The Rotational Spectrum of Ketene Isotopomers with ^{18}O and ^{13}C Revisited

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The pure rotational spectra of [^{18}O]ketene, $H_2C{=}C^{18}O$, [1-^{13}C]ketene, $H_2C{=}^{13}CO$, and [2-^{13}C]ketene, $H_2{}^{13}C{=}CO$, have been revisited in the frequency region 200 – 350 GHz in the ground vibrational state.

From more than 100 *R*-branch transitions for each isotopomer a set of rotational and centrifugal distortion constants could be derived using the Watson *S*-reduction formalism. The values obtained for the rotational constants *B* and *C* agree very well with results of former investigations. The agreement is worse with respect to the *A* constants, but our newly determined *A* values agree well with the corresponding values of the main species and the ^{17}O isotopomer.

Key words: Rotational Spectra; Ketene; Isotopomers; Structure.

Introduction

The microwave and millimeter-wave spectra of ketene, in several isotopic forms, have been the subjects of a large number of studies.

The first measurement of the rotational spectrum of ketene was reported in 1950 [1]. Since that time, this molecule has received considerable attention from microwave, millimeter-wave, and infrared spectroscopists, and many studies dealt with more than only one isotopomer as can be seen in Table 1.

The papers [10, 17] contain recent reviews summarizing much of the work, but new measurements continue to be made. The spectrum, particularly that of the most abundant isotopic species in its excited vibrational states, has been subject to increasingly refined analyses.

In 1994, for example, effective rotational constants for the three lowest vibrational states have been published [18], followed 1996 by measurements of the dipole moments of the same states for ketene and [D$_2$]ketene [19].

In 1999 and 2000, infrared analyses have been worked out, taking into account different Coriolis interactions among excited vibrational states [20, 21], and two years ago we published the first rotational analysis of [^{17}O]ketene [22].

Table 1. Selection of publications on different ketene isotopomers.

1950	$H_2C{=}CO$, $D_2C{=}CO$, $HDC{=}CO$	[1]
1951	$H_2C{=}CO$, $HDC{=}CO$, $D_2C{=}CO$	[2]
1959	$H_2^{13}C{=}CO$, $H_2C{=}C^{18}O$	[3]
1963	$H_2^{13}C{=}CO$, $H_2C{=}C^{18}O$	[4]
1966	$H_2C{=}CO$, $HDC{=}CO$, $D_2C{=}CO$	[5]
1972	$H_2C{=}CO$	[6]
1976	$HDC{=}CO$, $D_2C{=}CO$	[7]
1977	$H_2C{=}CO$, $D_2C{=}CO$	[8]
1978	$H_2C{=}CO$	[9]
1987	$H_2C{=}CO$, $HDC{=}CO$, $D_2C{=}CO$, $H_2^{13}C{=}CO$, $H_2C{=}^{13}CO$	[11]
1987	$H_2C{=}CO$, $D_2C{=}CO$, $H_2^{13}C{=}CO$, $H_2C{=}^{13}CO$	[12]
1987	$H_2C{=}CO$, $H_2^{13}C{=}CO$, $H_2C{=}^{13}CO$	[13]
1987	$D_2C{=}CO$	[14]
1990	$H_2C{=}CO$, $HDC{=}CO$, $D_2C{=}CO$, $H_2^{13}C{=}CO$, $H_2C{=}^{13}CO$, $H_2C{=}C^{18}O$	[15]
1992	$H_2C{=}CO$	[16]
2001	$H_2C{=}C^{17}O$	[22]

The present paper deals with millimeter-wave spectra of the species $H_2{}^{13}C{=}CO$, $H_2C{=}^{13}CO$, and $H_2C{=}C^{18}O$.

Even though some transitions of these isotopomers have been reported earlier [15], the observed spectra were not extensive enough to supply a value for the rotational constant *A* of the three isotopomers in agreement with the values obtained for the main species [16] and for the ^{17}O isotopomer [22].

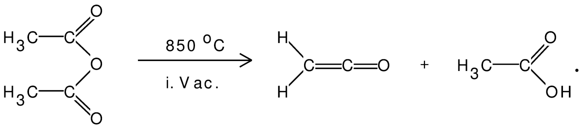
Table 2. Constants of reinvestigated isotopomers (a) compared with those obtained in [15] (b) and in [16] (c).

