The Millimeterwave Spectrum of Four Rare Ketene Isotopomers

Antonio Guarnieri

Technische Fakultät – Hochfrequenztechnik, Institut für Physikalische Chemie der Universität Kiel, D-24143 Kiel, Germany

Reprint requests to Prof. A. G.; E-mail: ag@tf.uni-kiel.de

Z. Naturforsch. **60a,** 619 – 628 (2005); received May 17, 2005

The pure rotational spectra in the ground vibrational state of (1,2-^{13}C)ketene, $H_2{}^{13}C{=}{}^{13}CO$, (D_2,1-^{13}C)ketene, $D_2C{=}{}^{13}CO$, (D_2,2-^{13}C)ketene, $D_2{}^{13}C{=}CO$, and (D_2,^{18}O)ketene, $D_2C{=}C^{18}O$, have been observed in the frequency region 200 – 350 GHz. All the spectral lines have been measured in natural abundances with a source modulated millimeterwave spectrometer.

From the measured R-branch transitions a set of rotational and centrifugal distortion constants for each isotopomer could be derived, using the Watson S-reduction formalism. Further, the rotational spectra of the two isotopomers (4,5-D)ketene, D_2CCO, and (4-D)ketene, DHCCO, which were already measured several years ago, have been extended to higher *J*-values and higher frequencies, as it is the case for all investigated isotopomers of this work. As a result of these studies a calculation of a mass-dependent structure will be the topic of a next paper.

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

1. Introduction

Ketene is significant as a simple asymmetric top molecule for spectroscopy, theoretical chemistry and reaction dynamics. Papers [1 – 3] contain recent reviews summarizing much of the work of the last 55 years.

Few years ago, Watson et al. [4] presented a valuable method, the r_m-method, to relate the ground state and the equilibrium moments of inertia of a molecule.

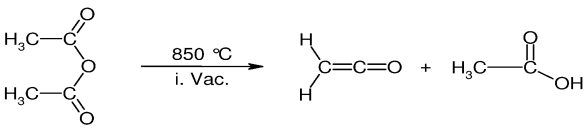
They analysed the up to that time observed moments of inertia of six isotopic ketenes to obtain a corresponding r_m-structure, but due to the reduced number of available isotopomers compared with the number of parameters to be determined, they got values for parameters not completely satisfactory.

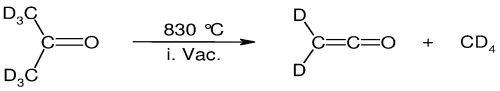
In the mean time the spectrum of the monosubstituted isotopic species in its ground vibrational state has been subject to increasingly refined analysis [1], and further the spectrum of (^{17}O)ketene has also been measured [5]. The present paper is concerned with millimeterwave spectra of rare species containing (1,2-^{13}C)ketene, $H_2{}^{13}C{}^{13}CO$, (D_2,1-^{13}C)ketene, $D_2C{}^{13}CO$, (D_2,2-^{13}C)ketene, $D_2{}^{13}CCO$ and (D_2,^{18}O)ketene, $D_2CC^{18}O$.

To my knowledge no spectra of these last four isotopomers have been reported earlier. The observed spectra are sufficient to supply also an acceptable value for the rotational constant *A* in agreement with the values obtained for all the other species investigated hitherto.

2. Experimental

Ketene was prepared by vacuum pyrolysis of acetic anhydride at 850 °C and perdeutereted ketene from d_6-acetone at 830 °C:





After intermediate trapping of the by-product acetic acid in one case and unreacted d_6-acetone in the other case by a dry ice cold trap, ketene was collected in a trap held at liquid nitrogen temperature and purified through repeated distillations if necessary. Enough (4-D)ketene for a spectrum analysis was also obtained by the second reaction using partially deutereted acetone.

