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The Ground State Rotational Spectrum of Formaldehyde

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The ground state rotational spectrum has been measured from 1 to 2600 GHz. These new measurements together with the older ones have been fitted to a standard *A*-reduced Watson-type Hamiltonian. The accuracy of the rotational and centrifugal distortion (including some octic ones) constants has been notably improved. The experimental constants are compared to the *ab initio* ones.

INTRODUCTION

Formaldehyde (H_2CO) is one of the molecules most extensively studied by microwave spectroscopy: more than 365 papers have been published on this subject to date. The reasons for this interest are numerous:

(i) With the advent of high-resolution spectroscopy in the terahertz region, it is of great interest to check the limits of the vibration–rotation theory and the applicability of the Watsonian approach to fitting the data. For light molecules such as, e.g., H_2S, the Padé formalism might be used as an alternative approach (*1*).

(ii) It is a small tetraatomic molecule and its properties may be easily predicted by *ab initio* calculations. Particularly, many papers are devoted to the calculation of the harmonic and anharmonic force field of H_2CO. A list of references may be found in Ref. (*2*). To check the quality of the force field, it is desirable to experimentally determine parameters which depend on this force field (centrifugal distortion constants, rovibrational constants, . . .).

(iii) Formaldehyde is one of the first polyatomic molecules to be detected in interstellar clouds (1968), and it is one of the most widely distributed interstellar molecules. In fact all its isotopic species have been detected including D_2CO (see, for instance, Ref. (*3*) for a list of references). Recently, it was also identified in several comets at submillimeter wavelengths (*4*).

The most recent centrifugal distortion analysis was published by Cornet and Winnewisser in 1980 (*5*). However, the measurement of the pure rotational spectrum was limited to the very low frequency range of the submillimeter-wave spectrum (460 GHz). Since H_2CO possesses large rotational constants ($A \approx 282$ GHz, $B \approx 39$ GHz, and $C \approx 34$ GHz), it would be extremely useful to measure the rotational spectrum at higher frequencies in order to improve the accuracy of the centrifugal distortion constants. Indeed to obtain accurate sextic constants, Cornet and Winnewisser (*5*) were obliged to combine the rotational data with infrared and ultraviolet combination differences. Nevertheless, the sextic constant Φ_J could still not be determined accurately: 0.031(7) Hz.

The recent development of submillimeter-wave radioastronomy has raised the interest for highly precise line predictions in the far-infrared range. In fact, the two recent Caltec-Submillimeterwave Observatory's CSO-frequency surveys from 325 to 360 GHz (*6*) and from 580 to 720 GHz (*7*) show that the higher *J* rotational transitions of H_2CO carry very strong intensities in high excitation sources such as Orion A. In fact, the $J = 9 \leftarrow 8$, $K = 0$ and $K = 1$ (upper/lower) transitions emit intensely from the cores of star-forming regions with antenna temperatures of about 15 K for Orion A. Precise rest frequency positions are required to establish unambiguously the Doppler corrections of the source. This fact assumes importance in determining experimentally the dynamics of the source and possibly in this manner can one derive from which part of the core region the emission emanates. This is the reason why we undertook a new and more complete study of the rotational spectrum of H_2CO.

EXPERIMENTAL DETAILS

The rotational spectrum of H_2CO was measured between 1 and 2600 GHz using several spectrometers in three different laboratories.

In Lille, the submillimeter-wave spectrum was measured between 800 and 2600 GHz with a far-infrared microwave sideband spectrometer (*8*). The outputs of

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a computer-controlled synthesizer (2–18 GHz) and an optically pumped far-infrared laser are mixed on a Schottky diode. A heterodyne receiver is used to detect the sideband signal. The length of the laser cavity is adjusted at the top of the Doppler profile of the laser line. The accuracy of the frequency measurements depends on the accuracy of the frequency of the laser line. For most measurements, it is between 500 kHz and 1 MHz, but, at 2500 GHz, the total width at half maximum due to the Doppler broadening is on the order of 7 MHz, giving an uncertainty of a few MHz for the frequency of the laser line. Additional interesting millimeter-wave lines were measured in the range 100–470 GHz with a source-modulated millimeter-wave spectrometer whose radiation source is either BWOs (340–470 GHz) or a GaAs Schottky multiplier driven by Gunn diodes (100–300 GHz). The frequency of the measurements is generally better than 50 kHz.

At Cologne, we have used the recently constructed terahertz spectrometer. As fundamental frequency sources, phase- and frequency-locked BWOs are used (*9*). Recently, we have achieved operation up to about 1.3 THz (*10*) and have reached measurement accuracies for unblended strong lines of about 10 kHz. This high measurement accuracy can be used in the region of frequency overlap with other techniques, such as laser sideband or Fourier FIR spectroscopy, for calibration purposes. Further details of the Cologne spectrometer have been published (*11, 12*). At Cologne, we have measured and analysed in addition to the parent molecule the terahertz spectra of the astrophysically relevant ^{13}C- and ^{18}O-isotopomers. These results will be published independently.

