Improved Spectroscopic Constants for $^{14}C^{16}O_2$ Obtained from the ν_3 Band

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The absorption spectra of carrier free $^{14}C^{16}O_2$ in the spectral range of 2290–2150 cm^{-1} by a medium resolution FTIR spectrometer, and the spectral region of 2258–2229 cm^{-1} with a high resolution tunable diode laser spectrometer have been recorded. Spectroscopic constants were calculated from the 00^01-00^00 and 01^11-01^10 transitions.

Introduction

The radioactive isotope ^{14}C is present in all living plants and animals. Its concentration is about 10^{-12} relative to natural carbon ^{12}C. Conventional radiocarbon dating techniques measure the beta activity of carbon samples to determine the remaining ^{14}C concentration, and hence the sample age (the half life time of ^{14}C is 5730 years). However, the accuracy of these methods is generally limited because of the low fraction of ^{14}C atoms which disintegrate during the counting periode. It is clear that any more sensitive method of radiocarbon dating should directly measure the ^{14}C remaining in the sample. CO_2 gas is an obvious choice for radiocarbon detection by infrared absorption techniques. In this respect a detailed study of the rotational-vibrational spectra of carrier free $^{14}CO_2$ has become important.

CO_2 also occurs in planetary atmospheres (e.g. Venus, Mars, and the Saturn's moon Titan). However, due to the lack of accurate spectroscopic data, the isotopic species $^{14}CO_2$ has not been discovered, as yet, although its concentration in planetary atmospheres in comparison to that of $^{12}CO_2$, might be of high interest, especially in the atmosphere of Venus.

The O=C=O molecule has a linear configuration and therefore it shows two infrared active bands (ν_2, ν_3) and one Raman active (ν_1) fundamental band. The Raman band is a doublet formed by Fermi resonance between the symmetric stretching mode ν_1 and one of the overtones of the ν_2 bending mode ($2\nu_2$).

Both absorption and emission infrared spectra of the carbon dioxide molecule have been widely studied [1–6]. However, very few spectroscopic data are known for the isotopic species $^{14}CO_2$. Nielsen et al. in 1954 recorded the ν_3 and ν_2 region of $^{14}CO_2$ enriched samples with a dispersion instrument. In the ν_3 stretching region 17 R-branch and 31 P-branch lines were recorded [7]. Eng et al. detected 3 P and 5 R bands of $^{14}CO_2$ [8], by using a tunable diode laser. Unfortunately they used for calibration old data of insufficient accuracy of $^{12}CO_2$ and $^{13}CO_2$ [9, 10]. Using natural CO_2, Sams and DeVoe determined 5 P and 8 R lines with a precision of ± 0.0013 cm^{-1} by a tunable diode laser spectrometer [11].

The present work deals with the medium resolution (0.18 cm^{-1}) FTIR and high resolution tunable diode laser spectra of the ν_3 and $(\nu_2^1+\nu_3)-\nu_2^1$ region of $^{14}C^{16}O_2$.

Experimental

The $^{14}C^{16}O_2$ gas was prepared in the Institute of Isotopes of the Hungarian Academy of Sciences by adding H_2SO_4 to $Ba^{14}CO_3$ under vacuum. The evolving CO_2 was passed through a series of cold traps to remove water vapor and was then frozen to a bulb. A 160 ml volume cylindrical glass cuvette of 10 cm path length with KBr windows was used to record infrared spectra at a resolution of 0.18 cm^{-1} with a Digilab FTS 20C interferometer equipped with a Data General Nova 3 computer (Inst. Isotopes, Budapest).

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$^{13}C^{16}O_2$ and $^{12}C^{16}O_2$ lines were used for calibration [2–6]. The wave numbers of $^{14}C^{16}O_2$ lines could be located to an accuracy of 0.02 cm^{-1}.