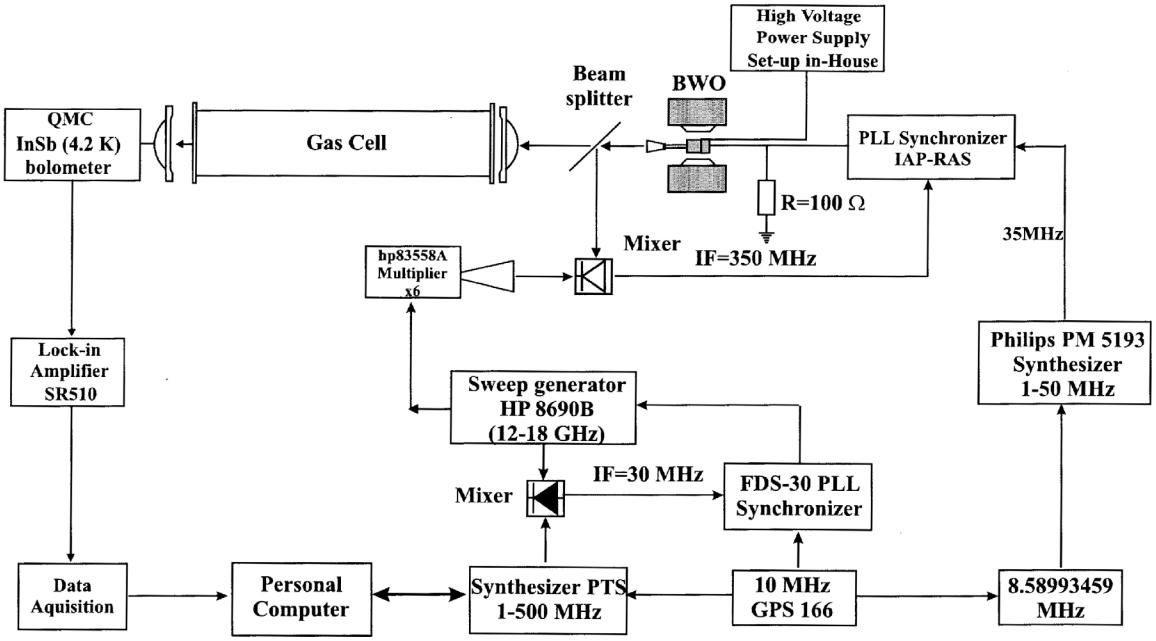


Fig. 1. Absorption submillimeterwave BWO-based spectrometer (Technische Fakultät der Universität Kiel). List of used devices: Istok BWO's OB 30, OB 32, OB 53; PLL Synchronizer – Inst. Appl. Physics, Russ. Acad. Sci., Nizhnii Novgorod; mixer with parabolic mirror – Inst. Appl. Physics, Russ. Acad. Sci., Nizhnii Novgorod; mixer 30 MHz IF – prepared in-house; sextupler hp 83558A; sweep Generator hp 8690B (12 – 18 GHz); Schomandl FDS 30 Synchronizer; synthesizer PTS 1 – 500 MHz; GPS 166 for 10 MHz Standard; Converter 10 MHz to 8.58993459 MHz for driving the Philips PM 5193 Synthesizer; QMC InSb chip cooled down by a GM/JT refrigerator of Quantum Technology; Lock-in Amplifier Stanford Res. Instr. 510; data acquisition prepared in-house.

All measurements for the normal and the deuterated species have been performed without any ^{13}C and ^{18}O isotopic enrichment.

The millimeterwave spectra have been recorded using a PC-controlled spectrometer operating in the source modulation mode with Istok BWO's (backward wave oscillator) as direct radiation sources. 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 an InSb bolometer cooled at 4.2 K by a cryocooler system of Quantum Technology (see Fig. 1).

Measurements in the frequency range 200 – 350 GHz were carried out at room temperature (27 °C) at a pressure of about 1 – 3 Pa. With respect to the weak intensity of the absorption lines and taking in account that several lines are partially overlapped by other strong lines of the ground state or excited vibrational states, the accuracy of the frequency measurements has been estimated to be ±10 kHz for strong lines and ± 20 kHz for week unperturbed lines.

3. Results of the Rotational Analysis

3.1. $H_2{}^{13}C={}^{13}CO$

Due to the weakness of the spectrum (abundance 0.02%) the reported rotational lines of this isotopomer have been identified using the rotational constants calculated applying the mass dependence method of Watson et al. [4, 6, 7] to the set of rotational constants of seven known isotopomers [1, 5].

The lines were found within intervals of 3 – 4 MHz with respect to the frequencies obtained using the calculated constants.

$K_a = 3$ doublets at high frequencies, moreover, 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 as strong as the latter – have been added. Through successive fits performed by use of Watson's S-reduced Hamiltonian [8, 9] 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

Table 1a. Selection of measured transition frequencies for the isotopomer $H_2{}^{13}C^{13}CO$.

No.	J	K_a	K_c	J'	K_a'	K_c'	f_{obs} (MHz)	f_{o-c} (kHz)
1	11	0	11	10	0	10	215154.799	−30
2	11	1	10	10	1	9	217147.388	22
3	11	3	8	10	3	7	215150.905	87
4	11	5	6	10	5	5	214978.519	−4
5	11	7	4	10	7	3	214711.475	56
6	12	0	12	11	0	11	234695.134	27
7	12	1	11	11	1	10	236880.444	−9
8	12	1	12	11	1	11	232636.972	−6
9	12	2	10	11	2	9	234832.871	−70
10	12	2	11	11	2	10	234735.039	−16
11	12	3	10	11	3	9	234708.228	1
12	12	3	9	11	3	8	234708.636	−1
13	12	4	8	11	4	7	234624.605	45
14	13	2	12	12	2	11	254289.263	9
15	13	3	10	12	3	9	254266.152	36
16	13	3	11	12	3	10	254265.511	9
17	13	4	9	12	4	8	254173.888	6
18	13	5	8	12	5	7	254059.463	0
19	14	0	14	13	0	13	273760.187	−32
20	14	1	13	13	1	12	276340.474	−5
21	15	4	11	14	4	10	293270.488	−25
22	15	5	10	14	5	9	293137.347	−23
23	15	7	8	14	7	7	292771.813	24
24	16	0	16	15	0	15	312802.030	23
25	16	1	15	15	1	14	315791.170	10
26	16	1	16	15	1	15	310136.293	−19
27	16	2	14	15	2	13	313173.658	45
28	16	3	14	15	3	13	312934.559	7
29	17	1	16	16	1	15	335512.526	−35
30	17	2	15	16	2	14	332766.622	11

The standard deviation of the complete least squares fit of 86 transition frequencies is 30 kHz. A complete list of all measured transition frequencies is available under the number TNA 41 at the central library of the University of Kiel or at the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

$K_a = 7$ could be identified. Like in the case of the papers [1, 5, 10], increasing deviations from the predicted frequencies occurred for higher K_a values. Thus only lines up to $K_{a,\max} = 7$ were included in the fit. Table 1a gives a selection of measured transitions, and Table 1b reports the obtained parameters with the corresponding correlation matrix of the least squares fit. A complete list of all measured transition frequencies is deposited under the number TNA 41 at the central library of the University of Kiel. It is also available upon request from the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

The reported molecular parameters of Table 1b are considered to give a reliable description of the rotational spectrum in the vibrational ground state of $H_2{}^{13}C={}^{13}CO$.

Because of the C_{2v} symmetry of the molecule, only a-type transitions, $\Delta K_a = 0$, could be observed. Thus

Table 1b. Rotational constants, centrifugal distortion constants and correlation coefficients of the least squares fit analysis of 86 transitions of $H_2{}^{13}C^{13}CO$. Standard deviation is 30 kHz. Values labelled with * are not determinable; they are fixed to that of the main isotopomer as given in [10].