Parameter	Main Isotopomer[c] [16]	H_2CCO[a]	$H_2CC^{18}O$[b]	$H_2CC^{18}O$[a]	$H_2C^{13}CO$[b]	$H_2C^{13}CO$[a]	$H_2{}^{13}CCO$[b]	$H_2\ {}^{13}CCO$[a]
A (MHz)	282101.185(409)	282032(22)	287350(910)	282002(22)	282334(521)	282037(26)	282112(334)	282044(14)
B (MHz)	10293.32117(80)	10293.31963(81)	9761.2368(33)	9761.23954(96)	10293.6209(58)	10293.6281(11)	9960.9659(79)	9960.97994(61)
C (MHz)	9915.90548(82)	9915.90393(80)	9421.1236(33)	9421.12530(92)	9916.2046(57)	9916.2102(11)	9607.1276(84)	9607.14130(60)
D_J (kHz)	3.27896(122)	3.2804(18)	2.873(19)	2.947(18)	3.318(27)	3.2723(22)	3.318(16)	3.0903(12)
D_{JK}(kHz)	479.180(97)	478.27(11)	437.7(15)	435.33(11)	470.0(14)	477.53(14)	441.7(18)	452.111(78)
D_K(MHz)	22.840(55)	22.84[d]	22.577	22.84[d]	22.543	22.84[d]	22.561	22.84[d]
d_I(Hz)	−147.46(23)	−147.57(84)	−126(11)	−129.1(14)	−143(15)	−146.7(14)	−132(24)	−132.97(75)
d_2(Hz)	−56.328(55)	−56.21(51)	131(21)	−48.8(10)	−50	−58.9(14)	−44	−48.72(57)
H_J(mHz)	−2.04(52)	−2.04[d]	–	−2.04[d]	–	−2.04[d]	–	−2.04[d]
H_{JK}(Hz)	2.059(65)	2.27(21)	–	1.84(19)	–	1.77(25)	–	2.29(14)
H_{KJ}(Hz)	−467.5(30)	−526.2(45)	−386(57)	−499.3(44)	−831(23)	−537.4(52)	−1182(74)	−489.1(28)
H_K(kHz)	5.23(159)	5.23[d]	–	5.23[d]	–	5.23[d]	–	5.23[d]
L_{JJKK}(mHz)	25.71(132)	−21.3(46)	–	−21.2(36)	–	−29.2(53)	–	−14.0(28)
L_{JKKK}(Hz)	−4.329(25)	3.475(59)	−4.14(66)	3.263(57)	–	3.930(65)	7.53(88)	3.224(34)
σ_{Fit}(kHz)	Rms 106 kHz for MMW Rms 10.6 MHz for IR	40	–	42	–	46	–	33.3
No. of transitions fitted	2250[e]	156	32	142	26	141	26	132

[a] This work. L_{JJKK} and L_{JKKK} are defined with reversed sign with respect to the same values given in [16]; [b] Brown et al. [15]; [c] Johns et al. [16]; [d] Not determinable. Value fixed to that of the main isotopomer H_2CCO as given in [16]; [e] 1700 IR-Lines, 300 Combination Differences, 250 MMW.

Experimental

Ketene was prepared by vacuum pyrolysis of acetic anhydride at 850 °C:



After intermediate trapping of the by-product acetic acid in a dry ice cold trap, the ketene was collected in a trap held at liquid nitrogen temperature.

In spite of the fact that the natural abundances of the ^{18}O and ^{13}C are only 0.2 and 1.1%, respectively, all measurements have been performed without isotopic enrichment during the search for and the measurement of the even weaker lines of the ^{17}O isotopomer [22].

The millimeter-wave spectra were recorded using a PC-controlled spectrometer operating in the source modulation mode. The radiation was obtained either directly from a BWO (Backward Wave Oscillator: Istok OB 30) or from a *Ku*- or *K*-band BWO (hp 8695A or hp 8696A) combined with an active frequency multiplier (hp 83556A or hp 83558A).

The free-space absorption cell consisted of a 10-cm-diameter glass tube, 4.20 m in length and capped at the ends with Teflon collimating lenses. Low-noise detection was achieved by use of a liquid-helium cooled InSb bolometer (“Putley detector”).

Measurements in the frequency range 200 – 350 GHz were carried out at room temperature (28 °C) and a pressure of about 1 – 3 Pa. Because of the weak intensity of the absorption lines, and taking into account that several lines are disturbed by other strong lines of the ground state or excited vibrational states, we estimate the accuracy of the frequency measurements to be ± 20 kHz.