The high resolution IR spectra were obtained with a tunable diode laser system at the University of Cologne [12]. A double sealed 25 cm long glass cell with NaCl windows was used with about 1 Torr sample pressure. The spectra were recorded in the second derivative form by a 2f-detection method of the source frequency modulation technique, where laser frequency was modulated externally by a 5 kHz sine wave. The line positions were calibrated using the lines of N_2O which have been measured by Guelachvili [13]. The precision of the lines measured with the diode laser spectrometer is better than 0.001 cm^{-1}.

Results

Medium Resolution Spectrum

The ν_3 rotational-vibrational band system of $^{14}C^{16}O_2$ is shown in Figure 1. In the region of 2290–2150 cm^{-1} 179 lines were recorded. On the high frequency side a few lines of $^{12}C^{16}O_2$ (P(62), P(64) and P(66)) were observed, and a number of bands belonging to the P branch of $^{13}C^{16}O_2$ (P(2)–P(28)) were also detected. From R(82) to P(68) as many as 76 rotational-vibrational bands were assigned to the 00^01-00^00 transitions of $^{14}C^{16}O_2$. Several bands from R(49) to P(38) of the 01^11-01^10 transition have also been detected, although some of them, at medium resolution remained unresolved due to confusion with much stronger 00^01-00^00 bands.

The selected lines of the 00^10-00^00, 01^11-01^10 ee and 01^11-01^10 ff transitions are summarized in Tables 1–3, respectively.

Diode Laser Spectrum

Diode laser spectral scans have been recorded in the frequency range of 2229–2259 cm^{-1}. However, the recorded spectra cover only short parts of this range interrupted by varying sized gaps, which basically reflects the tunability of the diode employed. Consequently, several bands belonging to the above frequency range have not been recorded. Furthermore, the range covered by the diode laser we used is out of the range of the P branch. The located R bands of the 00^01-00^00, 01^11-01^10 ee and 01^11-01^10 ff transitions are also summarized in Tables 1–3, respectively.

Interpretation of the Spectra

The spectra show the expected pattern of a linear molecule. The nuclear spin statistics confirmed the assignment.

The spectroscopic constants have been determined by use of a least-squares program with which the experimental data were fitted to the following standard expression:

$$\begin{aligned}\nu(J'-J'') = \nu_{10} &+ B'(J'(J'+1)-l'^2) - D'(J'(J'+1)-l'^2)^2 \\ &+ H'(J'(J'+1)-l'^2)^3 - B''(J''(J''+1)-l''^2) \\ &+ D''(J''(J''+1)-l''^2)^2 - H''(J''(J''+1)-l''^2)^3,\end{aligned}$$

where the band origin is $\nu_0 = G(v') - G(v'')$. Concerning the accuracy and range of our measurements, the influence of H constants was expected tobe negligible.

We have generally performed the calculations using both data sets, i.e. the FTIR data and those obtained by the diode laser. However, due to their different experimental accuracies, different weights in the fitting routine were employed. The employed weights are inversely proportional to the square of the estimated error in the measurments, as indicated in Tables 1–3.

In Table 1 we have also included the 00^01-00^00 band frequencies measured with a tunable diode laser by Sams and DeVoe [11], and the calculations were performed using their frequencies, as well; those of P(2) and P(16) with lower weight because of their higher uncertainties of ± 0.005 cm^{-1}. In the case of the 00^01-00^00 band, the medium resolution frequencies were not included into the calculations because the laser data were sufficient.

$\Sigma-\Sigma$ Transition

The calculated spectroscopic constants are given in Table 4 where respective data of other CO_2 isotopic species are also collected. As expected, the accuracy of our measurements is not sufficient to calculate the constants H' and H''. Therefore, we used a fixed value of 3.17×10^{-4} cm^{-1}, calculated by Freed et al. from measurements of $00^01-[10^00, 02^00]$ CO_2 laser transitions [14] for both H' and H''. For B' and D' we used the values of 0.387390283 and 1.3283×10^{-7} also given in [14]. Using the latter values we have obtained considerably inproved values for ν_0 and B'', which seem to be realistic in comparison with those of $^{13}C^{16}O_2$ and $^{12}C^{16}O_2$.