	Watson S-reduction		A	B	C	D_J	D_{JK}	d_1	d_2	H_{JJK}	H_{JKK}	L_{JJKK}	L_{JKKK}
A	/MHz	282031(22)	1										
B	/MHz	9960.8650(25)	0.0732	1									
C	/MHz	9607.0550(27)	−0.0626	−0.7665	1								
D_J	/kHz	3.0881(21)	0.2590	0.2727	0.3836	1							
D_{JK}	/kHz	451.12(11)	−0.2529	0.1944	0.2736	0.5270	1						
D_K	/kHz	22840*	−0.0487	−0.9136	0.9150	0.0722	0.0402	1					
d_1	/kHz	−0.1331(27)	0.7121	0.0250	0.0507	0.3081	−0.1254	0.0241	1				
d_2	/kHz	−0.0509(11)	0.2140	0.1974	0.2649	0.7331	0.7387	0.0377	0.2042	1			
H_{JJJ}	/ Hz	−0.00204*	−0.4651	0.1063	0.1492	0.1419	0.8247	−0.0196	−0.2881	0.2689	1		
H_{JJK}	/ Hz	2.07(23)	−0.1666	−0.1620	−0.2082	−0.5841	−0.7289	−0.0260	−0.1479	−0.9603	−0.3208	1	
H_{JKK}	/ Hz	−506.9(42)	0.5214	−0.0305	−0.0493	0.1236	−0.4863	−0.0064	0.3353	0.1808	−0.8818	−0.1463	1
H_{KKK}	/ Hz	5230*											
L_{JJKK}	/mHz	18.7(47)											
L_{JKKK}	/mHz	−3545(53)											

Table 1c. Constants of the $H_2{}^{13}C^{13}CO$ isotopomer compared with ^{13}C monosubstituted isotopomers.

Parameter		$H_2{}^{13}C^{13}CO$	$H_2C^{13}CO$[a]	$H_2{}^{13}CCO$[a]
A	/MHz	282031(22)	282037(26)	282044(14)
B	/MHz	9960.8650(25)	10293.6281(11)	9960.9799(6)
C	/MHz	9607.0550(27)	9916.2102(11)	9607.1413(6)
D_J	/kHz	3.0881(21)	3.272(2)	3.0903(12)
D_{JK}	/kHz	451.12(11)	477.53(14)	452.11(8)
D_K	/kHz	22840*	22840*	22840*
d_1	/kHz	−0.1331(27)	-0.1467(14)	−0.13297(57)
d_2	/kHz	−0.0509(11)	-0.0589(14)	−0.04872(57)
H_{JJJ}	/ Hz	−0.00204*	-0.00204*	−0.00204*
H_{JJK}	/ Hz	2.07(23)	1.77(25)	2.29(14)
H_{KKJ}	/ Hz	−506.9(42)	−537.4(52)	−489.1(28)
H_{KKK}	/ Hz	5230*	5230*	5230*
L_{JJKK}	/mHz	18.7(47)	29.2(53)	14.0(28)
L_{JKKK}	/mHz	−3545(53)	−3930(60)	−3224(34)
σ_{Fit}	/kHz	30	46	25
No. of lines fitted		86	141	132

* Not determinable. Value fixed to that of the main isotopomer H_2CCO as given in [10]. [a] Data of [1].

the purely K-dependent centrifugal distortion constants D_K and H_{KKK} were fixed to the corresponding H_2C=CO values [10]. The value of the D_K constant has not been adjusted in dependence of the mass change of the 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 of [10]; further two octic constants, L_{JJKK} and L_{JKKK}, were included in the fit, as it has been done for all isotopomers [1, 5]. The value obtained for the rotational constant A is comparable with the values obtained for the main and other isotopomers [1, 5].

For the presently investigated isotopomer, the least squares fit has been carried out using 86 transitions of the type $\Delta J = 1$, $\Delta K_a = 0$ with a resulting standard deviation of 30 kHz. A few lines with a least squares fit deviation larger than one standard deviation but smaller than three standard deviations have been nevertheless included in the complete list: their frequency measurements were influenced by the closeness of other strong lines.

In Table 1c the resulting data are reported in comparison with those of the monosubstituted ^{13}C-isotopomers of investigation [1].

3.2. $D_2{}^{13}C$=CO, D_2C=^{13}CO and D_2C=$C^{18}O$

The reported rotational lines of these three isotopomers have been first calculated with rotational constants obtained by the r_m-program, as in the preceding case, but using now the set of 8 known isotopomers and adding then each time the constants of the newly assigned one. The natural abundance of these species in the prepared D_2C=CO is 1 % for both ^{13}C isotopomers and 0.2 % for the ^{18}O isotopomer. The differences between observed and predicted values of the transition frequencies were in the range of about 1 to 3 MHz, thus confirming the reliability of the r_m-parameters for a prediction of the spectrum of isotopically substituted species with low abundance [4].

Like in (4,5-D)ketene [11] it is possible, by these isotopomers, to consider in the fit also lines with $K_a = 8$ or 9 without having deviations due to coupling with low excited vibrational states through a centrifugal distortion resonance with high K_a [12]. Due to the C_{2v} symmetry of the molecule and the measurements of only a-type lines, ΔK_a=0, purely K-dependent centrifugal distortion constants D_K and H_{KKK} could not be determined and were fixed to the value of Δ_K and H_{KKK} published in [13], knowing that the difference between D_K and Δ_K is negligible [14]. Also for H_{JJJ} the *ab initio* value given in [3] for D_2C=CO has been used. For each of these species a set of more than 100 transitions for each isotopomer in the range 200 – 340 GHz has been employed for the least squares analysis.

Tables 2a, 3a and 4a report a selection of measured transition frequencies while the complete lists can be requested from the central library of the University of Kiel under the number TNA 41 or at the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

Tables 2b, 3b and 4b report the results of the least squares fit with the corresponding standard deviations and correlation matrices.

