. Johnson, F. Lovas, W.H. Kirchoff *J. Phys. Chem. Ref. Data*, 1 (1972) 1011–1045.
- [60] A. Perrin, A. Valentin, L. Daumont, *J. Mol. Struct.* 780–781 (2006) 28–44.