Table 1. Band 00^01-00^00. * wt. = 0 not included into calculation. Standard deviation 0.0012 cm^{-1}.

	Medium resolution FTIR				Laser diode			Laser diode Ref. [11]		
	calc.	obs.	obs.-calc.	wt.*	obs.	obs.-calc.	wt.	obs.	obs.-calc.	wt.
P										
2	2224.2356	4.280	0.044	0.0				4.2403	0.0047	0.2
4	2222.6460	2.636	−0.010	0.0						
6	2221.0335	5.018	−0.017	0.0						
8	2219.3982	2.399	0.001	0.0				2.3983	0.0001	0.5
10	2217.7340	7.733	−0.007	0.0						
12	2216.0591	6.073	0.014	0.0				6.0594	0.0003	1.0
14	2214.3554	4.362	0.007	0.0				4.3553	−0.0001	1.0
16	2212.6290	2.625	−0.004	0.0				2.6268	−0.0022	1.0
18	2210.8799	0.860	−0.019	0.0						
20	2209.1081	9.108	0.000	0.0				9.1080	−0.0001	1.0
22	2207.3136	7.346	0.032	0.0						
24	2205.4966	5.471	−0.026	0.0						
26	2203.6569	3.641	−0.016	0.0				3.6577	0.0008	1.0
28	2201.7947	1.765	−0.030	0.0						
30	2199.9100	9.877	−0.033	0.0				9.9126	0.0026	1.0
32	2198.0028	8.998	−0.005	0.0						
34	2196.0731	6.108	0.035	0.0						
36	2194.1210	4.109	−0.012	0.0						
38	2192.1465	2.127	−0.019	0.0						
40	2190.1496	0.127	−0.023	0.0						
42	2188.1304	8.054	−0.076	0.0						
44	2186.0889	6.064	−0.025	0.0						
46	2184.0251	4.023	−0.002	0.0						
48	2181.9390	1.970	0.031	0.0						
50	2179.8308	9.801	−0.030	0.0						
52	2177.7004	7.688	−0.012	0.0						
54	2175.5478	5.518	−0.030	0.0						
56	2173.3732	3.370	−0.003	0.0						
58	2171.1764	1.127	−0.049	0.0						
60	2168.9577	8.954	−0.104	0.0						
62	2166.7169	6.672	−0.045	0.0						
64	2164.4542	4.429	−0.025	0.0						
66	2162.1695	2.158	−0.012	0.0						
68	2159.8630	9.891	0.028	0.0						
R										
0	2226.5772	6.514	−0.063	0.0						
2	2228.1095	8.083	−0.027	0.0				8.1103	0.0008	1.0
4	2229.6189	9.628	0.009	0.0	9.6177	−0.0012	1	9.6199	0.0010	1.0
6	2231.1054	1.106	0.001	0.0	1.1057	0.0003	1	1.1078	0.0024	1.0
8	2232.5688	2.537	−0.032	0.0						
10	2234.0092	4.006	−0.003	0.0						
12	2235.4265	5.434	0.007	0.0	5.4257	−0.0008	1			
14	2236.8208	6.812	−0.009	0.0	6.8199	−0.0009	1			
16	2238.1919	8.185	−0.007	0.0						
18	2239.5400	9.548	0.008	0.0	9.5394	−0.0006	1			
20	2240.8649	0.788	−0.079	0.0						
22	2242.1666	2.158	−0.009	0.0	2.1663	−0.0003	1			
24	2243.4452	3.440	−0.005	0.0	3.4440	−0.0012	1	3.4433	−0.0019	1.0
26	2244.7005	4.691	−0.009	0.0	4.7002	−0.0003	1	4.7017	0.0012	1.0
28	2245.9326	5.946	0.014	0.0						
30	2247.1415	7.133	−0.008	0.0	7.1416	0.0001	1			
32	2248.3271	8.340	0.013	0.0						
34	2249.4893	9.478	−0.011	0.0	9.4892	−0.0001	1			
36	2250.6283	0.631	0.003	0.0						
38	2251.7440	1.730	−0.014	0.0	1.7447	0.0007	1			
40	2252.8363	2.826	−0.010	0.0						
42	2253.9052	3.895	−0.010	0.0						
44	2254.9507	4.948	−0.003	0.0	4.9500	−0.0007	1			
46	2255.9729	5.970	−0.003	0.0						
48	2256.9716	6.964	−0.008	0.0						
50	2257.9469	8.015	0.061	0.0						
52	2258.8987	8.888	−0.011	0.0	8.8986	−0.0001	1			
54	2259.8270	9.744	−0.083	0.0						
56	2260.7319	0.727	−0.005	0.0						
58	2261.6132	1.678	0.065	0.0						
60	2262.4711	2.512	0.041	0.0						
62	2263.3054	3.270	−0.035	0.0						
64	2264.1161	4.098	−0.018	0.0						
66	2264.9033	4.912	0.009	0.0						
68	2265.6669	5.630	−0.040	0.0						
70	2266.4069	6.390	−0.017	0.0						
72	2267.1234	7.103	−0.020	0.0						
74	2267.8161	7.778	−0.038	0.0						
76	2268.4853	8.540	0.055	0.0						