In Kiel, a few very weak high J, low K, direct K-doublet Q-branch transitions located in the microwave region were measured. These lines are useful from the point of view of the centrifugal distortion and were recorded with waveguide microwave Fourier transform spectrometers in the frequency range from 1 to 26.5 GHz. The 1–4 GHz measurements have been performed with a setup using a 10-m coaxial cell (*13*). A circular waveguide cell has been used in the 18–26.5 GHz range (*14*). Standard setups containing waveguide cells with rectangular or quadratic cross sections and lengths from 2 to 12 m have been used in the 5–18 GHz range (*15, 16*). The microwave pulse power was about 10–100 mW, and the pulse length about 200 nsec. All measurements have been performed at room temperature with pressures between 2 and 5 mTorr.

The formaldehyde was freshly prepared before the measurements. Paraformaldehyde was heated *in vacuo*, and the reaction products were pumped through two traps connected in series and held at −20°C and liquid nitrogen temperature. The content of the second trap was used for the measurements.

ANALYSIS

First, the existing data were used to estimate the rotational parameters together with their variance–covariance matrix, which were then used to predict unmeasured transitions and their standard deviation. Only transitions with a standard deviation significantly larger than the measurement accuracy were retained. It appeared that most of these transitions are in the submillimeter-wave range. The newly measured transitions are listed in Table 1. A total of 273 transitions with $J \leqslant 44$ and $K_a \leqslant 12$ have been assigned. The new transitions combined with those of Ref. (*5*) were fitted to the Hamiltonian of Watson using the I^r representation in the A-reduction (*17*). It was found necessary to extend this Hamiltonian up to J^8 terms by adding (*18*):

$$\begin{aligned} H^{(8)} = {} & L_J\hat{J}^8 + L_{JJK}\hat{J}^6\hat{J}_z^2 + L_{JK}\hat{J}^4\hat{J}_z^4 + L_{KKJ}\hat{J}^2\hat{J}_z^6 + L_K\hat{J}_z^8 \\ & + 2\ell_J\hat{J}^6(\hat{J}_x^2 - \hat{J}_y^2) + \ell_{JK}\hat{J}^4[\hat{J}_z^2(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^2] \\ & + \ell_{KJ}\hat{J}^2[\hat{J}_z^4(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^4] \\ & + \ell_K[\hat{J}_z^6(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^6]. \end{aligned} \quad [1]$$

The rotational and centrifugal distortion constants are given in Table 2 together with their standard deviation and their correlation matrix. The older experimental constants of Ref. (*5*) and the *ab initio* values of Ref. (*2*) are also given in Table 3. Although H_2CO is a near-symmetric top, the S-reduction does not give better results. It can be seen that most of our constants are in fair agreement with the older ones, and that Φ_J and Φ_{KJ} are much more precise: $\Phi_J/\sigma(\Phi_J) = 86$ and $\Phi_{KJ}/\sigma(\Phi_{KJ}) = 161$ (instead of 4 and 12, respectively). It is for these two parameters that the difference between the new values and the older ones is the largest. Nevertheless, this difference is also large for some other parameters (δ_K, φ_K, . . .), more than 50 standard deviations. This result is surely not satisfactory but, in fact, rather common. It is due to the fact that more parameters are determined (three octic parameters) and that the system of normal equations is not well conditioned (*19*): in our best fit, the condition number is still $\kappa = 482$, indicating the presence of collinearity (according to Belsley (*20*) a system is well conditioned when its condition number κ is less than 30). This collinearity involves the sextic constant Φ_{JK} and the two octic constants L_{JJK} and ℓ_{KJ}. However, these three parameters are rather well determined (better than 17 times the standard deviation) and, in keeping one of them (or all) fixed at zero, the fit deteriorates significantly and the conditioning

TABLE 1

Observed Rotational Frequencies (MHz) of H_2CO Used in the Analysis[a]