Results of the Rotational Analysis

The reported rotational lines of the three isotopomers ($H_2C{=}C^{18}O$, $H_2C{=}^{13}CO$ and $H_2{}^{13}C{=}CO$) have been identified during the search and the assignment of the rotational spectrum of the ^{17}O isotopomer [22].

K_a = 3 doublets at high frequencies were of great help for a correct identification of the lines. Other lines with odd K_a values and finally those with even K_a values (due to spin statistics the former are three times stronger than the latter) have been added. Through successive fits, performed by use of Watson’s *S*-reduced Hamiltonian [24] in the I^r representation (with an asymmetry parameter of $\kappa = -0.997$ ketene is very near to the prolate top limit), several lines up to K_a = 7 could be identified. They were found within intervals of some 20 kHz with respect to the frequencies calculated using constants given in [15].

For higher K_a values, increasing deviations from the predicted frequencies occured. This discrepancy, the

Table 3. Rotational constants (MHz), principal moments of inertia and inertial defects (amu $\cdot$ Å^2) of the investigated isotopomers.

	H_2CCO[a]	H_2CCO[b]	$H_2CC^{18}O$[b]	$H_2\ ^{13}CCO$[b]	$H_2C^{13}CO$[b]	$H_2CC^{17}O$[c]	DHCCO[d]	D_2CCO[d]
$A^{(S)}$	282101.185(409)	282032(22)	282002(22)	282044(14)	282037(26)	282072(22)	194305(38)	141497.3(70)
$B^{(S)}$	10293.32117(80)	10293.31963(81)	9761.23954(96)	9960.97994(61)	10293.6281(11)	10013.4764(28)	9647.0664(13)	9120.8310(10)
$C^{(S)}$	9915.90548(82)	9915.90393(80)	9421.12530(92)	9607.14130(60)	9916.2102(11)	9655.9118(24)	9174.6457(13)	8552.7013(10)
I_a	1.7914813(27)	1.79192(17)	1.79211(17)	1.79184(10)	1.79189(23)	1.79167(14)	2.60096(51)	3.57165(18)
I_b	49.0977597(43)	49.0977661(34)	51.7740598(51)	50.7358717(31)	49.0962948(52)	50.469888(15)	52.3868064(71)	55.4093152(57)
I_c	50.9665013(42)	50.9665083(41)	53.6431672(52)	52.6045141(33)	50.9649342(56)	52.338818(14)	55.0843070(74)	59.0899860(69)
Δ	0.077260	0.076823	0.076997	0.076798	0.076750	0.077263	0.096543	0.106917

The coefficient 505379 MHz · amu · Å^2 has been used for the conversion. $\kappa = -0.9974$; [a] [16]; [b] this work; [c] [22]; [d] [7]. Data refitted to *S*-reduced Hamiltonian [see text].

Table 4. Selection of lines of the isotopomer $H_2CC^{18}O$.

No.	J	K_a	K_c	J'	K'_a	K'_c	ν_{obs} (MHz)	ν_{calc} (MHz)	o – c (kHz)
1	10	1	9	10	1	10	18702.843	18702.849	−6
2	11	1	10	11	1	11	22442.493	22442.499	−6
3	10	0	10	9	0	9	191759.314	191759.314	0
4	10	1	10	9	1	9	190090.387	190090.420	−33
5	10	2	8	9	2	7	191821.182	191821.188	−6
6	10	2	9	9	2	8	191769.024	191769.030	−6
7	10	3	7	9	3	6	191739.878	191739.947	−69
8	10	3	8	9	3	7	191739.878	191739.803	72
9	10	5	6	9	5	5	191589.892	191589.907	−21
10	10	7	4	9	7	3	191355.790	191355.790	0
11	13	0	13	12	0	12	249229.003	249228.985	21
12	13	1	12	12	1	11	251514.393	251514.381	12
13	13	1	13	12	1	12	247095.686	247095.707	−21
14	13	2	11	12	2	10	249396.425	249396.419	3
15	13	2	12	12	2	11	249281.413	249281.419	−6
16	13	3	10	12	3	9	249257.532	249257.541	−6
17	13	3	11	12	3	10	249257.004	249256.995	9
18	13	4	10	12	4	9	249168.823	249168.826	−6
19	13	5	9	12	5	8	249058.484	249058.493	−12
20	13	6	8	12	6	7	248921.443	248921.425	15
21	13	7	7	12	7	6	248753.446	248753.440	9
22	14	3	11	13	3	10	268429.382	268429.373	9
23	14	3	12	13	3	11	268428.594	268428.582	12
24	14	4	11	13	4	10	268332.588	268332.588	0
25	14	5	10	13	5	9	268213.307	268213.304	3
26	14	7	8	13	7	7	267884.485	267884.488	−3
27	17	0	17	16	0	16	325782.956	325782.917	36
28	17	1	17	16	1	16	323075.965	323075.788	174
29	17	2	15	16	2	14	326199.131	326199.164	−36
30	17	2	16	16	2	15	325941.696	325941.735	−42
31	17	3	14	16	3	13	325942.482	325942.464	18
32	17	3	15	16	3	14	325940.371	325940.359	12
33	17	4	14	16	4	13	325819.579	325819.579	6
34	17	5	13	16	5	12	325672.788	325672.797	−3
35	17	7	11	16	7	10	325272.257	325272.284	−27