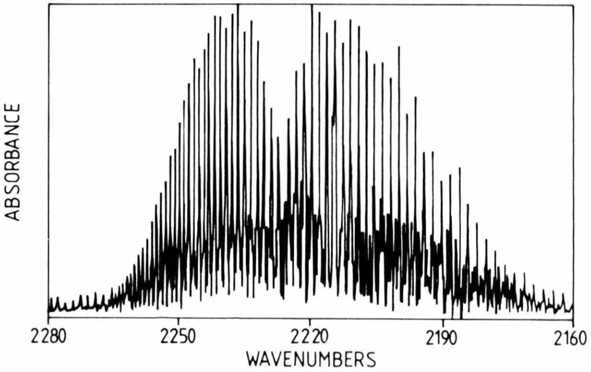

Fig. 1. The ν_3 band system of $^{14}C^{16}O_2$.

Table 2. Band 01^11-01^10 ee. Standard deviation 0.0015 cm^{-1}.

	Medium resolution FTIR				Laser diode		
	calc.	obs.	obs.-calc.	wt.	obs.	obs.-calc.	wt.
P							
3	2212.3877						
5	2210.7863						
7	2209.1624						
9	2207.5160						
11	2205.8472	5.863	0.016	0.0025			
13	2204.1558	4.153	−0.003	0.0025			
15	2202.4421	2.464	0.022	0.0025			
17	2200.7060	0.712	0.006	0.0025			
19	2198.9475	8.957	0.010	0.0025			
21	2197.1666	7.182	0.015	0.0025			
23	2195.3635	5.392	0.029	0.0025			
25	2193.5380	3.527	−0.011	0.0025			
27	2191.6903	1.663	−0.027	0.0025			
29	2189.8204	9.790	−0.030	0.0025			
31	2187.9283						
33	2186.0140						
35	2184.0776						
R							
1	2216.2923						
3	2217.8146						
5	2219.3143						
7	2220.7912						
9	2222.2455	2.221	−0.024	0.0025			
11	2223.6770	3.726	0.049	0.0025			
13	2225.0859	5.112	0.026	0.0025			
15	2226.4719						
17	2227.8351						
19	2229.1755	9.192	0.016	0.0025			
21	2230.4931	0.496	0.003	0.0006	0.4933	0.0002	1
23	2231.7878	1.808	−0.020	0.0025			
25	2233.0596	3.051	−0.009	0.0025			
27	2234.3085	4.286	−0.023	0.0025			
29	2235.5345				5.5352	0.0007	1
31	2236.7375				6.7371	−0.0004	1
33	2237.9175						
35	2239.0745	9.091	0.016	0.0006	9.0751	0.0006	1
37	2240.2085	0.207	−0.001	0.0025			
39	2241.3194	1.331	0.012	0.0006	1.3192	−0.0002	1
41	2242.4073				2.4068	−0.0005	1
43	2243.4720				3.4717	−0.0003	1
45	2244.5137				4.5134	−0.0003	1
47	2245.5322	5.551	0.019	0.0025			
49	2246.5276	6.578	0.050	0.0006	6.5263	−0.0013	1
51	2247.4998						
53	2248.4488						
55	2249.3746				9.3758	0.0012	1
57	2250.2771						
59	2251.1564				1.1565	0.0001	1
61	2252.0124				2.0128	0.0004	1
63	2252.8451						
65	2253.6545						
67	2254.4406				4.4403	−0.0003	1
69	2255.2033						