3.3. D_2C=CO and DHC=CO

The spectra of these two isotopomers have been investigated and measured several years ago in the millimeterwave range by L. Nemes and M. Winnewisser [11]. In addition to several Q-branch frequencies ($\Delta J = 0$, $\Delta K_a = 0$), they reported R-branch ($\Delta J = 1$, $\Delta K_a = 0$) transition frequencies up to $J = 10$, but because all the presently investigated isotopomers have been measured up to higher J-values and higher frequencies, the spectra of these two isotopomers have been supplemented with higher J-values in order to have comparable spectral informations for the least squares fit.

Table 2a. Selection of measured transition frequencies for the isotopomer $D_2{}^{13}CCO$.

No.	J	K_a	K_c	J'	K_a'	K_c'	f_{obs} (MHz)	f_{o-c} (kHz)
1	11	2	10	10	2	9	189547.654	−10
2	11	2	9	10	2	8	189908.343	−5
3	11	3	9	10	3	8	189616.132	1
4	11	3	8	10	3	7	189620.133	−1
5	11	4	8	10	4	7	189548.618	18
6	12	2	11	11	2	10	206764.129	−5
7	12	3	9	11	3	8	206866.166	8
8	12	3	10	11	3	9	206859.930	−3
9	12	4	8	11	4	7	206782.776	−21
10	13	0	13	12	0	12	223506.642	−2
11	13	1	12	12	1	11	227455.443	−14
12	13	1	13	12	1	12	220440.099	15
13	13	2	12	12	2	11	223976.646	−13
14	13	3	10	12	3	9	224114.425	−5
15	13	3	11	12	3	10	224105.089	−5
16	13	4	10	12	4	9	224017.587	14
17	14	4	11	13	4	10	241253.117	43
18	14	5	10	13	5	9	241155.001	−4
19	14	5	9	13	5	8	241155.001	−4
20	14	6	9	13	6	8	241047.450	−5
21	14	6	8	13	6	7	241047.450	−5
22	14	7	8	13	7	7	240924.996	2
23	14	7	7	13	7	6	240924.996	2
24	18	3	16	17	3	15	310351.765	−6
25	18	3	15	17	3	14	310399.854	8
26	18	4	15	17	4	14	310203.019	−1
27	18	4	14	17	4	13	310203.581	−2
28	19	2	18	18	2	17	327150.714	−10
29	19	2	17	18	2	16	328971.763	26
30	19	3	17	18	3	16	327605.08	−12
31	19	3	16	18	3	15	327668.129	−6
32	19	7	13	18	7	12	326959.123	−12
33	19	8	12	18	8	11	326765.275	0

The standard deviation of the complete least squares fit of 131 transition frequencies is 22 kHz. A complete list of all measured transition frequencies is available under the number TNA 41 at the central library of the University of Kiel or at the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

Tables 5a and 6a give a selection of the transitions measured for extending the frequency range of these two isotopomers while the complete list of lines including those measured in [11], are deposited in the central library of the University of Kiel under the number TNA 41 and can be requested as in the preceding cases.

The fit of all the available transition frequencies has been performed using the Watson S-reduction centrifugal distortion program [8, 9] up to the 8th order. Also in the case of $D_2C{=}CO$ the same values for D_K, H_{KKK}, and H_{JJJ} have been used as it was made for the preceding considered perdeuterated isotopomers. In the case of DHC=CO the value of D_K has been taken from [15], and the values for H_{KKK} and H_{JJJ} were fixed

Table 2b. Rotational constants, centrifugal distortion constants and correlation coefficients of the least squares fit analysis of 131 transitions for $D_2{}^{13}CCO$. Standard deviation is 22 kHz. Values labelled with * are not determinable they are fixed to that of the D_2CCO species as given in text.

	Watson S-reduction		A	B	C	D_J	D_{JK}	d_1	d_2	H_{JJK}	H_{JKK}	L_{JJKK}	L_{JKKK}
A	/MHz	141483.7(10)	1										
B	/MHz	8890.4753(17)	0.2998	1									
C	/MHz	8349.8413(15)	−0.3227	−0.8204	1								
D_J	/kHz	2.36147(88)	0.1455	0.3870	0.1768	1							
D_{JK}	/kHz	310.195(49)	−0.0901	0.3662	0.1029	0.6975	1						
D_K	/kHz	5387.7*	−0.2421	−0.9307	0.9243	−0.1171	−0.1451	1					
d_1	/kHz	−0.2010(13)	0.5085	−0.0017	0.0161	0.1071	−0.0571	0.0355	1				
d_2	/kHz	−0.10380(38)	0.1839	0.3190	0.1114	0.7898	0.8197	−0.1148	0.1147	1			
H_{JJJ}	/ Hz	−0.0012*	−0.2537	0.2667	0.0568	0.3802	0.8672	−0.1159	−0.1649	0.4686	1		
H_{JJK}	/ Hz	1.919(83)	−0.1778	−0.2565	−0.0842	−0.6389	−0.7519	0.0952	−0.1077	−0.9534	−0.4440	1	
H_{JKK}	/ Hz	−119.2(12)	0.3696	−0.0807	0.0020	0.0686	−0.3357	0.0460	0.2363	0.2131	−0.7168	−0.2884	1
H_{KKK}	/ Hz	941*											
L_{JJKK}	/mHz	2.1(14)											
L_{JKKK}	/mHz	−168(11)											

Table 3a. Selection of measured transition frequencies for the isotopomer $D_2C^{13}CO$.