The standard deviation of the complete fit on 142 transitions is 42 kHz. A complete list of transitions is available under TNA 40 at the Library of the University Kiel or at mb@tf.uni-kiel.de.

Table 5. Selection of lines of the isotopomer $H_2C^{13}CO$.

No.	J	K_a	K_c	J'	K'_a	K'_c	ν_{obs} (MHz)	ν_{calc} (MHz)	o – c (kHz)
1	4	0	4	3	0	3	80834.509	80834.584	−75
2	4	1	4	3	1	3	80079.110	80079.107	3
3	4	1	3	3	1	2	81588.595	81588.703	−108
4	4	2	2	3	2	1	80826.589	80826.775	−186
5	4	2	3	3	2	2	80822.830	80822.874	−45
6	4	3	1	3	3	0	80804.569	80804.554	15
7	4	3	2	3	3	1	80804.569	80804.551	15
8	10	0	10	9	0	9	202020.442	202020.478	−36
9	10	1	9	9	1	8	203946.465	203946.417	45
10	10	2	9	9	2	8	202037.329	202037.231	96
11	10	2	8	9	2	7	202101.611	202101.578	33
12	10	3	8	9	3	7	202007.335	202007.215	120
13	10	3	7	9	3	6	202007.335	202007.413	−78
14	10	4	7	9	4	6	201934.573	201934.567	3
15	10	5	6	9	5	5	201842.183	201842.213	−30
16	10	6	5	9	6	4	201726.795	201726.807	−12
17	10	7	4	9	7	3	201584.916	201584.913	3
18	13	7	7	12	7	6	262050.428	262050.419	6
19	13	6	8	12	6	7	262235.139	262235.139	−3
20	13	5	9	12	5	8	262385.782	262385.794	−12
21	13	4	10	12	4	9	262507.258	262507.225	33
22	13	3	11	12	3	10	262604.825	262604.786	39
23	13	3	10	12	3	9	262605.566	262605.533	33
24	13	2	11	12	2	10	262768.983	262768.959	21
25	13	2	12	12	2	11	262627.100	262627.094	6
26	13	1	13	12	1	12	260200.043	260200.037	6
27	13	1	12	12	1	11	265103.143	265103.146	−3
28	13	0	13	12	0	12	262556.256	262556.241	15
29	16	7	10	15	7	9	322508.113	322508.122	−12
30	16	6	11	15	6	10	322735.887	322735.866	18
31	16	5	12	15	5	11	322922.253	322922.262	−9
32	16	4	13	15	4	12	323073.840	323073.843	−6
33	16	3	14	15	3	13	323198.559	323198.532	24
34	16	3	13	15	3	12	323200.640	323200.664	−21
35	16	2	14	15	2	13	323465.006	323465.000	3
36	16	2	15	15	2	14	323200.286	323200.289	−3
37	16	1	16	15	1	15	320206.601	320206.613	−15
38	16	1	15	15	1	14	326238.320	326238.365	−42
39	16	0	16	15	0	15	323037.238	323037.145	96

The standard deviation of the complete fit on 141 transitions is 46 kHz. A complete list of transitions is available under TNA 40 at the Library of the University Kiel or at mb@tf.uni-kiel.de.

need of octic parameters in the fit [25], and the anomalously large value of some centrifugal distortion parameters (cf. Table 2) indicate that the ground state rotational levels are perturbed by the lowest excited vibrational states through a centrifugal distortion resonance in high K_a levels. A theoretical investigation of this effect has been done by Urban and Yamada [23], and it should be pointed out that the most recent investigation of the main isotopomer [16] revealed the same phenomenon.