Table 3. Band 01^11-01^10 ff. Standard deviation 0.0020 cm^{-1}.

	Medium resolution FTIR				Laser diode		
	calc.	obs.	obs.-calc.	wt.	obs.	calc.-obs.	wt.
P							
2	2213.1772	3.148	−0.029	0.0025			
4	2211.5843	1.574	−0.010	0.0025			
6	2209.9686	9.994	0.025	0.0025			
8	2208.3302	8.337	0.007	0.0025			
10	2206.6692	6.695	0.026	0.0025			
12	2202.9854	4.994	0.009	0.0025			
14	2203.2791	3.311	0.032	0.0025			
16	2201.5502						
18	2199.7986						
20	2198.0246						
22	2196.2280						
24	2194.4090						
26	2192.5675	2.552	−0.015	0.0025			
28	2190.7035	0.667	−0.036	0.0025			
30	2188.8171	8.792	−0.025	0.0025			
32	2186.9084	6.940	0.032	0.0025			
34	2184.9773	4.994	0.016	0.0025			
36	2183.0239	3.010	−0.014	0.0025			
38	2181.0482	1.046	−0.002	0.0025			
40	2179.0503						
42	2177.0301						
44	2174.9877						
R							
2	2217.0600	7.069	0.009	0.0025			
4	2218.5732	8.590	0.017	0.0025			
6	2220.0635	0.099	0.035	0.0025			
8	2221.5310	1.490	−0.041	0.0025			
10	2222.9755	2.975	−0.000	0.0025			
12	2224.3972						
14	2225.7959	5.797	0.001	0.0025			
16	2227.1716						
18	2228.5243	8.541	−0.001	0.0025			
20	2229.8540				9.8528	−0.0012	1
22	2231.1607						
24	2232.4443						
26	2233.7048						
28	2234.9422	4.971	0.029	0.0025			
30	2236.1564	6.148	−0.008	0.000625	6.1561	−0.0003	1
32	2237.3474	7.330	−0.017	0.000625	7.3478	0.0004	1
34	2238.5153	8.496	−0.019	0.0025			
36	2239.6600				9.6601	0.0001	1
38	2240.7814						
40	2241.8796				1.8796	0.0000	1
42	2242.9544	2.953	−0.001	0.0025			
44	2244.0060	4.008	0.002	0.000625	4.0073	0.0013	1
46	2245.0343	4.998	−0.036	0.0025			
48	2246.0392						
50	2247.0207						
52	2247.9788						

Table 4. Spectroscopic constants for 00^01-00^00 (−) transition of CO_2 (units in cm^{-1}).