No.	J	K_a	K_c	J'	K_a'	K_c'	f_{obs} (MHz)	f_{o-c} (kHz)
1	12	0	12	11	0	11	211514.844	−1
2	12	1	11	11	1	10	215300.818	−2
3	12	2	11	11	2	10	211921.499	−10
4	12	3	9	11	3	8	212036.956	−5
5	12	3	10	11	3	9	212029.736	15
6	12	4	9	11	4	8	211948.122	24
7	12	5	8	11	5	7	211864.354	−8
8	12	6	7	11	6	6	211770.399	−10
9	12	7	6	11	7	5	211662.300	−4
10	12	8	4	11	8	3	211538.004	−27
11	13	0	13	12	0	12	229040.847	−17
12	13	1	13	12	1	12	225844.302	15
13	13	1	12	12	1	11	233212.832	23
14	13	2	12	12	2	11	229562.086	−12
15	13	2	11	12	2	10	230219.146	−26
16	13	3	11	12	3	10	229706.473	−31
17	13	3	10	12	3	9	229717.355	−6
18	15	0	15	14	0	14	264021.587	7
19	15	1	15	14	1	14	260522.940	−4
20	15	1	14	14	1	13	269013.766	−8
21	15	2	14	14	2	13	264828.863	−4
22	15	2	13	14	2	12	265834.140	9
23	15	3	13	14	3	12	265064.735	16
24	15	3	12	14	3	11	265087.090	16
25	17	0	17	16	0	16	298898.779	−20
26	17	1	17	16	1	16	295174.942	−6
27	17	1	16	16	1	15	304779.321	−8
28	17	2	16	16	2	15	300074.056	4
29	17	2	15	16	2	14	301526.037	−3
30	18	0	18	17	0	17	316296.122	4
31	18	1	18	17	1	17	312490.189	−8
32	18	1	17	17	1	16	322646.963	12
33	18	2	16	17	2	15	319403.896	−35
34	19	0	19	18	0	18	333665.025	7

The standard deviation of the complete least squares fit on 102 transition frequencies is 33 kHz. A complete list of all measured transition frequencies is available under the number TNA 41 at the central library of the University of Kiel or at the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

to the mean values of the two isotopomers H_2C=CO and D_2C=CO.

The results of the least squares fit procedure are reported in Tables 5b and 6b, together with the corresponding correlation matrix, the standard deviation and the number of transitions used.

4. Conclusions

Table 7 gives the values of the rotational constants together with the inertial moments and the inertia defect for all the ketene isotopomers so far investigated.

The data reported for the mother species, written in italics, are only given for comparison because they re-

Table 3b. Rotational constants, centrifugal distortion constants and correlation coefficients of the least squares fit analysis of 103 transitions of $D_2C^{13}CO$. Standard deviation is 30 kHz. Values labelled with * are not determinable; they are fixed to that of the D_2CCO species as given in text.

	Watson S-reduction		A	B	C	D_J	D_{JK}	d_1	d_2	H_{JJK}	H_{JKK}	L_{JJKK}	L_{JKKK}
A	141484.0(14)	/MHz	1										
B	9119.4284(24)	/MHz	0.2472	1									
C	8551.4841(23)	/MHz	−0.1943	−0.8070	1								
D_J	2.4878(14)	/kHz	0.29345	0.3325	0.2497	1							
D_{JK}	322.152(76)	/kHz	−0.1059	0.2829	0.1469	0.5631	1						
D_K	5387.7*	/kHz	−0.1424	−0.9265	0.9159	−0.0586	−0.0841	1					
d_1	−0.2216(22)	/kHz	0.5346	−0.0384	0.1017	0.2356	−0.0607	0.1023	1				
d_2	−0.11403(76)	/kHz	0.2374	0.2703	0.1472	0.7234	0.7987	−0.0762	0.1608	1			
H_{JJJ}	−0.0012*	/ Hz	−0.3030	0.1873	0.0795	0.2308	0.8609	−0.0655	−0.1903	0.4231	1		
H_{JJK}	2.04(13)	/ Hz	−0.1964	−0.2252	−0.1107	−0.5831	−0.7751	0.0696	−0.1254	−0.9639	−0.4521	1	
H_{JKK}	−126.1(19)	/ Hz	0.4146	−0.0685	−0.0180	0.0834	−0.4737	0.0304	0.2593	0.0993	−0.8369	−0.0898	1
H_{KKK}	941*	/ Hz											
L_{JJKK}	4.0(21)	/mHz											
L_{JKKK}	−240(17)	/mHz											

Table 4a. Selection of measured transitions frequencies for the isotopomer $D_2CC^{18}O$.

No.	J	K_a	K_c	J'	K_a'	K_c'	f_{obs} (MHz)	f_{o-c} (kHz)
1	12	2	10	11	2	9	201572.257	13
2	12	3	9	11	3	8	201242.297	31
3	12	3	10	11	3	9	201237.029	25
4	13	0	13	12	0	12	217480.836	−13
5	13	1	12	12	1	11	221196.386	−10
6	13	2	11	12	2	10	218432.321	−6
7	14	1	14	13	1	13	231033.635	−5
8	14	1	13	13	1	12	238183.075	−6
9	14	2	12	13	2	11	235306.879	−15
10	14	2	13	13	2	12	234642.69	−2
11	14	3	12	13	3	11	234789.769	4
12	14	3	11	13	3	10	234801.256	18
13	14	0	14	13	0	13	234115.630	−14
14	15	0	15	14	0	14	250730.117	−11
15	15	1	14	14	1	13	255163.166	−13
16	15	2	14	14	2	13	251381.346	3
17	15	2	13	14	2	12	252196.795	12
18	15	3	13	14	3	12	251567.968	−44
19	15	3	12	14	3	11	251584.227	−33
20	16	0	16	15	0	15	267323.201	−9
21	16	1	16	15	1	15	263976.159	5
22	16	1	15	15	1	14	272136.138	17
23	16	2	15	15	2	14	268115.530	−15
24	16	2	14	15	2	13	269102.754	26
25	16	3	14	15	3	13	268347.522	15
26	17	4	14	16	4	13	285002.137	8
27	17	4	13	16	4	12	285002.431	2
28	17	5	13	16	5	12	284880.721	−43
29	17	6	12	16	6	11	284752.389	3
30	17	7	11	16	7	10	284608.562	−6
31	17	8	10	16	8	9	284445.369	8
32	20	0	20	19	0	19	333464.293	−7
33	20	1	20	19	1	19	329789.429	4
34	20	2	19	19	2	18	335002.010	−6
35	20	2	18	19	2	17	336897.100	64

The standard deviation of the complete least squares fit of 115 transition frequencies is 29 kHz. A complete list of all measured transition frequencies is available under the number TNA 41 at the central library of the University Kiel or at the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

sult from an IR + MW combined fit [10]. All other data are the result of a pure rotational spectrum investigation.