Thus only lines up to K_a = 7 were included in the fit, resulting in the molecular parameters of Table 2, which are considered to give a reliable description of the vibrational ground state of $H_2C{=}C^{18}O$, $H_2C{=}^{13}CO$ and $H_2{}^{13}C{=}CO$.

Because of the C_{2v} symmetry of the molecule, only *a*-type transitions, ΔK_a = 0, have been observed. Thus

Table 6. Selection of lines of the isotopomer $H_2{}^{13}CCO$.

No.	J	K_a	K_c	J'	K'_a	K'_c	ν_{obs} (MHz)	ν_{calc} (MHz)	o – c (kHz)
1	10	0	10	9	0	9	195611.950	195611.947	3
2	10	1	10	9	1	9	193877.419	193877.422	−3
3	10	1	9	9	1	8	197414.575	197414.584	−6
4	10	2	8	9	2	7	195680.527	195680.536	−9
5	10	2	9	9	2	8	195624.034	195624.019	15
6	10	3	8	9	3	7	195594.469	195594.391	78
7	10	3	7	9	3	6	195594.469	195594.553	−84
8	10	4	7	9	4	6	195525.960	195525.972	−12
9	10	5	6	9	5	5	195438.892	195438.907	−15
10	10	6	5	9	6	4	195330.292	195330.265	27
11	13	0	13	12	0	12	254232.968	254232.956	15
12	13	1	12	12	1	11	256614.289	256614.301	−9
13	13	1	13	12	1	12	252017.349	252017.349	0
14	13	2	11	12	2	10	254416.327	254416.345	−18
15	13	2	12	12	2	11	254291.758	254291.740	18
16	13	3	10	12	3	9	254268.518	254268.542	−24
17	13	3	11	12	3	10	254267.972	254267.927	45
18	13	4	10	12	4	9	254176.247	254176.241	6
19	13	5	9	12	5	8	254061.850	254061.862	−12
20	13	6	8	12	6	7	253920.084	253920.075	6
21	13	7	7	12	7	6	253746.666	253746.687	−21
22	17	0	17	16	0	16	332316.480	332316.489	−6
23	17	1	16	16	1	15	335516.135	335516.144	−9
24	17	1	17	16	1	16	329508.489	329508.492	−3
25	17	2	15	16	2	14	332769.907	332769.949	−42
26	17	2	16	16	2	15	332491.064	332491.040	24
27	17	3	14	16	3	13	332495.405	332495.384	21
28	17	3	15	16	3	14	332493.028	332493.004	24
29	17	4	14	16	4	13	332367.268	332367.205	63
30	17	5	13	16	5	12	332214.883	332214.913	−30
31	17	6	12	16	6	11	332028.269	332028.248	21
32	17	7	11	16	7	10	331800.957	331800.972	−15

The standard deviation of the complete fit on 134 transitions is 33.3 kHz. A complete list of transitions is available under TNA 40 at the Library of the University Kiel or at mb@tf.uni-kiel.de.

the purely K-dependent centrifugal distortion constants D_K and H_{KKK} could not be determined and were fixed to the corresponding $H_2C{=}CO$ values [16]. We also did not change the value of the D_K constant, which might in principle vary for different isotopomers, because this change would have been within the given uncertainty. Together with H_{KKK}, also the very small H_{JJJ} centrifugal distortion constant has been held fixed to the value given in [16]. The value obtained for the rotational constant A is comparable with the values obtained for the main and the ^{17}O isotopomer, though the given (statistical) error of the fit may be too optimistic because of the difficulty of determining a precise value of the A constant from a-type transitions only. As mentioned above, we included two octic constants, L_{JJKK} and L_{JKKK}, in the fit, as it has been done for the main isotopomer [16].

For the isotopomers investigated in this work, the fit has been carried out considering 145 transitions for $H_2C{=}C^{18}O$, 140 for $H_2C{=}{}^{13}CO$, and 132 for $H_2{}^{13}C{=}CO$. All these transitions are of the type $\Delta J = 1$, $\Delta K_a = 0$ or $\Delta J = 0$, $\Delta K_a = 0$. A selection of measured lines for each isotopomer is given in the Tables 4, 5, and 6. A complete list of all transition frequencies is deposited under the name TNA 40 at the Library of the University of Kiel. It is also available upon request from mb@tf.uni-kiel.de.