J	Ka	Kc	←J	Ka	Kc	fexp.	o-c	σ	S	El	Ref.
10	5	5	10	5	6	0.103	0.001	1	4.770	337.91	CW
16	6	10	16	6	11	0.142	0.003	4	4.362	624.11	CW
11	5	6	11	5	7	0.271	0.000	1	4.353	364.63	CW
18	6	12	18	6	13	0.580	0.002	2	3.886	709.07	CW
25	7	18	25	7	19	0.606	0.003	3	3.828	1188.02	CW
3	3	0	3	3	1	0.655	0.002	1	5.250	88.24	CW
12	5	7	12	5	8	0.657	0.001	1	4.003	393.77	CW
26	7	19	26	7	20	1.044	0.000	1	3.681	1251.07	CW
19	6	13	19	6	14	1.111	0.002	2	3.684	755.19	CW
13	5	8	13	5	9	1.476	0.001	1	3.704	425.35	CW
27	7	20	27	7	21	1.776	0.006	10	3.544	1316.54	CW
20	6	14	20	6	15	2.056	0.000	1	3.502	803.74	CW
8	4	4	8	4	5	2.454	0.002	2	3.776	218.33	CW
28	7	21	28	7	22	2.939	0.001	2	3.416	1384.43	CW
14	5	9	14	5	10	3.110	0.000	1	3.446	459.36	CW
21	6	15	21	6	16	3.692	0.001	2	3.337	854.72	CW
4	3	1	4	3	2	4.573	0.000	1	4.050	97.96	CW
15	5	10	15	5	11	6.210	0.000	1	3.222	495.80	CW
9	4	5	9	4	6	6.369	0.000	1	3.375	240.20	B2
22	6	16	22	6	17	6.442	0.001	1	3.186	908.14	CW
23	6	17	23	6	18	10.955	0.000	1	3.047	963.97	CW
16	5	11	16	5	12	11.833	0.000	1	3.024	534.67	CW
10	4	6	10	4	7	14.845	-0.001	2	3.051	264.51	CW
5	3	2	5	3	3	18.283	0.000	1	3.299	110.11	CW
17	5	12	17	5	13	21.646	0.000	1	2.848	575.98	CW
11	4	7	11	4	8	31.773	0.000	2	2.783	291.24	CW
18	5	13	18	5	14	38.201	0.000	1	2.692	619.72	CW
6	3	3	6	3	4	54.818	0.001	1	2.784	124.69	CW
12	4	8	12	4	9	63.446	0.000	0	2.558	320.42	CW
19	5	14	19	5	15	65.301	0.000	1	2.550	665.90	CW
2	2	0	2	2	1	71.140	0.001	1	3.333	40.04	CW
20	5	15	20	5	16	108.483	0.000	1	2.423	714.51	B1
13	4	9	13	4	10	119.615	0.000	0	2.365	352.02	CW
7	3	4	7	3	5	136.925	0.000	1	2.408	141.71	CW
21	5	16	21	5	17	175.641	-0.001	1	2.306	765.56	B1
14	4	10	14	4	11	214.812	0.000	1	2.199	386.07	B1
22	5	17	22	5	18	277.811	-0.001	1	2.199	819.04	B1
8	3	5	8	3	6	300.870	0.000	1	2.121	161.16	CW
3	2	1	3	2	2	355.568	0.001	1	2.333	47.33	CW
15	4	11	15	4	12	370.019	0.000	1	2.054	422.55	B1
9	2	7	9	2	8	22965.630	0.005	10	0.827	141.94	CW
17	3	14	17	3	15	24068.353	0.000	10	0.991	445.88	CW
35	5	30	35	5	31	24730.539	0.003	10	1.309	1736.35	CW
26	4	22	26	4	23	26358.798	0.007	10	1.140	985.02	CW
3	1	2	3	1	3	28974.805	0.003	10	0.583	22.28	CW
31	3	28	32	1	31	30724.378	-0.078	200	0.023	1294.85	CW
36	5	31	36	5	32	32148.522	-0.003	10	1.260	1823.99	CW
30	1	29	29	3	26	32345.456	-0.004	20	0.027	1143.96	CW
18	3	15	18	3	16	33270.587	-0.002	10	0.928	489.70	CW
10	2	8	10	2	9	34100.050	-0.001	10	0.741	166.17	CW
27	4	23	27	4	24	34982.292	0.001	10	1.087	1050.80	CW
26	1	25	25	3	22	40254.701	-0.015	20	0.029	870.63	CW
37	5	32	37	5	33	41402.359	-0.004	30	1.213	1914.06	CW
19	3	16	19	3	17	45063.028	0.004	20	0.870	535.94	CW
28	4	24	28	4	25	45834.995	-0.006	20	1.037	1119.02	CW
4	1	3	4	1	4	48284.547	0.034	20	0.450	31.67	CW
11	2	9	11	2	10	48618.033	0.032	20	0.669	192.80	CW
29	1	28	28	3	25	49516.276	-0.047	50	0.028	1071.79	CW
27	1	26	26	3	23	53589.200	-0.602	600	0.029	935.12	CW
28	1	27	27	3	24	56661.500	0.213	600	0.029	1002.18	CW
22	3	19	23	1	22	59352.700	-0.834	900	0.025	690.56	CW
20	3	17	20	3	18	59896.870	-0.040	100	0.817	584.60	CW
12	2	10	12	2	11	66973.580	0.041	100	0.607	221.82	CW
5	1	4	5	1	5	72409.090	0.005	100	0.367	43.41	CW
1	0	1	0	0	0	72837.948	-0.001	10	1.000	0.00	CW
22	3	19	22	3	20	100511.100	-0.053	150	0.719	689.19	CW
6	1	5	6	1	6	101332.991	0.011	44	0.310	57.48	CW
7	1	6	7	1	7	135030.440	-0.004	100	0.269	73.89	CW
2	1	2	1	1	1	140839.502	-0.016	10	1.500	10.54	CW
2	0	2	1	0	1	145602.949	-0.003	10	2.000	2.43	CW
18	2	16	19	0	19	148655.337	0.118	100	0.013	450.29	L
15	2	13	15	2	14	148679.198	-0.024	30	0.464	323.26	CW
2	1	1	1	1	0	150498.334	-0.004	10	1.500	10.70	CW
13	2	11	14	0	14	154025.270	-0.039	30	0.014	251.10	L
24	3	21	24	3	22	158528.320	-0.093	100	0.633	803.42	L
20	3	17	21	1	20	170589.029	0.002	10	0.020	580.91	CW
8	1	7	8	1	8	173461.705	-0.003	30	0.238	92.63	CW
12	2	10	13	0	13	181017.384	0.000	50	0.013	218.02	CW
16	2	14	16	2	15	185607.137	-0.013	30	0.427	361.83	CW
3	1	3	2	1	2	211211.468	0.016	10	2.667	15.24	CW