Molecule	ν_0	B'	B''	$D' \times 10^{-7}$	$D'' \times 10^{-7}$	$H' \times 10^{-14}$	$H'' \times 10^{-14}$	Ref.
$^{14}C^{16}O_2$	2225.80239(16)	0.387390283(17) [a]	0.39025488(18)	1.32831(29) [a]	1.3372(20)	3.17 [a]	3.17 [b]	this work
$^{13}C^{16}O_2$	2283.487570(6)	0.3872735(1)	0.390237(1)	1.3293(5)	1.3392(5)	2.5241 [b]	2.5241 [b]	[4]
$^{13}C^{18}O_2$	2247.29139(1)	0.3442086(1)	0.3468342(2)	1.055(1)	1.02(1)			[4]
$^{12}C^{16}O_2$	2249.143277	0.387141483	0.39219027	1.3299	1.3335	1.32 [b]	1.32 [b]	[2]
$^{12}C^{18}O_2$	2314.04880(8)	0.3440905(1)	0.3468173(1)	1.0520(4)	1.0544(4)	2.7759 [b]	2.7759 [b]	[3]

[a] Fixed value taken from [14]. – [b] Fixed value.

Table 5. Spectroscopic constants for 01^11-01^10 ($\Pi-\Pi$) transition of CO_2 (units in cm^{-1}). * Fixed values.

Molecule	ν_0	B', B'' f sublevels	D', $D'' \times 10^{-7}$ f sublevels	B^e-B^f $\times 10^{-4}$	$D^e D^f$ $\times 10^{-10}$	Ref.
$^{14}C^{16}O_2$	2214.74458(30)	0.388277(13) 0.391125(13)	1.348* 1.352*	−6.35(17) −6.59(17)	0 0	this work
$^{13}C^{16}O_2$	2271.76045(1)	0.3882928(2) 0.3912439(2)	1.3544(2) 1.3582(5)	−6.134(3) −6.334(3)	−10.4(7) − 8.2(7)	[4]
$^{13}C^{18}O_2$	2235.82547(6)	0.345099(1) 0.347715(1)	1.065(3) 1.070(3)	−4.95(1) −5.08(1)	0* 0*	[4]
$^{12}C^{16}O_2$	2336.632921	0.38819047 0.391254823	1.3467722 1.3524503	−5.977 −6.156	−13.7 −13.7	[2]
$^{12}C^{18}O_2$	2301.79939	0.3450080(2) 0.3477237(2)	1.0723(4) 1.0749(3)	−4.821(3) −4.93(3)	−5.7(6) −4.7(6)	[3]

$\Pi-\Pi$ Transition

The spectroscopic constants calculated from the experimental data of Tables 2 and 3 are shown in Table 5. For D' and D'' constants at both e and f levels we have used constrained values extrapolated from the respective data for $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ taken from [2, 3]. First we performed separated calculations for e and f subgroups. We found that the band centers were practically equal in the e and f components. Constraining common band centers for both ee and ff transitions we calculated the final constants shown in Table 5. By this treatment the constants ν_0, B', B'' and differences of B^e-B^f are consistent with the respective constants of the molecules $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$.

Force Constant Calculation

From the point of view of force constant calculation the CO_2 is a very simple molecule. A least-squares adjustment of anharmonic potential constants was developed by Pariseau, Suzuki, and Overend [16, 17] and applied to $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$.

We were able to collect the observed (anharmonic) and zero order (harmonic) frequencies of CO_2 for nine isotopic species (Table 6). The infrared active ν_3 band was observed for all nine molecules, the deformation mode, ν_2, was available for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{14}C^{16}O_2$, $^{12}C^{18}O_2$, $^{13}C^{18}O_2$, $^{12}C^{16}O^{17}O$ and $^{12}C^{16}O^{18}O$, but the Raman active symmetric stretching mode ν_1 is strongly perturbated by Fermi-resonance with the $2\nu_2$ mode. The unperturbed ν_1 frequencies were calculated from the shifted experimental data and assumed to be equal for the first three carbon isotopic species in Table 6. Surprisingly (to our best knowledge) there are no available ν_1 fundamental frequencies for symmetrically and asymmetrically oxygen labelled CO_2 species. A sufficient number of overtones and combination bands has been observed only for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ (see e.g. [17, 18]) to allow rather precise corrections for anharmonicity. For most of the isotopic species we used the Dennison approximation (22) to determine the zero-order frequencies. The harmonic frequencies are also listed in Table 6.