Table 7. Selection of lines of the main isotopomer H_2CCO for comparison.

No.	J	K_a	K_c	J'	K'_a	K'_c	ν_{obs} (MHz)	ν_{calc} (MHz)	o – c (kHz)
1	1	0	1	0	0	0	20209.204	20209.210	−6
2	3	1	2	3	1	3	2264.452	2264.452	0
3	4	0	4	3	0	3	80832.117	80832.123	−6
4	4	1	3	3	1	2	81586.230	81586.230	0
5	4	1	3	4	1	4	3774.042	3774.036	6
6	4	1	4	3	1	3	80076.652	80076.646	6
7	4	2	2	3	2	1	80824.290	80824.293	−3
8	4	2	3	3	2	2	80820.395	80820.389	6
9	4	3	1	3	3	0	80802.057	80802.051	6
10	4	3	2	3	3	1	80802.057	80802.048	9
11	12	0	12	11	0	11	242375.715	242375.703	12
12	12	1	11	11	1	10	244712.099	244712.237	−138
13	12	1	12	11	1	11	240185.794	240185.788	6
14	12	2	10	11	2	9	242536.152	242536.164	−12
15	12	2	11	11	2	10	242424.650	242424.632	18
16	12	3	9	11	3	8	242398.814	242398.928	−114
17	12	3	10	11	3	9	242398.565	242398.430	135
18	12	4	9	11	4	8	242309.407	242309.377	30
19	12	5	8	11	5	7	242197.911	242197.821	90
20	15	0	15	14	0	14	302874.399	302874.372	27
21	15	1	14	14	1	13	305853.311	305853.293	18
22	15	1	15	14	1	14	300197.583	300197.580	3
23	15	2	13	14	2	12	303220.036	303220.060	−24
24	15	2	14	14	2	13	303001.925	303001.889	36
25	15	3	12	14	3	11	302993.228	302993.207	21
26	15	3	13	14	3	12	302991.675	302991.666	9
27	15	4	12	14	4	11	302876.258	302876.261	−3
28	15	5	11	14	5	10	302734.936	302734.966	−30
29	15	6	10	14	6	9	302560.945	302560.951	−6
30	15	7	9	14	7	8	302348.596	302348.593	3
31	16	4	13	15	4	12	323063.752	323063.740	12
32	16	5	12	15	5	11	322912.254	322912.272	−18
33	16	6	11	15	6	10	322726.308	322726.308	0
34	16	7	10	15	7	9	322499.647	322499.647	0

The standard deviation of the complete fit on 156 transitions is 40 kHz. A complete list of transitions is available under TNA 40 at the Library of the University Kiel or at mb@tf.uni-kiel.de.

The vast majority of the lines has been measured during this work, but we have also included lines reported in [15] in the fit, provided that their deviations from the calculated ones did not exceed three standard deviations of the fit. A few lines, which have not satisfied this condition, have been included in the list, but not weighted in the fit.

In Table 2, we report the resulting data and oppose it to those reported in former studies [15, 16]. For comparison, we have included the results of a fit on 156 pure rotational transitions of the main isotopomer (mostly measured by us), a selection of which is listed in Table 7. The obtained parameters agree well with those obtained for the other isotopomers and with those published in [16].

The parameters of the isotopomers HDC=CO and D_2C=CO reported in Table 3 were refitted with the Watson *S*-reduced formalism using the original data of [7]. To this aim, we fixed the constant D_K to the value of Δ_K (published in [14] for D_2C=CO and in [11] for HDC=CO), knowing that the difference between D_K and Δ_K is negligible [26]. For H_{JJJ} and H_{KKK}, the values for D_2C=CO obtained in [17] by an *ab initio* treatment have been applied, while for DHC=CO a mean value of the two isotopomers H_2C=CO and D_2C=CO has been used.

Conclusions

The derived rotational and centrifugal distortion constants, given in Table 2, represent a significant improvement in accuracy compared to previously published values, particularly in the case of the *A* constant. In fact, this constant has now been proven to have practically the same value for all the investigated isotopomers (within the respective uncertainty) which is perfectly consistent with the molecular geometry. The constants can be considered reliable, in spite of the necessity to fix some parameters in the fits and to limit them to lines with $K_a \leq 7$.

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