9	3	6	9	3	7	600.740	0.000	1	1.894	183.05	B1
4	2	2	4	2	3	1065.869	0.000	1	1.798	57.04	B1
10	3	7	10	3	8	1113.190	0.000	1	1.710	207.37	B1
26	5	21	26	5	22	1428.685	-0.004	5	1.848	1057.37	K
18	4	14	18	4	15	1547.359	-0.001	5	1.709	546.65	K
11	3	8	11	3	9	1942.451	0.000	5	1.558	234.13	K
27	5	22	27	5	23	2063.262	-0.004	5	1.775	1123.05	K
19	4	15	19	4	16	2360.186	0.001	5	1.616	592.89	K
5	2	3	5	2	4	2483.408	0.000	5	1.463	69.18	K
28	5	23	28	5	24	2936.930	-0.004	5	1.705	1191.17	K
12	3	9	12	3	10	3225.423	0.000	5	1.429	263.33	K
20	4	16	20	4	17	3518.794	0.001	5	1.532	641.58	K
1	1	0	1	1	1	4829.660	0.000	1	1.500	10.54	CW
6	2	4	6	2	5	4954.760	0.049	100	1.232	83.75	CW
13	3	10	13	3	11	5136.539	0.001	5	1.318	294.97	K
21	4	17	21	4	18	5138.492	0.000	5	1.454	692.72	K
39	6	33	39	6	34	5427.157	-0.008	10	1.733	2188.02	K
31	1	30	30	3	27	5461.220	0.001	10	0.025	1218.66	K
30	5	25	30	5	26	5718.241	-0.003	5	1.579	1334.74	K
40	6	34	40	6	35	7248.848	0.000	5	1.680	2285.19	K
22	4	18	22	4	19	7362.640	0.001	5	1.383	746.29	K
31	5	26	31	5	27	7833.287	-0.001	5	1.520	1410.18	K
14	3	11	14	3	12	7892.034	0.002	5	1.222	329.04	K
7	2	5	7	2	6	8884.820	-0.001	10	1.063	100.73	CW
41	6	35	41	6	36	9600.263	-0.001	5	1.630	2384.79	K
23	4	19	23	4	20	10366.520	0.003	10	1.316	802.31	CW
32	5	27	32	5	28	10608.668	-0.002	10	1.464	1488.07	CW
32	2	30	31	4	27	11345.861	0.016	50	0.033	1341.45	K
15	3	12	15	3	13	11753.122	0.001	10	1.136	365.56	CW
42	6	36	42	6	37	12610.781	0.007	10	1.580	2486.82	K
33	5	28	33	5	29	14211.795	0.002	5	1.410	1568.39	K
24	4	20	24	4	21	14360.927	0.002	5	1.254	860.78	K
2	1	1	2	1	2	14488.479	0.000	1	0.833	15.24	CW
8	2	6	8	2	7	14726.637	0.000	5	0.932	120.13	K
23	3	20	24	1	23	16583.764	-0.003	5	0.027	748.79	K
25	1	24	24	3	21	16769.270	-0.001	5	0.028	808.70	K
16	3	13	16	3	14	17027.482	0.002	5	1.060	404.50	K
34	5	29	34	5	30	18841.428	0.006	10	1.359	1651.15	CW
25	4	21	25	4	22	19595.163	0.031	20	1.195	921.68	CW
44	6	38	44	6	39	21253.251	0.000	5	1.485	2698.17	K
9	1	8	9	1	9	216568.651	-0.016	30	0.213	113.70	CW
3	0	3	2	0	2	218222.192	0.003	10	2.999	7.29	CW
3	2	2	2	2	1	218475.632	-0.008	10	1.667	40.04	CW
3	2	1	2	2	0	218760.066	-0.003	10	1.667	40.04	CW
3	1	2	2	1	1	225697.775	0.000	10	2.667	15.72	CW
17	2	15	17	2	16	227583.553	0.003	30	0.395	402.78	L
26	3	23	26	3	24	236589.150	0.001	30	0.558	927.23	L
19	3	16	20	1	19	237482.325	-0.005	30	0.017	529.52	L
10	1	9	10	1	10	264270.140	-0.001	200	0.194	137.10	CW
18	2	16	18	2	17	274617.580	-0.017	200	0.366	446.09	CW
4	1	4	3	1	3	281526.929	0.006	10	3.750	22.28	CW
4	0	4	3	0	3	290623.405	-0.010	10	3.999	14.57	CW
4	2	3	3	2	2	291237.780	0.007	200	3.000	47.33	CW
4	3	2	3	3	1	291380.488	0.033	100	1.750	88.24	CW
4	3	1	3	3	0	291384.264	-0.110	100	1.750	88.24	CW
4	2	2	3	2	1	291948.060	-0.014	200	3.000	47.34	CW
4	1	3	3	1	2	300836.635	0.001	10	3.750	23.25	CW
27	4	23	28	2	26	341039.674	0.014	30	0.019	1040.60	L
5	1	5	4	1	4	351768.645	0.004	30	4.800	31.67	CW
5	0	5	4	0	4	362736.048	0.033	30	4.997	24.26	CW
5	2	4	4	2	3	363945.894	0.020	30	4.200	57.04	CW
5	4	2	4	4	1	364103.249	0.026	30	1.800	155.17	CW
5	4	1	4	4	0	364103.249	-0.013	30	1.800	155.17	CW
5	3	3	4	3	2	364275.141	-0.065	100	3.200	97.96	CW
5	3	2	4	3	1	364288.884	-0.032	100	3.200	97.96	CW
5	2	3	4	2	2	365363.428	0.015	30	4.200	57.08	CW
12	1	11	12	1	12	372986.243	-0.012	50	0.166	190.84	L
5	1	4	4	1	3	375893.216	0.003	30	4.800	33.28	CW
20	2	18	20	2	19	383592.517	-0.040	50	0.319	539.77	L
17	3	14	18	1	17	389364.903	0.014	30	0.012	433.70	L
29	3	26	29	3	27	394068.595	-0.100	100	0.465	1130.81	L
6	1	6	5	1	5	421920.772	0.168	200	5.833	43.41	CW
6	0	6	5	0	5	434492.995	0.048	30	5.995	36.36	CW
6	2	5	5	2	4	436586.486	-0.009	30	5.333	69.18	L
6	5	1	5	5	0	436751.040	-0.021	30	1.833	240.78	L
6	4	3	5	4	2	436957.406	0.073	500	3.333	167.31	L
6	3	4	5	3	3	437199.519	0.023	30	4.500	110.11	L
6	3	3	5	3	2	437235.976	-0.054	30	4.500	110.11	L
6	2	4	5	2	3	439057.786	-0.012	30	5.333	69.27	L
26	4	22	27	2	25	442896.100	-0.010	30	0.017	971.13	L