It can be seen that the values for the constant A of the six hydrogenated isotopic species are now all contained in a range of 36 MHz with a mean value of 282,036 MHz and therefore practically of a similar value for all the investigated isotopomers. The determination uncertainty is due to measurements of the only allowed μ_a-spectrum and to the changed mass of the substituted isotopomer. This fact is also apparent for the four perdeutereted isotopomers with C_{2v} symmetry, where the variability range reduces to 8 MHz in agreement with the smaller oscillation amplitude of

Table 4b. Rotational constants, centrifugal distortion constants and correlation coefficients of the least squares fit analysis of 115 transitions of $D_2CC^{18}O$. Standard deviation is 29 kHz. Values labelled with * are not determinable; they are fixed to that of the D_2CCO species as given in text.

	Watson S-reduction		A	B	C	D_J	D_{JK}	d_1	d_2	H_{JJK}	H_{JKK}	L_{JJKK}	L_{JKKK}
A	/MHz	141490.0(13)	1										
B	/MHz	8641.8429(21)	0.2941	1									
C	/MHz	8130.0534(21)	−0.3573	−0.8133	1								
D_J	/kHz	2.2384(10)	0.0439	0.3323	0.2488	1							
D_{JK}	/kHz	294.490(72)	−0.1900	0.2526	0.1874	0.6205	1						
D_K	/kHz	5387.7*	−0.2476	−0.9378	0.9114	−0.0876	−0.0637	1					
d_1	/kHz	−0.1885(16)	0.5262	−0.0325	−0.0059	0.0308	−0.1286	0.0405	1				
d_2	/kHz	−0.09410(44)	0.0547	0.2909	0.1444	0.7454	0.8623	−0.1085	0.0273	1			
H_{JJJ}	/ Hz	−0.0012*	−0.3077	0.1520	0.1408	0.3196	0.8748	−0.0238	−0.2023	0.5530	1		
H_{JJK}	/ Hz	1.94(10)	−0.0457	−0.2458	−0.1081	−0.6030	−0.8349	0.0975	−0.0207	−0.9563	−0.5996	1	
H_{JKK}	/ Hz	−115.8(17)	0.3801	−0.0052	−0.0796	0.0553	−0.4281	−0.0360	0.2434	0.0406	−0.7809	0.0136	1
H_{KKK}	/ Hz	941*											
L_{JJKK}	/mHz	−0.4(17)											
L_{JKKK}	/mHz	−187(14)											

Table 5a. Selection of transition frequencies of the isotopomer D_2CCO measured in this investigation.

No.	J	K_a	K_c	J'	K_a'	K_c'	f_{obs} (MHz)	f_{o-c} (kHz)
1	12	0	12	11	0	11	211545.992	29
2	12	1	11	11	1	10	215333.278	−16
3	12	2	10	11	2	9	212470.447	−6
4	12	2	11	11	2	10	211952.834	14
5	13	0	13	12	0	12	229074.506	−9
6	13	2	12	12	2	11	229596.001	−6
7	13	2	11	12	2	10	230253.499	1
8	13	3	11	12	3	10	229740.433	3
9	13	3	10	12	3	9	229751.301	3
10	13	4	10	12	4	9	229647.615	31
11	13	4	9	12	4	8	229647.615	−37
12	13	6	8	12	6	7	229451.060	−1
13	13	7	7	12	7	6	229333.080	−13
14	13	8	6	12	8	5	229197.972	−8
15	13	9	5	12	9	4	229044.108	9
16	15	0	15	14	0	14	264060.244	−13
17	15	1	15	14	1	14	260560.623	−22
18	15	1	14	14	1	13	269054.296	−28
19	15	2	14	14	2	13	264867.982	15
20	15	2	13	14	2	12	265873.866	−3
21	15	3	13	14	3	12	265103.891	8
22	15	3	12	14	3	11	265126.274	15
23	15	4	12	14	4	11	264986.811	117
24	15	4	11	14	4	10	264986.811	−72
25	19	0	19	18	0	18	333713.550	−5
26	19	1	19	18	1	18	329845.572	25
27	19	1	18	18	1	17	340554.631	−23
28	19	2	18	18	2	17	335344.258	−13
29	19	2	17	18	2	16	337352.344	−1
30	19	3	17	18	3	16	335848.900	4
31	19	3	16	18	3	15	335922.273	10
32	19	4	16	18	4	15	335676.406	−11
33	19	4	15	18	4	14	335677.458	30

The standard deviation of the complete least squares fit of 183 transition frequencies is 27 kHz. A complete list of all measured transition frequencies is available under the number TNA 41 at the central library of the University of Kiel or at the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

Table 5b. Rotational constants, centrifugal distortion constants and correlation coefficients of the least squares fit analysis of 181 transitions of D_2CCO. Standard deviation of the fit is 27 kHz. Values labelled with * are not determinable; they are fixed to the values given in text.