For nine isotopic species we have 19 experimental frequencies, and the three force constants, K(CO), F(CO, CO) and H(OCO) can be determined with high accuracy. The missing eight experimental frequencies can be predicted quite precisely with the final set of force constants. According to the isotopic rules,

Table 6. Observed and zero order frequencies for CO_2.

Isotope species	i	ν_i (cm^{-1})	ν_i (cm^{-1})	Ref.
$^{12}C^{16}O_2$	1	1338.45	1354.91	[17]
	2	667.38	673.00	[19]
	3	2349.14	2396.49	[2]
$^{13}C^{16}O_2$	1	1338.45	1354.91	a)
	2	648.48	653.45	[19]
	3	2283.49	2328.22	[4]
$^{14}C^{16}O_2$	1	1338.45	1354.95	a)
	2	632.15	636.02	[15]
	3	2225.80	2268.28	this work
$^{12}C^{18}O_2$	1	(1262.18)	(1277.25)	b)
	2	657.30	662.69	[20]
	3	2314.05	2359.84	[3]
$^{13}C^{18}O_2$	1	(1262.18)	(1277.25)	b)
	2	638.40	642.78	[21]
	3	2247.29	2290.53	[4]
$^{12}C^{16}O^{17}O$	1	(1318.41)	(1334.63)	b)
	2	664.73	670.33	[19]
	3	2340.01	2387.18	[1]
$^{12}C^{16}O^{18}O$	1	(1229.95)	(1315.94)	b)
	2	662.37	667.95	[19]
	3	2332.11	2379.12	[1]
$^{13}C^{16}O^{17}O$	1	(1318.41)	(1334.63)	b)
	2	(645.80)	(651.12)	b)
	3	2274.09	2318.63	[6]
$^{13}C^{16}O^{18}O$	1	(1299.88)	(1315.87)	b)
	2	(643.34)	(648.23)	b)
	3	2265.97	2310.36	[6]

Remarks: a) See text. – b) Calculated frequencies with refined force fields. In brackets are the frequencies calculated with the final set of force constants.

Table 7. Calculated force constants from anharmonic and harmonic frequencies.

Force constants	Anharmonic	Harmonic		
		Ref. [24]	Present work	
K(CO)	15.5453(36)	16.0250(60)	16.0329(23)	a)
F(CO, CO)	1.3434(36)	1.2630(60)	1.2692(23)	a)
H(OCO)	0.7737 (6)	0.7854(20)	0.7858 (4)	b)

Units: a) 10^1 N m^{-1}; b) 10^{-18} N m rad^{-2}.
Remarks: Atomic masses used for calculations: $^{12}C=12$; $^{13}C=13.003554$; $^{14}C=14.003242$ [25]; $^{16}O=15.9994915$; $^{17}O=17.99916$ [26]; $^{18}O=17.9991600$ [26]; interatomic distance $r(CO)=116.21$ pm. In brackets are the digits for the dispersion of the force constants.

the frequencies of some isotopic species yield no new information, but we can consider in general that, the greater the number of isotopic molecules available, the lower is the indeterminacy in the calculated force constants.

A FORTRAN program was used for calculating G matrices and for refining the force constants [23]. The force constant refinement was performed for both sets of frequencies, namely for anharmonic (ν_i) and for zero-order frequencies (ω_i) as well. The final sets of force constants are presented in Table 7. The ν_i experimental frequencies were reproduced with an accuracy better than 0.9 cm^{-1}, and the ν_i values better than 0.3 cm^{-1} for all 19 experimental fundamental vibrations of nine isotopic species. The harmonic force constants are rather close to those determined by Johns [24] on the basis of two carbon isotopic species of CO_2. According to the correlation between the harmonic valence force constants and the anharmonic potential constants, $K(CO)=2K_{11}$, $F(CO, CO)=K_{13}$, and $H(OCO)=K_{22}/r^2$ (where $r=$CO bond length), the Pariseau, Suzuki, and Overend [16] force field with $K_{11}=8.014(3)$, $K_{12}=1.268(6)\times10^2$ N m^{-1} and $K_{22}=0.3930(50)\times10^{-8}$ N rad^{-1} practically equals our values in Table 7.