TABLE 1—*Continued*

J	Ka	Kc	←J	Ka	Kc	fexp.	o-c	σ	S	El	Ref.
21	2	19	21	2	20	445274.162	-0.025	30	0.300	590.13	L
6	1	5	5	1	4	450844.412	-0.087	100	5.832	45.82	L
30	3	27	30	3	28	457331.271	-0.129	100	0.439	1203.40	L
8	1	8	7	1	7	561899.318	0.004	100	7.873	73.89	C
15	1	14	15	1	15	566608.786	0.027	100	0.140	288.77	C
8	0	8	7	0	7	576708.315	0.005	100	7.989	67.73	C
8	2	7	7	2	6	581611.847	-0.011	100	7.499	100.73	C
8	7	2	7	7	1	581749.983	0.019	100	1.875	467.71	C
23	2	21	23	2	22	582058.559	0.052	100	0.269	697.84	C
8	6	3	7	6	2	582070.795	-0.008	100	3.500	361.98	C
8	5	4	7	5	3	582382.070	-0.014	100	4.875	272.34	C
8	4	5	7	4	4	582722.953	0.127	100	6.000	198.90	C
8	4	4	7	4	3	582724.280	-0.180	100	6.000	198.90	C
8	3	6	7	3	5	583144.604	-0.015	100	6.875	141.71	C
8	3	5	7	3	4	583308.558	-0.006	100	6.875	141.71	C
8	2	6	7	2	5	587453.659	-0.015	100	7.499	101.02	C
8	1	7	7	1	6	600330.566	-0.011	100	7.873	78.39	C
4	2	2	5	0	5	621133.112	0.099	200	0.001	36.36	C
9	1	9	8	1	8	631702.813	-0.013	100	8.886	92.63	C
16	1	15	16	1	16	638263.261	0.033	50	0.134	326.00	C
9	0	9	8	0	8	647081.735	-0.004	30	8.984	86.96	C
14	3	11	15	1	14	648802.628	0.027	150	0.006	307.67	C
9	2	8	8	2	7	653970.155	-0.015	40	8.554	120.13	C
9	8	2	8	8	1	654065.180	0.065	50	1.889	608.85	C
9	7	3	8	7	2	654463.345	0.009	30	3.556	487.12	C
9	6	4	8	6	3	654838.225	-0.017	40	5.000	381.39	C
9	4	6	8	4	5	655639.907	0.089	50	7.222	218.33	C
9	4	5	8	4	4	655643.676	-0.059	50	7.222	218.33	C
9	3	7	8	3	6	656164.708	-0.014	50	8.000	161.16	C
9	3	6	8	3	5	656464.572	-0.020	30	8.000	161.17	C
24	2	22	24	2	23	656658.582	0.080	100	0.257	755.18	C
9	1	8	8	1	7	674809.776	-0.010	100	8.885	98.42	C
3	2	1	4	0	4	691921.105	0.152	100	0.000	24.26	C
10	1	10	9	1	9	701370.458	-0.009	100	9.896	113.70	C
17	1	16	17	1	17	712908.776	0.060	100	0.129	365.53	C
12	11	2	11	11	1	870063.852	0.176	100	1.917	1141.47	C
12	2	11	11	2	10	870273.480	-0.001	100	11.663	192.80	C
12	9	4	11	9	3	871410.665	0.062	100	5.250	819.15	C
12	8	5	11	8	4	872016.071	0.026	100	6.667	681.57	C
12	7	6	11	7	5	872590.976	-0.008	100	7.917	559.89	C
14	6	9	13	6	8	1018726.640	0.020	30	11.429	514.88	C
14	5	10	13	5	9	1019557.779	0.820	2080	12.215	425.35	C
10	3	7	11	1	10	1020448.368	0.017	100	0.002	173.37	C
11	2	10	11	0	11	1022509.473	-0.007	150	0.032	158.69	C
12	2	11	12	0	12	1037631.665	-0.003	150	0.039	187.21	C
14	2	12	13	2	11	1040865.220	0.117	1000	13.716	256.24	L
15	1	15	14	1	14	1047532.292	0.014	100	14.923	253.82	C
13	2	12	13	0	13	1056120.368	-0.008	120	0.047	218.02	C
17	1	17	16	1	16	1184994.400	0.012	1000	16.928	326.00	L
16	1	15	15	1	14	1187985.860	0.235	1000	15.912	307.67	L
17	1	16	16	1	15	1259640.550	0.674	1000	16.910	347.29	L
18	0	18	17	0	17	1261740.250	0.387	1000	17.944	363.87	L
19	7	12	18	7	11	1381452.419	0.375	1000	16.422	814.56	L
19	5	15	18	5	14	1384332.480	-0.002	1000	17.685	619.72	L
19	5	14	18	5	13	1384359.880	0.298	1000	17.685	619.72	L
19	3	17	18	3	16	1386263.090	0.426	1000	18.523	489.70	L
19	4	16	18	4	15	1386464.730	0.148	1000	18.158	546.65	L