	Watson S-reduction		A	B	C	D_J	D_{JK}	d_1	d_2	H_{JJK}	H_{JKK}	L_{JJKK}	L_{JKKK}
A	/MHz	141490.52(88)	1										
B	/MHz	9120.83101(34)	0.0112	1									
C	/MHz	8552.70127(34)	−0.1019	0.7439	1								
D_J	/kHz	2.48706(62)	0.1534	0.8218	0.8062	1							
D_{JK}	/kHz	322.972(36)	−0.1099	0.6588	0.6707	0.5559	1						
D_K	/kHz	5387.7*	−0.1095	−0.1740	0.2016	−0.0255	0.0401	1					
d_1	/kHz	−0.21841(26)	0.9577	0.0224	−0.1140	0.1558	−0.1151	−0.3622	1				
d_2	/kHz	−0.11369(24)	0.1715	0.5716	0.5611	0.7111	0.7846	−0.0142	0.1712	1			
H_{JJJ}	/ Hz	−0.0012*	−0.2031	0.4929	0.5122	0.3214	0.9172	0.0553	−0.2100	0.5470	1		
H_{JJK}	/ Hz	2.053(63)	−0.1562	−0.4400	−0.4321	−0.5581	−0.7159	0.0096	−0.1555	−0.9351	−0.5467	1	
H_{JKK}	/ Hz	−123.85(75)	0.3172	−0.2385	−0.2640	0.0142	−0.5425	−0.0648	0.3244	0.0155	−0.7819	−0.0699	1
H_{KKK}	/ Hz	941*											
L_{JJKK}	/mHz	2.55(99)											
L_{JKKK}	/mHz	−187.5(45)											

deuterium. The derived rotational constants given in Table 7 represent now, with the new investigated isotopomers, a group of eleven sets of data, which will be the basis for a mass-dependent structure calculation after Watson et al. [4] in a following paper. Due to the definition of an r_m-structure, a good agreement with the *ab initio* r_e-structure of paper [3] is now to be expected, reflecting the increased number of available rotational constants.

Aknowledgements

I wish to thank Prof. R. Knoechel and the Technical Faculty of the University of Kiel for research facilities. My gratitude goes also to the central workshop of

Table 6a. Selection of transition frequencies of the isotopomer DHCCO measured in this investigation.

No.	J	K_a	K_c	J'	K_a'	K_c'	f_{obs} (MHz)	f_{o-c} (kHz)
1	12	0	12	11	0	11	225581.294	−1
2	12	1	12	11	1	11	222936.522	−24
3	12	1	11	11	1	10	228600.345	−7
4	12	2	11	11	2	10	225767.935	−11
5	12	2	10	11	2	9	226025.242	12
6	13	1	13	12	1	12	241499.152	−4
7	13	1	12	12	1	11	247633.465	−8
8	13	2	12	12	2	11	244570.010	38
9	13	2	11	12	2	10	244897.165	−2
10	13	3	11	12	3	10	244620.361	23
11	13	3	10	12	3	9	244623.539	−1
12	13	4	10	12	4	9	244541.841	24
13	15	0	15	14	0	14	281780.467	−6
14	15	1	15	14	1	14	278613.289	7
15	15	1	14	14	1	13	285686.932	3
16	15	2	14	14	2	13	282165.200	9
17	15	2	13	14	2	12	282667.453	−29
18	15	3	13	14	3	12	282258.556	−6
19	15	3	12	14	3	11	282265.153	−3
20	15	4	12	14	4	11	282162.067	11
21	15	4	11	14	4	10	282162.067	−22
22	15	5	11	14	5	10	282058.120	7
23	15	6	10	14	6	9	281938.087	−22
24	15	7	9	14	7	8	281797.484	19
25	17	0	17	16	0	16	319177.003	14
26	17	1	17	16	1	16	315711.039	21
27	17	1	16	16	1	15	323720.925	−25
28	17	2	16	16	2	15	319747.179	7
29	17	2	15	16	2	14	320476.799	18
30	17	3	15	16	3	14	319898.065	−3
31	17	3	14	16	3	13	319910.455	4
32	17	4	14	16	4	13	319781.615	11
33	17	4	13	16	4	12	319781.615	−70
34	17	5	13	16	5	12	319659.820	5
35	17	6	12	16	6	11	319521.789	9
36	17	7	11	16	7	10	319361.288	27

The standard deviation of the complete least squares fit of 159 transition frequencies is 23 kHz. A complete list of all measured transition frequencies is available under the number TNA 41 at the central library of the University of Kiel or at the Sektion für Spektren und Strukturdokumentation, University of Ulm (Germany).

the Technical Faculty, which gave the necessary assistance. Further I would like to thank Prof. H. Dreizler, Kiel and Dr. L. Nemes, Budapest for reading and commenting the manuscript.

Table 6b. Rotational constants, centrifugal distortion constants and correlation coefficients of the Least Squares fit analysis of 159 transitions of DHCCO. Standard deviation is 23 kHz. Values labelled with * are not determinable; they are fixed to the values given in text.

	Watson S-reduction		A	B	C	D_J	D_{JK}	d_1	d_2	H_{JJK}	H_{JKK}	L_{JJKK}	L_{JKKK}
A	/MHz	194285.8(33)	A	1									
B	/MHz	9647.06575(44)	B	−0.0087	1								
C	/MHz	9174.64485(45)	C	−0.0895	0.7826	1							
D_J	/kHz	3.00867(97)	D_J	0.1594	0.8573	0.8460	1						
D_{JK}	/kHz	328.483(56)	D_{JK}	−0.1924	0.6620	0.6778	0.5412	1					
D_K	/kHz	14465.7*	d_1	−0.1286	−0.1424	0.2178	0.0035	0.0690	1				
d_1	/kHz	−0.22491(34)	d_2	0.9837	0.0010	−0.1065	0.1561	−0.1968	−0.2925	1			
d_2	/kHz	−0.08326(34)	H_{JJK}	0.1418	0.6361	0.6330	0.7369	0.7835	0.0173	0.1379	1		
H_{JJJ}	/ Hz	−0.00162*	H_{JKK}	−0.3014	0.4468	0.4684	0.2621	0.9010	0.0758	−0.3050	0.5042	1	
H_{JJK}	/ Hz	2.14(10)	L_{JJKK}	−0.1007	−0.5140	−0.5146	−0.5830	−0.7815	−0.0226	−0.0969	−0.9508	−0.5861	1
H_{JKK}	/ Hz	−240.0(17)	L_{JKKK}	0.3743	−0.2360	−0.2592	−0.0080	−0.6422	−0.0713	0.3766	−0.1094	−0.8927	0.1908
H_{KKK}	/ Hz	3025*											
L_{JJKK}	/mHz	5.0(20)											
L_{JKKK}	/mHz	−517(16)											

Table 7. Derived rotational constants (in MHz), moments of inertia and inertia defects (in amu Å^2) for 11 isotopomers of ketene.