The dispersions of the fitted harmonic force constants are 3–5 times smaller in our calculation than those in [16] and [24]. It is also interesting to note that a slightly better accuracy of force constants was obtained for harmonic values.

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[1] A. Baldacci, V. Malathy Devi, Da-Wun Chen, and K. Narahari Rao, J. Mol. Spectrosc. **70,** 143 (1978).
[2] D. Bailly, R. Farreng, G. Guelachvili, and C. Rossetti, J. Mol. Spectrosc. **90,** 74 (1981).
[3] D. Bailly and C. Rossetti, J. Mol. Spectrosc. **105,** 215 (1984).
[4] D. Bailly and C. Rossetti, J. Mol. Spectrosc. **105,** 219 (1984).
[5] D. Bailly and C. Rossetti, J. Mol. Spectrosc. **105,** 331 (1984).
[6] D. Bailly and C. Rossetti, J. Mol. Spectrosc. **119,** 388 (1986).
[7] A. H. Nielsen and R. T. Lageman, J. Chem. Phys. **22,** 36 (1954).
[8] R. S. Eng, K. W. Nill, and M. Wahlen, Appl. Opt. **16,** 3072 (1977).

[9] R. A. McClatchey, W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Rothman, and J. C. Caring, AFCRL-TR-0096, Environmental Research Paper, No. 434 (1973).

[10] T. R. Todd, C. M. Clayton, W. B. Telfair, T. C. McCubbin, and J. Pilva, J. Mol. Spectrosc. **62,** 601 (1976).

[11] R. L. Sams and J. R. DeVoe, J. Mol. Spectrosc. **128,** 296 (1988).

[12] K. M. T. Yamada and G. Winnewisser, Z. Naturforsch. **36 a,** 1052 (1981).

[13] G. Guelachvili and K. Naharahari Rao, Handbook of Infrared Standards, Academic Press, Orlando 1986, p. 656–667.

[14] C. Freed, L. C. Bradley, and R. G. O'Donnell, J. Quant. Electr. QE-**16,** 1195 (1980).

[15] A. T. Ayoub, Ph.D. Thesis, Budapest 1982.

[16] M. A. Pariseau, I. Suzuki, and J. Overend, J. Chem. Phys. **42,** 2335 (1965).

[17] I. Suzuki, J. Mol. Spectrosc. **25,** 477 (1968).

[18] J. Dupre-Maquiare and P. Pinson, J. Mol. Spectrosc. **62,** 181 (1976).

[19] R. Paso, J. Kauppinen, and R. Anttila, J. Mol. Spectrosc. **79,** 236 (1980).

[20] C. Jr. Chakerian and D. F. Jr. Eggers, J. Chem. Phys. **43,** 754 (1965).

[21] C. Jr. Chakerian and D. F. Jr. Eggers, J. Mol. Spectrosc. **27,** 59 (1968).

[22] M. D. Denninson, Rev. Modern Phys. **12,** 175 (1940).

[23] J. Mink and L. M. Mink, Computer Program System for Vibrational Analysis of Molecules, Erlangen 1983.

[24] L. M. Jones, Inorganic Vibrational Spectroscopy, Vol. 1, Marcel Decker, New York 1971.

[25] Atomic Weight of the Elements, Pure and Appl. Chem. **21,** 91 (1970).

[26] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Chemical Application of Spectroscopy (W. West, ed.), Wiley-Intersci. 1970, Appendix V.