12	6	7	11	6	6	873159.787	-0.004	100	9.000	454.20	C
12	5	8	11	5	7	873775.413	0.177	100	9.917	364.63	C
12	4	9	11	4	8	874557.380	-0.010	100	10.667	291.24	C
12	4	8	11	4	7	874589.043	-0.020	100	10.667	291.24	C
12	3	10	11	3	9	875366.175	-0.005	100	11.250	234.13	C
12	3	9	11	3	8	876649.150	-0.002	100	11.250	234.20	C
12	2	10	11	2	9	888629.012	-0.008	30	11.666	194.42	C
12	1	11	11	1	10	896805.097	-0.004	150	11.907	173.37	C
27	2	25	27	2	26	901481.861	0.268	500	0.230	941.06	C
13	1	13	12	1	12	909507.566	-0.111	150	12.916	190.84	C
13	0	13	12	0	12	923587.825	0.002	50	12.963	187.21	C
11	3	8	12	1	11	926754.911	0.031	200	0.002	203.28	C
13	12	2	12	12	1	941690.074	-0.065	150	1.923	1354.94	C
13	2	12	12	2	11	942076.535	0.004	50	12.687	221.82	C
13	11	3	12	11	2	942510.238	0.003	30	3.692	1170.49	C
13	10	4	12	10	3	943273.417	0.010	30	5.308	1001.54	C
13	9	5	12	9	4	943984.915	0.030	30	6.769	848.21	C
13	8	6	12	8	5	944653.527	-0.003	30	8.077	710.66	C
13	8	5	12	8	4	944653.527	-0.003	30	8.077	710.66	C
13	7	7	12	7	6	945295.262	-0.004	50	9.231	588.99	C
13	7	6	12	7	5	945295.262	-0.004	50	9.231	588.99	C
13	6	8	12	6	7	945941.087	-0.002	30	10.231	483.33	C
13	6	7	12	6	6	945941.087	-0.008	30	10.231	483.33	C
13	5	9	12	5	8	946658.419	0.415	1000	11.077	393.77	C
13	5	8	12	5	7	946658.419	-0.403	1000	11.077	393.77	C
13	4	10	12	4	9	947591.820	0.003	30	11.769	320.42	C
13	4	9	12	4	8	947647.981	-0.005	80	11.769	320.42	C
13	3	11	12	3	10	948453.819	0.007	100	12.307	263.33	C
13	3	10	12	3	9	950364.931	0.004	100	12.307	263.44	C
13	2	11	12	2	10	964668.054	0.001	50	12.693	224.06	C
8	2	7	8	0	8	994322.727	0.076	250	0.014	86.96	C
9	2	8	9	0	9	1001211.089	0.006	200	0.019	108.55	C
10	2	9	10	0	10	1010480.968	-0.005	200	0.025	132.46	C
14	2	13	13	2	12	1013711.409	0.020	50	13.708	253.25	C
14	12	3	13	12	2	1014053.257	-0.608	1120	3.714	1386.35	C
14	11	4	13	11	3	1014942.457	-0.199	120	5.357	1201.93	C
14	10	5	13	10	4	1015771.991	-0.107	150	6.857	1033.00	C
14	9	6	13	9	5	1016548.672	-0.059	40	8.215	879.70	C
14	8	7	13	8	6	1017283.605	-0.023	30	9.429	742.17	C
14	7	8	13	7	7	1017996.678	-0.004	30	10.500	620.52	C
19	4	15	18	4	14	1387277.490	0.083	1000	18.158	546.70	L
20	1	20	19	1	19	1390236.900	-0.209	1000	19.932	451.44	L
19	1	18	18	1	17	1401314.410	0.137	1000	18.901	433.70	L
21	4	17	20	4	16	1534564.900	-0.214	1000	20.238	641.70	L
22	4	18	21	4	17	1608419.900	1.037	1000	21.272	692.89	L
22	1	21	21	1	20	1609503.280	0.617	1000	21.881	580.91	L
25	4	21	24	4	20	1831086.500	0.558	1000	24.359	861.26	L
26	5	22	25	5	21	1895910.000	0.493	1000	25.039	994.13	L
26	5	21	25	5	20	1896364.980	0.864	1000	25.039	994.16	L
26	4	23	25	4	22	1898997.300	0.944	1000	25.383	921.68	L
34	4	30	33	4	29	2513626.720	2.133	2500	33.534	1501.44	L
35	3	33	34	3	32	2525928.640	0.222	1000	34.700	1517.18	L
34	3	31	33	3	30	2539009.750	-0.547	1000	33.754	1457.83	L
36	2	35	35	2	34	2539183.030	2.116	2500	35.816	1537.20	L
37	1	37	36	1	36	2539404.460	0.967	1000	36.934	1547.32	L
37	0	37	36	0	36	2539580.000	0.382	1000	36.934	1547.29	L