Isotopomer	*A*	*B*	*C*	I_a	I_b	I_c	Δ
H_2CCO[a]	*282101.185(409)*	*10293.32117(80)*	*9915.90548(82)*	*1.7914813(27)*	*49.0977597(43)*	*50.9665013(42)*	*0.077260*
H_2CCO[b]	282032(22)	10293.31963(81)	9915.90393(80)	1.79192(14)	49.0977759(34)	50.9665184(41)	0.076821
$H_2C^{13}CO$[b]	282037(26)	10293.6281(11)	9916.2102(11)	1.79189(16)	49.0963045(52)	50.9649442(56)	0.076750
$H_2{}^{13}CCO$[b]	282044(14)	9960.97994(61)	9607.14130(60)	1.79184(10)	50.7358817(31)	52.6045245(33)	0.076798
$H_2CC^{18}O$[b]	282002(22)	9761.23954(92)	9421.12530(92)	1.79211(17)	51.7740701(51)	53.6431778(52)	0.076996
$H_2CC^{17}O$[c]	282072(22)	10013.4764(28)	9655.9118(24)	1.79167(14)	50.469895(15)	52.338827(14)	0.077265
$H_2{}^{13}C^{13}CO$[d]	282031(22)	9960.8654(27)	9607.0546(28)	1.79193(14)	50.736465(14)	52.604999(15)	0.076607
D_2CCO[d,e]	141490.52(88)	9120.83101(34)	8552.70127(35)	3.571823(22)	55.4093261(21)	59.0899898(24)	0.108849
$D_2{}^{13}CCO$[d]	141483.7(10)	8890.4753(17)	8349.8413(15)	3.571995(25)	56.845004(11)	60.525593(11)	0.108595
$D_2C^{13}CO$[d]	141484.0(14)	9119.4284(24)	8551.4841(23)	3.571988(35)	55.417848(15)	59.098408(16)	0.108572
$D_2CC^{18}O$[d]	141490.0(13)	8641.8429(21)	8130.0534(21)	3.571836(33)	58.480478(14)	62.161843(16)	0.109529
$DHCCO$[d,e]	194285.8(33)	9647.06578(44)	9174.64485(45)	2.601214(44)	52.3868201(25)	55.0843230(27)	0.096288

[a] [10]. Data, reported for comparison, are results of IR + MW fit; [b] [1]; [c] [5]; [d] this work; [e] [11]. The coefficient 505379.1 MHz·amu·Å^2 has been used for the conversion.

[1] A. Guarnieri and A. Huckauf, Z. Naturforsch. **58a**, 275 (2003).

[2] L. Nemes, in: Spectroscopy: Perspectives and Frontiers (Ed. A. P. Roy), Narosa Publishing House, New Delhi, India 1997.

[3] A. L. L. East, W. D. Allen, and J. Klippenstein, J. Chem. Phys. **102**, 8506 (1995).

[4] J. K. G. Watson, A. Roytburg, and W. Ulrich, J. Mol. Spectrosc. **196**, 102 (1999).

[5] A. Guarnieri and A. Huckauf, Z. Naturforsch. **56a**, 440 (2001).

[6] J. K. G. Watson, J. Mol. Spectrosc. **207**, 16 (2001).

[7] Z. Kisiel, J. Mol. Spectrosc. **218**, 58 (2003); Z. Kisiel, Strfit Program in PROSPE (Programs for ROtational SPEctroscopy). http://info.ifpan.edu.pl/∼kisiel /prospe.htm.

[8] J. K. G. Watson, Aspects of Quartic and Sextic Centrifugal Effects on Rotational Energy Levels, in: Vibrational Spectra and Structure, Vol. 6 (Ed. J. R. Durig), Elsevier, Amsterdam 1977, pp. 1 – 89; W. Gordy and R. L. Cook, Microwave Molecular Spectra, Wiley Interscience Equations 8.111, 8.112,.8.113 and 8.117, pp. 334, 335.

[9] Program kindly delivered by Dr. Laszlo Nemes, Central Research Institute for Chemistry, Hungarian Academie of Sciences, Budapest, Hungary; Z. Kisiel, Asfit Program in PROSPE (Programs for ROtational SPEctroscopy). http://info.ifpan.edu.pl/∼kisiel/prospe.htm.

[10] J. W. C. Johns, L. Nemes, K. M. T. Yamada, T. Y. Wang, J. L. Doménech, J. Santos, P. Cancio, D. Bermejo, J. Ortigoso, and R. Escribano, J. Mol. Spectrosc. **156**, 501 (1992).

[11] L. Nemes and M. Winnewisser, Z. Naturforsch. **31a**, 272 (1976).

[12] Š. Urban and K. M. T. Yamada, J. Mol. Spectrosc. **160**, 279 (1993).

[13] F. Hegelund, J. Kauppinen, and F. Winther, Mol. Phys. **61**, 261 (1987).

[14] W. Gordy and R. Cook, Microwave Molecular Spectra, Wiley Interscience, New York 1984, p. 335.

[15] J. L. Duncan, A. M. Ferguson, J. Harper, and K. H. Tonge, J. Mol. Spectrosc. **125**, 196 (1987).