[a] The uncertainties assumed in the present analysis are given in the column σ(kHz), S is the line strength and El (cm^{-1}) the energy of the lower level.
The frequencies indicated by C have been measured in Cologne, K in Kiel and L in Lille. The other frequencies are taken from the literature: CW from Ref. (**5**), B1 from Ref. (**25**) and B2 from Ref. (**26**).

does not improve. It is still possible to slightly improve the fit by freeing the octic constant L_{JK}, but it is not accurate ($L_{JK}/\sigma(L_{JK}) = 6$) and, in the final fit, it was fixed at zero. The situation is still worse for the older parameters where $\Phi_J/\sigma(\Phi_J) = 4$ and $\Phi_{KJ}/\sigma(\Phi_{KJ}) = 12$. In the latter case, we are clearly in a situation of harmful collinearity, and it may explain the differences found for some parameters. Although the collinearity is generally much less harmful for the prediction of a spectrum than for the estimation of the parameters, it is clearly desirable to continue to improve the conditioning of the data. It could be achieved by combining the rotational data with the high resolution infrared data.

The *ab initio* and experimental centrifugal distortion constants are also compared in Table 3. The agreement is rather satisfactory for the quartic constants where the mean deviation is 6%, the *ab initio* constants being systematically smaller than the experimental ones. The largest deviation is for δ_K: 13%; this result seems to be rather general, δ_K being more difficult to determine accu-

TABLE 2
Molecular Parameters of H_2CO in the Ground Vibrational State Determined Using an *A*-reduced Hamiltonian in the I^r Representation[a]

			Correlation matrix																	
A	MHz	281970.5418(84)	1.00																	
B	MHz	38836.05020(32)	0.16	1.00																
C	MHz	34002.20056(30)	0.35	0.77	1.00															
Δ_J	kHz	75.3244(12)	0.22	0.67	0.62	1.00														
Δ_{JK}	kHz	1290.967(26)	0.10	0.50	0.39	0.29	1.00													
Δ_K	kHz	19421.9(15)	0.79	-0.12	0.11	0.21	-0.46	1.00												
δ_J	kHz	10.45394(16)	-0.17	0.31	0.11	0.38	0.13	-0.15	1.00											
δ_K	kHz	1028.024(37)	-0.19	0.25	-0.26	0.02	0.23	-0.31	-0.27	1.00										
Φ_J	Hz	0.0949(11)	0.11	0.42	0.38	0.79	0.26	0.10	0.43	-0.03	1.00									
Φ_{JK}	Hz	32.006(73)	-0.04	0.30	-0.02	0.08	0.63	-0.37	-0.08	0.67	0.22	1.00								
Φ_{KJ}	Hz	-80.14(50)	0.09	0.34	0.36	0.36	0.70	-0.29	0.21	-0.09	0.11	0.01	1.00							
Φ_K	Hz	4386(64)	0.68	-0.16	0.08	0.16	-0.56	0.97	-0.24	-0.31	0.00	-0.49	-0.31	1.00						
φ_J	Hz	0.04423(19)	0.14	0.20	0.23	0.54	0.01	0.25	0.62	-0.36	0.69	0.09	-0.12	0.14	1.00					
φ_{JK}	Hz	16.953(49)	-0.42	0.16	-0.24	-0.16	0.29	-0.60	0.12	0.61	-0.06	0.30	0.19	-0.59	-0.53	1.00				
φ_K	Hz	1483.9(25)	-0.08	0.23	-0.18	0.03	0.26	-0.20	-0.24	0.85	-0.07	0.81	-0.17	-0.22	-0.09	0.24	1.00			
L_{JJK}	mHz	-1.404(51)	0.27	-0.19	0.19	0.20	-0.53	0.56	0.09	-0.76	0.14	-0.83	-0.07	0.61	0.34	-0.69	-0.75	1.00		
L_{KKJ}	mHz	51.0(30)	-0.06	-0.34	-0.28	-0.37	-0.69	0.29	-0.16	-0.08	-0.12	-0.15	-0.96	0.32	0.10	-0.21	-0.04	0.19	1.00	
ℓ_{KJ}	mHz	-71.3(23)	0.42	-0.22	0.25	0.14	-0.42	0.63	-0.08	-0.80	0.08	-0.72	-0.05	0.66	0.31	-0.81	-0.70	0.95	0.17	1.00
273 lines																				

[a] Standard errors in parentheses are shown in units of the last digit.

rately. It is known that the choice of the rotational constants (either equilibrium or ground state) has a nonnegligible effect on the calculated value of δ_K (*21*). Furthermore, the agreement is systematically better with the *T* constants than with the Δ constants for most of the molecules studied so far (*22*). There is a systematic deviation

TABLE 3
Comparison of the Experimental and *ab Initio* Centrifugal Distortion Constants[a]

	Old values (5)		Present values			*Ab initio* (2)	
	$p_o(\sigma)$	p_o/σ	$p_n(\sigma)$	p_n/σ	$\Delta p/p$[b]	p_a	$\Delta p/p$[c]
Δ_J	75.2953(70)	10756	75.3244(12)	64711	0.04	72.730	3.44
Δ_{JK}	1 290.51(12)	10464	1 290.967(26)	48865	0.04	1265.244	1.99
Δ_K	19424(2)	8324	19421.9(15)	12784	-0.01	18609.317	4.18
δ_J	10.45676(30)	34856	10.45394(15)	66143	-0.03	9.563	8.52
δ_K	1 026.031(83)	12312	1 028.024(37)	27637	0.19	896.290	12.81
Φ_J	0.0314(70)	4	0.0949(11)	86	66.87	0.090	5.22
Φ_{JK}	29.02(23)	126	32.006(73)	440	9.33	25.812	19.35
Φ_{KJ}	-112.2(93)	12	-80.14(50)	161	-39.98	-58.190	27.39
Φ_K	4499(67)	67	4386(64)	69	-2.58	3789.197	13.61
φ_J	0.04240(57)	75	0.04423(19)	235	4.14	0.030	32.22
φ_{JK}	15.67(10)	152	16.953(49)	344	7.59	13.760	18.83
φ_K	1372(6)	229	1483.9(25)	588	7.53	1156.030	22.09

[a]) p = parameter (quartic in kHz, sextic in Hz), σ = its standard deviation.
[b]) $(p_n - p_o)/p_n$ in %.
[c]) $(p_n - p_a)/p_n$ in %.

of 20% between the *ab initio* sextic constants and the experimental ones, the *ab initio* constants being smaller.

H_2CO is a planar molecule. Indeed its inertial defect is very small, $\Delta = 0.0559(1)$ uÅ^2, in good agreement with the empirical value calculated using the formulation of Watson (*23*): 0.0576 uÅ^2. The planarity defect in centrifugal distortion, whose defining equation is

$$\Delta\tau = 4\left(T_{cc} - \frac{T_2 - CT_1}{A + B}\right), \qquad [2]$$

is also very small, but significantly different from zero, $\Delta\tau = -0.00398(1)$ MHz, and it has the right order of magnitude and is negative, as was previously found for all planar molecules studied thus far (*24*). The defect in the sextic planarity relation (*18*)

$$\begin{aligned}\Delta H = 6C\Phi_J - (B - C)\Phi_{JK} - 2(2A + B + 3C)\varphi_J \\ + 2(B - C)\varphi_{JK} + 4\Delta_J^2 \qquad [3] \\ - 4\delta_J(4\Delta_J + \Delta_{JK} - 2\delta_J - 2\delta_K)\end{aligned}$$

is also significantly different from zero, $\Delta H = 0.00916(57)$ MHz^2.

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